Textbook for Class XI

Chemistry

Part 1

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UNIT 1

SOME BASIC CONCEPTS OF CHEMISTRY

Objectives

After studying this unit, you will be able to

- understand and appreciate the role of chemistry in different spheres of life;
- explain the characteristics of three states of matter;
- classify different substances into elements, compounds and mixtures;
- define SI base units and list some commonly used prefixes;
- use scientific notations and perform simple mathematical operations on numbers;
- differentiate between precision and accuracy;
- determine significant figures;
- convert physical quantities from one system of units to another;
- explain various laws of chemical combination;
- appreciate significance of atomic mass, average atomic mass, molecular mass and formula mass;
- describe the terms – mole and molar mass;
- calculate the mass per cent of different elements constituting a compound;
- determine empirical formula and molecular formula for a compound from the given experimental data;
- perform the stoichiometric calculations.

"Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them ..."

Roald Hoffmann

Chemistry deals with the composition, structure and properties of matter. These aspects can be best described and understood in terms of basic constituents of matter: **atoms** and **molecules**. That is why chemistry is called the science of atoms and molecules. Can we see, weigh and perceive these entities? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and number of these particles (atoms and molecules)? We will like to answer some of these questions in this Unit. We would further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.

1.1 IMPORTANCE OF CHEMISTRY

Science can be viewed as a continuing human effort to systematize knowledge for describing and understanding nature. For the sake of convenience science is sub-divided into various disciplines: chemistry, physics, biology, geology etc. Chemistry is the branch of science that studies the composition, properties and interaction of matter. Chemists are interested in knowing how chemical transformations occur. Chemistry plays a central role in science and is often intertwined with other branches of science like physics, biology, geology etc. Chemistry also plays an important role in daily life.

Chemical principles are important in diverse areas, such as: weather patterns, functioning of brain and operation

of a computer. Chemical industries manufacturing fertilizers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys and other inorganic and organic chemicals, including new materials, contribute in a big way to the national economy.

Chemistry plays an important role in meeting human needs for food, health care products and other materials aimed at improving the quality of life. This is exemplified by the large scale production of a variety of fertilizers, improved varieties of pesticides and insecticides. Similarly many life saving drugs such as **cisplatin** and **taxol**, are effective in cancer therapy and AZT (Azidothymidine) used for helping AIDS victims, have been isolated from plant and animal sources or prepared by synthetic methods.

With a better understanding of chemical principles it has now become possible to design and synthesize new materials having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres and large scale miniaturization of solid state devices. In recent years chemistry has tackled with a fair degree of success some of the pressing aspects of environmental degradation. Safer alternatives to environmentally hazardous refrigerants like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases like methane, carbon dioxide etc. Understanding of bio-chemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic materials are some of the intellectual challenges for the future generation of chemists. A developing country like India needs talented and creative chemists for accepting such challenges.

1.2 NATURE OF MATTER

You are already familiar with the term **matter** from your earlier classes. Anything which has mass and occupies space is called **matter**.

Fig. 1.1 *Arrangement of particles in solid, liquid and gaseous state*

Everything around us, for example, book, pen, pencil, water, air, all living beings etc. are composed of matter. You know that they have mass and they occupy space.

You are also aware that matter can exist in three physical states *viz.* **solid**, **liquid** and **gas**. The constituent particles of matter in these three states can be represented as shown in Fig. 1.1. In **solids**, these particles are held very close to each other in an orderly fashion and there is not much freedom of movement. In **liquids**, the particles are close to each other but they can move around. However, in **gases**, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. Because of such arrangement of particles, different states of matter exhibit the following characteristics:

(i) Solids have *definite volume* and *definite shape*.

(ii) Liquids have *definite volume* but *not* the *definite shape*. They take the shape of the container in which they are placed.

(iii) Gases have *neither definite volume nor definite shape*. They completely occupy the container in which they are placed.

These three states of matter are interconvertible by changing the conditions of temperature and pressure.

$$\text{Solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftarrows}} \text{liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftarrows}} \text{Gas}$$

On heating a solid usually changes to a liquid and the liquid on further heating

changes to the gaseous (or vapour) state. In the reverse process, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid.

At the macroscopic or bulk level, matter can be classified as **mixtures** or **pure substances**. These can be further sub-divided as shown in Fig. 1.2.

Fig. 1.2 *Classification of matter*

Many of the substances present around you are **mixtures**. For example, sugar solution in water, air, tea etc., are all mixtures. A mixture contains two or more substances present in it (in any ratio) which are called its components. A mixture may be **homogeneous** or **heterogeneous**. In a **homogeneous mixture**, the components completely mix with each other and its composition is uniform throughout. Sugar solution, and air are thus, the examples of homogeneous mixtures. In contrast to this, in **heterogeneous mixtures**, the composition is not uniform throughout and sometimes the different components can be observed. For example, the mixtures of salt and sugar, grains and pulses along with some dirt (often stone) pieces, are heterogeneous mixtures. You can think of many more examples of mixtures which you come across in the daily life. It is worthwhile to mention here that the components of a mixture can be separated using physical methods such as simple hand picking, filtration, crystallisation, distillation etc.

Pure substances have characteristics different from the mixtures. They have fixed composition, whereas mixtures may contain the components in any ratio and their composition is variable. Copper, silver, gold, water, glucose are some examples of pure substances. Glucose contains carbon, hydrogen and oxygen in a fixed ratio and thus, like all other pure substances has a fixed composition. Also, the constituents of pure substances cannot be separated by simple physical methods.

Pure substances can be further classified into **elements** and **compounds**. An **element** consists of only one type of particles. These particles may be **atoms** or **molecules**. You may be familiar with atoms and molecules from the previous classes; however, you will be studying about them in detail in Unit 2. Sodium, copper, silver, hydrogen, oxygen etc. are some examples of elements. They all contain atoms of one type. However, the atoms of different elements are different in nature. Some elements such as sodium or copper, contain single atoms held together as their constituent particles whereas in some others, two or more atoms combine to give **molecules** of the element. Thus, hydrogen, nitrogen and oxygen gases consist of molecules in which two atoms combine to give their respective molecules. This is illustrated in Fig. 1.3.

When two or more atoms of different elements combine, the molecule of a **compound** is obtained. The examples of some compounds are water, ammonia, carbon

Fig. 1.3 *A representation of atoms and molecules*

dioxide, sugar etc. The molecules of water and carbon dioxide are represented in Fig 1.4.

Water molecule (H_2O) Carbon dioxide molecule (CO_2)

Fig. 1.4 *A depiction of molecules of water and carbon dioxide*

You have seen above that a water molecule comprises two hydrogen atoms and one oxygen atom. Similarly, a molecule of carbon dioxide contains two oxygen atoms combined with one carbon atom. Thus, the atoms of different elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound. Also, the properties of a compound are different from those of its constituent elements. For example, hydrogen and oxygen are gases whereas the compound formed by their combination *i.e.*, water is a liquid. It is interesting to note that hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher.

Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods.

1.3 PROPERTIES OF MATTER AND THEIR MEASUREMENT

Every substance has unique or characteristic properties. These properties can be classified into two categories – **physical properties** and **chemical properties**.

Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. Some examples of physical properties are colour, odour, melting point, boiling point, density etc. The measurement or observation of **chemical properties** require a chemical change to occur. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc.

Many properties of matter such as length, area, volume, etc., are quantitative in nature. Any quantitative observation or measurement is represented by a number followed by units in which it is measured. For example length of a room can be represented as 6 m; here 6 is the number and m denotes *metre* – the unit in which the length is measured.

Two different systems of measurement, i.e. the **English System** and the **Metric System** were being used in different parts of the world. The metric system which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. The need of a common standard system was being felt by the scientific community. Such a system was established in 1960 and is discussed below in detail.

1.3.1 The International System of Units (SI)

The International System of Units (in French *Le Systeme International d'Unités* – abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from *Conference Generale des Poids at Measures*). The CGPM is an inter governmental treaty organization created by a diplomatic treaty known as Meter Convention which was signed in Paris in 1875.

The SI system has seven *base units* and they are listed in Table 1.1. These units pertain to the seven fundamental scientific quantities. The other physical quantities such as speed, volume, density etc. can be derived from these quantities.

The definitions of the SI base units are given in Table 1.2.

The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit. These prefixes are listed in Table 1. 3.

Let us now quickly go through some of the quantities which you will be often using in this book.

Table 1.1 Base Physical Quantities and their Units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

Table 1.2 Definitions of SI Base Units

Unit of length	**metre**	The *metre* is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
Unit of mass	**kilogram**	The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Unit of time	**second**	The *second* is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	**ampere**	The *ampere* is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to $2 \quad 10^{-7}$ newton per metre of length.
Unit of thermodynamic temperature	**kelvin**	The *kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Unit of amount of substance	**mole**	1. The *mole* is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is "mol." 2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	**candela**	The *candela* is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \quad 10^{12}$ hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

Table 1.3 Prefixes used in the SI System

Multiple	Prefix	Symbol
10^{-24}	yocto	y
10^{-21}	zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zeta	Z
10^{24}	yotta	Y

1.3.2 Mass and Weight

Mass of a substance is the amount of matter present in it while **weight** is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity. You should be careful in using these terms.

The mass of a substance can be determined very accurately in the laboratory by using an analytical balance (Fig. 1.5).

The SI unit of mass as given in Table 1.1 is kilogram. However, its fraction gram (1 kg = 1000 g), is used in laboratories due to the smaller amounts of chemicals used in chemical reactions.

Volume

Volume has the units of (length)^3. So in SI system, volume has units of m^3. But again, in chemistry laboratories, smaller volumes are used. Hence, volume is often denoted in cm^3 or dm^3 units.

Fig. 1.5 *Analytical balance*

Maintaining the National Standards of Measurement

The system of units including unit definitions keeps on changing with time. Whenever the accuracy of measurement of a particular unit was enhanced substantially by adopting new principles, member nations of *metre treaty* (signed in 1875), agreed to change the formal definition of that unit. Each modern industrialized country including India has a National Metrology Institute (NMI) which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL), New Delhi. This laboratory establishes experiments to realize the *base units* and *derived units* of measurement and maintains National Standards of Measurement. These standards are periodically inter-compared with standards maintained at other National Metrology Institutes in the world as well as those established at the International Bureau of Standards in Paris.

A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids.

$$1\ L = 1000\ mL\ ,\ \ 1000\ cm^3 = 1\ dm^3$$

Fig. 1.6 helps to visualise these relations.

In the laboratory, volume of liquids or solutions can be measured by graduated cylinder, burette, pipette etc. A volumetric flask is used to prepare a known volume of a solution. These measuring devices are shown in Fig. 1.7.

Fig. 1.6 *Different units used to express volume*

Density

Density of a substance is its amount of mass per unit volume. So SI units of density can be obtained as follows:

$$\text{SI unit of density} = \frac{\text{SI unit of m}}{\text{SI unit of vo}}$$

$$= \frac{kg}{m^3} \text{ or } kg\ m^{-3}$$

This unit is quite large and a chemist often expresses density in g cm^{-3}, where mass is expressed in gram and volume is expressed in cm^3.

Fig 1.7 *Some volume measuring devices*

Temperature

There are three common scales to measure temperature — C (degree celsius), F (degree fahrenheit) and K (kelvin). Here, K is the SI unit. The thermometers based on these scales are shown in Fig. 1.8. Generally, the thermometer with celsius scale are calibrated from 0 to 100 where these two temperatures are the freezing point and the boiling point of water respectively. The fahrenheit scale is represented between 32 to 212 .

The temperatures on two scales are related to each other by the following relationship:

$$°F = \frac{9}{5}(°C) + 3$$

The kelvin scale is related to celsius scale as follows :

$$K = °C + 273.1$$

Fig. 1.8 *Thermometers using different temperature scales*

It is interesting to note that temperature below 0 C (i.e. negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

Reference Standard

After defining a unit of measurement such as the kilogram or the metre, scientists agreed on reference standards that make it possible to calibrate all measuring devices. For getting reliable measurements, all devices such as *metre sticks* and *analytical balances* have been calibrated by their manufacturers to give correct readings. However, each of these devices is standardised or calibrated against some reference. The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time.

Scientists are in search of a new standard for mass. This is being attempted through accurate determination of Avogadro constant. Work on this new standard focuses on ways to measure accurately the number of atoms in a well-defined mass of sample. One such method, which uses X-rays to determine the atomic density of a crystal of ultrapure silicon, has an accuracy of about 1 part in 10^6 but has not yet been adopted to serve as a standard. There are other methods but none of them are presently adequate to replace the Pt-Ir cylinder. No doubt, changes are expected within this decade.

The metre was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0 C (273.15 K). In 1960 the length of the metre was defined as 1.65076373 10^6 times the wavelength of light emitted by a krypton laser. Although this was a cumbersome number, it preserved the length of the metre at its agreed value. The metre was redefined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Similar to the length and the mass, there are reference standards for other physical quantities.

1.4 UNCERTAINTY IN MEASUREMENT

Many a times in the study of chemistry, one has to deal with experimental data as well as theoretical calculations. There are meaningful ways to handle the numbers conveniently and present the data realistically with certainty to the extent possible. These ideas are discussed below in detail.

1.4.1 Scientific Notation

As chemistry is the study of atoms and molecules which have extremely low masses and are present in extremely large numbers, a chemist has to deal with numbers as large as 602, 200,000,000,000,000,000,000 for the molecules of 2 g of hydrogen gas or as small as 0.000000000000000000000000166 g mass of a H atom. Similarly other constants such as Planck's constant, speed of light, charges on particles etc., involve numbers of the above magnitude.

It may look funny for a moment to write or count numbers involving so many zeros but it offers a real challenge to do simple mathematical operations of addition, subtraction, multiplication or division with such numbers. You can write any two numbers of the above type and try any one of the operations you like to accept the challenge and then you will really appreciate the difficulty in handling such numbers.

This problem is solved by using scientific notation for such numbers, *i.e.*, exponential notation in which any number can be represented in the form N 10^n where n is an exponent having positive or negative values and N can vary between 1 to 10.

Thus, we can write 232.508 as 2.32508×10^2 in scientific notation. Note that while writing it, the decimal had to be moved to the *left* by two places and same is the exponent (2) of 10 in the scientific notation.

Similarly, 0.00016 can be written as 1.6×10^{-4}. Here the decimal has to be moved four places to the *right* and (–4) is the exponent in the scientific notation.

Now, for performing mathematical operations on numbers expressed in scientific

notations, the following points are to be kept in mind.

Multiplication and Division

These two operations follow the same rules which are there for exponential numbers, i.e.

$$\left(5.6\times10^{5}\right)\times($$

$$\left(9.8\times10^{-2}\right)\times($$

$$=(9.8\times2.5)(1$$

$$= 24.50 \quad 10^{-}$$

$$\frac{2.7\times10^{-3}}{5.5\times10^{4}}=(2.$$

Addition and Subtraction

For these two operations, first the numbers are written in such a way that they have same exponent. After that, the coefficient are added or subtracted as the case may be.

Thus, for adding 6.65 10^4 and 8.95 10^3, 6.65 10^4 + 0.895 10^4 exponent is made same for both the numbers.

Then, these numbers can be added as follows (6.65 + 0.895) 10^4 = 7.545 10^4

Similarly, the subtraction of two numbers can be done as shown below :

2.5 10^{-2} – 4.8 10^{-3}

= (2.5 10^{-2}) – (0.48 10^{-2})

= (2.5 – 0.48) 10^{-2} = 2.02 10^{-2}

1.4.2 Significant Figures

Every experimental measurement has some amount of uncertainty associated with it. However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk about the measurement.

Precision refers to the closeness of various measurements for the same quantity. However, **accuracy** is the agreement of a particular value to the true value of the result. For example, if the true value for a result is 2.00 g and a student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate. Another student repeats the experiment and obtains 1.94 g and 2.05 g as the results for two measurements. These observations are neither precise nor accurate. When a third student repeats these measurements and reports 2.01g and 1.99g as the result. These values are both precise and accurate. This can be more clearly understood from the data given in Table 1.4

Table 1.4 Data to Illustrate Precision and Accuracy

	Measurements/g		
	1	2	Average (g)
Student A	1.95	1.93	1.940
Student B	1.94	2.05	1.995
Student C	2.01	1.99	2.000

The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. **Significant figures** are meaningful digits which are known with certainty. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be ±1 in the last digit. Unless otherwise stated, an uncertainty of ±1 in the last digit is always understood.

There are certain rules for determining the number of significant figures. These are stated below:

(1) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.

(2) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point.

Thus, 0.03 has one significant figure and 0.0052 has two significant figures.

(3) Zeros between two non-zero digits are

significant. Thus, 2.005 has four significant figures.

(4) Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures.

But, if otherwise, the zeros are not significant. For example, 100 has only one significant figure.

(5) Exact numbers have an infinite number of significant figures. For example, in 2 balls or 20 eggs, there are infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000

When numbers are written in scientific notation, the number of digits between 1 and 10 gives the number of significant figures. Thus,

$4.01 \quad 10^2$ has three significant figures, and $8.256 \quad 10^3$ has four significant figures.

Addition and Subtraction of Significant Figures

The result cannot have more digits to the right of the decimal point than either of the original numbers.

$$\begin{array}{r} 12.11 \\ 18.0 \\ 1.012 \\ \hline 31.122 \\ \hline \end{array}$$

Here, 18.0 has only one digit after the decimal point and the result should be reported only up to one digit after the decimal point which is 31.1.

Multiplication and Division of Significant Figures

In these operations, the result must be reported with no more significant figures as are there in the measurement with the few significant figures.

$2.5 \quad 1.25 = 3.125$

Since 2.5 has two significant figures, the result should not have more than two significant figures, thus, it is 3.1.

While limiting the result to the required number of significant figures as done in the above mathematical operation, one has to keep in mind the following points for rounding off the numbers

1. If the rightmost digit to be removed is more than 5, the preceding number is increased by one. for example

   1.386

   If we have to remove 6, we have to round it to 1.39

2. If the rightmost digit to be removed is less than 5, the preceding number is not changed. For example, 4.334 if 4 is to be removed, then the result is rounded upto 4.33.

3. If the rightmost digit to be removed is 5, then the preceding number is not changed if it is an even number but it is increased by one if it is an odd number. For example, if 6.35 is to be rounded by removing 5, we have to increase 3 to 4 giving 6.4 as the result. However, if 6.25 is to be rounded off it is rounded off to 6.2.

1.4.3 Dimensional Analysis

Often while calculating, there is a need to convert units from one system to other. The method used to accomplish this is called **factor label method** or **unit factor method** or **dimensional analysis**. This is illustrated below.

Example

A piece of metal is 3 inch (represented by in) long. What is its length in cm?

We know that 1 in = 2.54 cm

From this equivalence, we can write

$$\frac{1 \text{ in}}{2.54 \text{ cm}} = 1 =$$

thus $\frac{1 \text{ in}}{2.54 \text{ cm}}$ equals 1 and $\frac{2.54 \text{ cm}}{1 \text{ in}}$ also equals 1. Both of these are called **unit factors**. If some number is multiplied by these unit factors (i.e. 1), it will not be affected otherwise.

Say, the 3 in given above is multiplied by the unit factor. So,

$$3 \text{ in} = 3 \text{ in} \quad \frac{2.54 \text{ cm}}{1 \text{ in}} = 3 \quad 2.54 \text{ cm} = 7.62 \text{ cm}$$

Now the unit factor by which multiplication is to be done is that unit factor ($\frac{2.54 \text{ cm}}{1 \text{ in}}$ in the above case) which gives the desired units i.e., the numerator should have that part which is required in the desired result.

It should also be noted in the above example that units can be handled just like other numerical part. It can be cancelled, divided, multiplied, squared etc. Let us study one more example for it.

Example

A jug contains 2 L of milk. Calculate the volume of the milk in m^3.

Since 1 L = 1000 cm^3

and 1 m = 100 cm which gives

$$\frac{1 \text{ m}}{100 \text{ cm}} = 1 =$$

To get m^3 from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1 \text{m}}{100 \text{m}}\right)^3 \Rightarrow \frac{}{1}$$

Now 2 L = 2 1000 cm^3

The above is multiplied by the unit factor

$$2 \times 1000 \text{ cm}^3 :$$

Example

How many seconds are there in 2 days?

Here, we know 1 day = 24 hours (h)

$$\text{or} \quad \frac{1 \text{day}}{24 \text{h}} = 1 = \frac{2}{1}$$

then 1h = 60 min

$$\text{or} \quad \frac{1 \text{h}}{60 \text{min}} = 1 = \frac{}{}$$

so, for converting 2 days to seconds,

i.e., 2 days ----- seconds

The unit factors can be multiplied in series in one step only as follows:

$$2 \text{day} \times \frac{24 \text{h}}{1 \text{day}} \times$$

= 2 24 60 60 s

= 172800 s

1.5 LAWS OF CHEMICAL COMBINATIONS

The combination of elements to form compounds is governed by the following five basic laws.

Antoine Lavoisier (1743 1794)

1.5.1 Law of Conservation of Mass

It states that *matter can neither be created nor destroyed.*

This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions for reaching to the above conclusion. This law formed the basis for several later developments in chemistry. Infact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.

1.5.2 Law of Definite Proportions

This law was given by, a French chemist, Joseph Proust. He stated that *a given compound always contains exactly the same proportion of elements by weight.*

Joseph Proust (1754 1826)

Proust worked with two samples of cupric carbonate — one of which was of natural origin and the other was synthetic one. He found that the composition of elements present in it was same for both the samples as shown below :

	% of copper	% of oxygen	% of carbon
Natural Sample	51.35	9.74	38.91
Synthetic Sample	51.35	9.74	38.91

Thus, irrespective of the source, a given compound always contains same elements in the same proportion. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as **Law of definite composition**.

1.5.3 Law of Multiple Proportions

This law was proposed by Dalton in 1803. According to this law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.*

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.

Hydrogen + Oxygen → Water

2g 16g 18g

Hydrogen + Oxygen → Hydrogen Peroxide

2g 32g 34g

Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e. 16:32 or 1: 2.

1.5.4 Gay Lussac's Law of Gaseous Volumes

This law was given by Gay Lussac in 1808. He observed that *when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.*

Joseph Louis Gay Lussac

Thus, 100 mL of hydrogen combine with 50 mL of oxygen to give 100 mL of water vapour.

Hydrogen + Oxygen → Water

100 mL 50 mL 100 mL

Thus, the volumes of hydrogen and oxygen which combine together (i.e. 100 mL and 50 mL) bear a simple ratio of 2:1.

Gay-Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume. The law of definite proportions, stated earlier, was with respect to mass. The Gay-Lussac's law was explained properly by the work of Avogadro in 1811.

1.5.5 Avogadro Law

In 1811, Avogadro proposed that *equal volumes of gases at the same temperature and pressure should contain equal number of molecules.* Avogadro made a distinction between **atoms** and **molecules** which is quite understandable in the present times. If we consider again the reaction of hydrogen and oxygen to produce water, we see that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any unreacted oxygen.

Lorenzo Romano Amedeo Carlo Avogadro di Quareqa edi Carreto (1776 1856)

Note that in the Fig. 1.9, each box contains equal number of molecules. In fact, Avogadro could explain the above result by considering the molecules to be **polyatomic.** If hydrogen

Fig. 1.9 *Two volumes of hydrogen react with One volume of oxygen to give Two volumes of water vapour*

and oxygen were considered as **diatomic** as recognised now, then the above results are easily understandable. However, Dalton and others believed at that time that atoms of the same kind cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro's proposal was published in the French **Journal de Physidue**. In spite of being correct, it did not gain much support.

After about 50 years, in 1860, first international conference on chemistry was held in Karlsruhe, Germany to resolve various ideas. At the meeting, Stanislao Cannizaro presented a sketch of a course of chemical philosophy which emphasised the importance of Avogadro's work.

1.6 DALTON'S ATOMIC THEORY

John Dalton
(1776 1884)

Although the origin of idea that matter is composed of small indivisible particles called *'a tomio'* (meaning — *indivisible*), dates back to the time of Democritus, a Greek Philosopher (460 — 370 BC), it again started emerging as a result of several experimental studies which led to the Laws mentioned above.

In 1808, Dalton published 'A New System of Chemical Philosophy' in which he proposed the following :

1. Matter consists of indivisible atoms.
2. All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
3. Compounds are formed when atoms of different elements combine in a fixed ratio.
4. Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

   Dalton's theory could explain the laws of chemical combination.

1.7 ATOMIC AND MOLECULAR MASSES

After having some idea about the terms atoms and molecules, it is appropriate here to understand what we mean by atomic and molecular masses.

1.7.1 Atomic Mass

The atomic mass or the mass of an atom is actually very-very small because atoms are extremely small. Today, we have sophisticated techniques e.g., mass spectrometry for determining the atomic masses fairly accurately. But, in the nineteenth century, scientists could determine mass of one atom **relative** to another by experimental means, as has been mentioned earlier. Hydrogen, being lightest atom was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it. However, the present system of atomic masses is based on carbon - 12 as the standard and has been agreed upon in 1961. Here, Carbon - 12 is one of the *isotopes* of carbon and can be represented as ^{12}C. In this system, ^{12}C is assigned a mass of exactly 12 atomic mass unit (**amu**) and masses of all other atoms are given relative to this standard. One **atomic mass unit** is defined as a mass exactly equal to one-twelfth the mass of one carbon - 12 atom.

And 1 amu $= 1.66056\ 10^{-24}$ g

Mass of an atom of hydrogen

$= 1.6736\ 10^{-24}$ g

Thus, in terms of amu, the mass

of hydrogen atom $= \dfrac{1.6736 \times 10^{-2}}{1.66056 \times 10^{-}}$

$= 1.0078$ amu

$= 1.0080$ amu

Similarly, the mass of oxygen - 16 (^{16}O) atom would be 15.995 amu.

Today, **'amu'** has been replaced by **'u'** which is known as **unified mass**.

When we use atomic masses of elements in calculations, we actually use *average atomic masses* of elements which are explained below.

1.7.2 Average Atomic Mass

Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence),

the average atomic mass of that element can be computed. For example, carbon has the following three isotopes with relative abundances and masses as shown against each of them.

Isotope	Relative Abundance (%)	Atomic Mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2 10^{-10}	14.00317

From the above data, the average atomic mass of carbon will come out to be :

(0.98892) (12 u) + (0.01108) (13.00335 u) + (2 10^{-12}) (14.00317 u)

= 12.011 u

Similarly, average atomic masses for other elements can be calculated. In the periodic table of elements, the atomic masses mentioned for different elements actually represented their average atomic masses.

1.7.3 Molecular Mass

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together. For example, molecular mass of methane which contains one carbon atom and four hydrogen atoms can be obtained as follows :

Molecular mass of methane,

(CH_4) = (12.011 u) + 4 (1.008 u)

= 16.043 u

Similarly, molecular mass of water (H_2O)

= 2 atomic mass of hydrogen + 1 atomic mass of oxygen

= 2 (1.008 u) + 16.00 u

= 18.02 u

Problem 1.1

Calculate molecular mass of glucose ($C_6H_{12}O_6$) molecule.

Solution

Molecular mass of glucose ($C_6H_{12}O_6$)

= 6(12.011 u) + 12(1.008 u) + 6(16.00 u)

= (72.066 u) + (12.096 u) + (96.00 u)

= 180.162 u

1.7.4 Formula Mass

Some substances such as sodium chloride do not contain discrete molecules as their constituent units. In such compounds, positive (sodium) and negative (chloride) entities are arranged in a three-dimensional structure, as shown in Fig. 1.10.

Fig. 1.10 *Packing of Na^+ and Cl^- ions in sodium chloride*

It may be noted that in sodium chloride, one Na^+ is surrounded by six Cl and *vice versa*.

The formula such as NaCl is used to calculate the **formula mass** instead of molecular mass as in the solid state sodium chloride does not exist as a single entity.

Thus, formula mass of sodium chloride = atomic mass of sodium + atomic mass of chlorine

= 23.0 u + 35.5 u = 58.5 u

1.8 MOLE CONCEPT AND MOLAR MASSES

Atoms and molecules are extremely small in size and their numbers in even a small amount of any substance is really very large. To handle such large numbers, a unit of similar magnitude is required.

Just as we denote one dozen for 12 items, score for 20 items, gross for 144 items, we use the idea of mole to count entities at the microscopic level (i.e. atoms/molecules/particles, electrons, ions, etc).

In SI system, **mole** (symbol, mol) was introduced as seventh base quantity for the amount of a substance.

One mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the ^{12}C isotope. It may be emphasised that the mole of a substance always contain the same number of entities, no matter what the substance may be. In order to determine this number precisely, the mass of a carbon–12 atom was determined by a mass spectrometer and found to be equal to $1.992648 \quad 10^{-23}$ g. Knowing that one mole of carbon weighs 12 g, the number of atoms in it is equal to :

$$\frac{12\,g/1}{1.992648 \times 10}$$

$$= 6.0221367$$

This number of entities in 1 mol is so important that it is given a separate name and symbol, known as **'Avogadro'** constant, denoted by (N_A) in honour of Amedeo Avogadro. To really appreciate largeness of this number, let us write it with all the zeroes without using any powers of ten.

602213670000000000000000

Hence, so many entities (atoms, molecules or any other particle) constitute one mole of a particular substance.

We can, therefore, say that 1 mol of hydrogen atoms = $6.022 \quad 10^{23}$ atoms

1 mol of water molecules = $6.022 \quad 10^{23}$ water molecules

Fig. 1.11 *One mole of various substances*

1 mol of sodium chloride = $6.022 \quad 10^{23}$ formula units of sodium chloride

Having defined the mole, it is easier to know mass of one mole of the substance or the constituent entities. **The mass of one mole of a substance in grams is called its molar mass.** The molar mass in grams is numerically equal to atomic/molecular/formula mass in u.

Molar mass of water = 18.02 g
Molar mass of sodium chloride = 58.5 g

1.9 PERCENTAGE COMPOSITION

So far, we were dealing with the number of entities present in a given sample. But many a time, the information regarding the percentage of a particular element present in a compound is required. Suppose an unknown or new compound is given to you, the first question you would ask is: what is its formula or what are its constituents and in what ratio are they present in the given compound? For known compounds also, such information provides a check whether the given sample contains the same percentage of elements as is present in a pure sample. In other words, one can check the purity of a given sample by analysing this data.

Let us understand it by taking the example of water (H_2O). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows :

Mass % of an element =

$$\frac{\text{mass of that e}}{\text{molar}}$$

Molar mass of water = 18.02 g

Mass % of hydrogen $= \frac{2 \quad 1.008}{18.02} \quad 10$

$= 11.18$

Mass % of oxygen $= \frac{16.00}{18.02} \quad 100$

$= 88.79$

Let us take one more example. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Molecular formula of ethanol is : C_2H_5OH

Molar mass of ethanol is : (2 12.01 + 6 1.008 + 16.00) g

= 46.068 g

Mass per cent of carbon

$$= \frac{24.02\,g}{46.068\,g} \quad 10 \quad = 52.14\%$$

Mass per cent of hydrogen

$$= \frac{6.048\,g}{46.068\,g} \quad 10 \quad = 13.13\%$$

Mass per cent of oxygen

$$= \frac{16.00\,g}{46.068\,g} \quad 10 \quad = 34.73\%$$

After understanding the calculation of per cent of mass, let us now see what information can be obtained from the per cent composition data.

1.9.1 Empirical Formula for Molecular Formula

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound whereas the **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound.

If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following example illustrates this sequence.

Problem 1.2

A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas ?

Solution

Step 1. Conversion of mass per cent to grams.

Since we are having mass per cent, it is convenient to use 100 g of the compound as the starting material. Thus, in the 100 g sample of the above compound, 4.07g hydrogen is present, 24.27g carbon is present and 71.65 g chlorine is present.

Step 2. Convert into number moles of each element

Divide the masses obtained above by respective atomic masses of various elements.

Moles of hydrogen $= \frac{4.07\,g}{1.008\,g} = 4.04$

Moles of carbon $= \frac{24.27\,g}{12.01\,g} = 2.021$

Moles of chlorine $= \frac{71.65\,g}{35.453\,g} = 2.021$

Step 3. Divide the mole value obtained above by the smallest number

Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl.

In case the ratios are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient.

Step 4. Write empirical formula by mentioning the numbers after writing the symbols of respective elements.

CH_2Cl is, thus, the empirical formula of the above compound.

Step 5. Writing molecular formula

(a) Determine empirical formula mass

Add the atomic masses of various atoms present in the empirical formula.

For CH_2Cl, empirical formula mass is

12.01 + 2 1.008 + 35.453

= 49.48 g

(b) Divide Molar mass by empirical formula mass

$$\frac{\text{Molar 1}}{\text{Empirical for}}$$

= 2 = (n)

(c) Multiply empirical formula by n obtained above to get the molecular formula

Empirical formula = CH_2Cl, n = 2. Hence molecular formula is $C_2H_4Cl_2$.

1.10 STOICHIOMETRY AND STOICHIOMETRIC CALCULATIONS

The word 'stoichiometry' is derived from two Greek words - *stoicheion* (meaning *element*) and *metron* (meaning *measure*). Stoichiometry, thus, deals with the calculation of masses (sometimes volumes also) of the reactants and the products involved in a chemical reaction. Before understanding how to calculate the amounts of reactants required or those produced in a chemical reaction, let us study what information is available from the *balanced* chemical equation of a given reaction. Let us consider the combustion of methane. A balanced equation for this reaction is as given below :

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

Balancing a chemical equation

According to the law of conservation of mass, a balanced chemical equation has the *same number of atoms of each element on both sides* of the equation. Many chemical equations can be balanced by *trial and error*. Let us take the reactions of a few metals and non-metals with oxygen to give oxides

$4\,Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ (a) balanced equation

$2\,Mg(s) + O_2(g) \rightarrow 2MgO(s)$ (b) balanced equation

$P_4(s) + O_2\,(g) \rightarrow P_4O_{10}(s)$ (c) unbalanced equation

Equations (a) and (b) are balanced since there are same number of metal and oxygen atoms on each side of equations. However equation (c) is not balanced. In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance it, we must place the coefficient 5 on the left of oxygen on the left side of the equation to balance the oxygen atoms appearing on the right side of the equation.

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$ balanced equation

Now let us take combustion of propane, C_3H_8. This equation can be balanced in steps.

Step 1 Write down the correct formulas of reactants and products. Here propane and oxygen are reactants, and carbon dioxide and water are products.

$C_3H_8(g) + O_2(g) \rightarrow CO_2\,(g) + H_2O(l)$ unbalanced equation

Step 2 *Balance the number of C atoms:* Since 3 carbon atoms are in the reactant, therefore, three CO_2 molecules are required on the right side.

$C_3H_8\,(g) + O_2\,(g) \rightarrow 3CO_2\,(g) + H_2O\,(l)$

Step 3 *Balance the number of H atoms* : on the left there are 8 hydrogen atoms in the reactants however, each molecule of water has two hydrogen atoms, so four molecules of water will be required for eight hydrogen atoms on the right side.

$C_3H_8\,(g) + O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(l)$

Step 4 *Balance the number of O atoms*: There are ten oxygen atoms on the right side ($3 \times 2 = 6$ in CO_2 and $4 \times 1 = 4$ in water). Therefore, five O_2 molecules are needed to supply the required ten oxygen atoms.

$C_3H_8\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(l)$

Step 5 *Verify that the number of atoms of each element is balanced in the final equation.* The equation shows three carbon atoms, eight hydrogen atoms, and ten oxygen atoms on each side.

All equations that have correct formulas for all reactants and products can be balanced. Always remember that subscripts in formulas of reactants and products cannot be changed to balance an equation.

Here, methane and dioxygen are called *reactants* and carbon dioxide and water are called *products*. Note that all the reactants and the products are gases in the above reaction and this has been indicated by letter (g) in the brackets next to its formula. Similarly, in the case of solids and liquids, (s) and (l) are written respectively.

The coefficients 2 for O_2 and H_2O are called stoichiometric coefficients. Similarly the coefficient for CH_4 and CO_2 is one in each case. They represent the number of molecules (and moles as well) taking part in the reaction or formed in the reaction.

Thus, according to the above chemical reaction,

- One **mole** of CH_4(g) reacts with two **moles** of O_2(g) to give one **mole** of CO_2(g) and two **moles** of H_2O(g)
- One **molecule** of CH_4(g) reacts with 2 **molecules** of O_2(g) to give one **molecule** of CO_2(g) and 2 molecules of H_2O(g)
- 22.4 L of CH_4(g) reacts with 44.8 L of O_2 (g) to give 22.4 L of CO_2 (g) and 44.8 L of H_2O(g)
- 16 g of CH_4 (g) reacts with 2 32 g of O_2 (g) to give 44 g of CO_2 (g) and 2 18 g of H_2O (g).

From these relationships, the given data can be interconverted as follows :

mass *f* mole

$$\frac{\text{Mass}}{\text{Volume}} = \text{Den}$$

Problem 1.3

Calculate the amount of water (g) produced by the combustion of 16 g of methane.

Solution

The balanced equation for combustion of methane is :

$$CH_4(g) + 2O_2$$

(i) 16 g of CH_4 corresponds to one mole.

(ii) From the above equation, 1 mol of CH_4 (g) gives 2 mol of H_2O (g).

2 mol of water (H_2O) = 2 (2+16)
= 2 18 = 36 g

$$1 \text{ mol } H_2O = 18 \text{ g } H_2O \Rightarrow \frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O} = 1$$

$$\text{Hence 2 mol } H_2O \quad \frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O}$$

$$= 2 \quad 18 \text{ g } H_2O = 36 \text{ g } H_2O$$

Problem 1.4

How many moles of methane are required to produce 22 g CO_2 (g) after combustion?

Solution

According to the chemical equation,

$$CH_4(g) + 2O_2$$

44 g CO_2 (g) is obtained from 16 g CH_4 (g).

[Q 1 mol CO_2(g) is obtained from 1 mol of CH_4(g)]

mole of CO_2 (g)

$$= 22 \text{ g } CO_2 \text{ (g)} \quad \frac{1 \text{ mol } CO_2 \text{ (g)}}{44 \text{ g } CO_2 \text{ (g)}}$$

= 0.5 mol CO_2 (g)

Hence, 0.5 mol CO_2 (g) would be obtained from 0.5 mol CH_4 (g) or 0.5 mol of CH_4 (g) would be required to produce 22 g CO_2 (g).

1.10.1 Limiting Reagent

Many a time, the reactions are carried out when the reactants are not present in the amounts as required by a balanced chemical reaction. In such situations, one reactant is in excess over the other. The reactant which is present in the lesser amount gets consumed after sometime and after that no further reaction takes place whatever be the amount of the other reactant present. Hence, the reactant which gets consumed, limits the amount of product formed and is, therefore, called the **limiting reagent**.

In performing stoichiometric calculations, this aspect is also to be kept in mind.

Problem 1.5

50.0 kg of N_2 (g) and 10.0 kg of H_2 (g) are mixed to produce NH_3 (g). Calculate the NH_3 (g) formed. Identify the limiting reagent in the production of NH_3 in this situation.

Solution

A balanced equation for the above reaction is written as follows :

Calculation of moles :

$N_2(g) + 3H_2($

moles of N_2

$= 50.0 \text{ kg } N_2 \quad \frac{1000 \text{ g } N_2}{1 \text{ kg } N_2}$

$= 17.86 \quad 10^2$ mol

moles of H_2

$= 10.00 \text{ kg } H_2 \quad \frac{1000 \text{ g } H_2}{1 \text{ kg } H_2} \quad \frac{}{2}$

$= 4.96 \quad 10^3$ mol

According to the above equation, 1 mol N_2 (g) requires 3 mol H_2 (g), for the reaction. Hence, for 17.86 10^2 mol of N_2, the moles of H_2 (g) required would be

$17.86 \quad 10^2 \text{ mol } N_2 \quad \frac{3 \text{ mol } H_2 \text{ (g)}}{1 \text{ mol } N_2 \text{ (g)}}$

$= 5.36 \quad 10^3 \text{ mol } H_2$

But we have only 4.96 10^3 mol H_2. Hence, dihydrogen is the limiting reagent in this case. So NH_3(g) would be formed only from that amount of available dihydrogen *i.e.*, 4.96 10^3 mol

Since 3 mol H_2(g) gives 2 mol NH_3(g)

$4.96 \quad 10^3 \text{ mol } H_2 \text{ (g)} \quad \frac{2 \text{ mol } NH_3 \text{ (g)}}{3 \text{ mol } H_2 \text{ (g)}}$

$= 3.30 \quad 10^3 \text{ mol } NH_3$ (g)

3.30 10^3 mol NH_3 (g) is obtained.

If they are to be converted to grams, it is done as follows :

1 mol NH_3 (g) = 17.0 g NH_3 (g)

$3.30 \quad 10^3 \text{ mol } NH_3 \text{ (g)} \quad \frac{17.0 \text{ g } NH_3 \text{ (g)}}{1 \text{ mol } NH_3 \text{ (g)}}$

$= 3.30 \quad 10^3 \quad 17 \text{ g } NH_3$ (g)

$= 56.1 \quad 10^3 \text{ g } NH_3$

$= 56.1 \text{ kg } NH_3$

1.10.2 Reactions in Solutions

A majority of reactions in the laboratories are carried out in solutions. Therefore, it is important to understand as how the amount of substance is expressed when it is present in the form of a solution. The concentration of a solution or the amount of substance present in its given volume can be expressed in any of the following ways.

1. Mass per cent or weight per cent (w/w %)
2. Mole fraction
3. Molarity
4. Molality

Let us now study each one of them in detail.

1. Mass per cent

It is obtained by using the following relation:

Mass per cen

Problem 1.6

A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.

Solution

Mass per cent

$= \frac{2 \text{ g}}{2 \text{ g of A} + 18}$

$= \frac{2 \text{ g}}{20 \text{ g}} \times 100$

= 10 %

2. Mole Fraction

It is the ratio of number of moles of a particular component to the total number of moles of the solution. If a substance 'A' dissolves in substance 'B' and their number of moles are n_A and n_B respectively; then the mole fractions of A and B are given as

$$\text{Mole fraction} = \frac{\text{No. of m}}{\text{No. of moles}} = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction} = \frac{\text{No. of m}}{\text{No. of moles}} = \frac{n_B}{n_A + n_B}$$

3. Molarity

It is the most widely used unit and is denoted by M. It is defined as the number of moles of the solute in 1 litre of the solution. Thus,

$$\text{Molarity (M)} = \frac{\text{No. of m}}{\text{Volume of s}}$$

Suppose we have 1 M solution of a substance, say NaOH and we want to prepare a 0.2 M solution from it.

1 M NaOH means 1 mol of NaOH present in 1 litre of the solution. For 0.2 M solution we require 0.2 moles of NaOH in 1 litre solution.

Hence, we have to take 0.2 moles of NaOH and make the solution to 1 litre.

Now how much volume of concentrated (1M) NaOH solution be taken which contains 0.2 moles of NaOH can be calculated as follows:

If 1 mol is present in 1 L or 1000 mL

then 0.2 mol is present in

$$\frac{1000 \text{ mL}}{1 \text{ mol}} \times 0.$$

= 200 mL

Thus, 200 mL of 1M NaOH are taken and enough water is added to dilute it to make it 1 litre.

In fact for such calculations, a general formula, $M_1 \quad V_1 = M_2 \quad V_2$ where M and V are molarity and volume respectively can be used. In this case, M_1 is equal to 0.2; V_1 = 1000 mL and, M_2 = 1.0; V_2 is to be calculated. Substituting the values in the formula:

$$0.2 \text{ M} \quad 1000 \text{ mL} = 1.0 \text{ M} \quad V_2$$

$$\therefore V_2 = \frac{0.2 \text{ M}}{1} = 200 \text{ mL}$$

Note that the **number of moles of solute** (NaOH) was 0.2 in 200 mL and *it has remained the same*, i.e., 0.2 even after dilution (in 1000 mL) as we have changed just the amount of solvent (i.e. water) and have not done anything with respect to NaOH. But keep in mind the concentration.

Problem 1.7

Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Solution

Since molarity (M)

$$= \frac{\text{No. of m}}{\text{Volume of}}$$

$$= \frac{\text{Mass of Na}}{}$$

$$= \frac{4 \text{ g} / 40 \text{ g}}{0.250 \text{ L}}$$

= 0.4 mol L^{-1}

= 0.4 M

Note that molarity of a solution depends upon temperature because volume of a solution is temperature dependent.

4. Molality

It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m.

$$\text{Thus, Molality (m)} = \frac{\text{No. of mole}}{\text{Mass of so}}$$

Problem 1.8

The density of 3 M solution of NaCl is 1.25 g mL^{-1}. Calculate molality of the solution.

Solution

M = 3 mol L^{-1}

Mass of NaCl
in 1 L solution = 3 58.5 = 175.5 g

Mass of
1L solution = 1000 1.25 = 1250 g
(since density = 1.25 g mL^{-1})

Mass of
water in solution = 1250 –175.5
= 1074.5 g

$$\text{Molality} = \frac{\text{No. of mole}}{\text{Mass of so}}$$

$$= \frac{3 \text{ mol}}{1.0745 \text{ kg}}$$

$$= 2.79\ m$$

Often in a chemistry laboratory, a solution of a desired concentration is prepared by diluting a solution of known higher concentration. The solution of higher concentration is also known as stock solution. Note that molality of a solution does not change with temperature since mass remains unaffected with temperature.

SUMMARY

The study of chemistry is very important as its domain encompasses every sphere of life. Chemists study the properties and structure of substances and the changes undergone by them. All substances contain matter which can exist in three states – solid, liquid or gas. The constituent particles are held in different ways in these states of matter and they exhibit their characteristic properties. Matter can also be classified into elements, compounds or mixtures. An **element** contains particles of only one type which may be **atoms** or **molecules**. The compounds are formed where atoms of two or more elements combine in a fixed ratio to each other. Mixtures occur widely and many of the substances present around us are mixtures.

When the properties of a substance are studied, measurement is inherent. The quantification of properties requires a system of measurement and units in which the quantities are to be expressed. Many systems of measurement exist out of which the English and the Metric Systems are widely used. The scientific community, however, has agreed to have a uniform and common system throughout the world which is abbreviated as SI units (International System of Units).

Since measurements involve recording of data which are always associated with a certain amount of uncertainty, the proper handling of data obtained by measuring the quantities is very important. The measurements of quantities in chemistry are spread over a wide range of 10^{-31} to 10^{+23}. Hence, a convenient system of expressing the numbers in **scientific notation** is used. The uncertainty is taken care of by specifying the number of **significant figures** in which the observations are reported. The **dimensional analysis** helps to express the measured quantities in different systems of units. Hence, it is possible to interconvert the results from one system of units to another.

The combination of different atoms is governed by basic laws of chemical combination – these being the **Law of Conservation of Mass, Law of Definite Properties, Law of Multiple Proportions, Gay Lussac's Law of Gaseous Volumes** and **Avogadro Law**. All these laws led to the **Dalton's atomic theory** which states that atoms are building blocks of matter. The **atomic mass** of an element is expressed relative to ^{12}C isotope of carbon which has an exact value of 12. Usually, the atomic mass used for an element is

the **average atomic mass** obtained by taking into account the natural abundance of different isotopes of that element. The **molecular mass** of a molecule is obtained by taking sum of the atomic masses of different atoms present in a molecule. The **molecular formula** can be calculated by determining the mass per cent of different elements present in a compound and its molecular mass.

The number of atoms, molecules or any other particles present in a given system are expressed in the terms of **Avogadro constant** ($6.022 \quad 10^{23}$). This is known as **1 mol** of the respective particles or entities.

Chemical reactions represent the chemical changes undergone by different elements and compounds. A **balanced** chemical equation provides a lot of information. The coefficients indicate the molar ratios and the respective number of particles taking part in a particular reaction. The quantitative study of the reactants required or the products formed is called **stoichiometry**. Using stoichiometric calculations, the amounts of one or more reactant(s) required to produce a particular amount of product can be determined and vice-versa. The amount of substance present in a given volume of a solution is expressed in number of ways, e.g., mass per cent, mole fraction, molarity and molality.

EXERCISES

1.1 Calculate the molecular mass of the following :

(i) H_2O (ii) CO_2 (iii) CH_4

1.2 Calculate the mass per cent of different elements present in sodium sulphate (Na_2SO_4).

1.3 Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass.

1.4 Calculate the amount of carbon dioxide that could be produced when

(i) 1 mole of carbon is burnt in air.

(ii) 1 mole of carbon is burnt in 16 g of dioxygen.

(iii) 2 moles of carbon are burnt in 16 g of dioxygen.

1.5 Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass per cent of nitric acid in it being 69%.

1.7 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$) ?

1.8 Determine the molecular formula of an oxide of iron in which the mass per cent of iron and oxygen are 69.9 and 30.1 respectively.

1.9 Calculate the atomic mass (average) of chlorine using the following data :

	% Natural Abundance	Molar Mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

1.10 In three moles of ethane (C_2H_6), calculate the following :

(i) Number of moles of carbon atoms.

(ii) Number of moles of hydrogen atoms.

(iii) Number of molecules of ethane.

1.11 What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume up to 2L?

1.12 If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

1.13 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below :

1Pa = 1N m^{-2}

If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

1.14 What is the SI unit of mass? How is it defined?

1.15 Match the following prefixes with their multiples:

	Prefixes	**Multiples**
(i)	micro	10^6
(ii)	deca	10^9
(iii)	mega	10^{-6}
(iv)	giga	10^{-15}
(v)	femto	10

1.16 What do you mean by significant figures ?

1.17 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(i) Express this in percent by mass.

(ii) Determine the molality of chloroform in the water sample.

1.18 Express the following in the scientific notation:

(i) 0.0048

(ii) 234,000

(iii) 8008

(iv) 500.0

(v) 6.0012

1.19 How many significant figures are present in the following?

(i) 0.0025

(ii) 208

(iii) 5005

(iv) 126,000

(v) 500.0

(vi) 2.0034

1.20 Round up the following upto three significant figures:

(i) 34.216

(ii) 10.4107

(iii) 0.04597

(iv) 2808

1.21 The following data are obtained when dinitrogen and dioxygen react together to form different compounds :

	Mass of dinitrogen	**Mass of dioxygen**
(i)	14 g	16 g
(ii)	14 g	32 g

(iii)	28 g	32 g
(iv)	28 g	80 g

(a) Which law of chemical combination is obeyed by the above experimental data? Give its statement.

(b) Fill in the blanks in the following conversions:

(i) 1 km = ... mm = ... pm

(ii) 1 mg = ... kg = ... ng

(iii) 1 mL = ... L = ... dm^3

1.22 If the speed of light is 3.0 10^8 m s^{-1}, calculate the distance covered by light in 2.00 ns.

1.23 In a reaction

$A + B_2 \rightarrow AB_2$

Identify the limiting reagent, if any, in the following reaction mixtures.

(i) 300 atoms of A + 200 molecules of B

(ii) 2 mol A + 3 mol B

(iii) 100 atoms of A + 100 molecules of B

(iv) 5 mol A + 2.5 mol B

(v) 2.5 mol A + 5 mol B

1.24 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:

$N_2(g) + H_2(g) \rightarrow 2NH_3(g)$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.

(ii) Will any of the two reactants remain unreacted?

(iii) If yes, which one and what would be its mass?

1.25 How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different?

1.26 If ten volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced?

1.27 Convert the following into basic units:

(i) 28.7 pm

(ii) 15.15 pm

(iii) 25365 mg

1.28 Which one of the following will have largest number of atoms?

(i) 1 g Au (s)

(ii) 1 g Na (s)

(iii) 1 g Li (s)

(iv) 1 g of $Cl_2(g)$

1.29 Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040.

1.30 What will be the mass of one ^{12}C atom in g ?

1.31 How many significant figures should be present in the answer of the following calculations?

(i) $\frac{0.02856 \times 29}{0.5}$ (ii) 5×5.364

(iii) 0.0125 + 0.7864 + 0.0215

1.32 Use the data given in the following table to calculate the molar mass of naturally occuring *argon* isotopes:

Isotope	**Isotopic molar mass**	**Abundance**
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

1.33 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

1.34 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide , 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

1.35 Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3$ (s) + 2 HCl (aq) $\rightarrow$ $CaCl_2$ (aq) + CO_2(g) + H_2O(l)
What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

1.36 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction
4 HCl (aq) + MnO_2(s) $\rightarrow$ $2H_2O$ (l) + $MnCl_2$(aq) + Cl_2 (g)
How many grams of HCl react with 5.0 g of manganese dioxide?

UNIT 2

STRUCTURE OF ATOM

Objectives

After studying this unit you will be able to

- know about the discovery of electron, proton and neutron and their characteristics;
- describe Thomson, Rutherford and Bohr atomic models;
- understand the important features of the quantum mechanical model of atom;
- understand nature of electromagnetic radiation and Planck's quantum theory;
- explain the photoelectric effect and describe features of atomic spectra;
- state the de Broglie relation and Heisenberg uncertainty principle;
- define an atomic orbital in terms of quantum numbers;
- state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity;
- write the electronic configurations of atoms.

"The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements."

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word '*a tomio*' which means 'uncutable' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter (Unit 1).

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into sub-atomic particles, i.e., electrons, protons and neutrons—a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behaviour of one element from other in terms of both physical and chemical properties,

- to explain the formation of different kinds of molecules by the combination of different atoms and,
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

2.1 SUB-ATOMIC PARTICLES

Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century. However, in this section we will talk about only two particles, namely electron and proton.

2.1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in class XII. These results suggested the particulate nature of electricity.

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other".

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. It is depicted in Fig. 2.1. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through a

Fig. 2.1(a) *A cathode ray discharge tube*

stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed(same thing happens in a television set) [Fig. 2.1(b)].

Fig. 2.1(b) *A cathode ray discharge tube with perforated anode*

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 2.2).

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons.**

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituent of all the atoms.

2.1.2 Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \quad 10^{11} \text{ C kg}^{-1} \qquad (2.1)$$

Where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is –e.

Fig. 2.2 *The apparatus to determine the charge to the mass ratio of electron*

2.1.3 Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found that the charge on the electron to be – 1.6 10^{-19} C. The present accepted value of electrical charge is – 1.6022 10^{-19} C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} =$$

$$= 9.1094 \ 10^{-31} \text{ kg} \qquad (2.2)$$

2.1.4 Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as **canal rays.** The characteristics of these positively charged particles are listed below.

(i) unlike cathode rays, the positively charged particles depend upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles is found to depend on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called **proton**. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles. When electrically neutral particles having a mass slightly greater than that of the protons was emitted. He named these particles as **neutrons**. The important properties of these fundamental particles are given in Table 2.1.

Millikan's Oil Drop Method

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets.The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, $q = n$ e, where n = 1, 2, 3... .

Fig. 2.3 *The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

2.2 ATOMIC MODELS

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different

Table 2.1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.00054	0
Proton	p	$+1.6022\times10^{-19}$	+1	1.67262×10^{-27}	1.00727	1
Neutron	n	0	0	1.67493×10^{-27}	1.00867	1

atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by J. J. Thomson and Ernest Rutherford are discussed below.

2.2.1 Thomson Model of Atom

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.** This model

Fig.2.4 *Thomson model of atom*

can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. *An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom.* Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhalm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since Röentgen did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called targets. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electro-magnetic character (Section 2.3.1).

Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as **radioactivity** and the elements known as **radioactive elements.** This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed that three kinds of rays i.e., α, β- and γ-rays are emitted. Rutherford found that α-rays consists of high energy particles carrying two units of positive charge and four unit of atomic mass. He

concluded that α- particles are helium nuclei as when α- particles combined with two electrons yielded helium gas. β-rays are negatively charged particles similar to electrons. The γ-rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, α-particles are the least, followed by β-rays (100 times that of α–particles) and γ-rays (1000 times of that α-particles).

2.2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous **α–particle scattering experiment** is represented in Fig. 2.5. A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.

A. *Rutherford's scattering experiment*

B. *Schematic molecular view of the gold foil*

Fig.2.5 *Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.*

The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α– particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that :

(i) most of the α– particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α– particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180 .

On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom :

(i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected.

(ii) A few positively charged α– particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α– particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate

this difference in size by realising that if a cricket ball represents a nucleus, then the radius of atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom (after the discovery of protons). According to this model :

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called **nucleus** by Rutherford.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

2.2.3 Atomic Number and Mass Number

The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number (Z). For example, the number of protons in the hydrogen nucleus is 1, in sodium atom it is 11, therefore their atomic numbers are 1 and 11 respectively. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively.

Atomic number (Z) = number of protons in the nucleus of an atom

= number of electrons in a nuetral atom (2.3)

While the positive charge of the nucleus is due to protons, the mass of the nucleus, due to protons and neutrons. As discussed earlier protons and neutrons present in the nucleus are collectively known as **nucleons**. The total number of nucleons is termed as **mass number (A)** of the atom.

mass number (A) = number of protons (Z) + number of neutrons (n) (2.4)

2.2.4 Isobars and Isotopes

The composition of any atom can be represented by using the normal element symbol (X) with super-script on the left hand side as the atomic mass number (A) and subscript (Z) on the left hand side as the atomic number (i.e., $^{A}_{Z}X$).

Isobars are the atoms with same mass number but different atomic number for example, $^{14}_{6}C$ and $^{14}_{7}N$. On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. In other words (according to equation 2.4), it is evident that difference between the isotopes is due to the presence of different number of neutrons present in the nucleus. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called **protium($^{1}_{1}H$)**. Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called **deuterium** ($^{2}_{1}D$, 0.015%) and the other one possessing 1 proton and 2 neutrons is called **tritium ($^{3}_{1}T$)**. The latter isotope is found in trace amounts on the earth. Other examples of commonly occuring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons ($^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$); chlorine atoms containing 18 and 20 neutrons besides 17 protons ($^{35}_{17}Cl$, $^{37}_{17}Cl$).

Lastly an important point to mention regarding isotopes is that *chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus.* Number of neutrons present in the nucleus have very little effect on the chemical properties of an element. Therefore, all the isotopes of a given element show same chemical behaviour.

Problem 2.1

Calculate the number of protons, neutrons and electrons in $^{80}_{35}Br$.

Solution

In this case, $^{80}_{35}Br$, Z = 35, A = 80, species is neutral

Number of protons = number of electrons = Z = 35

Number of neutrons = 80 – 35 = 45, (equation 2.4)

Problem 2.2

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons

= 16 + 16 = 32

Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = 18 – 16 = 2. Symbol is $^{32}_{16}S^{2-}$.

Note : Before using the notation $^{A}_{Z}X$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (2.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by A–Z, whether the species is neutral or ion.

2.2.5 Drawbacks of Rutherford Model

Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. Further, the coulomb force (kq_1q_2/r^2 where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force $\left(G.\frac{m_1m_2}{r^2}\right)$ where m_1 and m_2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements. The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. However, when a body is moving in an orbit, it undergoes acceleration (even if the body is moving with a constant speed in an orbit, it must accelerate because of changing direction). So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary around the nucleus. If the electrons were stationary, electrostatic attraction between

* *Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.*

the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson's model of atom.

Another serious drawback of the Rutherford model is that it says nothing about the electronic structure of atoms i.e., how the electrons are distributed around the nucleus and what are the energies of these electrons.

2.3 DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra which can be explained only by assuming quantized (Section 2.4) electronic energy levels in atoms.

2.3.1 Wave Nature of Electromagnetic Radiation

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called **electromagnetic waves** or **electromagnetic radiation**.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscules). It was only in the 19th century when wave nature of light was established.

Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character (Fig. 2.6). Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 2.6.

Fig.2.6 *The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.*

(ii) Unlike sound waves or water waves, electromagnetic waves do not require medium and can move in vacuum.

(iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called **electromagnetic spectrum** (Fig. 2.7). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6 Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region

around 10^{16}Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called **visible light**. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

(iv) Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterised by the properties, namely, frequency (ν) and wavelength (λ).

The SI unit for frequency (ν) is hertz (Hz, s^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second.

Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig.2.7 shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies.

In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0 10^8 m s^{-1} (2.997925 10^8 m s^{-1}, to be precise). This is called **speed of light** and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (2.5).

$$c = \nu \lambda \qquad (2.5)$$

The other commonly used quantity specially in spectroscopy, is the **wavenumber** ($\bar{\nu}$). *It is defined as the number of wavelengths per unit length.* Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1} (not SI unit).

Problem 2.3

The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Solution

The wavelength, λ, is equal to c/ν, where c is the speed of electromagnetic radiation in vacuum and ν is the

Fig. 2.7 *(a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum .*

frequency. Substituting the given values, we have

$$\lambda = \frac{c}{\nu}$$

$$= \frac{3.00 \times 10^8 \text{ m}}{1368 \text{ kHz}}$$

$$= \frac{3.00 \times 10^8 \text{ m}}{1368 \times 10^3 \text{ s}}$$

$$= 219.3 \text{ m}$$

This is a characteristic radiowave wavelength.

Problem 2.4

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). (1nm = 10^{-9} m)

Solution

Using equation 2.5, frequency of violet light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times}{400}$$

$$= 7.50 \quad 10^{14} \text{ Hz}$$

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 1}{750 \times 1} \qquad = 4.00 \quad 10^{14} \text{ Hz}$$

The range of visible spectrum is from 4.0 10^{14} to 7.5 10^{14} Hz in terms of frequency units.

Problem 2.5

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution

(a) Calculation of wavenumber ($\bar{\nu}$)

$$\lambda = 5800 \text{Å} = 58$$

$$= 58$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800 \quad 1}$$

$$= 1.724$$

$$= 1.724$$

(b) Calculation of the frequency (ν)

$$\nu = \frac{c}{\lambda} = \frac{3 \quad 10^8}{5800}$$

2.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies (black -body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature

(iv) line spectra of atoms with special reference to hydrogen.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation was given by Max Planck in 1900. This phenomenon is given below:

When solids are heated they emit radiation over a wide range of wavelengths. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. In terms of

* *Diffraction is the bending of wave around an obstacle.*

** *Interference is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the algebraic or vector sum of disturbances at that point resulting from each interfering wave.*

frequency, it means that the radiation emitted goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies in the lower frequency region while blue colour belongs to the higher frequency region of the electromagnetic spectrum. *The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation.* The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature. At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength, as shown in Fig. 2.8.

Fig. 2.8 *Wavelength-intensity relationship*

The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner, a belief popular at that time. Planck gave the name **quantum** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation (2.6).

$$E = h\nu \qquad (2.6)$$

The proportionality constant, 'h' is known as Planck's constant and has the value $6.626\ 10^{-34}$ J s.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown in Fig.2.9. The phenomenon is called

Fig.2.9 *Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.*

Max Planck
(1858 - 1947)

Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

Photoelectric effect. The results observed in this experiment were:

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [ν = (4.3 to 4.6) 10^{14} Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light (ν = 5.1–5.2 10^{14} Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (ν_0) for potassium metal is 5.0 10^{14} Hz.

Albert Einstein (1879 - 1955)

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point,

Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0; Table 2.2), then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 2.7.

$$h\nu = h\nu_0 + \frac{1}{2}m \qquad (2.7)$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it

Table 2.2 Values of Work Function (W_0) for a Few Metals

Metal	Li	Na	K	Mg	Cu	Ag
W_0 /ev	2.42	2.3	2.25	3.7	4.8	4.3

could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Problem 2.6

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$E = h\nu$

$h = 6.626 \quad 10^{-34}$ J s

$\nu = 5 \quad 10^{14}$ s^{-1} (given)

$E = (6.626 \quad 10^{-34}$ J s) $\quad (5 \quad 10^{14}$ s$^{-1})$

$= 3.313 \quad 10^{-19}$ J

Energy of one mole of photons

$= (3.313 \quad 10^{-19}$ J) $\quad (6.022 \quad 10^{23}$ mol$^{-1})$

$= 199.51$ kJ mol^{-1}

Problem 2.7

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

Power of the bulb = 100 watt

= 100 J s^{-1}

Energy of one photon $E = h\nu = hc/\lambda$

$$= \frac{6.626 \times 10^{-3}}{4(}$$

$= 4.969 \times 10^{-1}$

Number of photons emitted

$$\frac{100 \text{ J s}^{-1}}{4.969 \times 10^{-19} \text{ J}}$$

Problem 2.8

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68×10^5 J mol^{-1}. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted ?

Solution

The energy (E) of a 300 nm photon is given by

$h\nu = hc/\lambda$

$$= \frac{6.626 \times 1}{}$$

$= 6.626 \times 10^{-19}$ J

The energy of one mole of photons

$= 6.626 \times 10^{19}$ J $\times 6.022 \times 10^{23}$ mol^{-1}

$= 3.99 \times 10^5$ J mol^{-1}

The minimum energy needed to remove a mole of electrons from sodium

$= (3.99 - 1.68)\ 10^5$ J mol^{-1}

$= 2.31 \times 10^5$ J mol^{-1}

The minimum energy for one electron

$$= \frac{2.31\times}{6.022\times10^{23}}$$

$$= 3.84\times10^{-19}$$

This corresponds to the wavelength

$$\therefore \lambda = \frac{hc}{E}$$

$$= \frac{6.626\times1}{}$$

$$= 517 \text{ nm}$$

(This corresponds to green light)

Problem 2.9

The threshold frequency ν_0 for a metal is 7.0×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times10^{15}$ s^{-1} hits the metal.

Solution

According to Einstein's equation

Kinetic energy = $\frac{1}{2} m_e v^2 = h(\nu - \nu_0)$

$= (6.626 \times10^{-34}$ J s) $(1.0 \times 10^{15}$ s^{-1} – 7.0×10^{14} $s^{-1})$

$= (6.626 \times10^{-34}$ J s) $(10.0 \times10^{14}$ s^{-1} – 7.0×10^{14} $s^{-1})$

$= (6.626 \times10^{-34}$ J s) $(3.0 \times10^{14}$ $s^{-1})$

$= 1.988 \times10^{-19}$ J

2.3.3 Evidence for the quantized* Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called **continuous spectrum.** Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.2.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be **"excited"**. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from

* *The restriction of any property to discrete values is called quantization.*

red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig, 2.10)

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of *discrete frequencies*. The hydrogen spectrum consists of several series of *lines* named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula :

$$\bar{\nu} = 109,677 \left(\qquad (2.8)$$

where n is an integer equal to or greater than 3 (i.e., n = 3,4,5,....)

Fig. 2.10 ***(a) Atomic emission.*** *The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum.* ***(b) Atomic absorption****. When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.*

The series of lines described by this formula are called the **Balmer series**. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

$$\bar{\nu} = 109,677 \left(\qquad \right. \tag{2.9}$$

where n_1=1,2.....

$n_2 = n_1 + 1,\ n_1 + 2$.....

The value 109,677 cm^{-1} is called the **Rydberg constant** for hydrogen. The first five series of lines that correspond to n_1 = 1, 2, 3, 4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively, Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig 2.11 shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes more and more complex for heavier atom. There are however certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are : What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

2.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of hydrogen atom structure and its spectrum. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

ii) The energy of an electron in the orbit does not change with time. However, the

Table 2.3 The Spectral Lines for Atomic Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

Fig. 2.11 *Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)*

electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner.

Angular Momentum

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e, moving in a circular path of radius r around the nucleus,

angular momentum = $I \times \omega$

Since $I = m_e r^2$, and $\omega = v/r$ where v is the linear velocity,

$\therefore$ angular momentum = $m_e r^2 \times v/r = m_e vr$

iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 -}{h} \qquad (2.10)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

Niels Bohr (1885–1962)

Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

iv) The angular momentum of an electron in a given stationary state can be expressed as in equation (2.11)

$$m_e v r = n.\frac{h}{2\pi} \qquad n = 1,2,3..... \qquad (2.11)$$

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered $n = 1,2,3.....$ These integral numbers (Section 2.6.2) are known as **Principal quantum numbers**.

b) The radii of the stationary states are expressed as :

$$r_n = n^2 a_0 \qquad (2.12)$$

where a_0 = 52,9 pm. Thus the radius of the first stationary state, called the **Bohr radius**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n=1). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -R_H\left(\frac{1}{n^2}\right. \qquad n = 1,2,3.... \qquad (2.13)$$

where R_H is called **Rydberg constant** and its value is 2.18×10^{-18} J. The energy of the lowest state, also called as the ground state, is $E_1 = -2.18\times10^{-18}\ (\frac{1}{1^2}) = -2.18\times10^{-18}$ J. The energy of the stationary state for n = 2, will be : $E_2 = -2.18\times10^{-18}$J $(\frac{1}{2^2}) = -0.545\times10^{-18}$ J.

Fig. 2.11 depicts the energies of different

stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 2.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (2.13) so that E_∞=0. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by n=1 which corresponds to the most stable orbit. We call this the ground state.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number = n = ∞ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and n = ∞.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 1($$ (2.14)

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z}$$ (2.15)

where Z is the atomic number and has values 2, 3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

2.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 2.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (2.16)

$$\Delta E = E_f - E_i$$ (2.16)

Combining equations (2.13) and (2.16)

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) -$$ (where n_i and n_f stand for initial orbit and final orbits)

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

(2,17)

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\right.$$

$$= \frac{2.18 \times 10^{-18}}{6.626 \times 10^{-34}}$$ (2.18)

$$= 3.29 \times 10^{15} \left(\frac{}{} \right. \qquad (2.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc} \left(\frac{1}{n} \right. \qquad (2.20)$$

$$= \frac{3.29 \times 10^{15} s}{3 \times 10^{8} m s^{-}}$$

$$= 1.09677 \times 1(\qquad (2.21)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, ΔE is negative and energy is released.

The expression (2.17) is similar to that used by Rydberg (2.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Problem 2.10

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (2.17)

$$\Delta E = 2.18 \times 1($$

$$= -4.58 \times 1$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h}$$

$$= \frac{4.58 \quad 10^{-1}}{6.626 \quad 10^{-3}}$$

$$= 6.91 \quad 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times}{6.91}$$

Problem 2.11

Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18 \times 1}{1} \qquad \text{atom}^{-1}$$

For He^+, $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18 \times 1}{}$$

The radius of the orbit is given by equation (2.15)

$$r_n = \frac{(0.0529 \text{ n}}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_n = \frac{(0.0529 \text{ n}}{2}$$

2.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+, Li^{2+}, Be^{3+}, and so on). However, Bohr's model was too simple to account for the following points.

i) It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed

by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

ii) It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

2.5 TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were :

1. Dual behaviour of matter,
2. Heisenberg uncertainty principle.

2.5.1 Dual Behaviour of Matter

The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (2.22)$$

where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

Louis de Broglie (1892-1987)

Louis de Broglie, a French physicist, studied history as an undergraduate in the early 1910's. His interest turned to science as a result of his assignment to radio communications in World War I. He received his Dr. Sc. from the University of Paris in 1924. He was professor of theoretical physics at the University of Paris from 1932 untill his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively.

Problem 2.12

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Solution

According to de Brogile equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.2}{(0.1}$$

= 6.626 10^{-34} m (J = kg m^2 s^{-2})

Problem 2.13

The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

Solution

Since K. E. = ½ mv^2

$$v = \left(\frac{2K.E.}{m}\right)^{1/2} :$$

$= 812 \text{ m s}^{-1}$

$$\lambda = \frac{h}{m\,v} = \frac{\quad}{(9.1}$$

$= 8967 \quad 10^{-10}$ m = 896.7 nm

Problem 2.14

Calculate the mass of a photon with wavelength 3.6 Å.

Solution

$\lambda = 3.6$ Å = 3.(

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{\quad}{(3.6}$$

$= 6.135 \quad 10^{-29}$ kg

2.5.2 Heisenberg's Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. **It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.**

Mathematically, it can be given as in equation (2.23).

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi} \qquad (2.23)$$

or $\Delta x \times \Delta(mv_x) \geq$

or $\Delta x \times \Delta v_x \geq \frac{h}{4\pi r}$

where Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(v_x)$ is small), then the position of the electron will be uncertain (Δx will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless, In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light $\left(p = \frac{h}{\lambda}\right)$ would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles.** The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible

simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron.

The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples.

If uncertainty principle is applied to an object of mass, say about a milligram (10^{-6} kg), then

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

$$= \frac{6.62}{4 \quad 3.1}$$

The value of $\Delta v \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that **in dealing with milligram-sized or heavier objects, the associated uncertainties are hardly of any real consequence.**

In the case of a microscopic object like an electron on the other hand. $\Delta v.\Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11 10^{-31} kg., according to Heisenberg uncertainty principle

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

$$= \frac{6.626}{4 \quad 3.1416}$$

$$= 10^{\ 4} m^2 s^{\ 1}$$

It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10^{-8} m, then the uncertainty Δv in velocity would be

$$\frac{10^{-4} m^2 s^{-1}}{10^{-8} m} \approx 1($$

which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. **It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.**

Problem 2.15

A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

Solution

$$\Delta x \, \Delta p = \frac{h}{4\pi} \text{ or}$$

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

$$\Delta v = \frac{}{4 \quad 3.14 \quad 0}$$

$= 0.579 \ 10^7$ m s^{-1} (1J = 1 kg $m^2 s^{-2}$

$= 5.79 \ 10^6$ m s^{-1}

Problem 2.16

A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Werner Heisenberg (1901-1976) Werner Heisenberg (1901-1976) received his Ph.D. in physics from the University of Munich in 1923. He then spent a year working with Max Born at Gottingen and three years with Niels Bohr in Copenhagen. He was professor of physics at the University of Leipzig from 1927 to 1941. During World War II, Heisenberg was in charge of German research on the atomic bomb. After the war he was named director of Max Planck Institute for physics in Gottingen. He was also accomplished mountain climber. Heisenberg was awarded the Nobel Prize in Physics in 1932.

Solution

The uncertainty in the speed is 2%, i.e.,

$$45 \quad \frac{2}{100} = 0.9$$

Using the equation (2.22)

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

$$= \frac{6}{4 \;\; 3.14 \;\; 40}$$

$$= 1.46 \;\; 10^{-33} \text{ m}$$

This is nearly ~ 10^{18} times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Erwin Schrödinger (1887-1961)

Erwin Schrödinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrödinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrödinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrödinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.

Reasons for the Failure of the Bohr Model

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. *Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.* In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

2.6 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum

mechanics was developed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as

$\hat{H}\psi = E\psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ.

Hydrogen Atom and the Schrödinger Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number** n, **azimuthal quantum number** l **and magnetic quantum number** m_l) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrödinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That

is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.

4. **An atomic orbital is the wave function ψ for an electron in an atom**. Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These "one electron orbital wave functions" or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. ***From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.***

2.6.1 Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, l and m_l.

The principal quantum number 'n' is a positive integer with value of n = 1,2,3..... . The principal quantum number determines the *size and to large extent the energy of the orbital.* For hydrogen atom and hydrogen like species (He^+, Li^{2+}, ... etc.) energy and size of the orbital depends only on 'n'.

The principal quantum number also identifies the **shell**. With the increase in the value of 'n', the number of allowed orbital increases and **are given by 'n^2' All the orbitals of a given value of 'n' constitute a single shell of atom** and are represented by the following letters

n =	1	2	3	4	.....
Shell =	K	L	M	N	.....

Size of an orbital increases with increase of principal quantum number 'n'. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n.

Azimuthal quantum number. 'l' is also known as **orbital angular momentum or subsidiary quantum number.** It defines the three dimensional shape of the orbital. For a given value of n, l can have n values ranging from 0 to $n-1$, that is, for a given value of n, the possible value of l are : l = 0, 1, 2, ... (n–1)

For example, when n = 1, value of l is only 0. For n = 2, the possible value of l can be 0 and 1. For n = 3, the possible l values are 0, 1 and 2.

Each shell consists of one or more **sub-shells** or **sub-levels**. The number of sub-shells in a principal shell is equal to the value of n. For example in the first shell (n = 1), there is only one sub-shell which corresponds to l = 0. There are two sub-shells (l = 0, 1) in the second shell (n = 2), three (l = 0, 1, 2) in third shell (n = 3) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols.

Value for l :	0	1	2	3	4	5	.....
notation for sub-shell	s	p	d	f	g	h	.....

Table 2.4 shows the permissible values of 'l' for a given principal quantum number and the corresponding sub-shell notation.

Table 2.4 Subshell Notations

n	l	Subshell notation
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

Magnetic orbital quantum number. 'm_l' gives information about **the spatial orientation of the orbital with respect to standard set of co-ordinate axis.** For any **sub-shell (defined by 'l' value)** $2l+1$ values of m_l are possible and these values are given by :

$m_l = -l, -(l-1), -(l-2) \ldots 0, 1 \ldots (l-2), (l-1), l$

Thus for $l = 0$, the only permitted value of $m_l = 0$, [2(0)+1 = 1, one s orbital]. For $l = 1$, m_l can be −1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For $l = 2$, $m_l = -2, -1, 0, +1$ and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of m_l are derived from l and that the value of l are derived from n.

Each orbital in an atom, therefore, is defined by a set of values for n, l and m_l. An orbital described by the quantum numbers $n = 2$, $l = 1$, $m_l = 0$ is an orbital in the p sub-shell of the second shell. The following chart gives the relation between the sub-shell and the number of orbitals associated with it.

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
number of orbitals	1	3	5	7	9	11

Electron spin 's' : The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers.

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth

Orbit, orbital and its importance

Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and m_l) and its value depends upon the coordinates of the electron. ψ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital.

quantum number known as the **electron spin quantum number (m_s).** An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers m_s which can take the values of +½ or –½. These are called the **two spin states of the electron** and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different m_s values (one +½ and the other –½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information :

i) ***n*** defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n subshells in the nth shell. ***l*** identifies the subshell and determines the shape of the orbital (see section 2.6.2). There are ($2l$+1) orbitals of each type in a subshell, that is, one s orbital (l = 0), three p orbitals (l = 1) and five d orbitals (l = 2) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) $\boldsymbol{m_l}$ designates the orientation of the orbital. For a given value of l, m_l has ($2l$+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) $\boldsymbol{m_s}$ refers to orientation of the spin of the electron.

Problem 2.17

What is the total number of orbitals associated with the principal quantum number n = 3 ?

Solution

For n = 3, the possible values of l are 0, 1 and 2. Thus there is one 3s orbital (n = 3, l = 0 and m_l = 0); there are three 3p orbitals (n = 3, l = 1 and m_l = –1, 0, +1); there are five 3d orbitals (n = 3, l = 2 and m_l = –2, –1, 0, +1+, +2).

Therefore, the total number of orbitals is 1+3+5 = 9

The same value can also be obtained by using the relation; number of orbitals = n^2, i.e. 3^2 = 9.

Problem 2.18

Using s, p, d, f notations, describe the orbital with the following quantum numbers

(a) n = 2, l = 1, (b) n = 4, l = 0, (c) n = 5, l = 3, (d) n = 3, l = 2

Solution

	n	l	orbital
a)	2	1	2p
b)	4	0	4s
c)	5	3	5f
d)	3	2	3d

2.6.2 Shapes of Atomic Orbitals

The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. Fig. 2.12(a), (page 54) gives such plots for 1s (n = 1, l = 0) and 2s (n = 2, l = 0) orbitals.

According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for 1s and 2s orbitals is given in Fig. 2.12(b), (page 54). Here again, you may note that the curves for 1s and 2s orbitals are different.

It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move

Fig. 2.12 *The plots of (a) the orbital wave function $\psi(r)$; (b) the variation of probability density $\psi^2(r)$ as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.*

away from it. On the other hand, for 2*s* orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of *r* increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that *ns*-orbital has $(n - 1)$ nodes, that is, number of nodes increases with increase of principal quantum number *n*. In other words, number of nodes for 2*s* orbital is one, two for 3*s* and so on.

These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density of the dots in a region represents electron probability density in that region.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of

Fig. 2.13 *(a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.*

probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1*s* and 2*s* orbitals are given in Fig. 2.13(b). One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a *s* orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

* *If probability density $|\psi|^2$ is constant on a given surface, $|\psi|$ is also constant over the surface. The boundary surface for $|\psi|^2$ and $|\psi|$ are identical.*

Thus we see that 1*s* and 2*s* orbitals are spherical in shape. In reality all the *s*-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in *n*, that is, 4*s* > 3*s* > 2*s* > 1*s* and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three 2*p* orbitals (l = 1) are shown in Fig. 2.14. In these diagrams, the nucleus is at the origin. Here, unlike *s*-orbitals, the boundary surface diagrams are not spherical. Instead each *p* orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that *there is no simple relation between the values of* m_l *(1, 0 and +1) and the x, y and z directions.* For our purpose, it is sufficient to remember that,

Fig. 2.14 *Boundary surface diagrams of the three 2p orbitals.*

because there are three possible values of m_l, there are, therefore, three *p* orbitals whose axes are mutually perpendicular. Like *s* orbitals, *p* orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various *p* orbitals is 4*p* > 3*p* > 2*p*. Further, like s orbitals, the probability density functions for *p*-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the *n* –2, that is number of radial node is 1 for 3*p* orbital, two for 4*p* orbital and so on.

For l = 2, the orbital is known as *d*-orbital and the minimum value of principal quantum number (*n*) has to be 3. as the value of *l* cannot be greater than *n*–1. There are five m_l values (–2, –1, 0, +1 and +2) for l = 2 and thus there are five *d* orbitals. The boundary surface diagram of *d* orbitals are shown in Fig. 2.15, (page 56).

The five *d*-orbitals are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d_{z^2}, is different from others, but all five 3*d* orbitals are equivalent in energy. The *d* orbitals for which *n* is greater than 3 (4*d*, 5*d*...) also have shapes similar to 3*d* orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the n*p* and n*d* orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing *z*-axis. These are called angular nodes and number of angular nodes are given by '*l*', i.e., one angular node for *p* orbitals, two angular nodes for '*d*' orbitals and so on. **The total number of nodes are given by (*n*–1), i.e., *sum of l* angular nodes and (*n* – *l* – 1) radial nodes.**

2.6.3 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by the principal quantum

Fig. 2.15 *Boundary surface diagrams of the five 3d orbitals.*

number. Thus the energy of the orbitals increases as follows :

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \quad (2.23)$$

and is depicted in Fig. 2.16. Although the shapes of $2s$ and $2p$ orbitals are different, an electron has the same energy when it is in the $2s$ orbital as when it is present in $2p$ orbital. The orbitals having the same energy are called **degenerate.** The $1s$ in a hydrogen atom, as said earlier, corresponds to the most

Fig. 2.16 *Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms. Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom. In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.*

stable condition and is called the **ground state** and an electron residing in this orbital is most strongly held by the nucleus. An electron in the $2s$, $2p$ or higher orbitals in a hydrogen atom is in **excited state.**

The energy of an electron in a multi-electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, s, p, d, f... all have different energies. The main reason for having different energies of the subshells is the mutual repulsion among the electrons in a multi-electron atoms. The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged

nucleus. In multi-electron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion terms between every electron and other electrons present in the atom. Thus the stability of an electron in multi-electron atom is because total attractive interactions are more than the repulsive interactions. In general, the repulsive interaction of the electrons in the outer shell with the electrons in the inner shell are more important. On the other hand, the attractive interactions of an electron increases with increase of positive charge (Ze) on the nucleus. Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge on the nucleus (Ze), but will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the **shielding of the outshell electrons from the nucleus by the inner shell electrons,** and the net positive charge experienced by the electron from the nucleus is known as **effective nuclear charge** ($Z_{eff}\, e$). Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increase with increase of nuclear charge. In other words, the energy of interaction between, the nucleus and electron (that is orbital energy) decreases (that is more negative) with the increase of atomic number (**Z**).

Both the attractive and repulsive interactions depend upon the shell and shape of the orbital in which the electron is present. For example, being spherical in shape, the s orbital shields the electrons from the nucleus more effectively as compared to p orbital. Similarly because of difference in their shapes, p orbitals shield the electrons from the nucleus more than the d orbitals, even though all these orbitals are present in the same shell. Further due to spherical shape, s orbital electron spends more time close to the nucleus in comparison to p orbital and p orbital spends more time in the vicinity of nucleus in comparison to d orbital. In other words, for a given shell (principal quantum number), the Z_{eff} experienced by the orbital decreases with increase of azimuthal quantum number (l), that is, the *s orbital will be more tightly bound to the nucleus than p orbital and p orbital in turn will be better tightly bound than the d orbital*. The energy of s orbital will be lower (more negative) than that of p orbital and that of p orbital will be less, than that of d orbital and so on. Since the extent of shielding of the nucleus is different for different orbitals, it leads to the splitting of the energies of the orbitals within the same shell (or same principal quantum number), that is, energy of the orbital, as mentioned earlier, depends upon the values of n and l. Mathematically, the dependence of energies of the orbitals on n and l are quite complicated but one simple rule is that of combined value of n and l. **The lower the value of ($n + l$) for an orbital, the lower is its energy. If two orbitals have the same value of ($n + l$), the orbital with lower value of n will have the lower energy.** The Table 2.5, (page 57) illustrates the ($n + l$) rule and Fig. 2.16 depicts the energy levels of multi-electrons atoms. It may be noted that different subshells of a particular shell have different energies in case of multi-electrons atoms. However, in hydrogen atom, these have the same energy. Lastly it may be mentioned here that **energies of the orbitals in the same subshell decrease with increase in the atomic number (Z_{eff})**. For example, energy of 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K).

2.6.4 Filling of Orbitals in Atom

The filling of electrons into the orbitals of different atoms takes place according to the *aufbau* principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau Principle

The word '*aufbau*' in German means 'building up'. The building up of orbitals means the

Table 2.5 Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) Rule

Orbital	Value of n	Value of l	Value of (n + l)	
1s	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	
2p	2	1	2 + 1 = 3	2p (n=2) has lower energy than
3s	3	0	3 + 0 = 3	3s (n=3)
3p	3	1	3 + 1 = 4	3p (n =3) has lower energy than
4s	4	0	4 + 0 = 4	4s (n =4)
3d	3	2	3 + 2 = 5	3d (n =3) has lower energy than
4p	4	1	4 + 1 =5	4p (n =4)

filling up of orbitals with electrons. The principle states : **In the ground state of the atoms, the orbitals are filled in order of their increasing energies.** In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...

The order may be remembered by using the method given in Fig. 2.17. Starting from the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left.

Fig.2.17 *Order of filling of orbitals*

Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle : **No two electrons in an atom can have the same set of four quantum numbers.** Pauli exclusion principle can also be stated as : **"Only two electrons may exist in the same orbital and these electrons must have opposite spin."** This means that the two electrons can have the same value of three quantum numbers n, l and m_l, but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1s comprises of one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d

subshells, the maximum number of electrons can be 6 and 10 and so on. This can be summed up as : **the maximum number of electrons in the shell with principal quantum number *n* is equal to $2n^2$.**

Hund's Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called **degenerate orbitals).** It states : **pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.**

Since there are three *p*, five *d* and seven *f* orbitals, therefore, the pairing of electrons will start in the *p*, *d* and *f* orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry (see Section, 2.6.7).

2.6.5 Electronic Configuration of Atoms

The distribution of electrons into orbitals of an atom is called its **electronic configuration**. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The electronic configuration of different atoms can be represented in two ways. For example :

(i) $s^a p^b d^c$ ..... notation

(ii) Orbital diagram

In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c, ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow (↑) a positive spin or an arrow (↓) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers.

The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1*s*. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1*s* orbital. The second electron in helium (He) can also occupy the 1*s* orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram.

The third electron of lithium (Li) is not allowed in the 1*s* orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2*s* orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2*s* orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2\ 2s^2$ (see Table 2.6, page 62 for the electronic configurations of elements).

In the next six elements-boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the 2*p* orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows :

The electronic configuration of the elements sodium (Na, $1s^2 2s^2 2p^6 3s^1$) to argon (Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the $3s$ and $3p$ orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to argon can be written as (Na, [Ne]$3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called **valence electrons.** For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the $4s$ orbital, being lower in energy than the $3d$ orbitals, is occupied by one and two electrons respectively.

A new pattern is followed beginning with scandium (Sc). The $3d$ orbital, being lower in energy than the $4p$ orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five $3d$ orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in $3d$ orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and half-filled orbitals have extra stability (that is, lower energy). Thus p^3, p^6, d^5, d^{10}, f^7, f^{14} etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10} configuration (Section 2.6.7)[*caution: exceptions do exist*]

With the saturation of the $3d$ orbitals, the filling of the $4p$ orbital starts at gallium (Ga) and is complete at krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the $5s$, $4d$ and $5p$ orbitals are similar to that of $4s$, $3d$ and $4p$ orbitals as discussed above. Then comes the turn of the $6s$ orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in $4f$ and $5d$ orbitals. After this, filling of $6p$, then $7s$ and finally $5f$ and $6d$ orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known elements (as determined by spectroscopic methods) are tabulated in Table 2.6.

One may ask what is the utility of knowing the electron configuration? The modern approach to the chemistry, infact, depends almost entirely on electronic distribution to understand and explain chemical behaviour. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are non-metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern chemical knowledge.

2.6.6 Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in Section 2.6.5. However, in certain elements such as Cu, or Cr, where the two subshells ($4s$ and $3d$) differ slightly in their energies, an electron shifts from a subshell of lower energy ($4s$) to a subshell of higher energy ($3d$), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively and not $3d^4 4s^2$ and $3d^9 4s^2$. It has been found that there is extra stability associated with these electronic configurations.

Causes of Stability of Completely Filled and Half Filled Sub-shells

The completely filled and completely half filled sub-shells are stable due to the following reasons:

1. Symmetrical distribution of electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here *3d*) have equal energy but different spatial distribution. Consequently, their shielding of one-another is relatively small and the electrons are more strongly attracted by the nucleus.

2. Exchange Energy : The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 2.18). As a result the exchange energy is maximum and so is the stability.

You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic repulsion energy, and (iii) larger exchange energy. Details about the exchange energy will be dealt with in higher classes.

4 exchange by electron 1

3 exchange by electron 2

2 exchange by electron 3

1 exchange by electron 4

Fig. 2.18 *Possible exchange for a d^5 configuration*

Table 2.6 Electronic Configurations of the Elements

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

** Elements with exceptional electronic configurations*

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			
La*	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce*	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6			2			
Gd*	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt*	78	2	2	6	2	6	10	2	6	10	14	2	6	9		2			
Au*	79	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6	2
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2
Ds	110	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	8	2
Rg**	111	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10	1

*** Elements with atomic number 112 and above have been reported but not yet fully authenticated and named.*

SUMMARY

Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react. The first atomic theory, proposed by John Dalton in 1808, regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: **electrons**, **protons** and **neutrons**. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom.

Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom is made of a tiny positively charged **nucleus**, at its centre with electrons revolving around it in **circular orbits**. **Rutherford model**, which resembles the solar system, was no doubt an improvement over **Thomson model** but it could not account for the stability of the atom i.e., why the electron does not fall into the nucleus. Further, it was also silent about the electronic structure of atoms i.e., about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. **Bohr model**, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts **Heisenberg uncertainty principle**.

Erwin Schrödinger, in 1926, proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglie's concept of **wave-particle duality** and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function(s) (ψ) (which in fact are the mathematical functions) of the electron associated with each energy state]. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number** n, **azimuthal quantum number** l and **magnetic quantum number** m_l) arise as a natural consequence in the solution of the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into **shells**. The shells, in turn, are thought to consist of one or more **subshells** and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He^+, Li^{2+} etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and l. The lower the value of $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n + l)$ value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in

accordance with **Pauli exclusion principle** (no two electrons in an atom can have the same set of four quantum numbers) and **Hund's rule of maximum multiplicity** (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of atoms.

EXERCISES

2.1 (i) Calculate the number of electrons which will together weigh one gram.
(ii) Calculate the mass and charge of one mole of electrons.

2.2 (i) Calculate the total number of electrons present in one mole of methane.
(ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of ^{14}C. (Assume that mass of a neutron = 1.675×10^{-27} kg).
(iii) Find (a) the total number and (b) the total mass of protons in 34 mg of NH_3 at STP.
Will the answer change if the temperature and pressure are changed ?

2.3 How many neutrons and protons are there in the following nuclei ?
$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$,

2.4 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)
(i) Z = 17 , A = 35.
(ii) Z = 92 , A = 233.
(iii) Z = 4 , A = 9.

2.5 Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wavenumber ($\bar{\nu}$) of the yellow light.

2.6 Find energy of each of the photons which
(i) correspond to light of frequency 3 10^{15} Hz.
(ii) have wavelength of 0.50 Å.

2.7 Calculate the wavelength, frequency and wavenumber of a light wave whose period is 2.0 10^{-10} s.

2.8 What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy?

2.9 A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate (i) the energy of the photon (eV), (ii) the kinetic energy of the emission, and (iii) the velocity of the photoelectron (1 eV= 1.6020 10^{-19} J).

2.10 Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

2.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second.

2.12 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

2.13 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2?

2.14 How much energy is required to ionise a H atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from $n = 1$ orbit).

2.15 What is the maximum number of emission lines when the excited electron of a H atom in $n = 6$ drops to the ground state?

2.16 (i) The energy associated with the first orbit in the hydrogen atom is $-2.18 \quad 10^{-18}$ J atom^{-1}. What is the energy associated with the fifth orbit?
(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

2.17 Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen.

2.18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

2.19 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

2.20 Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 m s^{-1}.

2.21 The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wavelength.

2.22 Which of the following are isoelectronic species i.e., those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

2.23 (i) Write the electronic configurations of the following ions: (a) H^- (b) Na^+ (c) O^{2-} (d) F^-
(ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1$ (b) $2p^3$ and (c) $3p^5$?
(iii) Which atoms are indicated by the following configurations ?
(a) [He] $2s^1$ (b) [Ne] $3s^2\ 3p^3$ (c) [Ar] $4s^2\ 3d^1$.

2.24 What is the lowest value of n that allows g orbitals to exist?

2.25 An electron is in one of the $3d$ orbitals. Give the possible values of n, l and m_l for this electron.

2.26 An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.

2.27 Give the number of electrons in the species H_2^+, H_2 and O_2^+

2.28 (i) An atomic orbital has $n = 3$. What are the possible values of l and m_l ?
(ii) List the quantum numbers (m_l and l) of electrons for $3d$ orbital.
(iii) Which of the following orbitals are possible?
$1p$, $2s$, $2p$ and $3f$

2.29 Using s, p, d notations, describe the orbital with the following quantum numbers.
(a) n=1, l=0; (b) $n = 3$; l=1 (c) $n = 4$; l =2; (d) n=4; l=3.

2.30 Explain, giving reasons, which of the following sets of quantum numbers are not possible.

(a)	$n = 0$,	$l = 0$,	$m_l = 0$,	$m_s = +½$
(b)	$n = 1$,	$l = 0$,	$m_l = 0$,	$m_s = -½$
(c)	$n = 1$,	$l = 1$,	$m_l = 0$,	$m_s = +½$
(d)	$n = 2$,	$l = 1$,	$m_l = 0$,	$m_s = -½$

(e) $n = 3$, $l = 3$, $m_l = -3$, $m_s = +½$

(f) $n = 3$, $l = 1$, $m_l = 0$, $m_s = +½$

2.31 How many electrons in an atom may have the following quantum numbers?
(a) $n = 4$, $m_s = -½$ (b) $n = 3$, $l = 0$

2.32 Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

2.33 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum ?

2.34 Calculate the energy required for the process

$He^+(g) \rightarrow He^{2+}(g) + e^-$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J atom^{-1}

2.35 If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long.

2.36 2 10^8 atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.

2.37 The diameter of zinc atom is 2.6 Å.Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.

2.38 A certain particle carries 2.5 10^{-16}C of static electric charge. Calculate the number of electrons present in it.

2.39 In Milikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is –1.282 10^{-18}C, calculate the number of electrons present on it.

2.40 In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum etc. have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium etc. is used, what difference would be observed from the above results ?

2.41 Symbols $^{79}_{35}Br$ and ^{79}Br can be written, whereas symbols $^{35}_{79}Br$ and ^{35}Br are not acceptable. Answer briefly.

2.42 An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.

2.43 An ion with mass number 37 possesses one unit of negative charge. If the ion conatins 11.1% more neutrons than the electrons, find the symbol of the ion.

2.44 An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol to this ion.

2.45 Arrange the following type of radiations in increasing order of frequency: (a) radiation from microwave oven (b) amber light from traffic signal (c) radiation from FM radio (d) cosmic rays from outer space and (e) X-rays.

2.46 Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6 10^{24}, calculate the power of this laser.

2.47 Neon gas is generally used in the sign boards. If it emits strongly at 616 nm, calculate (a) the frequency of emission, (b) distance traveled by this radiation in 30 s (c) energy of quantum and (d) number of quanta present if it produces 2 J of energy.

2.48 In astronomical observations, signals observed from the distant stars are generally

weak. If the photon detector receives a total of 3.15 10^{-18} J from the radiations of 600 nm, calculate the number of photons received by the detector.

2.49 Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano second range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is 2.5 10^{15}, calculate the energy of the source.

2.50 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calcualte the frequency of each transition and energy difference between two excited states.

2.51 The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron.

2.52 Following results are observed when sodium metal is irradiated with different wavelengths. Calculate (a) threshold wavelength and, (b) Planck's constant.

λ (nm) 500 450 400

v 10^{-5} (cm s^{-1}) 2.554.35 5.35

2.53 The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal.

2.54 If the photon of the wavelength 150 pm strikes an atom and one of tis inner bound electrons is ejected out with a velocity of 1.5 10^{7} m s^{-1}, calculate the energy with which it is bound to the nucleus.

2.55 Emission transitions in the Paschen series end at orbit n = 3 and start from orbit n and can be represeted as υ = 3.29 10^{15} (Hz) [$1/3^2 - 1/n^2$]

Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.

2.56 Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum.

2.57 Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is 1.6 10^{6} ms^{-1}, calculate de Broglie wavelength associated with this electron.

2.58 Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron.

2.59 If the velocity of the electron in Bohr's first orbit is 2.19 10^{6} ms^{-1}, calculate the de Broglie wavelength associated with it.

2.60 The velocity associated with a proton moving in a potential difference of 1000 V is 4.37 10^{5} ms^{-1} . If the hockey ball of mass 0.1 kg is moving with this velocity, calcualte the wavelength associated with this velocity.

2.61 If the position of the electron is measured within an accuracy of $\pm$ 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $h/4\pi_m$ 0.05 nm, is there any problem in defining this value.

2.62 The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists:

1. $n = 4, l = 2, m_l = -2, m_s = -1/2$
2. $n = 3, l = 2, m_l = 1, m_s = +1/2$

3. $n = 4, l = 1, m_l = 0, m_s = +1/2$
4. $n = 3, l = 2, m_l = -2, m_s = -1/2$
5. $n = 3, l = 1, m_l = -1, m_s = +1/2$
6. $n = 4, l = 1, m_l = 0, m_s = +1/2$

2.63 The bromine atom possesses 35 electrons. It contains 6 electrons in $2p$ orbital, 6 electrons in $3p$ orbital and 5 electron in $4p$ orbital. Which of these electron experiences the lowest effective nuclear charge ?

2.64 Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge? (i) $2s$ and $3s$, (ii) $4d$ and $4f$, (iii) $3d$ and $3p$.

2.65 The unpaired electrons in Al and Si are present in $3p$ orbital. Which electrons will experience more effective nuclear charge from the nucleus ?

2.66 Indicate the number of unpaired electrons in : (a) P, (b) Si, (c) Cr, (d) Fe and (e) Kr.

2.67 (a) How many sub-shells are associated with $n = 4$? (b) How many electrons will be present in the sub-shells having m_s value of $-1/2$ for $n = 4$?

UNIT 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Objectives

After studying this Unit, you will be able to :

- appreciate how the concept of grouping elements in accordance to their properties led to the development of Periodic Table.
- understand the Periodic Law;
- understand the significance of atomic number and electronic configuration as the basis for periodic classification;
- name the elements with $Z > 100$ according to IUPAC nomenclature;
- classify elements into *s*, *p*, *d*, *f* blocks and learn their main characteristics;
- recognise the periodic trends in physical and chemical properties of elements;
- compare the reactivity of elements and correlate it with their occurrence in nature;
- explain the relationship between ionization enthalpy and metallic character;
- use scientific vocabulary appropriately to communicate ideas related to certain important properties of atoms e.g., atomic/ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity, valence of elements.

"The Periodic Table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families. An awareness of the Periodic Table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements."

Glenn T. Seaborg

In this Unit, we will study the historical development of the Periodic Table as it stands today and the Modern Periodic Law. We will also learn how the periodic classification follows as a logical consequence of the electronic configuration of atoms. Finally, we shall examine some of the periodic trends in the physical and chemical properties of the elements.

3.1 WHY DO WE NEED TO CLASSIFY ELEMENTS ?

We know by now that the elements are the basic units of all types of matter. In 1800, only 31 elements were known. By 1865, the number of identified elements had more than doubled to 63. At present 114 elements are known. Of them, the recently discovered elements are man-made. Efforts to synthesise new elements are continuing. With such a large number of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To ease out this problem, scientists searched for a systematic way to organise their knowledge by classifying the elements. Not only that it would rationalize known chemical facts about elements, but even predict new ones for undertaking further study.

3.2 GENESIS OF PERIODIC CLASSIFICATION

Classification of elements into groups and development of Periodic Law and Periodic Table are the consequences of systematising the knowledge gained by a number of scientists through their observations and experiments. The German chemist, Johann Dobereiner in early 1800's was the first to consider the idea of trends among properties of elements. By 1829 he noted a similarity among the physical and chemical properties of several groups of three elements (**Triads**). In each case, he noticed that the middle element of each of the **Triads** had an atomic weight about half way between the atomic weights of the other two (Table 3.1). Also the properties of the middle element were in between those of the other two members. Since Dobereiner's relationship, referred to as the **Law of Triads**, seemed to work only for a few elements, it was dismissed as coincidence. The next reported attempt to classify elements was made by a French geologist, A.E.B. de Chancourtois in 1862. He arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties. This also did not attract much attention. The English chemist, John Alexander Newlands in 1865 profounded the **Law of Octaves**. He arranged the elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element (Table 3.2). The relationship was just like every eighth note that resembles the first in octaves of music. Newlands's Law of Octaves seemed to be true only for elements up to calcium. Although his idea was not widely accepted at that time, he, for his work, was later awarded Davy Medal in 1887 by the Royal Society, London.

The Periodic Law, as we know it today owes its development to the Russian chemist, Dmitri Mendeleev (1834-1907) and the German chemist, Lothar Meyer (1830-1895). Working independently, both the chemists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals. Lothar Meyer plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern. Unlike Newlands, Lothar Meyer observed a change in length of that repeating pattern. By 1868, Lothar Meyer had developed a table of the

Table 3.1 Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	**Ca**	40	**Cl**	35.5
Na	23	**Sr**	88	**Br**	80
K	39	**Ba**	137	**I**	127

Table 3.2 Newlands's Octaves

Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
At. wt.	7	9	11	12	14	16	19
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
At. wt.	23	24	27	29	31	32	35.5
Element	**K**	**Ca**					
At. wt.	39	40					

elements that closely resembles the Modern Periodic Table. However, his work was not published until after the work of Dmitri Mendeleev, the scientist who is generally credited with the development of the Modern Periodic Table.

While Dobereiner initiated the study of periodic relationship, it was Mendeleev who was responsible for publishing the Periodic Law for the first time. It states as follows :

The properties of the elements are a periodic function of their atomic weights.

Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group. Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. He fully recognized the significance of periodicity and used broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. He ignored the order of atomic weights, thinking that the atomic measurements might be incorrect, and placed the elements with similar properties together. For example, iodine with lower atomic weight than that of tellurium (Group VI) was placed in Group VII along with fluorine, chlorine, bromine because of similarities in properties (Fig. 3.1). At the same time, keeping his primary aim of arranging the elements of similar properties in the same group, he proposed that some of the elements were still undiscovered and, therefore, left several gaps in the table. For example, both gallium and germanium were unknown at the time Mendeleev published his Periodic Table. He left the gap under aluminium and a gap under silicon, and called these elements **Eka-Aluminium** and **Eka-Silicon.** Mendeleev predicted not only the existence of gallium and germanium, but also described some of their general physical properties. These elements were discovered later. Some of the properties predicted by Mendeleev for these elements and those found experimentally are listed in Table 3.3.

The boldness of Mendeleev's quantitative predictions and their eventual success made him and his Periodic Table famous. Mendeleev's Periodic Table published in 1905 is shown in Fig. 3.1.

Table 3.3 Mendeleev's Predictions for the Elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

Property	Eka-aluminium (predicted)	Gallium (found)	Eka-silicon (predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density / (g/cm^3)	5.9	5.94	5.5	5.36
Melting point /K	Low	29.78	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES

SERIES	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	-	Hydrogen H 1.008	-	-					
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Cobalt Nickel Fe Co Ni (Cu) 55.9 59 59
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	-	Ruthenium Rhodium Palladium Ru Rh Pd (Ag) 101.7 103.0 106.5
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Iodine I 126.9	
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-	
9		-	-	-	-	-	-	-	
10	-	-	-	Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184	-	Osmium Iridium Platinum Os Ir Pt (Au) 191 193 194.9
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	-	-	
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239		
	R	R_2O	RO	R_2O_3	HIGHER SALINE OXIDES RO_2	R_2O_5	RO_3	R_2O_7	RO_4
					HIGHER GASEOUS HYDROGEN COMPOUNDS RH_4	RH_3	RH_2	RH	

Fig. 3.1 *Mendeleev's Periodic Table published earlier*

Dmitri Ivanovich Mendeleev (1834-1907)

Dmitri Mendeleev was born in Tobalsk, Siberia in Russia. After his father's death, the family moved to St. Petersburg. He received his Master's degree in Chemistry in 1856 and the doctoral degree in 1865. He taught at the University of St.Petersburg where he was appointed Professor of General Chemistry in 1867. Preliminary work for his great textbook "Principles of Chemistry" led Mendeleev to propose the ***Periodic Law*** *and to construct his* ***Periodic Table*** *of elements. At that time, the structure of atom was unknown and Mendeleev's idea to consider that the properties of the elements were in someway related to their atomic masses was a very imaginative one. To place certain elements into the correct group from the point of view of their chemical properties, Mendeleev reversed the order of some pairs of elements and asserted that their atomic masses were incorrect. Mendeleev also had the foresight to leave gaps in the Periodic Table for elements unknown at that time and predict their properties from the trends that he observed among the properties of related elements. Mendeleev's predictions were proved to be astonishingly correct when these elements were discovered later.*

Mendeleev's Periodic Law spurred several areas of research during the subsequent decades. The discovery of the first two noble gases helium and argon in 1890 suggested the possibility that there must be other similar elements to fill an entire family. This idea led Ramsay to his successful search for krypton and xenon. Work on the radioactive decay series for uranium and thorium in the early years of twentieth century was also guided by the Periodic Table.

Mendeleev was a versatile genius. He worked on many problems connected with Russia's natural resources. He invented an accurate barometer. In 1890, he resigned from the Professorship. He was appointed as the Director of the Bureau of Weights and Measures. He continued to carry out important research work in many areas until his death in 1907.

You will notice from the modern Period Table (Fig. 3.2) that Mendeleev's name has been immortalized by naming the element with atomic number 101, as Mendelevium. This name was proposed by American scientist Glenn T. Seaborg, the discoverer of this element, "in recognition of the pioneering role of the great Russian Chemist who was the first to use the periodic system of elements to predict the chemical properties of undiscovered elements, a principle which has been the key to the discovery of nearly all the transuranium elements".

3.3 MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

We must bear in mind that when Mendeleev developed his **Periodic Table**, chemists knew nothing about the internal structure of atom. However, the beginning of the 20th century witnessed profound developments in theories about sub-atomic particles. In 1913, the English physicist, Henry Moseley observed regularities in the characteristic *X ray spectra* of the elements. A plot of $\sqrt{\nu}$ (where ν is frequency of *X*-rays emitted) against atomic number (Z) gave a straight line and not the plot of $\sqrt{\nu}$ *vs* atomic mass. He thereby showed that the atomic number is a more fundamental property of an element than its atomic mass. **Mendeleev's Periodic Law** was, therefore, accordingly modified. This is known as the **Modern Periodic Law** and can be stated as :

The physical and chemical properties of the elements are periodic functions of their atomic numbers.

The **Periodic Law** revealed important analogies among the 94 naturally occurring elements (neptunium and plutonium like actinium and protoactinium are also found in pitch blende – an ore of uranium). It stimulated renewed interest in Inorganic Chemistry and has carried into the present with the creation of artificially produced short-lived elements.

You may recall that the atomic number is equal to the nuclear charge (*i.e.*, number of protons) or the number of electrons in a neutral atom. It is then easy to visualize the significance of quantum numbers and electronic configurations in periodicity of elements. In fact, it is now recognized that the Periodic Law is essentially the consequence of the periodic variation in electronic configurations, which indeed determine the physical and chemical properties of elements and their compounds.

Numerous forms of Periodic Table have been devised from time to time. Some forms emphasise chemical reactions and valence, whereas others stress the electronic configuration of elements. A modern version, the so-called "**long form**" of the **Periodic Table** of the elements (Fig. 3.2), is the most convenient and widely used. The horizontal rows (which Mendeleev called **series**) are called **periods** and the vertical columns, **groups**. Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as **groups** or **families**. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA ... VIIA, VIII, IB ... VIIB and 0.

There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom*.

3.4 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100

The naming of the new elements had been traditionally the privilege of the discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversy. The new elements with very high atomic numbers are so unstable that only minute quantities, sometimes only a few atoms of them are obtained. Their synthesis and characterisation, therefore, require highly

* *Glenn T. Seaborg's work in the middle of the 20th century starting with the discovery of plutonium in 1940, followed by those of all the transuranium elements from 94 to 102 led to reconfiguration of the periodic table placing the actinoids below the lanthanoids. In 1951, Seaborg was awarded the* ***Nobel Prize*** *in chemistry for his work. Element 106 has been named Seaborgium (Sg) in his honour.*

Representative elements — GROUP NUMBER 1, 2 (I A, II A)

Representative elements — GROUP NUMBER 13–17 (III B, IV B, V B, VI B, VII B)

Noble gases — 18 (0)

d-Transition elements — GROUP NUMBER 3–12 (III A, IV A, V A, VI A, VII A, ← VIII →, I B, II B)

PERIOD NUMBER 1–7

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	I A	II A	III A	IV A	V A	VI A	VII A	← VIII →			I B	II B	III B	IV B	V B	VI B	VII B	0
	1 H $1s^1$																	2 He $1s^2$
1																		
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	–	114 Uuq	–	Uuh	–	–

f - Inner transition elements

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^06s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^16s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

Fig. 3.2 *Long form of the Periodic Table of the Elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA–VIIA, VIII, IB–VIIB and 0 for the elements.*

sophisticated costly equipment and laboratory. Such work is carried out with competitive spirit only in some laboratories in the world. Scientists, before collecting the reliable data on the new element, at times get tempted to claim for its discovery. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium whereas Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognized, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9. These are shown in Table 3.4. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 100 are shown in Table 3.5.

Table 3.4 Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Table 3.5 Nomenclature of Elements with Atomic Number Above 100

Atomic Number	Name	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassnium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Unnnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium*	Rg*
112	Ununbium	Uub	*	*
113	Ununtrium	Uut	+	
114	Ununquadium	Uuq	*	*
115	Ununpentium	Uup	+	
116	Ununhexium	Uuh	*	*
117	Ununseptium	Uus	+	
118	Ununoctium	Uuo	+	

* Official IUPAC name yet to be announced + Elements yet to be discovered

Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later permanent name and symbol are given by a vote of IUPAC representatives from each country. The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a notable scientist. As of now, elements with atomic numbers up to 112, 114 and 116 have been discovered. Elements with atomic numbers 113, 115, 117 and 118 are not yet known.

Problem 3.1

What would be the IUPAC name and symbol for the element with atomic number 120?

Solution

From Table 3.4, the roots for 1, 2 and 0 are un, bi and nil, respectively. Hence, the symbol and the name respectively are Ubn and unbinilium.

3.5 ELECTRONIC CONFIGURATIONS OF ELEMENTS AND THE PERIODIC TABLE

In the preceding unit we have learnt that an electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number (n) defines the main energy level known as **shell**. We have also studied about the filling of electrons into different subshells, also referred to as **orbitals** (s, p, d, f) in an atom. The distribution of electrons into orbitals of an atom is called its **electronic configuration**. An element's location in the Periodic Table reflects the quantum numbers of the last orbital filled. In this section we will observe a direct connection between the electronic configurations of the elements and the long form of the Periodic Table.

(a) Electronic Configurations in Periods

The period indicates the value of n for the outermost or valence shell. In other words, successive period in the Periodic Table is associated with the filling of the next higher principal energy level ($n = 1$, $n = 2$, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic **orbitals** available in the energy level that is being filled. The first period ($n = 1$) starts with the filling of the lowest level ($1s$) and therefore has two elements — hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed. The second period ($n = 2$) starts with lithium and the third electron enters the $2s$ orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the $2p$ orbitals are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period ($n = 3$) begins at sodium, and the added electron enters a $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals gives rise to the third period of 8 elements from sodium to argon. The fourth period ($n = 4$) starts at potassium, and the added electrons fill up the $4s$ orbital. Now you may note that before the $4p$ orbital is filled, filling up of $3d$ orbitals becomes energetically favourable and we come across the so called $3d$ **transition series** of elements. This starts from scandium ($Z = 21$) which has the electronic configuration $3d^1 4s^2$. The $3d$ orbitals are filled at zinc (Z=30) with electronic configuration $3d^{10} 4s^2$. The fourth period ends at krypton with the filling up of the $4p$ orbitals. Altogether we have 18 elements in this fourth period. The fifth period ($n = 5$) beginning with rubidium is similar to the fourth period and contains the $4d$ **transition series** starting at yttrium ($Z = 39$). This period ends at xenon with the filling up of the $5p$ orbitals. The sixth period ($n = 6$) contains 32 elements and successive electrons enter $6s$, $4f$, $5d$ and $6p$ orbitals, in the order — filling up of the $4f$ orbitals begins with cerium ($Z = 58$) and ends at lutetium ($Z = 71$) to give the $4f$-**inner transition series** which is called the **lanthanoid series**. The seventh period ($n = 7$) is similar to the sixth period with the successive filling up of the $7s$, $5f$, $6d$ and $7p$ orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the $5f$ orbitals after actinium ($Z = 89$) gives the $5f$-**inner transition**

series known as the **actinoid series**. The 4*f*- and 5*f*-**inner transition series** of elements are placed separately in the Periodic Table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

Problem 3.2

How would you justify the presence of 18 elements in the 5th period of the Periodic Table?

Solution

When $n = 5$, $l = 0, 1, 2, 3$. The order in which the energy of the available orbitals $4d$, $5s$ and $5p$ increases is $5s < 4d < 5p$. The total number of orbitals available are 9. The maximum number of electrons that can be accommodated is 18; and therefore 18 elements are there in the 5th period.

(b) Groupwise Electronic Configurations

Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) all have ns^1 valence shell electronic configuration as shown below.

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ **(or)** [He]$2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ **(or)** [Ne]$3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ **(or)** [Ar]$4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ **(or)** [Kr]$5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ **(or)** [Xe]$6s^1$
87	Fr	[Rn]$7s^1$

Thus it can be seen that the properties of an element have periodic dependence upon its atomic number and not on relative atomic mass.

3.6 ELECTRONIC CONFIGURATIONS AND TYPES OF ELEMENTS: *s*-, *p*-, *d*-, *f*- BLOCKS

The *aufbau* (build up) principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the Periodic Table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals. We can classify the elements into four blocks *viz.*, ***s*-block**, ***p*-block**, ***d*-block** and ***f*-block** depending on the type of atomic orbitals that are being filled with electrons. This is illustrated in Fig. 3.3. We notice two exceptions to this categorisation. Strictly, helium belongs to the *s*-block but its positioning in the *p*-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has a lone *s*-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table as shown in Fig. 3.2 and Fig. 3.3. We will briefly discuss the salient features of the four types of elements marked in the Periodic Table. More about these elements will be discussed later. During the description of their features certain terminology has been used which has been classified in section 3.7.

3.6.1 The *s*-Block Elements

The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1

Fig. 3.3 *The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broad division of elements into METALS ( ), NON-METALS ( ) and METALLOIDS ( ).*

and ns^2 outermost electronic configuration belong to the ***s*-Block Elements**. They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1+ ion (in the case of alkali metals) or 2+ ion (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. Because of high reactivity they are never found pure in nature. The compounds of the *s* block elements, with the exception of those of lithium and beryllium are predominantly ionic.

3.6.2 The *p*-Block Elements

The ***p*-Block Elements** comprise those belonging to Group 13 to 18 and these together with the ***s*-Block Elements** are called the **Representative Elements or Main Group Elements**. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. At the end of each period is a noble gas element with a closed valence shell ns^2np^6 configuration. All the orbitals in the valence shell of the **noble gases** are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of non-metals. They are the **halogens** (Group 17) and the **chalcogens** (Group 16). These two groups of elements have high negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

3.6.3 The *d*-Block Elements (Transition Elements)

These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner *d* orbitals by electrons and are therefore referred to as ***d*-Block Elements**. These elements have the general outer electronic configuration $(n\ 1)d^{1\text{-}10}ns^{0\text{-}2}$. They are all metals. They mostly form coloured ions, exhibit variable valence (oxidation states), paramagnetism and oftenly used as catalysts. However, Zn, Cd and Hg which have the electronic configuration, $(n\ 1)\ d^{10}ns^2$ do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of *s* block elements and the less active elements of Groups 13 and 14 and thus take their familiar name **"Transition Elements"**.

3.6.4 The *f*-Block Elements (Inner-Transition Elements)

The two rows of elements at the bottom of the Periodic Table, called the **Lanthanoids,** Ce(Z = 58) – Lu(Z = 71) and **Actinoids**, Th(Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n\text{-}2)f^{1\text{-}14}(n\text{-}1)d^{0\text{-}1}ns^2$. The last electron added to each element is filled in *f* orbital. These two series of elements are hence called the **Inner-Transition Elements (*f*-Block Elements)**. They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or even less by nuclear reactions and their chemistry is not fully studied. The elements after uranium are called **Transuranium Elements**.

Problem 3.3

The elements Z = 117 and 120 have not yet been discovered. In which family / group would you place these elements and also give the electronic configuration in each case.

Solution

We see from Fig. 3.2, that element with Z = 117, would belong to the halogen family (Group 17) and the electronic configuration would be [Rn] $5f^{14}6d^{10}7s^27p^5$. The element with Z = 120, will be placed in Group 2 (alkaline earth metals), and will have the electronic configuration [Uuo]$8s^2$.

3.6.5 Metals, Non-metals and Metalloids

In addition to displaying the classification of elements into ***s*-, *p*-, *d*-**, and ***f*-blocks**, Fig. 3.3 shows another broad classification of elements based on their properties. The elements can be divided into **Metals** and **Non-Metals**. Metals comprise more than 78% of all known elements and appear on the left side of the **Periodic Table**. Metals are usually solids at room temperature [mercury is an exception; gallium and caesium also have very low melting points (303K and 302K, respectively)]. Metals usually have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast, non-metals are located at the top right hand side of the **Periodic Table**. In fact, in a horizontal row, the property of elements change from metallic on the left to non-metallic on the right. Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the **Periodic Table**. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 3.3. The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering this line and running diagonally across the **Periodic Table** show properties that are characteristic of both metals and non-metals. These elements are called **Semi-metals** or **Metalloids**.

Problem 3.4

Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character : Si, Be, Mg, Na, P.

Solution

Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is: P < Si < Be < Mg < Na.

3.7 PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

There are many observable patterns in the physical and chemical properties of elements as we descend in a group or move across a period in the Periodic Table. For example, within a period, chemical reactivity tends to be high in Group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the Group 17 non-metals. Likewise within a group of representative metals (say alkali metals) reactivity increases on moving down the group, whereas within a group of non-metals (say halogens), reactivity decreases down the group. But why do the properties of elements follow these trends? And how can we explain periodicity? To answer these questions, we must look into the theories of atomic structure and properties of the atom. In this section we shall discuss the periodic trends in certain physical and chemical properties and try to explain them in terms of number of electrons and energy levels.

3.7.1 Trends in Physical Properties

There are numerous physical properties of elements such as melting and boiling points, heats of fusion and vaporization, energy of atomization, etc. which show periodic variations. However, we shall discuss the periodic trends with respect to atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity.

(a) Atomic Radius

You can very well imagine that finding the size of an atom is a lot more complicated than measuring the radius of a ball. Do you know why? Firstly, because the size of an atom (~ 1.2 Å i.e., 1.2 10^{-10} m in radius) is very small. Secondly, since the electron cloud surrounding the atom does not have a sharp boundary, the determination of the atomic size cannot be precise. In other words, there is no

practical way by which the size of an individual atom can be measured. However, an estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. One practical approach to estimate the size of an atom of a non-metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value, the "**Covalent Radius**" of the element can be calculated. For example, the bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine. For metals, we define the term "**Metallic Radius**" which is taken as half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm. For simplicity, in this book, we use the term **Atomic Radius** to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal. Atomic radii can be measured by *X*-ray or other spectroscopic methods.

The atomic radii of a few elements are listed in Table 3.6 . Two trends are obvious. We can explain these trends in terms of nuclear charge and energy level. The atomic size generally decreases across a period as illustrated in Fig. 3.4(a) for the elements of the second period. It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Within a family or vertical column of the **periodic table**, the atomic radius increases regularly with atomic number as illustrated in Fig. 3.4(b). For alkali metals and halogens, as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

Note that the atomic radii of noble gases are not considered here. Being monoatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

Table 3.6(a) Atomic Radii/pm Across the Periods

Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Atomic radius	152	111	88	77	70	74	72
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Atomic radius	186	160	143	117	110	104	99

Table 3.6(b) Atomic Radii/pm Down a Family

Atom (Group I)	**Atomic Radius**	**Atom (Group 17)**	**Atomic Radius**
Li	152	**F**	72
Na	186	**Cl**	99
K	231	**Br**	114
Rb	244	**I**	133
Cs	262	**At**	140

Fig. 3.4 (a) *Variation of atomic radius with atomic number across the second period*

Fig. 3.4 (b) *Variation of atomic radius with atomic number for alkali metals and halogens*

(b) Ionic Radius

The removal of an electron from an atom results in the formation of a **cation**, whereas gain of an electron leads to an **anion**. The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 72 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

When we find some atoms and ions which contain the same number of electrons, we call them **isoelectronic species**. For example, O^{2-}, F^-, Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

Problem 3.5

Which of the following species will have the largest and the smallest size?
Mg, Mg^{2+}, Al, Al^{3+}.

Solution

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic species, the one with the larger positive nuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}.

(c) Ionization Enthalpy

A quantitative measure of the tendency of an element to lose electron is given by its **Ionization Enthalpy**. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an

element X is the enthalpy change ($\Delta_i H$) for the reaction depicted in equation 3.1.

$$X(g) \rightarrow X^+(g) + e \qquad (3.1)$$

The ionization enthalpy is expressed in units of kJ mol^{-1}. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation 3.2.

$$X^+(g) \rightarrow X^{2+}(g) + e \qquad (3.2)$$

Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on. The term "ionization enthalpy", if not qualified, is taken as the first ionization enthalpy.

The first ionization enthalpies of elements having atomic numbers up to 60 are plotted in Fig. 3.5. The periodicity of the graph is quite striking. You will find maxima at the noble gases which have closed electron shells and very stable electron configurations. On the other hand, minima occur at the alkali metals and their low ionization enthalpies can be correlated

Fig. 3.5 *Variation of first ionization enthalpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60*

with their high reactivity. In addition, you will notice two trends the first ionization enthalpy generally increases as we go across a period and decreases as we descend in a group. These trends are illustrated in Figs. 3.6(a) and 3.6(b) respectively for the elements of the second period and the first group of the periodic table. You will appreciate that the ionization enthalpy and atomic radius are closely related properties. To understand these trends, we have to consider two factors : (i) the attraction of electrons towards the nucleus, and (ii) the repulsion of electrons from each other. The effective nuclear charge experienced by a valence electron in an atom will be less than

3.6 (a)

3.6 (b)

Fig. 3.6(a) *First ionization enthalpies ($\Delta_i H$) of elements of the second period as a function of atomic number (Z) and* ***Fig. 3.6(b)*** *$\Delta_i H$ of alkali metals as a function of Z.*

the actual charge on the nucleus because of **"shielding"** or **"screening"** of the valence electron from the nucleus by the intervening core electrons. For example, the 2*s* electron in lithium is shielded from the nucleus by the inner core of 1*s* electrons. As a result, the valence electron experiences a net positive charge which is less than the actual charge of +3. In general, shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have a lone *ns*-outermost electron preceded by a noble gas electronic configuration.

When we move from lithium to fluorine across the second period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period. As we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

From Fig. 3.6(a), you will also notice that the first ionization enthalpy of boron ($Z = 5$) is slightly less than that of beryllium ($Z = 4$) even though the former has a greater nuclear charge. When we consider the same principal quantum level, an *s*-electron is attracted to the nucleus more than a *p*-electron. In beryllium, the electron removed during the ionization is an *s*-electron whereas the electron removed during ionization of boron is a *p*-electron. The penetration of a 2*s* electron to the nucleus is more than that of a 2*p* electron; hence the 2*p* electron of boron is more shielded from the nucleus by the inner core of electrons than the 2*s* electrons of beryllium. Therefore, it is easier to remove the 2*p*-electron from boron compared to the removal of a 2*s* electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another "anomaly" is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2*p* electrons reside in different atomic orbitals (Hund's rule) whereas in the oxygen atom, two of the four 2*p* electrons must occupy the same 2*p* orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2*p*-electron from oxygen than it is, to remove one of the three 2*p*-electrons from nitrogen.

Problem 3.6

The first ionization enthalpy ($\Delta_i H$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol^{-1}? Justify your answer.

Solution

It will be more close to 575 kJ mol^{-1}. The value for Al should be lower than that of Mg because of effective shielding of 3*p* electrons from the nucleus by 3*s*-electrons.

(d) Electron Gain Enthalpy

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy** ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation 3.3.

$$X(g) + e^- \rightarrow X\ (g) \qquad (3.3)$$

Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have

Table 3.7 Electron Gain Enthalpies* / (kJ mol^{-1}) of Some Main Group Elements

Group 1	$\Delta_{eg}H$	Group 16	$\Delta_{eg}H$	Group 17	$\Delta_{eg}H$	Group 0	$\Delta_{eg}H$
H	– 73					**He**	+ 48
Li	– 60	**O**	– 141	**F**	– 328	**Ne**	+ 116
Na	– 53	**S**	– 200	**Cl**	– 349	**Ar**	+ 96
K	– 48	**Se**	– 195	**Br**	– 325	**Kr**	+ 96
Rb	– 47	**Te**	– 190	**I**	– 295	**Xe**	+ 77
Cs	– 46	**Po**	– 174	**At**	– 270	**Rn**	+ 68

large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases.

The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 3.7). However, electron gain enthalpy of O or F is less than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from the other electrons present in this level. For the $n = 3$ quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

Problem 3.7

Which of the following will have the most negative electron gain enthalpy and which the least negative?

P, S, Cl, F.

Explain your answer.

Solution

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2*p* orbital leads to greater repulsion than adding an electron to the larger 3*p* orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

(e) Electronegativity

A qualitative measure of the ability of an atom in a **chemical compound** to attract shared electrons to itself is called **electronegativity**. Unlike ionization enthalpy and electron gain enthalpy, it is not a measureable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale have been developed. The one which is the most

* *In many books, the negative of the enthalpy change for the process depicted in equation 3.3 is defined as the ELECTRON AFFINITY (A_e) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined as absolute zero and, therefore at any other temperature (T) heat capacities of the reactants and the products have to be taken into account in $\Delta_{eg}H = -A_e - 5/2\ RT$.*

widely used is the Pauling scale. Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 3.8(a)

The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together – a relationship that you will explore later.

Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table. How can these trends be explained? Can the electronegativity be related to atomic radii, which tend to decrease across each period from left to right, but increase down each group ? The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. The electronegativity also increases. On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization enthalpy.

Knowing the relationship between electronegativity and atomic radius, can you now visualise the relationship between electronegativity and non-metallic properties?

Fig. 3.7 *The periodic trends of elements in the periodic table*

Table 3.8(a) Electronegativity Values (on Pauling scale) Across the Periods

Atom (Period II)	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 3.8(b) Electronegativity Values (on Pauling scale) Down a Family

Atom (Group I)	**Electronegativity Value**	**Atom (Group 17)**	**Electronegativity Value**
Li	1.0	**F**	4.0
Na	0.9	**Cl**	3.0
K	0.8	**Br**	2.8
Rb	0.8	**I**	2.5
Cs	0.7	**At**	2.2

Non-metallic elements have strong tendency to gain electrons. Therefore, electronegativity is directly related to that non-metallic properties of elements. It can be further extended to say that the electronegativity is inversely related to the metallic properties of elements. Thus, the increase in electronegativities across a period is accompanied by an increase in non-metallic properties (or decrease in metallic properties) of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties (or increase in metallic properties) of elements.

All these periodic trends are summarised in figure 3.7.

3.7.2 Periodic Trends in Chemical Properties

Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanoid contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine).

(a) Periodicity of Valence or Oxidation States

The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and / or equal to eight minus the number of outermost electrons as shown below.

Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: OF_2 and Na_2O. The order of electronegativity of the three elements involved in these compounds is F > O > Na. Each of the atoms of fluorine, with outer electronic configuration $2s^2 2p^5$, shares one electron with oxygen in the OF_2 molecule. Being highest electronegative element, fluorine is given oxidation state –1. Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2. In Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state –2. On the other hand sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state +1. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

Problem 3.8

Using the Periodic Table, predict the formulas of compounds which might be formed by the following pairs of elements; (a) silicon and bromine (b) aluminium and sulphur.

Solution

(a) Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence the formula of the compound formed would be $SiBr_4$.

(b) Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be Al_2S_3.

Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 3.9. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in this book.

Group	1	2	13	14	15	16	17	18
Number of valence electron	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3,5	2,6	1,7	0,8

Table 3.9 Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds

Group	1	2	13	14	15	16	17
Formula of hydride	LiH NaH KH	CaH_2	B_2H_6 AlH_3	CH_4 SiH_4 GeH_4 SnH_4	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2S H_2Se H_2Te	HF HCl HBr HI
Formula of oxide	Li_2O Na_2O K_2O	MgO CaO SrO BaO	B_2O_3 Al_2O_3 Ga_2O_3 In_2O_3	CO_2 SiO_2 GeO_2 SnO_2 PbO_2	N_2O_3, N_2O_5 P_4O_6, P_4O_{10} As_2O_3, As_2O_5 Sb_2O_3, Sb_2O_5 Bi_2O_3 –	SO_3 SeO_3 TeO_3 –	– Cl_2O_7 – –

There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids, which we shall study later.

(b) Anomalous Properties of Second Period Elements

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the following group i.e., magnesium and aluminium, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties.

What are the reasons for the different chemical behaviour of the first member of a group of elements in the ***s***- and ***p*-blocks** compared to that of the subsequent members in the same group? The anomalous behaviour is attributed to their small size, large charge/radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2*s* and 2*p*) available for bonding, whereas the second member of the groups have nine valence orbitals (3*s*, 3*p*, 3*d*). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium forms $[AlF_6]^{3-}$). Furthermore, the first member of *p*-block elements displays greater ability to form $p_\pi - p_\pi$ multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group.

Property	Element		
Metallic radius M/ pm	**Li** 152 **Na** 186	**Be** 111 **Mg** 160	**B** 88 **Al** 143
Ionic radius M^+ / pm	**Li** 76 **Na** 102	**Be** 31 **Mg** 72	

Problem 3.9

Are the oxidation state and covalency of Al in $[AlCl(H_2O)_5]^{2+}$ same ?

Solution

No. The oxidation state of Al is +3 and the covalency is 6.

3.7.3 Periodic Trends and Chemical Reactivity

We have observed the periodic trends in certain fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and valence. We know by now that the periodicity is related to electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements. We shall now try to explore relationships between these fundamental properties of elements with their chemical reactivity.

The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions as outlined in section 3.7.1(a)) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note : noble gases having completely filled shells have rather positive electron gain enthalpy values). This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However, here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period. The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left is the most basic (e.g., Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g., Al_2O_3, As_2O_3) or neutral (e.g., CO, NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

Problem 3.10

Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

Solution

Na_2O with water forms a strong base whereas Cl_2O_7 forms strong acid.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$

Their basic or acidic nature can be qualitatively tested with litmus paper.

Among transition metals (3*d* series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4*f* series). The ionization enthalpies are intermediate between those of *s* and *p* blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements as shown in section 3.7.1(d)) in electron gain enthalpies in the case of main group elements.

Thus, the metallic character increases down the group and non-metallic character decreases. This trend can be related with their reducing and oxidizing property which you will learn later. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy.

SUMMARY

In this Unit, you have studied the development of the **Periodic Law** and the **Periodic Table**. Mendeleev's **Periodic Table** was based on atomic masses. Modern **Periodic Table** arranges the elements in the order of their atomic numbers in seven horizontal rows (**periods**) and eighteen vertical columns (**groups** or **families**). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern. Elements of the same group have similar **valence shell** electronic configuration and, therefore, exhibit similar chemical properties. However, the elements of the same period have incrementally increasing number of electrons from left to right, and, therefore, have different valencies. Four types of elements can be recognized in the periodic table on the basis of their electronic configurations. These are ***s*-block, *p*-block, *d*-block** and ***f*-block** elements. **Hydrogen** with one electron in the 1*s* orbital occupies a unique position in the periodic table. **Metals** comprise more than seventy eight per cent of the known elements. **Non-metals**, which are located at the top of the periodic table, are less than twenty in number. Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As) are called **metalloids** or **semi-metals**. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers.

Periodic trends are observed in **atomic sizes, ionization enthalpies, electron gain enthalpies**, **electronegativity** and **valence.** The atomic radii decrease while going from left to right in a period and increase with atomic number in a group. Ionization enthalpies generally increase across a period and decrease down a group. Electronegativity also shows a similar trend. Electron gain enthalpies, in general, become more negative across a period and less negative down a group. There is some periodicity in valence, for example, among representative elements, the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number. **Chemical reactivity** is hightest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy). Highly reactive elements do not occur in nature in free state; they usually occur in the combined form. Oxides formed of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral.

EXERCISES

3.1 What is the basic theme of organisation in the periodic table?

3.2 Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that?

3.3 What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law?

3.4 On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements.

3.5 In terms of period and group where would you locate the element with $Z = 114$?

3.6 Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

3.7 Which element do you think would have been named by

(i) Lawrence Berkeley Laboratory

(ii) Seaborg's group?

3.8 Why do elements in the same group have similar physical and chemical properties?

3.9 What does atomic radius and ionic radius really mean to you?

3.10 How do atomic radius vary in a period and in a group? How do you explain the variation?

3.11 What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.

(i) F^- (ii) Ar (iii) Mg^{2+} (iv) Rb^+

3.12 Consider the following species :

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

(a) What is common in them?

(b) Arrange them in the order of increasing ionic radii.

3.13 Explain why cation are smaller and anions larger in radii than their parent atoms?

3.14 What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy?

Hint : Requirements for comparison purposes.

3.15 Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1}.

Hint: Apply the idea of mole concept to derive the answer.

3.16 Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne.

Explain why

(i) Be has higher $\Delta_i H$ than B

(ii) O has lower $\Delta_i H$ than N and F?

3.17 How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?

3.18 What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?

3.19 The first ionization enthalpy values (in kJ mol^{-1}) of group 13 elements are :

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend ?

3.20 Which of the following pairs of elements would have a more negative electron gain enthalpy?

(i) O or F (ii) F or Cl

3.21 Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer.

3.22 What is the basic difference between the terms electron gain enthalpy and electronegativity?

3.23 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

3.24 Describe the theory associated with the radius of an atom as it
(a) gains an electron
(b) loses an electron

3.25 Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different? Justify your answer.

3.26 What are the major differences between metals and non-metals?

3.27 Use the periodic table to answer the following questions.
(a) Identify an element with five electrons in the outer subshell.
(b) Identify an element that would tend to lose two electrons.
(c) Identify an element that would tend to gain two electrons.
(d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

3.28 The increasing order of reactivity among group 1 elements is Li < Na < K < Rb <Cs whereas that among group 17 elements is F > CI > Br > I. Explain.

3.29 Write the general outer electronic configuration of *s*-, *p*-, *d*- and *f*- block elements.

3.30 Assign the position of the element having outer electronic configuration (i) ns^2np^4 for n=3 (ii) $(n\text{-}1)d^2ns^2$ for n=4, and (iii) $(n\text{-}2)\ f^7\ (n\text{-}1)d^1ns^2$ for n=6, in the periodic table.

3.31 The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg}H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below:

Elements	ΔH_1	ΔH_2	$\Delta_{eg}H$
I	520	7300	–60
II	419	3051	–48
III	1681	3374	–328
IV	1008	1846	–295
V	2372	5251	+48
VI	738	1451	–40

Which of the above elements is likely to be :
(a) the least reactive element.
(b) the most reactive metal.
(c) the most reactive non-metal.
(d) the least reactive non-metal.
(e) the metal which can form a stable binary halide of the formula MX_2(X=halogen).
(f) the metal which can form a predominantly stable covalent halide of the formula MX (X=halogen)?

3.32 Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements.
(a) Lithium and oxygen (b) Magnesium and nitrogen
(c) Aluminium and iodine (d) Silicon and oxygen
(e) Phosphorus and fluorine (f) Element 71 and fluorine

3.33 In the modern periodic table, the period indicates the value of :
(a) atomic number
(b) atomic mass
(c) principal quantum number
(d) azimuthal quantum number.

3.34 Which of the following statements related to the modern periodic table is incorrect?
(a) The *p*-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a *p*-shell.

(b) The *d*-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a *d*-subshell.

(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell.

(d) The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration.

3.35 Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell?

(a) Valence principal quantum number (n)

(b) Nuclear charge (Z)

(c) Nuclear mass

(d) Number of core electrons.

3.36 The size of isoelectronic species — F^-, Ne and Na^+ is affected by

(a) nuclear charge (Z)

(b) valence principal quantum number (n)

(c) electron-electron interaction in the outer orbitals

(d) none of the factors because their size is the same.

3.37 Which one of the following statements is incorrect in relation to ionization enthalpy?

(a) Ionization enthalpy increases for each successive electron.

(b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.

(c) End of valence electrons is marked by a big jump in ionization enthalpy.

(d) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.

3.38 Considering the elements B, Al, Mg, and K, the correct order of their metallic character is :

(a) B > Al > Mg > K (b) Al > Mg > B > K

(c) Mg > Al > K > B (d) K > Mg > Al > B

3.39 Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is :

(a) B > C > Si > N > F (b) Si > C > B > N > F

(c) F > N > C > B > Si (d) F > N > C > Si > B

3.40 Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is :

(a) F > Cl > O > N (b) F > O > Cl > N

(c) Cl > F > O > N (d) O > F > N > Cl

UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Objectives

After studying this Unit, you will be able to :

- understand Kössel-Lewis approach to chemical bonding;
- explain the octet rule and its limitations, draw Lewis structures of simple molecules;
- explain the formation of different types of bonds;
- describe the VSEPR theory and predict the geometry of simple molecules;
- explain the valence bond approach for the formation of covalent bonds;
- predict the directional properties of covalent bonds;
- explain the different types of hybridisation involving *s*, *p* and *d* orbitals and draw shapes of simple covalent molecules;
- describe the molecular orbital theory of homonuclear diatomic molecules;
- explain the concept of hydrogen bond.

"Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts."

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. **The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.** Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic coniguration of elements and the periodic table. Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability.

4.1 KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gases.

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement. **Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.** In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl ions. In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**.

Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as **valence electrons**. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:

Significance of Lewis Symbols : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or **group valence** of the element. The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

Kössel, in relation to chemical bonding, drew attention to the following facts:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases;
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms;
- The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.
- The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

$$Na \rightarrow Na^+ + e$$
$$[Ne]\ 3s^1 \qquad [Ne]$$
$$Cl + e \rightarrow Cl$$
$$[Ne]\ 3s^2\ 3p^5 \qquad [Ne]\ 3s^2\ 3p^6 \text{ or } [Ar]$$
$$Na^+ + Cl \rightarrow NaCl \text{ or } Na^+Cl$$

Similarly the formation of CaF_2 may be shown as:

$$Ca \rightarrow Ca^{2+} + 2e$$
$$[Ar]4s^2 \qquad [Ar]$$
$$F + e \rightarrow F$$
$$[He]\ 2s^2\ 2p^5 \qquad [He]\ 2s^2\ 2p^6 \text{ or } [Ne]$$
$$Ca^{2+} + 2F \rightarrow CaF_2 \text{ or } Ca^{2+}(F\ )_2$$

The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as

the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion. Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one.

Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into these concepts.

4.1.1 Octet Rule

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory** of **chemical bonding**. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as **octet rule**.

4.1.2 Covalent Bond

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term **covalent bond**. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule, Cl_2. The Cl atom with electronic configuration, [Ne]$3s^2\ 3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

Covalent bond between two Cl atoms

The dots represent electrons. Such structures are referred to as Lewis dot structures.

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes at least one electron to the shared pair.
- The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.
- Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

H atoms attain a duplet of electrons and O, the octet

Each of the four Cl atoms along with the C atom attains octet of electrons

Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

Double bonds in CO_2 molecule

C_2H_4 molecule

When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.

N_2 molecule

C_2H_2 molecule

4.1.3 Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the following steps:

- The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).
- For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the CO_3^{2-} ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For NH_4^+ ion, one positive charge indicates the loss of one electron from the group of neutral atoms.
- Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

  Lewis representations of a few molecules/ ions are given in Table 4.1.

Table 4.1 The Lewis Representation of Some Molecules

Molecule/Ion		Lewis Representation
H_2	H : H*	H – H
O_2	:Ö::Ö:	:Ö=Ö:
O_3		
NF_3		
CO_3^{2-}		
HNO_3		

* *Each H atom attains the configuration of helium (a duplet of electrons)*

Problem 4.1

Write the Lewis dot structure of CO molecule.

Solution

Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are: $2s^2\ 2p^2$ and $2s^2\ 2p^4$, respectively. The valence electrons available are 4 + 6 =10.

Step 2. The skeletal structure of CO is written as: C O

Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.

This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.

Problem 4.2

Write the Lewis structure of the nitrite ion, NO_2^-.

Solution

Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

$N(2s^2\ 2p^3)$, $O\ (2s^2\ 2p^4)$

5 + (2 6) +1 = 18 electrons

Step 2. The skeletal structure of NO_2^- is written as : O N O

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.

Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.

or

4.1.4 Formal Charge

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

$$\text{Formal charge (F.C.) on an atom in a Lewis structure} = \left[\text{total number of valence electrons in the free atom}\right] - \left[\text{total number of non bonding (lone pair) electrons}\right] - (1/2)\left[\text{total number of bonding(shared) electrons}\right]$$

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair.

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 may be drawn as :

The atoms have been numbered as 1, 2 and 3.

- The central O atom marked 1

$$= 6 - 2 - \frac{1}{2}(6) = +1$$

- The end O atom marked 2

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

- The end O atom marked 3

$$= 6 - 6 - \frac{1}{2}(2) = -1$$

Hence, we represent O_3 along with the formal charges as follows:

We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. **Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.**

4.1.5 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.

Li, Be and B have 1,2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3.

Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms

The expanded octet

Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.

PF_5 — 10 electrons around the P atom

SF_6 — 12 electrons around the S atom

H_2SO_4 — 12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.

Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

4.2 IONIC OR ELECTROVALENT BOND

From the K ssel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

$M(g) \rightarrow M^+(g) + e$; Ionization enthalpy

$X(g) + e \rightarrow X(g)$; Electron gain enthalpy

$M^+(g) + X(g) \rightarrow MX(s)$

The **electron gain enthalpy,** $\Delta_{eg}H$**,** is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.

Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for $Na^+(g)$ formation from Na(g) is 495.8 kJ mol ^{1} ; while the electron gain enthalpy for the change $Cl(g) + e \rightarrow Cl(g)$ is, – 348.7 kJ mol ^{1} only. The sum of the two, 147.1 kJ mol ^{1} is more than compensated for by the enthalpy of lattice formation of NaCl(s) (–788 kJ mol ^{1}). Therefore, the energy released in the

processes is more than the energy absorbed. **Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.**

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

4.2.1 Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol ^{1}. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na^+ (g) and one mole of Cl (g) to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

4.3 BOND PARAMETERS

4.3.1 Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 4.1). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. **The van der Waals radius represents the overall size of the atom which includes its valence shell in a nonbonded situation.** Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in Fig.4.2

Fig. 4.1 *The bond length in a covalent molecule AB.*
$R = r_A + r_B$ *(R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively)*

Fig. 4.2 *Covalent and van der Waals radii in a chlorine molecule .The inner circles correspond to the size of the chlorine atom (r_{vdw} and r_c are van der Waals and covalent radii respectively).*

Some typical average bond lengths for single, double and triple bonds are shown in Table 4.2. Bond lengths for some common molecules are given in Table 4.3.

The covalent radii of some common elements are listed in Table 4.4.

4.3.2 Bond Angle

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under :

4.3.3 Bond Enthalpy

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}. For example, the H – H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

$H_2(g) \rightarrow H(g) + H(g); \Delta_a H^{\ominus} = 435.8 \text{ kJ mol}^{-1}$

Similarly the bond enthalpy for molecules containing multiple bonds, for example O_2 and N_2 will be as under :

O_2 (O = O) (g) $\rightarrow$ O(g) + O(g);

$\Delta_a H^{\ominus} = 498 \text{ kJ mol}^{-1}$

N_2 (N ≡ N) (g) $\rightarrow$ N(g) + N(g);

$\Delta_a H^{\ominus} = 946.0 \text{ kJ mol}^{-1}$

It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a heteronuclear diatomic molecules like HCl, we have

$HCl (g) \rightarrow H(g) + Cl (g); \Delta_a H^{\ominus} = 431.0 \text{ kJ mol}^{-1}$

In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H_2O molecule, the enthalpy needed to break the two O – H bonds is not the same.

Table 4.2 Average Bond Lengths for Some Single, Double and Triple Bonds

Bond Type	Covalent Bond Length (pm)
O–H	96
C–H	107
N–O	136
C–O	143
C–N	143
C–C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

Table 4.3 Bond Lengths in Some Common Molecules

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N ≡ N)	109
O_2 (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

Table 4.4 Covalent Radii, *r_{cov}/(pm)

H	37						
C	77(1)	N	74 (1)	O	66(1)	F	64
	67 (2)		65(2)		57 (2)	Cl	99
	60(3)		55(3)				
		P	110	S	104(1)	Br	114
					95(2)		
		As	121	Se	104	I	133
		Sb	141	Te	137		

* *The values cited are for single bonds, except where otherwise indicated in parenthesis. (See also Unit 3 for periodic trends).*

$H_2O(g) \rightarrow H(g) + OH(g); \Delta_a H_1^{\ominus} = 502 \text{ kJ mol}^{-1}$

$OH(g) \rightarrow H(g) + O(g); \Delta_a H_2^{\ominus} = 427 \text{ kJ mol}^{-1}$

The difference in the $\Delta_a H^{\ominus}$ value shows that the second O – H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O – H bond in different molecules like C_2H_5OH (ethanol) and water. Therefore in polyatomic molecules the term **mean or average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,

$$\text{Average bond enthalpy} = \frac{502 + 427}{2}$$

$$= 464.5 \text{ kJ mol}^{-1}$$

4.3.4 Bond Order

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1,2,3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H^{\ominus}$ is 946 kJ mol ^{1}; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

A general correlation useful for understanding the stablities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

4.3.5 Resonance Structures

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:

Fig. 4.3 *Resonance in the O_3 molecule*

(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O–O single bond and a O=O double bond. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3. **According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.** Thus for O_3, the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 more accurately. This is also called **resonance hybrid**. Resonance is represented by a double headed arrow.

Some of the other examples of resonance structures are provided by the **carbonate ion and the carbon dioxide molecule.**

Problem 4.3

Explain the structure of CO_3^{2-} ion in terms of resonance.

Solution

The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.

I II III

Fig.4.4 *Resonance in CO_3^{2} , I, II and III represent the three canonical forms.*

Problem 4.4

Explain the structure of CO_2 molecule.

Solution

The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond (C=O) and carbon to oxygen triple bond (C≡O) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in CO_2 (115 pm) lie between the values for C=O and C≡O. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III.

I II III

Fig. 4.5 *Resonance in CO_2 molecule, I, II and III represent the three canonical forms.*

In general, it may be stated that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single cannonical structure; and,
- Resonance averages the bond characteristics as a whole.

  Thus the energy of the O_3 resonance hybrid is lower than either of the two cannonical froms I and II (Fig 4.3).

Many **misconceptions** are associated with resonance and the same need to be dispelled. You should remember that :

- The cannonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms.
- There is no such equilibrium between the cannonical forms as we have between tautomeric forms (*keto* and *enol*) in tautomerism.
- The molecule as such has a single structure which is the resonance hybrid of the cannonical forms and which cannot as such be depicted by a single Lewis structure.

4.3.6 Polarity of Bonds

The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2, N_2 or F_2, the shared pair of electrons is equally

attracted by the two atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine (Unit 3) is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows :

Dipole moment (μ) = charge (Q) distance of separation (r)

Dipole moment is usually expressed in Debye units (D).The conversion factor is

$$1\ D = 3.33564 \quad 10^{-30}\ C\ m$$

where C is coulomb and m is meter.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as :

The shift in electron density is symbolised by crossed arrow (⟶) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in H_2O molecule, which has a bent structure, the two O–H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17 10^{-30} C m (1D = 3.33564 10^{-30} C m) is the resultant of the dipole moments of two O–H bonds.

(a) Bond dipole (b) Resultant dipole moment

Net Dipole moment, μ = 1.85 D

= 1.85 3.33564 10^{-30} C m = 6.17 10^{-30} C m

The dipole moment in case of BeF_2 is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.

Bond dipoles in BeF_2 Total dipole moment in BeF_2

In tetra-atomic molecule, for example in BF_3, the dipole moment is zero although the B – F bonds are oriented at an angle of 120° to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.

(a) (b)

BF_3 molecule; representation of (a) bond dipoles and (b) total dipole moment

Let us study an interesting case of NH_3 and NF_3 molecule. Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH_3 (4.90 10^{-30} C m) is greater than that of NF_3 (0.8 10^{-30} C m). This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in

Peter Debye, the Dutch chemist received Nobel prize in 1936 for his work on X-ray diffraction and dipole moments. The magnitude of the dipole moment is given in Deby units in order to honour him.

the direction opposite to the resultant dipole moment of the three N–F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3 as represented below :

Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ C m

Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ C m

Dipole moments of some molecules are shown in Table 4.5.

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n\text{-}1)d^n ns^o$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2\, np^6$, typical of alkali and alkaline earth metal cations.

  The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

4.4 THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick

Table 4.5 Dipole Moments of Selected Molecules

Type of Molecule	Example	Dipole Moment, μ(D)	Geometry
Molecule (AB)			
	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H_2	0	linear
Molecule (AB_2)			
	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule (AB_3)			
	NH_3	1.47	trigonal-pyramidal
	NF_3	0.23	trigonal-pyramidal
	BF_3	0	trigonal-planar
Molecule (AB_4)			
	CH_4	0	tetrahedral
	$CHCl_3$	1.04	tetrahedral
	CCl_4	0	tetrahedral

and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as **(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.**

Table 4.6 (page110) shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 4.7 (page 111) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 112) explains the reasons for the distortions in the geometry of the molecule.

As depicted in Table 4.6, in the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangement of electron pairs and the B atoms around the central atom A are : **linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral,** respectively. Such arrangement can be seen in the molecules like BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) as depicted below by their ball and stick models.

Fig. 4.6 *The shapes of molecules in which central atom has no lone pair*

The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of *p*-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

Table 4.6 Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	Trigonal planar	Trigonal planar	BF_3
4	Tetrahedral	Tetrahedral	CH_4, NH_4^+
5	Trigonal bipyramidal	Trigonal bipyramidal	PCl_5
6	Octahedral	Octahedral	SF_6

Table 4.7 Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E).

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	Tetrahedral	Trogonal pyramidal	NH_3
AB_2E_2	2	2	Tetrahedral	Bent	H_2O
AB_4E	4	1	Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	Octahedral	Square planar	XeF_4

Table 4.8 Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5 from 120 .
AB_3E	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107 from 109.5 .
AB_2E_2	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5 from 109.5 .
AB_4E	4	1		See-saw	In (a) the lp is present at axial position so there are three lp—bp repulsions at 90 . In(b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_3E_2	3	2	(a)	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).
			(b)		
			(c)		

4.5 VALENCE BOND THEORY

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 (435.8 kJ mol^{-1}, 74 pm) and F_2 (150.6 kJ mol^{-1}, 42 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules.

Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements (Units 2), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience, valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between:

(i) nucleus of one atom and its own electron that is $N_A - e_A$ and $N_B - e_B$.

(ii) nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

Similarly repulsive forces arise between (i) electrons of two atoms like $e_A - e_B$, (ii) nuclei of two atoms $N_A - N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 4.7).

Fig. 4.7 *Forces of attraction and repulsion during the formation of H_2 molecule.*

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in Fig. 4.8. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

$$H_2(g) + 435.8 \text{ kJ mol}^{-1} \rightarrow H(g) + H(g)$$

Fig. 4.8 *The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.*

4.5.1 Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

4.5.2 Directional Properties of Bonds

As we have already seen the formation of covalent bond depends on the overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1*s*-orbitals of two H atoms, when they combine with each other.

In case of polyatomic molecules like CH_4, NH_3 and H_2O, the geometry of the molecules is also important in addition to the bond formation. For example why is it so that CH_4 molecule has tetrahedral shape and HCH bond angles are 109.5 ? Why is the shape of NH_3 molecule pyramidal ?

The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4, NH_3 and H_2O, etc. in terms of overlap and hybridisation of atomic orbitals.

4.5.3 Overlapping of Atomic Orbitals

When two atoms come close to each other, there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of *s* and *p* orbitals resulting in positive, negative and zero overlap are depicted in Fig. 4.9.

Fig.4.9 *Positive, negative and zero overlaps of s and p atomic orbitals*

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4, NH_3 and H_2O, the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the CH_4 (methane) molecule. The electronic configuration of carbon in its ground state is [He]$2s^2\ 2p^2$ which in the excited state becomes [He] $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the hydrogen.The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1*s* orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at 90 to one another, the HCH angle for these will also be 90 . That is three C-H bonds will be oriented at 90 to one another. The 2*s* orbital of carbon and the 1*s* orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of 109.5 . Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similar procedure and arguments, it can be seen that in the

case of NH_3 and H_2O molecules, the HNH and HOH angles should be 90 . This is in disagreement with the actual bond angles of 107 and 104.5 in the NH_3 and H_2O molecules respectively.

4.5.4 Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping:

(i) Sigma(σ) bond, and (ii) pi(π) bond

(i) Sigma(σ) bond : This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

- ***s-s* overlapping :** In this case, there is overlap of two half filled *s*-orbitals along the internuclear axis as shown below :

- ***s-p* overlapping:** This type of overlap occurs between half filled *s*-orbitals of one atom and half filled *p*-orbitals of another atom.

- ***p–p* overlapping :** This type of overlap takes place between half filled *p*-orbitals of the two approaching atoms.

(ii) **pi(π) bond :** In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

p-orbital *p*-orbital *p-p* overlapping

4.5.5 Strength of Sigma and pi Bonds

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

4.6 HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3 and H_2O etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2*s* and three 2*p*-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.

3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

4.6.1 Types of Hybridisation

There are various types of hybridisation involving *s*, *p* and *d* orbitals. The different types of hybridisation are as under:

(I) *sp* hybridisation: This type of hybridisation involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent *sp* hybrid orbitals. The suitable orbitals for *sp* hybridisation are *s* and p_z, if the hybrid orbitals are to lie along the *z*-axis. Each *sp* hybrid orbitals has 50% *s*-character and 50% *p*-character. Such a molecule in which the central atom is *sp*-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

The two *sp* hybrids point in the opposite direction along the *z*-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of molecule having *sp* hybridisation

$BeCl_2$: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2*s*-electrons is promoted to vacant 2*p* orbital to account for its divalency. One 2*s* and one 2*p*-orbitals get hybridised to form two *sp* hybridised orbitals. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180 . Each of the *sp* hybridised orbital overlaps with the 2*p*-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in Fig. 4.10.

Fig.4.10 *(a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear $BeCl_2$ molecule*

(II) *sp^2 hybridisation :* In this hybridisation there is involvement of one *s* and two *p*-orbitals in order to form three equivalent sp^2 hybridised orbitals. For example, in BCl_3 molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2*s* electrons is promoted to vacant 2*p* orbital as

Fig.4.11 *Formation of sp^2 hybrids and the BCl_3 molecule*

a result boron has three unpaired electrons. These three orbitals (one 2*s* and two 2*p*) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2*p* orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl_3 (Fig. 4.11), the geometry is trigonal planar with ClBCl bond angle of 120 .

(III) sp^3 *hybridisation:* This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one *s*-orbital and three *p*-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% *s*-character and 75% *p*-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbital is 109.5 as shown in Fig. 4.12.

Fig.4.12 *Formation of sp^3 hybrids by the combination of s , p_x , p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule*

The structure of NH_3 and H_2O molecules can also be explained with the help of sp^3 hybridisation. In NH_3, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2s^2 2p_x^1 2p_y^1 2p_z^1$ having three unpaired electrons in the sp^3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1*s* orbitals of hydrogen atoms to form three N–H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107 from 109.5 . The geometry of such a molecule will be pyramidal as shown in Fig. 4.13.

Fig.4.13 *Formation of NH_3 molecule*

In case of H_2O molecule, the four oxygen orbitals (one 2*s* and three 2*p*) undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5 from 109.5 (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry.

Fig.4.14 *Formation of H_2O molecule*

4.6.2 Other Examples of sp^3, sp^2 and sp Hybridisation

sp^3 Hybridisation in C_2H_6 molecule: In ethane molecule both the carbon atoms assume sp^3 hybrid state. One of the four sp^3 hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form sp^3-sp^3 sigma bond while the other three hybrid orbitals of each carbon atom are used in forming sp^3–s sigma bonds with hydrogen atoms as discussed in section 4.6.1(iii). Therefore in ethane C–C bond length is 154 pm and each C–H bond length is 109 pm.

sp^2 Hybridisation in C_2H_4: In the formation of ethene molecule, one of the sp^2 hybrid orbitals of carbon atom overlaps axially with sp^2 hybridised orbital of another carbon atom to form C–C sigma bond. While the other two sp^2 hybrid orbitals of each carbon atom are used for making sp^2–s sigma bond with two hydrogen atoms. The unhybridised orbital ($2p_x$ or $2p_y$) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak π bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms.

Thus, in ethene molecule, the carbon-carbon bond consists of one sp^2–sp^2 sigma bond and one pi (π) bond between p orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C–H bond is sp^2–s sigma with bond length 108 pm. The H–C–H bond angle is 117.6 while the H–C–C angle is 121 . The formation of sigma and pi bonds in ethene is shown in Fig. 4.15.

Fig. 4.15 *Formation of sigma and pi bonds in ethene*

***sp* Hybridisation in C_2H_2 :** In the formation of ethyne molecule, both the carbon atoms undergo *sp*-hybridisation having two unhybridised orbital *i.e.*, $2p_y$ and $2p_x$.

One *sp* hybrid orbital of one carbon atom overlaps axially with *sp* hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled *s* orbital of hydrogen atoms forming σ bonds. Each of the two unhybridised *p* orbitals of both the carbon atoms overlaps sidewise to form two π bonds between the carbon atoms. So the triple bond between the two carbon atoms is made up of one sigma and two pi bonds as shown in Fig. 4.16.

Fig.4.16 *Formation of sigma and pi bonds in ethyne*

4.6.3 Hybridisation of Elements involving *d* Orbitals

The elements present in the third period contain *d* orbitals in addition to *s* and *p* orbitals. The energy of the 3*d* orbitals are comparable to the energy of the 3*s* and 3*p* orbitals. The energy of 3*d* orbitals are also comparable to those of 4*s* and 4*p* orbitals. As a consequence the hybridisation involving either 3*s*, 3*p* and 3*d* or 3*d*, 4*s* and 4*p* is possible. However, since the difference in energies of 3*p* and 4*s* orbitals is significant, no hybridisation involving 3*p*, 3*d* and 4*s* orbitals is possible.

The important hybridisation schemes involving *s*, *p* and *d* orbitals are summarised below:

Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp^2	$d+s+p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s+p(3)+d$	PF_5, PCl_5
Square pyramidal	dsp^3	$d+s+p(3)$	BrF_5, $XeOF_4$
Octahedral	sp^3d^2 d^2sp^3	$s+p(3)+d(2)$ $d(2)+s+p(3)$	SF_6, $[CrF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

(i) Formation of PCl_5 (sp^3d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below.

sp^3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

Now the five orbitals (*i.e.*, one *s*, three *p* and one *d* orbitals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the Fig. 4.17.

Fig. 4.17 *Trigonal bipyramidal geometry of PCl_5 molecule*

It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. In PCl_5 the five sp^3d orbitals of phosphorus overlap with the singly occupied *p* orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bond lie in one plane and make an angle of 120 with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds–one lying above and the other lying below the equatorial plane, make an angle of 90 with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl_5 molecule more reactive.

(ii) Formation of SF_6 (sp^3d^2 hybridisation): In SF_6 the central sulphur atom has the ground state outer electronic configuration $3s^2 3p^4$. In the exited state the available six orbitals *i.e.*, one *s*, three *p* and two *d* are singly occupied by electrons. These orbitals hybridise to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF_6. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry as shown in Fig. 4.18.

Fig. 4.18 *Octahedral geometry of SF_6 molecule*

4.7 MOLECULAR ORBITAL THEORY

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

(i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.

(ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

(iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus,

an atomic orbital is monocentric while a molecular orbital is polycentric.

(iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital**.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the *aufbau* principle obeying the Pauli's exclusion principle and the Hund's rule.

4.7.1 Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1*s* orbital. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B. Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below :

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals σ and σ* are formed as :

$$\sigma = \psi_A + \psi_B$$
$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital σ* formed by the subtraction of atomic orbital is called **antibonding molecular orbital** as depicted in Fig. 4.19.

Fig.4.19 *Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.*

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of

antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. Infact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilise a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilise the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

4.7.2 Conditions for the Combination of Atomic Orbitals

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

1. The combining atomic orbitals must have the same or nearly the same energy. This means that 1*s* orbital can combine with another 1*s* orbital but not with 2*s* orbital because the energy of 2*s* orbital is appreciably higher than that of 1*s* orbital. This is not true if the atoms are very different.

2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.

3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

4.7.3 Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical**. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as σ*1s* and σ**1s* [Fig. 4.20(a),page 124]. **If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of $2p_z$- orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$**. [Fig. 4.20(b)]

Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as π and π* [Fig. 4.20(c)]. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei.

4.7.4 Energy Level Diagram for Molecular Orbitals

We have seen that 1*s* atomic orbitals on two atoms form two molecular orbitals designated as σ1*s* and σ*1*s*. In the same manner, the 2*s* and 2*p* atomic orbitals (eight atomic orbitals

Fig. 4.20 *Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.*

on two atoms) give rise to the following eight molecular orbitals:

Antibonding MOs σ^*2s σ^*2p_z π^*2p_x π^*2p_y

Bonding MOs $\sigma 2s$ $\sigma 2p_z$ $\pi 2p_x$ $\pi 2p_y$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of

energies of various molecular orbitals for O_2 and F_2 is given below :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2 etc. the increasing order of energies of various molecular orbitals is

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals**.

4.7.5 Electronic Configuration and Molecular Behaviour

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule**. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

Stability of Molecules: If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then

(i) the molecule is stable if N_b is greater than N_a, and

(ii) the molecule is unstable if N_b is less than N_a.

In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

Bond order

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e.,

Bond order (b.o.) = ½ $(N_b - N_a)$

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

Nature of the bond

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

Bond-length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic nature

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

4.8 BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

In this section we shall discuss bonding in some homonuclear diatomic molecules.

1. Hydrogen molecule (H_2): It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1*s* orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in $\sigma 1s$ molecular orbital. So electronic configuration of hydrogen molecule is

$H_2 : (\sigma 1s)^2$

The bond order of H_2 molecule can be calculated as given below:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 -}{2}$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1}

and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

2. Helium molecule (He_2): The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals leading to electronic configuration:

He_2 : $(\sigma 1s)^2 (\sigma^* 1s)^2$

Bond order of He_2 is ½(2 – 2) = 0

He_2 *molecule is therefore unstable and does not exist.*

Similarly, it can be shown that Be_2 molecule $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ *also does not exist.*

3. Lithium molecule (Li_2): The electronic configuration of lithium is $1s^2, 2s^1$. There are six electrons in Li_2. The electronic configuration of Li_2 molecule, therefore, is

Li_2 : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

The above configuration is also written as $KK(\sigma 2s)^2$ where KK represents the closed K shell structure $(\sigma 1s)^2 (\sigma^* 1s)^2$.

From the electronic configuration of Li_2 molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its bond order, therefore, is ½ (4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

4. Carbon molecule (C_2): The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. The electronic configuration of C_2 molecule, therefore, is

C_2 : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma$

or $KK(\sigma 2s)^2 (\sigma$:

The bond order of C_2 is ½ (8 – 4) = 2 and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond. In a similar fashion the bonding in N_2 molecule can be discussed.

5. Oxygen molecule (O_2): The electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^4$. Each oxygen atom has 8 electrons, hence, in O_2 molecule there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is

O_2: $(\sigma 1s)^2 (\sigma^* 1$

$(\pi\ 2p_x{}^2 \equiv \pi\ 2$ or

O_2 : KK

$(\pi 2p_x^2 \equiv$

From the electronic configuration of O_2 molecule it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

Bond order =

So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ molecular orbitals, therefore, **O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation**. In this way, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written. In Fig.4.21 are given the molecular orbital occupancy and molecular properties for B_2 through Ne_2. The sequence of MOs and their electron population are shown. The bond energy, bond length, bond order, magnetic properties and valence electron configuration appear below the orbital diagrams.

Fig. 4.21 *MO occupancy and molecular properties for B_2 through Ne_2.*

4.9 HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the higly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below :

$$---H^{\delta+} \quad F^{\delta-}$$

Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (– – –) while a solid line represents the covalent bond. **Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.**

4.9.1 Cause of Formation of Hydrogen Bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (δ^+) while 'X' attain fractional negative charge

(δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as :

$$H^{\delta+} - X^{\delta-} - -$$

The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

4.9.2 Types of H-Bonds

There are two types of H-bonds

(i) Intermolecular hydrogen bond

(ii) Intramolecular hydrogen bond

(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in *o*-nitrophenol the hydrogen is in between the two oxygen atoms.

Fig. 4.20 *Intramolecular hydrogen bonding in o-nitrophenol molecule*

SUMMARY

K ssel's first insight into the mechanism of formation of electropositive and electronegative ions related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of **electrovalency**.

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the **enthalpy of lattice formation**.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone-pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. **Important parameters, associated with chemical bonds, like: bond length, bond angle, bond enthalpy, bond order and bond polarity have significant effect on the properties of compounds.**

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **resonance**. The contributing structures or *canonical forms* taken together constitute the resonance hybrid which represents the molecule or ion.

The ***VSEPR model*** used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, *molecular geometry is determined by repulsions between lone pairs and lone pairs* ; *lone pairs and bonding pairs* and *bonding pairs and bonding pairs*. The order of these repulsions being : lp-lp > lp-bp > bp-bp

The **valence bond (VB) approach** to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H_2 molecule from two hydrogen atoms involves the overlap of the 1*s* orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of **hybridisation of atomic orbitals**. sp, sp^2, sp^3 hybridizations of atomic orbitals of Be, B, C, N and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BCl_3, CH_4, NH_3 and H_2O. They also explain the formation of multiple bonds in molecules like C_2H_2 and C_2H_4.

The **molecular orbital (MO) theory** describes bonding in terms of the combination and arrangment of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals.

The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if the number of elctrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.

Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intramolecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds.

EXERCISES

4.1 Explain the formation of a chemical bond.

4.2 Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

4.3 Write Lewis symbols for the following atoms and ions:

S and S^{2-}; Al and Al^{3+}; H and H^-

4.4 Draw the Lewis structures for the following molecules and ions :

H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

4.5 Define octet rule. Write its significance and limitations.

4.6 Write the favourable factors for the formation of ionic bond.

4.7 Discuss the shape of the following molecules using the VSEPR model:

$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

4.8 Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

4.9 How do you express the bond strength in terms of bond order ?

4.10 Define the bond length.

4.11 Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

4.12 H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same.

(1) (2)

4.13 Write the resonance structures for SO_3, NO_2 and NO_3^-.

4.14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (a) K and S (b) Ca and O (c) Al and N.

4.15 Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

4.16 Write the significance/applications of dipole moment.

4.17 Define electronegativity. How does it differ from electron gain enthalpy ?

4.18 Explain with the help of suitable example polar covalent bond.

4.19 Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.

4.20 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.

4.21 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar ?

4.22 Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.

4.23 Which out of NH_3 and NF_3 has higher dipole moment and why ?

4.24 What is meant by hybridisation of atomic orbitals? Describe the shapes of *sp*, sp^2, sp^3 hybrid orbitals.

4.25 Describe the change in hybridisation (if any) of the Al atom in the following reaction.

$AlCl_3 + Cl^- \rightarrow A$

4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction ?

$BF_3 + NH_3 \rightarrow F_3]$

4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

4.28 What is the total number of sigma and pi bonds in the following molecules ?

(a) C_2H_2 (b) C_2H_4

4.29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) 1*s* and 1*s* (b) 1*s* and $2p_x$; (c) $2p_y$ and $2p_y$ (d) 1*s* and 2*s*.

4.30 Which hybrid orbitals are used by carbon atoms in the following molecules ?

CH_3–CH_3; (b) CH_3–CH=CH_2; (c) CH_3-CH_2-OH; (d) CH_3-CHO (e) CH_3COOH

4.31 What do you understand by bond pairs and lone pairs of electrons ? Illustrate by giving one exmaple of each type.

4.32 Distinguish between a sigma and a pi bond.

4.33 Explain the formation of H_2 molecule on the basis of valence bond theory.

4.34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

4.35 Use molecular orbital theory to explain why the Be_2 molecule does not exist.

4.36 Compare the relative stability of the following species and indicate their magnetic properties;

O_2, O_2^+, O_2^- (superoxide), O_2^{2-} (peroxide)

4.37 Write the significance of a plus and a minus sign shown in representing the orbitals.

4.38 Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds ?

4.39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

4.40 What is meant by the term bond order ? Calculate the bond order of : N_2, O_2, O_2^+ and O_2^-.

UNIT 5

STATES OF MATTER

Objectives

After studying this unit you will be able to

- explain the existence of different states of matter in terms of balance between intermolecular forces and thermal energy of particles;
- explain the laws governing behaviour of ideal gases;
- apply gas laws in various real life situations;
- explain the behaviour of real gases;
- describe the conditions required for liquifaction of gases;
- realise that there is continuity in gaseous and liquid state;
- differentiate between gaseous state and vapours;
- explain properties of liquids in terms of intermolecular attractions.

"The snowflake falls, yet lays not long
Its feath'ry grasp on Mother Earth
Ere Sun returns it to the vapors Whence it came,
Or to waters tumbling down the rocky slope."

Rod O' Connor

INTRODUCTION

In previous units we have learnt about the properties related to single particle of matter, such as atomic size, ionization enthalpy, electronic charge density, molecular shape and polarity, etc. Most of the observable characteristics of chemical systems with which we are familiar represent bulk properties of matter, *i.e.*, the properties associated with a collection of a large number of atoms, ions or molecules. For example, an individual molecule of a liquid does not boil but the bulk boils. Collection of water molecules have wetting properties; individual molecules do not wet. Water can exist as ice, which is a solid; it can exist as liquid; or it can exist in the gaseous state as water vapour or steam. Physical properties of ice, water and steam are very different. In all the three states of water chemical composition of water remains the same i.e., H_2O. Characteristics of the three states of water depend on the energies of molecules and on the manner in which water molecules aggregate. Same is true for other substances also.

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions do depend upon the physical state. Many times in calculations while dealing with data of experiments we require knowledge of the state of matter. Therefore, it becomes necessary for a chemist to know the physical

laws which govern the behaviour of matter in different states. In this unit, we will learn more about these three physical states of matter particularly liquid and gaseous states. To begin with, it is necessary to understand the nature of intermolecular forces, molecular interactions and effect of thermal energy on the motion of particles because a balance between these determines the state of a substance.

5.1 INTERMOLECULAR FORCES

Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds.

Attractive intermolecular forces are known as **van der Waals forces**, in honour of Dutch scientist Johannes van der Waals (1837-1923), who explained the deviation of real gases from the ideal behaviour through these forces. We will learn about this later in this unit. van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces. A particularly strong type of dipole-dipole interaction is hydrogen bonding. **Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category.** We have already learnt about this interaction in Unit 4.

At this point, it is important to note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces. We will now learn about different types of van der Waals forces.

5.1.1 Dispersion Forces or London Forces

Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other (Fig. 5.1a). It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.*, the charge cloud is more on one side than the other (Fig. 5.1 b and c). This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary

Fig. 5.1 *Dispersion forces or London forces between atoms.*

dipoles is known as **London force**. Another name for this force is **dispersion force**. These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$ where r is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle.

5.1.2 Dipole - Dipole Forces

Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess "partial charges" and these charges are shown by Greek letter *delta* (δ). Partial charges are always less than the unit electronic charge ($1.6\ 10^{-19}$ C). The polar molecules interact with neighbouring molecules. Fig 5.2 (a) shows electron cloud distribution in the dipole of hydrogen chloride and Fig. 5.2 (b) shows dipole-dipole interaction between two HCl molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules. Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$, where r is the distance between polar molecules. Besides dipole-dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the total of intermolecular forces in polar molecules increase.

Fig. 5.2 *(a) Distribution of electron cloud in HCl – a polar molecule, (b) Dipole-dipole interaction between two HCl molecules*

5.1.3 Dipole–Induced Dipole Forces

This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 5.3). Thus an induced dipole is developed in the other molecule. In this case also interaction energy is proportional to $1/r^6$ where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. We have already learnt in Unit 4 that molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.

Fig. 5.3 *Dipole - induced dipole interaction between permanent dipole and induced dipole*

In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.

5.1.4 Hydrogen bond

As already mentioned in section (5.1); this is special case of dipole-dipole interaction. We have already learnt about this in Unit 4. This

is found in the molecules in which highly polar N–H, O–H or H–F bonds are present. Although hydrogen bonding is regarded as being limited to N, O and F; but species such as Cl may also participate in hydrogen bonding. Energy of hydrogen bond varies between 10 to 100 kJ mol^{-1}. This is quite a significant amount of energy; therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids. Strength of the hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule. Following diagram shows the formation of hydrogen bond.

$$\overset{\delta+}{H}-\overset{\delta-}{F}\cdots\overset{\delta+}{H}-\overset{\delta-}{F}$$

Intermolecular forces discussed so far are all attractive. **Molecules also exert repulsive forces** on one another. When two molecules are brought into close contact with each other, the repulsion between the electron clouds and that between the nuclei of two molecules comes into play. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquids and solids are hard to compress. In these states molecules are already in close contact; therefore they resist further compression; as that would result in the increase of repulsive interactions.

5.2 THERMAL ENERGY

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called thermal motion.

5.3 INTERMOLECULAR FORCES *vs* THERMAL INTERACTIONS

We have already learnt that intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquified. Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows :

We have already learnt the cause for the existence of the three states of matter. Now we will learn more about gaseous and liquid states and the laws which govern the behaviour of matter in these states. We shall deal with the solid state in class XII.

5.4 THE GASEOUS STATE

This is the simplest state of matter. Throughout our life we remain immersed in the ocean of air which is a mixture of gases. We spend our life in the lowermost layer of the atmosphere called troposphere, which is held to the surface of the earth by gravitational force. The thin layer of atmosphere is vital to our life. It shields us from harmful radiations and contains substances like dioxygen, dinitrogen, carbon dioxide, water vapour, etc.

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure. A look at the periodic table shows that only eleven elements

Fig. 5.4 *Eleven elements that exist as gases*

exist as gases under normal conditions (Fig 5.4).

The gaseous state is characterized by the following physical properties.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas. Interdependence of these variables leads to the formulation of gas laws. In the next section we will learn about gas laws.

5.5 THE GAS LAWS

The gas laws which we will study now are the result of research carried on for several centuries on the physical properties of gases. The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as Boyle's Law. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from Avogadro and others provided lot of information about gaseous state.

5.5.1 Boyle's Law (Pressure - Volume Relationship)

On the basis of his experiments, Robert Boyle reached to the conclusion that **at constant temperature, the pressure of a fixed amount** (i.e., number of moles n) **of gas varies inversely with its volume**. This is known as **Boyle's law**. Mathematically, it can be written as

$$p \propto \frac{1}{V} \quad (\text{at constant } T \text{ and } n) \tag{5.1}$$

$$\Rightarrow p = k_1 \frac{1}{V} \tag{5.2}$$

where k_1 is the proportionality constant. The value of constant k_1 depends upon the amount of the gas, temperature of the gas and the units in which p and V are expressed.

On rearranging equation (5.2) we obtain

$$pV = k_1 \tag{5.3}$$

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure p_1 undergoes expansion, so that volume becomes V_2 and pressure becomes p_2, then according to Boyle's law :

$$p_1V_1 = p_2V_2 = \text{constant} \tag{5.4}$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1} \tag{5.5}$$

Fig. 5.5(a) *Graph of pressure, p vs. Volume, V of a gas at different temperatures.*

Fig. 5.5 (b) *Graph of pressure of a gas, p vs.* $\frac{1}{V}$

Figure 5.5 shows two conventional ways of graphically presenting Boyle's law. Fig. 5.5 (a) is the graph of equation (5.3) at different temperatures. The value of k_1 for each curve is different because for a given mass of gas, it varies only with temperature. Each curve corresponds to a different constant temperature and is known as an **isotherm** (constant temperature plot). Higher curves correspond to higher temperature. It should be noted that volume of the gas doubles if pressure is halved. Table 5.1 gives effect of pressure on volume of 0.09 mol of CO_2 at 300 K.

Fig 5.5 (b) represents the graph between p and $\frac{1}{V}$. It is a straight line passing through origin. However at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph.

Experiments of Boyle, in a quantitative manner prove that gases are highly compressible because when a given mass of a gas is compressed, the same number of molecules occupy a smaller space. This means that gases become denser at high pressure. A relationship can be obtained between density and pressure of a gas by using Boyle's law :

By definition, density 'd' is related to the mass 'm' and the volume 'V' by the relation $d = \frac{m}{V}$. If we put value of V in this equation

Table 5.1 Effect of Pressure on the Volume of 0.09 mol CO_2 Gas at 300 K.

Pressure/10^4 Pa	Volume/10^{-3} m^3	$(1/V)$/m^{-3}	pV/10^2 Pa m^3
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

from Boyle's law equation, we obtain the relationship.

$$d = \left(\frac{m}{k_1}\right) p = k' p$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Problem 5.1

A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded ?

Solution

According to Boyle's Law $p_1V_1 \quad p_2V_2$

If p_1 is 1 bar, V_1 will be 2.27 L

If p_2 = 0.2 bar, then $V_2 = \frac{p_1V_1}{p_2}$

$$\Rightarrow V_2 = \frac{1\,\text{bar} \times}{0.2} \qquad = 11.35\ \text{L}$$

Since balloon bursts at 0.2 bar pressure, the volume of balloon should be less than 11.35 L.

5.5.2 Charles' Law (Temperature - Volume Relationship)

Charles and Gay Lussac performed several experiments on gases independently to improve upon hot air balloon technology. Their investigations showed that for a fixed mass of a gas at constant pressure, volume of a gas increases on increasing temperature and decreases on cooling. They found that for each degree rise in temperature, volume of a gas increases by $\frac{1}{273.15}$ of the original volume of the gas at 0 C. Thus if volumes of the gas at 0 C and at t C are V_0 and V_t respectively, then

$$V_t = V_0 + \frac{}{2}$$

$$\Rightarrow V_t = V_0\left(1\right.$$

$$\Rightarrow V_t = V_0\left(\frac{2}{}\right. \qquad (5.6)$$

At this stage, we define a new scale of temperature such that t C on new scale is given by T = 273.15 + t and 0 C will be given by T_0 = 273.15. This new temperature scale is called the **Kelvin temperature scale** or **Absolute temperature scale**.

Thus 0 C on the celsius scale is equal to 273.15 K at the absolute scale. Note that degree sign is not used while writing the temperature in absolute temperature scale, i.e., Kelvin scale. Kelvin scale of temperature is also called **Thermodynamic scale** of temperature and is used in all scientific works.

Thus we add 273 (more precisely 273.15) to the celsius temperature to obtain temperature at Kelvin scale.

If we write T_t = 273.15 + t and T_0 = 273.15 in the equation (5.6) we obtain the relationship

$$V_t = V_0\left(\frac{T_t}{T_0}\right.$$

$$\Rightarrow \frac{V_t}{V_0} = \frac{T_t}{T_0} \qquad (5.7)$$

Thus we can write a general equation as follows.

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \qquad (5.8)$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{V}{T} = \text{const} \qquad (5.9)$$

Thus $V = k_2 T$ (5.10)

The value of constant k_2 is determined by the pressure of the gas, its amount and the units in which volume V is expressed.

Equation (5.10) is the mathematical expression for **Charles' law**, which states that **pressure remaining constant, the volume**

of a fixed mass of a gas is directly proportional to its absolute temperature. Charles found that for all gases, at any given pressure, graph of volume *vs* temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at – 273.15 C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at – 273.15 C (Fig. 5.6).

Fig. 5.6 *Volume vs Temperature (C) graph*

Each line of the volume *vs* temperature graph is called **isobar**.

Observations of Charles can be interpreted if we put the value of t in equation (5.6) as – 273.15 C. We can see that the volume of the gas at – 273.15 C will be zero. This means that gas will not exist. In fact all the gases get liquified before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **Absolute zero**.

All gases obey Charles' law at very low pressures and high temperatures.

Problem 5.2

On a ship sailing in pacific ocean where temperature is 23.4 C , a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1 C ?

Solution

$V_1 = 2$ L $\qquad T_2 = 26.1 + 273$

$T_1 = (23.4 + 273)$ K $\qquad = 299.1$ K

$= 296.4$ K

From Charles law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow V_2 = \frac{V_1 T_2}{T_1}$$

$$\Rightarrow V_2 = \frac{2\,\text{L} \times 2}{296}$$

$$= 2\,\text{L} \times 1.009$$

$$= 2.018\,\text{L}$$

5.5.3 Gay Lussac's Law (Pressure-Temperature Relationship)

Pressure in well inflated tyres of automobiles is almost constant, but on a hot summer day this increases considerably and tyre may burst if pressure is not adjusted properly. During winters, on a cold morning one may find the pressure in the tyres of a vehicle decreased considerably. The mathematical relationship between pressure and temperature was given by Joseph Gay Lussac and is known as Gay Lussac's law. It states that **at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.** Mathematically,

$$p \propto T$$

$$\Rightarrow \frac{p}{T} = \text{const}$$

This relationship can be derived from Boyle's law and Charles' Law. Pressure *vs* temperature (Kelvin) graph at constant molar volume is shown in Fig. 5.7. Each line of this graph is called **isochore.**

Fig. 5.7 *Pressure vs temperature (K) graph (Isochores) of a gas.*

5.5.4 Avogadro Law (Volume - Amount Relationship)

In 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes (Unit 1) which is now known as Avogadro law. **It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.** This means that as long as the temperature and pressure remain constant, the volume depends upon number of molecules of the gas or in other words amount of the gas. Mathematically we can write

$V \propto n$ where n is the number of moles of the gas.

$$\Rightarrow V = k_4 n \qquad (5.11)$$

The number of molecules in one mole of a gas has been determined to be 6.022 10^{23} and is known as **Avogadro constant**. You will find that this is the same number which we came across while discussing definition of a 'mole' (Unit 1).

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at **standard temperature and pressure (STP)*** **will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}.**

Molar volume of some gases is given in (Table 5.2).

Table 5.2 Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

Number of moles of a gas can be calculated as follows

$$n = \frac{m}{M} \qquad (5.12)$$

Where m = mass of the gas under investigation and M = molar mass

Thus,

$$V = k_4 \frac{m}{M} \qquad (5.13)$$

Equation (5.13) can be rearranged as follows :

$$M = k_4 \frac{m}{V} = k_4 d \qquad (5.14)$$

* *The previous standard is still often used, and applies to all chemistry data more than decade old. In this definition STP denotes the same temperature of 0 C (273.15 K), but a slightly higher pressure of 1 atm (101.325 kPa). One mole of any gas of a combination of gases occupies 22.413996 L of volume at STP.*

Standard ambient temperature and pressure *(SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e., exactly 10^5 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol^{-1}.*

Here 'd' is the density of the gas. We can conclude from equation (5.14) that the density of a gas is directly proportional to its molar mass.

A gas that follows Boyle's law, Charles' law and Avogadro law strictly is called **an ideal gas**. Such a gas is hypothetical. It is assumed that intermolecular forces are not present between the molecules of an ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations these deviate from ideal behaviour. You will learn about the deviations later in this unit.

5.6 IDEAL GAS EQUATION

The three laws which we have learnt till now can be combined together in a single equation which is known as **ideal gas equation**.

At constant T and n; $V \propto \frac{1}{p}$ **Boyle's Law**

At constant p and n; $V \propto T$ **Charles' Law**

At constant p and T ; $V \propto n$ **Avogadro Law**

Thus,

$$V \propto \frac{nT}{p} \qquad (5.15)$$

$$\Rightarrow \quad V = \mathrm{R}\frac{nT}{p} \qquad (5.16)$$

where R is proportionality constant. On rearranging the equation (5.16) we obtain

$$pV = n\,\mathrm{R}T \qquad (5.17)$$

$$\Rightarrow \quad \mathrm{R} = \frac{pV}{nT} \qquad (5.18)$$

R is called gas constant. It is same for all gases. Therefore it is also called **Universal Gas Constant**. Equation (5.17) is called **ideal gas equation.**

Equation (5.18) shows that the value of R depends upon units in which p, V and T are measured. If three variables in this equation are known, fourth can be calculated. From this equation we can see that at constant temperature and pressure n moles of any gas will have the same volume because $V = \frac{n\mathrm{R}T}{p}$ and n, R, T and p are constant. This equation will be applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour. Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710981 L mol^{-1}. Value of R for one mole of an ideal gas can be calculated under these conditions as follows :

$$\mathrm{R} = \frac{(10^5\ \mathrm{Pa})(}{(1\ \mathrm{mol}}$$

$$= 8.314\ \mathrm{Pa\ m^3\ K^{-1}\ mol^{-1}}$$

$$= 8.314 \quad 10^{-2}\ \mathrm{bar\ L\ K^{-1}\ mol^{-1}}$$

$$= 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

At STP conditions used earlier (0 C and 1 atm pressure), value of R is 8.20578 10^{-2} L atm K^{-1} mol^{-1}.

Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called **equation of state**.

Let us now go back to the ideal gas equation. This is the relationship for the simultaneous variation of the variables. If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2 then we can write

$$\frac{p_1V_1}{T_1} = n\mathrm{R} \quad \text{a}$$

$$\Rightarrow \quad \frac{p_1V_1}{T_1} = \frac{p_2}{T} \qquad (5.19)$$

Equation (5.19) is a very useful equation. If out of six, values of five variables are known, the value of unknown variable can be calculated from the equation (5.19). This equation is also known as **Combined gas law**.

Problem 5.3

At 25 C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is 10 C and volume of the gas is 640 mL.

Solution

p_1 = 760 mm Hg, V_1= 600 mL

T_1 = 25 + 273 = 298 K

V_2 = 640 mL and T_2 = 10 + 273 = 283 K

According to Combined gas law

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\Rightarrow p_2 = \frac{p_1V_1T_2}{T_1V_2}$$

$$\Rightarrow p_2 = \frac{(760\,\mathrm{m}}{}$$

= 676.6 mm Hg

5.6.1 Density and Molar Mass of a Gaseous Substance

Ideal gas equation can be rearranged as follows:

$$\frac{n}{V} = \frac{p}{RT}$$

Replacing n by $\frac{m}{M}$, we get

$$\frac{m}{M\,V} = \frac{p}{R\,T} \qquad (5.20)$$

$$\frac{d}{M} = \frac{p}{R\,T} \text{ (where } d \text{ is the density)} \qquad (5.21)$$

On rearranging equation (5.21) we get the relationship for calculating molar mass of a gas.

$$M = \frac{d\,RT}{p} \qquad (5.22)$$

5.6.2 Dalton's Law of Partial Pressures

The law was formulated by John Dalton in 1801. It states that **the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases** i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called **partial pressure**. Mathematically,

$$p_{\text{Total}} = p_1+p_2+p_3+\ldots\ldots \text{(at constant } T, V) \qquad (5.23)$$

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2 , p_3 etc. are partial pressures of gases.

Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also. Pressure exerted by saturated water vapour is called **aqueous tension**. Aqueous tension of water at different temperatures is given in Table 5.3.

$$p_{\text{Dry gas}} = p_{\text{Total}} - \text{Aqueous tension} \qquad (5.24)$$

Table 5.3 Aqueous Tension of Water (Vapour Pressure) as a Function of Temperature

Temp./K	Pressure/bar	Temp./K	Pressure/bar
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p_1, p_2 and p_3 respectively. then,

$$p_1 = \frac{n_1RT}{V} \qquad (5.25)$$

$$p_2 = \frac{n_2 RT}{V} \quad (5.26)$$

$$p_3 = \frac{n_3 RT}{V} \quad (5.27)$$

where n_1 n_2 and n_3 are number of moles of these gases. Thus, expression for total pressure will be

$$p_{Total} = p_1 + p_2 + p_3$$

$$= n_1 \frac{RT}{V} + n_2$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V} \quad (5.28)$$

On dividing p_1 by p_{total} we get

$$\frac{p_1}{p_{total}} = \left(\frac{n}{n_1+n}\right.$$

$$= \frac{n_1}{n_1+n_2+n_3}$$

where $n = n_1+n_2+n_3$

x_1 is called mole fraction of first gas.

Thus, $p_1 = x_1\, p_{total}$

Similarly for other two gases we can write

$p_2 = x_2\, p_{total}$ and $p_3 = x_3\, p_{total}$

Thus a general equation can be written as

$$p_i = x_i\, p_{total} \quad (5.29)$$

where p_i *and* x_i are partial pressure and mole fraction of ith gas respectively. If total pressure of a mixture of gases is known, the equation (5.29) can be used to find out pressure exerted by individual gases.

Problem 5.4

A neon-dioxygen mixture contains 70.6 g dioxygen and 167.5 g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture ?

Number of moles of dioxygen

$$= \frac{70.6\,g}{32\,g\,mol^{-1}}$$

$$= 2.21 \text{ mol}$$

Number of moles of neon

$$= \frac{167.5\,g}{20\,g\,mol^{-1}}$$

$$= 8.375 \text{ mol}$$

Mole fraction of dioxygen

$$= \frac{2.21}{2.21+8.375}$$

$$= \frac{2.21}{10.585}$$

$$= 0.21$$

Mole fraction of neon $= \frac{8.375}{2.21+8.375}$

$$= 0.79$$

Alternatively,

mole fraction of neon = 1– 0.21 = 0.79

Partial pressure of a gas = mole fraction total pressure

⇒ Partial pressure of oxygen = 0.21 (25 bar) = 5.25 bar

Partial pressure of neon = 0.79 (25 bar) = 19.75 bar

5.7 KINETIC MOLECULAR THEORY OF GASES

So far we have learnt the laws (e.g., Boyle's law, Charles' law etc.) which are concise statements of experimental facts observed in the laboratory by the scientists. Conducting careful experiments is an important aspect of scientific method and it tells us how the particular system is behaving under different conditions. However, once the experimental facts are established, a scientist is curious to know why the system is behaving in that way. For example, gas laws help us to predict that pressure increases when we compress gases

but we would like to know what happens at molecular level when a gas is compressed ? A theory is constructed to answer such questions. A theory is a model (i.e., a mental picture) that enables us to better understand our observations. The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory.

Assumptions or postulates of the kinetic-molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature. It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently thus exerting more pressure.

Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

5.8 BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

Our theoritical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation $pV = nRT$ reproduce actual pressure-volume-temperature relationship of gases. To test this point we plot pV *vs* p plot

of gases because at constant temperature, pV will be constant (Boyle's law) and pV *vs* p graph at all pressures will be a straight line parallel to x-axis. Fig. 5.8 shows such a plot constructed from actual data for several gases at 273 K.

Fig. 5.8 *Plot of pV vs p for real gas and ideal gas*

It can be seen easily that at constant temperature pV *vs* p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen.In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases. The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. It is thus, found that real gases do not follow ideal gas equation perfectly under all conditions.

Deviation from ideal behaviour also becomes apparent when pressure *vs* volume plot is drawn. The pressure *vs* volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig 5.9 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

Fig. 5.9 *Plot of pressure vs volume for real gas and ideal gas*

It is found that real gases do not follow, Boyle's law, Charles law and Avogadro law perfectly under all conditions. Now two questions arise.

(i) Why do gases deviate from the ideal behaviour?

(ii) What are the conditions under which gases deviate from ideality?

We get the answer of the first question if we look into postulates of kinetic theory once again. We find that two assumptions of the kinetic theory do not hold good. These are

(a) There is no force of attraction between the molecules of a gas.

(b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress.

This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volume. If assumption (b) is correct, the pressure *vs* volume graph of experimental data (real gas) and that theoritically calculated from Boyles law (ideal gas) should coincide.

Real gases show deviations from ideal gas law because molecules interact with each other. At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{ideal} = p_{real} \quad - \qquad (5.30)$$

observed pressure correction term

Here, a is a constant.

Repulsive forces also become significant. Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume V, these are now restricted to volume (V–nb) where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant. Having taken into account the corrections for pressure and volume, we can rewrite equation (5.17) as

$$\left(p + \frac{an^2}{V^2}\right)(V - \qquad (5.31)$$

Equation (5.31) is known as van der Waals equation. In this equation n is number of moles of the gas. Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas. Value of 'a' is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces. Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

The deviation from ideal behaviour can be measured in terms of **compressibility factor** Z, which is the ratio of product pV and nRT. Mathematically

$$Z = \frac{pV}{n\,\mathrm{R}T} \qquad (5.32)$$

For ideal gas Z = 1 at all temperatures and pressures because pV n RT. The graph of Z *vs* p will be a straight line parallel to pressure axis (Fig. 5.10). For gases which deviate from ideality, value of Z deviates from unity. At very low pressures all gases shown

Fig. 5.10 *Variation of compressibility factor for some gases*

have $Z \approx 1$ and behave as ideal gas. At high pressure all the gases have $Z > 1$. These are more difficult to compress. At intermediate pressures, most gases have $Z < 1$. **Thus gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it.** In other words, the behaviour of the gas becomes more ideal when pressure is very low. Upto what pressure a gas will follow the ideal gas law, depends upon nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point.** Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

More insight is obtained in the significance of Z if we note the following derivation

$$Z = \frac{pV_{\text{real}}}{n\,\text{R}T} \qquad (5.33)$$

If the gas shows ideal behaviour then $V_{\text{ideal}} = \frac{n\,\text{R}T}{p}$. On putting this value of $\frac{n\text{R}T}{p}$ in equation (5.33) we have

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \qquad (5.34)$$

From equation (5.34) we can see that compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

In the following sections we will see that it is not possible to distinguish between gaseous state and liquid state and that liquids may be considered as continuation of gas phase into a region of small volumes and very high molecular attraction. We will also see how we can use isotherms of gases for predicting the conditions for liquifaction of gases.

5.9 LIQUIFACTION OF GASES

First complete data on pressure - volume - temperature relations of a substance in both gaseous and liquid state was obtained by Thomas Andrews on carbon dioxide. He plotted isotherms of carbon dioxide at various temperatures (Fig. 5.11). Later on it was found that real gases behave in the same manner as carbon dioxide. Andrews noticed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquified even at very high pressure. As the temperature is lowered, shape of the curve changes and data shows considerable deviation from ideal behaviour. At 30.98 C

Fig. 5.11 *Isotherms of carbon dioxide at various temperatures*

carbon dioxide remains gas upto 73 atmospheric pressure. (Point E in Fig. 5.11). At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. The temperature 30.98 C is called **critical temperature (T_c)** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed. Above this temperature it is gas. Volume of one mole of the gas at critical temperature is called **critical volume (V_c)** and pressure at this temperature is called **critical pressure (p_c)**. The critical temperature, pressure and volume are called critical constants. Further increase in pressure simply compresses the liquid carbon dioxide and the curve represents the compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in steep rise in pressure indicating very low compressibility of the liquid. Below 30.98 C, the behaviour of the gas on compression is quite different. At 21.5 C, carbon dioxide remains as a gas only upto point B. At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide coexist and further application of pressure results in the condensation of more gas until the point C is reached. At point C, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by steep line. A slight compression from volume V_2 to V_3 results in steep rise in pressure from p_2 to p_3 (Fig. 5.11). Below 30.98 C (critical temperature) each curve shows the similar trend. Only length of the horizontal line increases at lower temperatures. At critical point horizontal portion of the isotherm merges into one point. Thus we see that a point like A in the Fig. 5.11 represents gaseous state. A point like D represents liquid state and a point under the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium. All the gases upon compression at constant temperature (isothermal compression) show the same behaviour as shown by carbon dioxide. Also above discussion shows that gases should be cooled below their critical temperature for liquification. Critical temperature of a gas is highest temperature at which liquifaction of the gas first occurs. Liquifaction of so called permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.

It is possible to change a gas into liquid or a liquid into gas by a process in which always a single phase is present. For example in Fig. 5.11 we can move from point A to F vertically by increasing the temperature, then we can reach the point G by compressing the gas at the constant temperature along this isotherm (isotherm at 31.1 C). The pressure will increase. Now we can move vertically down towards D by lowering the temperature. As soon as we cross the point H on the critical isotherm we get liquid. We end up with liquid but in this series of changes we do not pass through two-phase region. If process is carried out at the critical temperature, substance always remains in one phase.

Thus there is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognise this continuity. Thus a liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears (Section 5.10.1). A gas below the critical temperature can be liquified by applying pressure, and is called **vapour** of the substance. Carbon dioxide gas below its

critical temperature is called carbon dioxide vapour. Critical constants for some common substances are given in Table 5.4.

Table 5.4 Critical Constants for Some Substances

Substance	T_c /K	p_c /bar	V_c/dm^3 mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Problem 5.5

Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the gas particles. Critical temperatures of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquify first when you start cooling from 500 K to their critical temperature ?

Solution

Ammonia will liquify first because its critical temperature will be reached first. Liquifaction of CO_2 will require more cooling.

5.10 LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.

Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

5.10.1 Vapour Pressure

If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases. After some time it becomes constant, an equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as **equilibrium vapour pressure or saturated vapour pressure.**. Since process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid.

When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is given in (Fig. 5.12). At 1 atm pressure boiling temperature is called **normal boiling point**. If pressure is 1 bar then the boiling point is called **standard boiling point** of the liquid. Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100 C (373 K), its standard boiling point is 99.6 C (372.6 K).

At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food. In hospitals surgical

Fig. 5.12 *Vapour pressure vs temperature curve of some common liquids.*

instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called **critical temperature** about which we have already discussed in section 5.9.

5.10.2 Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface. Why do particles of soil at the bottom of river remain separated but they stick together when taken out ? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid ? All these phenomena are caused due to the characteristic property of liquids, called **surface tension**. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule, therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Fig. 5.13), due to the molecules below it. Since there are no molecules above it.

Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy.

Fig. 5.13 *Forces acting on a molecule on liquid surface and on a molecule inside the liquid*

Its dimensions are J m^{-2}. Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ (Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1}. The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition, that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.

The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

5.10.3 Viscosity

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid (Fig.5.14), the layer above it accelerates its flow and the layer below this retards its flow.

Fig. 5.14 *Gradation of velocity in the laminar flow*

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\frac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$f \propto A$ (A is the area of contact)

$f \propto \frac{du}{dz}$ (where, $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$$F \propto A.\frac{du}{dz}$$

$$\Rightarrow f = \eta A \frac{du}{dz}$$

'η' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m^{-2}) = pascal second (Pa s = 1kg $m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = 1 g $cm^{-1}s^{-1}$ = 10^{-1}kg $m^{-1}s^{-1}$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

SUMMARY

Intermolecular forces operate between the particles of matter. These forces differ from pure electrostatic forces that exist between two oppositely charged ions. Also, these do not include forces that hold atoms of a covalent molecule together through covalent bond. Competition between thermal energy and intermolecular interactions determines the state of matter. "Bulk" properties of matter such as behaviour of gases, characteristics of solids and liquids and change of state depend upon energy of constituent particles and the type of interaction between them. Chemical properties of a substance do not change with change of state, but the reactivity depends upon the physical state.

Forces of interaction between gas molecules are negligible and are almost independent of their chemical nature. Interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental studies on gases. **Boyle's law** states that under isothermal condition, pressure of a fixed amount of a gas is inversely proportional to its volume. **Charles' law** is a relationship between volume and absolute temperature under isobaric condition. It states that volume of a fixed amount of gas is directly proportional to its absolute temperature $(V \propto T)$. If state of a gas is represented by p_1, V_1 and T_1 and it changes to state at p_2, V_2 and T_2, then relationship between these two states is given by combined gas law according to which $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$. Any one of the variables of this gas can be found out if other five variables are known. **Avogadro law** states that equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules. **Dalton's law of partial pressure** states that total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them. Thus $p = p_1+p_2+p_3+ \ldots$. Relationship between pressure, volume, temperature and number of moles of a gas describes its state and is called equation of state of the gas. Equation of state for ideal gas is $pV=nRT$, where R is a gas constant and its value depends upon units chosen for pressure, volume and temperature.

At high pressure and low temperature intermolecular forces start operating strongly between the molecules of gases because they come close to each other. Under suitable temperature and pressure conditions gases can be liquified. Liquids may be considered as continuation of gas phase into a region of small volume and very strong molecular attractions. Some properties of liquids *e.g.*, surface tension and viscosity are due to strong intermolecular attractive forces.

EXERCISES

5.1 What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30 C?

5.2 A vessel of 120 mL capacity contains a certain amount of gas at 35 C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 C. What would be its pressure?

5.3 Using the equation of state $pV=nRT$; show that at a given temperature density of a gas is proportional to gas pressure p.

5.4 At 0 C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

5.5 Pressure of 1 g of an ideal gas A at 27 C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

5.6 The drain cleaner, Drainex contains small bits of aluminum which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20 C and one bar will be released when 0.15g of aluminum reacts?

5.7 What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27 C ?

5.8 What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27 C?

5.9 Density of a gas is found to be 5.46 g/dm^3 at 27 C at 2 bar pressure. What will be its density at STP?

5.10 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 C and 0.1 bar pressure. What is the molar mass of phosphorus?

5.11 A student forgot to add the reaction mixture to the round bottomed flask at 27 C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477 C. What fraction of air would have been expelled out?

5.12 Calculate the temperature of 4.0 mol of a gas occupying 5 dm^3 at 3.32 bar. (R = 0.083 bar dm^3 K^{1} mol^{1}).

5.13 Calculate the total number of electrons present in 1.4 g of dinitrogen gas.

5.14 How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second ?

5.15 Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27 C. R = 0.083 bar dm^3 K^{1} mol^{1}.

5.16 Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27 C. (Density of air = 1.2 kg m^{3} and R = 0.083 bar dm^3 K^{1} mol^{1}).

5.17 Calculate the volume occupied by 8.8 g of CO_2 at 31.1 C and 1 bar pressure. R = 0.083 bar L K^{1} mol^{1}.

5.18 2.9 g of a gas at 95 C occupied the same volume as 0.184 g of dihydrogen at 17 C, at the same pressure. What is the molar mass of the gas?

5.19 A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

5.20 What would be the SI unit for the quantity pV^2T^2/n ?

5.21 In terms of Charles' law explain why –273 C is the lowest possible temperature.

5.22 Critical temperature for carbon dioxide and methane are 31.1 C and –81.9 C respectively. Which of these has stronger intermolecular forces and why?

5.23 Explain the physical significance of van der Waals parameters.

UNIT 6

THERMODYNAMICS

Objectives

After studying this Unit, you will be able to

- explain the terms : system and surroundings;
- discriminate between close, open and isolated systems;
- explain internal energy, work and heat;
- state first law of thermodynamics and express it mathematically;
- calculate energy changes as work and heat contributions in chemical systems;
- explain state functions: U, H.
- correlate ΔU and ΔH;
- measure experimentally ΔU and ΔH;
- define standard states for ΔH;
- calculate enthalpy changes for various types of reactions;
- state and apply Hess's law of constant heat summation;
- differentiate between extensive and intensive properties;
- define spontaneous and non-spontaneous processes;
- explain entropy as a thermodynamic state function and apply it for spontaneity;
- explain Gibbs energy change (ΔG);
- establish relationship between ΔG and spontaneity, ΔG and equilibrium constant.

"It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown."

Albert Einstein

Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like:

How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?

What drives a chemical reaction/process?

To what extent do the chemical reactions proceed?

6.1 THERMODYNAMIC STATE

We are interested in chemical reactions and the energy changes accompanying them. In order to quantify these energy changes, we need to separate the system which is under observations, from remaining part of the universe.

6.1.1 The System and the Surroundings

A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings.** The surroundings include everything other than the system. System and the surroundings together constitute the universe .

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 6.1).

Fig. 6.1 *System and the surroundings*

Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall that separates the system from the surroundings is called **boundary**. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

6.1.2 Types of the System

We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 6.2 (a)]. The presence of reactants in an open beaker is an example of an open system*. Here the boundary is an imaginary surface enclosing the beaker and reactants.

2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 6.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

(a) Open System (b) Closed System

(c) Isolated System

Fig. 6.2 *Open, closed and isolated systems.*

* *We could have chosen only the reactants as system then walls of the beakers will act as boundary.*

3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 6.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

6.1.3 The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by **state functions** or **state variables**.

The **state** of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

6.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

These systems are classified accordingly as you have already studied in section 6.1.2.

(a) Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as **adiabatic**. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig 6.3).

Fig. 6.3 *An adiabatic system which does not permit the transfer of heat through its boundary.*

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as T_A. Let the

internal energy of the system in state A be called U_A. We can change the state of the system in two different ways.

One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B. It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$.

Second way: We now do an equal amount (i.e., 1kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$.

In fact, the experiments in the above manner were done by J. P. Joule between 1840–50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system.

So, it seems appropriate to define a quantity, the internal energy U, whose value is characteristic of the state of a system, whereby the adiabatic work, w_{ad} required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, ΔU *i.e.*,

$$\Delta U = U_2 - U_1 :$$

Therefore, internal energy, U, of the system is a state function.

The positive sign expresses that w_{ad} is positive when work is done **on** the system. Similarly, if the work is done **by** the system, w_{ad} will be negative.

Can you name some other familiar state functions? Some of other familiar state functions are V, p, and T. For example, if we bring a change in temperature of the system from 25 C to 35 C, the change in temperature is 35 C–25 C = +10 C, whether we go straight up to 35 C or we cool the system for a few degrees, then take the system to the final temperature. Thus, T is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both,

(b) Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q. Let us consider bringing about the same change in temperature (the same initial and final states as before in section 6.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 6.4).

Fig. 6.4 *A system which allows heat transfer through its boundary.*

We take water at temperature, T_A in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat reservoir at temperature, T_B. The heat absorbed by the system (water), q can be measured in terms of temperature difference , $T_B - T_A$. In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.

The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.

(c) The general case

Let us consider the general case in which a change of state is brought about both by

doing work and by transfer of heat. We write change in internal energy for this case as:

$$\Delta U = q + w \quad (6.1)$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if w = 0 and $q = 0$, then $\Delta U = 0$.

The equation 6.1 i.e., $\Delta U = q + w$ is mathematical statement of the **first law of thermodynamics**, which states that

The energy of an isolated system is constant.

It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed.

Note: There is considerable difference between the character of the thermodynamic property energy and that of a mechanical property such as volume. We can specify an unambiguous (absolute) value for volume of a system in a particular state, but not the absolute value of the internal energy. However, we can measure only the changes in the internal energy, ΔU of the system.

Problem 6.1

Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Solution

(i) $\Delta U = w_{ad}$, wall is adiabatic

(ii) $\Delta U = -q$, thermally conducting walls

(iii) $\Delta U = q - w$, closed system.

6.2 APPLICATIONS

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

6.2.1 Work

First of all, let us concentrate on the nature of work a system can do. We will consider only mechanical work i.e., pressure-volume work.

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change

Fig. 6.5(a) *Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.*

be achieved in a single step and the final volume be V_f. During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A [Fig. 6.5(a)].

then, volume change = l A = $\Delta V = (V_f - V_i)$

We also know, pressure = $\frac{\text{fo}}{\text{ar}}$

Therefore, force on the piston = p_{ex} . A

If w is the work done on the system by movement of the piston then

w = force × distance = p_{ex} . A .l

$$= p_{ex} . (-\Delta V) = - p_{ex} \Delta V = - p_{ex} (V_f - V_i) \qquad (6.2)$$

The negative sign of this expression is required to obtain conventional sign for w, which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p\Delta V$ [Fig. 6.5 (b)]

Fig. 6.5 (b) *pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex} dV \qquad (6.3)$$

Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression [Fig. 6.5(c)]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex} = (p_{in} \quad dp)$. In general case we can write, $p_{ex} = (p_{in} \pm dp)$. Such processes are called reversible processes.

A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes

Fig. 6.5 (c) *pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

other than reversible processes are known as irreversible processes.

In chemistry, we face problems that can be solved if we relate the work term to the **internal pressure of the system.** We can relate work to internal pressure of the system under **reversible conditions** by writing equation 6.3 as follows:

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex} d$$

Since dp dV is very small we can write

$$w_{rev} = -\int_{V_i}^{V_f} p_{in} d \qquad (6.4)$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., $pV = nRT$

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = -\int_{V_i}^{V_f} nRT$$

$$= -2.303\ nRT \log \frac{V_f}{V_i} \qquad (6.5)$$

Free expansion: Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation 6.2 and 6.3).

Now, we can write equation 6.1 in number of ways depending on the type of processes.

Let us substitute $w = -p_{ex}\Delta V$ (eq. 6.2) in equation 6.1, and we get

$$\Delta U = q - p_{ex}\Delta V$$

If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_V$$

the subscript V in q_V denotes that heat is supplied at constant volume.

Isothermal and free expansion of an ideal gas

For isothermal (T = constant) expansion of an ideal gas into vacuum ; w = 0 since $p_{ex} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$

Equation 6.1, $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change
   $q = -w = p_{ex}(V_f \quad V_i)$
2. For isothermal reversible change
   $$q = -w = nRT \ln \frac{V_f}{V_i}$$
   $$= 2.303\ nRT \log \frac{V_f}{V_i}$$
3. For adiabatic change, $q = 0$,
   $\Delta U = w_{ad}$

Problem 6.2

Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

Solution

We have $q = -w = p_{ex}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

Problem 6.3

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -w = p_{ex}(8) = 8$ litre-atm

Problem 6.4

Consider the same expansion, to a final volume of 10 litres conducted reversibly.

Solution

We have $q = -w = 2.303 \quad 10 \log \frac{10}{2}$

$= 16.1$ litre-atm

6.2.2 Enthalpy, *H*

(a) A useful new state function

We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation (6.1) as $\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$$U_2 - U_1 = q_p - p\,(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \qquad (6.6)$$

Now we can define another thermodynamic function, the enthalpy H [Greek word *enthalpien*, to warm or heat content] as :

$$H = U + pV \qquad (6.7)$$

so, equation (6.6) becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation 6.7 as

$$\Delta H = \Delta U + \Delta pV$$

Since p is constant, we can write

$$\Delta H = \Delta U + p\Delta V \qquad (6.8)$$

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

At constant volume ($\Delta V = 0$), $\Delta U = q_V$, therefore equation 6.8 becomes

$$\Delta H = \Delta U = q_V$$

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT$$

and $$pV_B = n_B RT$$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or $$p\,(V_B - V_A) = (n_B - n_A)\,RT$$

or $$p\,\Delta V = \Delta n_g RT \qquad (6.9)$$

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation 6.9 in equation 6.8, we get

$$\Delta H = \Delta U + \Delta n_g RT \qquad (6.10)$$

The equation 6.10 is useful for calculating ΔH from ΔU and *vice versa*.

Problem 6.5

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100 C is 41kJ mol^{-1}. Calculate the internal energy change, when

(i) 1 mol of water is vaporised at 1 bar pressure and 100 C.

(ii) 1 mol of water is converted into ice.

Solution

(i) The change $H_2O(l) \rightarrow H_2$

$\Delta H = \Delta U + \Delta$

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$\Delta U = 41.00$ kJ

$\times 8.3$ J

$= 41.00$ kJ m

$= 37.904$ kJ mol^{-1}

(ii) The change $H_2O(l) \rightarrow H_2O$

There is negligible change in volume,

So, we can put $p\Delta V = \Delta n_g RT$ in this case,

$$\Delta H \cong \Delta U$$

so, $\Delta U = 41.$

(b) Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An **extensive property** is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**. For example temperature, density, pressure etc. are intensive properties. A molar property, χ_m, is the value of an extensive property χ of the system for 1 mol of the substance. If n is the amount of matter, $\chi_m = \frac{\chi}{n}$ is independent of the amount of matter. Other examples are molar volume, V_m and molar heat capacity, C_m. Let us understand the distinction between extensive and intensive properties by considering a gas enclosed in a container of volume V and at temperature T [Fig. 6.6(a)]. Let us make a partition such that volume is halved, each part [Fig. 6.6 (b)] now has one half of the original volume, $\frac{V}{2}$, but the temperature will still remain the same i.e., T. It is clear that volume is an extensive property and temperature is an intensive property.

Fig. 6.6(a) *A gas at volume V and temperature T*

Fig. 6.6 (b) *Partition, each part having half the volume of the gas*

(c) Heat Capacity

In this sub-section, let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system.

The increase of temperature is proportional to the heat transferred

$$q = coeff \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as $q = C\,\Delta T$

The coefficient, C is called the heat capacity.

Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity.

When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature.

C is directly proportional to amount of substance. The molar heat capacity of a substance, $C_m = \left(\frac{C}{n}\right)$, is the heat capacity for

one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin). Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as

$$q = c \times m \times \Delta T \qquad (6.11)$$

(d) The relationship between C_p and C_V for an ideal gas

At constant volume, the heat capacity, C is denoted by C_V and at constant pressure, this is denoted by C_p. Let us find the relationship between the two.

We can write equation for heat, q

at constant volume as $q_V = C_V \Delta T = \Delta U$

at constant pressure as $q_p = C_p \Delta T = \Delta H$

The difference between C_p and C_V can be derived for an ideal gas as:

For a mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$$\therefore \Delta H = \Delta U + 1 \qquad (6.12)$$

On putting the values of ΔH and ΔU, we have

$$C_p \Delta T = C_V \Delta T$$

$$C_p = C_V + R$$

$$C_p - C_V = R \qquad (6.13)$$

6.3 MEASUREMENT OF ΔU AND ΔH: CALORIMETRY

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

i) at constant volume, q_v

ii) at constant pressure, q_p

(a) ΔU measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Fig. 6.7). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is

Fig. 6.7 *Bomb calorimeter*

done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_V, by using the known heat capacity of the calorimeter with the help of equation 6.11.

(b) ΔH measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig. 6.8. We know that $\Delta H = q_p$ (at constant p) and, therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, q_p will be negative and $\Delta_r H$ will also be negative. Similarly in an endothermic reaction, heat is absorbed, q_p is positive and $\Delta_r H$ will be positive.

Fig. 6.8 *Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).*

Problem 6.6

1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

C (graphite) + O_2 (g) $\rightarrow$ CO_2 (g)

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

Solution

Suppose q is the quantity of heat from the reaction mixture and C_V is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$q = C_V \quad \Delta T$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$q = - C_V \times \Delta T =$

$= -$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1g of graphite = – 20.7 kJK^{-1}

For combustion of 1 mol of graphite,

$= \dfrac{12.0 \text{ g mol}^{-1}}{1}$

$= - 2.48 \quad 10^2 \text{ kJ mol}^{-1}$

6.4 ENTHALPY CHANGE, $\Delta_r H$ OF A REACTION – REACTION ENTHALPY

In a chemical reaction, reactants are converted into products and is represented by,

Reactants $\rightarrow$ Products

The enthalpy change accompanying a reaction is called the **reaction enthalpy**. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

$\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

$$= \sum_i a_i H_{products} \quad (6.14)$$

(Here symbol $\sum$ (sigma) is used for summation and a_i and b_i are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation. For example, for the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r H = \sum_i a_i H_p$$

$$= [H_m(CO_2, g) + 2H_m(H_2O, l)] - [H_m(CH_4, g) + 2H_m(O_2, g)]$$

where H_m is the molar enthalpy.

Enthalpy change is a very useful quantity. Knowledge of this quantity is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

(a) Standard enthalpy of reactions

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript V to the symbol ΔH, e.g., ΔH^V

(b) Enthalpy changes during phase transformations

Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).

$$H_2O(s) \rightarrow H_2O$$

Here $\Delta_{fus}H$ is enthalpy of fusion in standard state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^0$.

Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires heat for evaporation. At constant temperature of its boiling point T_b and at constant pressure:

$$H_2O(l) \rightarrow H_2O$$

$\Delta_{vap}H$ is the standard enthalpy of vaporization.

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^0$.

Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimes at 195K with $\Delta_{sub}H$ =25.2 kJ mol^{-1}; naphthalene sublimes slowly and for this $\Delta_{sub}H^V = 73.0$.

Standard enthalpy of sublimation, $\Delta_{sub}H$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).

The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transfomations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular

Table 6.1 Standard Enthalpy Changes of Fusion and Vaporisation

Substance	T_f/K	$\Delta_{fus}H^{\ominus}$/(kJ mol^{-1})	T_b/K	$\Delta_{vap}H^{\ominus}$/(kJ mol^{-1})
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl_4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

(T_f and T_b are melting and boiling points, respectively)

dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mol of acetone than it does to vaporize 1 mol of water. Table 6.1 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

Problem 6.7

A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 100 C.

$\Delta_{vap}H^{V}$ for water

at 373K = 40.66 kJ mol^{-1}

Solution

We can represent the process of evaporation as

$18\,g\,H_2O(l) \longrightarrow$

No. of moles in 18 g $H_2O(l)$ is

$$= \frac{18g}{18\,g\,mol^{-1}} =$$

$\Delta_{vap}U = \Delta_{vap}H^{\vee}$

(assuming steam behaving as an ideal gas).

$\Delta_{vap}H^{V} - \Delta n_g R$

$-(1)(8.314$ J

$\Delta_{vap}U^{V} = 40.6$

$= 37.5$

(c) Standard enthalpy of formation

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^0$, where the subscript 'f' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25 C and 1 bar pressure. For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of formation are given below.

$H_2(g) + ½O_2(g$

$\Delta_f H^{V} = -285$

C (graphite, s) $+2H_2(g) \rightarrow$ CH

Table 6.2 Standard Molar Enthalpies of Formation ($\Delta_f H^\ominus$) at 298K of a Few Selected Substances

Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})	Substance	$\Delta_f H^\ominus$ /(kJ mol^{-1})
$Al_2O_3(s)$	-1675.7	HI(g)	+26.48
$BaCO_3(s)$	-1216.3	KCl(s)	-436.75
$Br_2(l)$	0	KBr(s)	-393.8
$Br_2(g)$	+30.91	MgO(s)	-601.70
$CaCO_3(s)$	-1206.92	$Mg(OH)_2(s)$	-924.54
C (diamond)	+1.89	NaF(s)	-573.65
C (graphite)	0	NaCl(s)	-411.15
CaO(s)	- 635.09	NaBr(s)	-361.06
$CH_4(g)$	-74.81	NaI(s)	-287.78
$C_2H_4(g)$	52.26	$NH_3(g)$	-46.11
$CH_3OH(l)$	-238.86	NO(g)	+ 90.25
$C_2H_5OH(l)$	-277.69	$NO_2(g)$	+33.18
$C_6H_6(l)$	+ 49.0	$PCl_3(l)$	-319.70
CO(g)	-110.53	$PCl_5(s)$	-443.5
$CO_2(g)$	-393.51	$SiO_2(s)$ (quartz)	-910.94
$C_2H_6(g)$	-84.68	$SnCl_2(s)$	-325.1
$Cl_2(g)$	0	$SnCl_4(l)$	-511.3
$C_3H_8(g)$	-103.85	$SO_2(g)$	-296.83
$n-C_4H_{10}(g)$	-126.15	$SO_3(g)$	-395.72
HgS(s) red	-58.2	$SiH_4(g)$	+ 34
$H_2(g)$	0	$SiCl_4(g)$	-657.0
$H_2O(g)$	-241.82	C(g)	+716.68
$H_2O(l)$	-285.83	H(g)	+217.97
HF(g)	-271.1	Cl(g)	+121.68
HCl(g)	-92.31	$Fe_2O_3(s)$	–824.2
HBr(g)	-36.40		

$$\Delta_f H^\vee = -74.8$$

$$2C(\text{graphite, s})$$

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H$, is just a special case of $\Delta_r H$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:

$$CaO(s) + CO_2($$

$$\Delta_f H^\vee = -178$$

is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H$ for HBr(g).

$$H_2(g) + Br_2(l)$$

Here two moles, instead of one mole of the product is formed from the elements, i.e., $\Delta_r H^\vee = 2\Delta_f H$.

Therefore, by dividing all coefficients in the balanced equation by 2, expression for

enthalpy of formation of HBr (g) is written as

$$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2$$

Standard enthalpies of formation of some common substances are given in Table 6.2.

By convention, standard enthalpy for formation, $\Delta_f H$, of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

Suppose, you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide, with all the substances in their standard state.

$$CaCO_3(s) \rightarrow C$$

Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation.

$$\Delta_r H^{\circ} = \sum_i a_i \Delta_f H^{\circ}$$

(6.15)

where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are 1 each.

Therefore,

$$\Delta_r H^{\circ} = \Delta_f H^{\circ}[$$

$$= 1(-635.1 \text{ kJ}$$

$$= 178.3 \text{ kJ mol}^{-1}$$

Thus, the decomposition of $CaCO_3$ (s) is an endothermic process and you have to heat it for getting the desired products.

(d) Thermochemical equations

A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation. We specify the physical state (alongwith allotropic state) of the substance in an equation. For example:

$$C_2H_5OH(l) + 3$$

The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

It would be necessary to remember the following conventions regarding thermochemical equations.

1. The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.
2. The numerical value of $\Delta_r H$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H$ will have units as kJ mol^{-1}.

To illustrate the concept, let us consider the calculation of heat of reaction for the following reaction :

$$Fe_2O_3(s) + 3H$$

From the Table (6.2) of standard enthalpy of formation ($\Delta_f H$), we find :

$$\Delta_f H^{\circ}(H_2O, l) = -285.83 \text{ kJ mol}^{-1};$$

$$\Delta_f H^{\circ}(Fe_2O_3, s = -824.2 \text{ kJ mol}^{-1};$$

Also $\Delta_f H^{\circ}(Fe$

$\Delta_f H^{\circ}(H$

Then,

$$\Delta_r H_1^{\circ} = 3(-285.83 \text{ kJ mol}^{-1}) - 1(-824.2 \text{ kJ mol}^{-1})$$

$$= (-857.5 + 824.2) \text{ kJ mol}^{-1}$$

$$= -33.3 \text{ kJ mol}^{-1}$$

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for $\Delta_r H$ is

kJ mol^{-1}, which means *per mole of reaction*. Once we balance the chemical equation in a particular way, as above, this defines the *mole of reaction*. If we had balanced the equation differently, for example,

$$\frac{1}{2}Fe_2O_3(s) + \frac{3}{2}$$

then this amount of reaction would be one mole of reaction and $\Delta_r H$ would be

$$\Delta_r H_2^{\ominus} = \frac{3}{2}(-2$$

$$-\frac{1}{2}(-824.2\,\text{k}$$

= (– 428.7 + 412.1) kJ mol^{-1}

= –16.6 kJ mol^{-1} = ½ $\Delta_r H_1^{\ominus}$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of $\Delta_r H$ is reversed in sign. For example

$$N_2(g) + 3H_2(g$$

$$2NH_3(g) \rightarrow N_2$$

(e) Hess's Law of Constant Heat Summation

We know that enthalpy is a state function, therefore the change in enthalpy is independent of the path between initial state (reactants) and final state (products). In other words, enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of Hess's Law.

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

Let us understand the importance of this law with the help of an example.

Consider the enthalpy change for the reaction

$$C(\text{graphite}, s)$$

Although CO(g) is the major product, some CO_2 gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:

$$C(\text{graphite}, s) \qquad \text{(i)}$$

$$CO(g) + \frac{1}{2}O_2 \qquad \text{(ii)}$$

We can combine the above two reactions in such a way so as to obtain the desired reaction. To get one mole of CO(g) on the right, we reverse equation (ii). In this, heat is absorbed instead of being released, so we change sign of $\Delta_r H$ value

$$CO_2(g) \rightarrow CO$$

$$\Delta_r H^{\ominus} = +283. \qquad \text{(iii)}$$

Adding equation (i) and (iii), we get the desired equation,

$$C(\text{graphite}, s)$$

for which $\Delta_r H^{\ominus}$ = (–39

= – 110.5 kJ mol^{-1}

In general, if enthalpy of an overall reaction A→B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... representing enthalpies of reactions leading to same product, B along another route,then we have

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots \qquad (6.16)$$

It can be represented as:

6.5 ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

It is convenient to give name to enthalpies specifying the types of reactions.

(a) Standard enthalpy of combustion (symbol : $\Delta_c H^0$)

Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane (C_4H_{10}). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:

$$C_4H_{10}(g) + \frac{13}{2}$$

Similarly, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is :

$$C_6H_{12}O_6(g) + ($$

$$\Delta$$

Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

Problem 6.8

The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $CO_2(g)$ and H_2O (l) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H$ of benzene. Standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are –393.5 kJ mol^{-1} and – 285.83 kJ mol^{-1} respectively.

Solution

The formation reaction of benezene is given by :

$$6C(\text{graphite})$$

The enthalpy of combustion of 1 mol of benzene is :

$$C_6H_6(l) + \frac{15}{2}($$

$$\Delta_c H$$

The enthalpy of formation of 1 mol of $CO_2(g)$:

$$C(\text{graphite}) +$$

$$\Delta_f H^{\backslash}$$

The enthalpy of formation of 1 mol of $H_2O(l)$ is :

$$H_2(g) + \frac{1}{2}O_2($$

$$\Delta_f H^{\vee} = -$$

multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:

$$6C(\text{graphite})$$

$$/$$

$$3H_2(g) + \frac{3}{2}O_2$$

$$/$$

Summing up the above two equations :

$$6C(\text{graphite}) +$$

$\Delta_f H^V = -3218$

Reversing equation (ii);

$6CO_2(g) + 3H_2$

$\Delta_f H^V$

Adding equations (v) and (vi), we get

$6C(\text{graphite})$

(b) Enthalpy of atomization (symbol: $\Delta_a H^0$)

Consider the following example of atomization of dihydrogen

$H_2(g) \rightarrow 2H(g)$; $\Delta_a H = 435.0$ kJ mol^{-1}

You can see that H atoms are formed by breaking H–H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization, $\Delta_a H$. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

In case of diatomic molecules, like dihydrogen (given above), the enthalpy of atomization is also the bond dissociation enthalpy. The other examples of enthalpy of atomization can be

$CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta_a H = 1665$ kJ mol^{-1}

Note that the products are only **atoms** of C and H in gaseous phase. Now see the following reaction:

$Na(s) \rightarrow Na(g)$; $\Delta_a H = 108.4$ kJ mol^{-1}

In this case, the enthalpy of atomization is same as the enthalpy of sublimation.

(c) Bond Enthalpy (symbol: $\Delta_{bond} H^0$)

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

(i) Bond dissociation enthalpy

(ii) Mean bond enthalpy

Let us discuss these terms with reference to diatomic and polyatomic molecules.

Diatomic Molecules: Consider the following process in which the bonds in one mole of dihydrogen gas (H_2) are broken:

$H_2(g) \rightarrow 2H(g)$; $\Delta_{H-H} H = 435.0$ kJ mol^{-1}

The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

$Cl_2(g) \rightarrow 2Cl(g)$; $\Delta_{C-Cl} H = 242$ kJ mol^{-1}

$O_2(g) \rightarrow 2O(g)$; $\Delta_{O\ O} H = 428$ kJ mol^{-1}

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

Polyatomic Molecules: Let us now consider a polyatomic molecule like methane, CH_4. The overall thermochemical equation for its atomization reaction is given below:

$CH_4(g) \rightarrow C(g$

In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :

$CH_4(g) \rightarrow CH_3($

$CH_3(g) \rightarrow CH_2($

$CH_2(g) \rightarrow CH(g$

$CH(g) \rightarrow C(g)$

Therefore,

$CH_4(g) \rightarrow C(g)$

In such cases we use **mean bond enthalpy of C – H bond**.

For example in CH_4, $\Delta_{C-H}H$ is calculated as:

$$\Delta_{C-H}H^{V} = (\Delta$$

$$= 416 \text{ kJ mol}^{-1}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in CH_3CH_2Cl, CH etc, but it does not differ in a great deal*. Using Hess's law, bond enthalpies can be calculated. Bond enthalpy values of some single and multiple bonds are given in Table 6.3. The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of the new bonds. We can predict enthalpy of a reaction in gas phase, if we know different bond enthalpies. The standard enthalpy of reaction, $\Delta_r H$ is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\Delta_r H^{V} = \sum \text{bon}$$

$$- \sum \text{b}$$

(6.17)**

This relationship is particularly more useful when the required values of $\Delta_f H$ are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Remember that this relationship is approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

(d) Enthalpy of Solution (symbol : $\Delta_{sol}H^0$)

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves

Table 6.3(a) Some Mean Single Bond Enthalpies in kJ mol^{-1}

H	C	N	O	F	Si	P	S	Cl	Br	I	
436	414	389	464	569	293	318	339	431	368	297	H
	347	293	351	439	289	264	259	330	276	238	C
		159	201	272	-	209	-	201	243	-	N
			138	184	368	351	-	205	-	201	O
				159	540	490	327	255	197	-	F
					176	213	226	360	289	213	Si
						213	230	331	272	213	P
							213	251	213	-	S
								243	218	209	Cl
									192	180	Br
										151	I

Table 6.3(b) Some Mean Multiple Bond Enthalpies in kJ mol^{-1}

N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

* *Note that symbol used for bond dissociation enthalpy and mean bond enthalpy is the same.*

** *If we use enthalpy of bond formation, ($\Delta_f H_{bond}$), which is the enthalpy change when one mole of a particular type of bond is formed from gaseous atom, then* $\Delta_r H^{V} = \sum \Delta_f H^{V}_{bonds}$

in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)

The enthalpy of solution of AB(s), $\Delta_{sol}H$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice}H$ and enthalpy of hydration of ions, $\Delta_{hyd}H$ as

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H$$

For most of the ionic compounds, $\Delta_{sol}H$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Why do many fluorides tend to be less soluble than the corresponding chlorides? Estimates of the magnitudes of enthalpy changes may be made by using tables of bond energies (enthalpies) and lattice energies (enthalpies).

Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$$Na^+Cl^-(s) \rightarrow$$

$$\Delta$$

Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a **Born-Haber Cycle** (Fig. 6.9).

Let us now calculate the lattice enthalpy of $Na^+Cl^-(s)$ by following steps given below :

1. $Na(s) \rightarrow Na(g)$, *sublimation of sodium metal,* $\Delta_{sub}H^{\ominus} = 108$.
2. $Na(g) \rightarrow Na^+(g)$, the *ionization of sodium atoms*, ionization enthalpy Δ_iH = 496 kJ mol^{-1}
3. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$, the *dissociation of chlorine*, the reaction enthalpy is half the

Fig. 6.9 *Enthalpy diagram for lattice enthalpy of NaCl*

bond dissociation enthalpy.

$$\frac{1}{2}\Delta_{bond}H^{\vee} = 1$$

4. $Cl(g) + e^{-1}(g)$ – *electron gained* by chlorine atoms. The electron gain enthalpy, $\Delta_{eg}H = -348.6$ kJ mol^{-1}.
You have learnt about ionization enthalpy and electron gain enthalpy in Unit 3. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms (see the box for justification).

Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for

$M(g) \rightarrow M^{+}(g) + e^{-}$ (for ionization)

$M(g) + e^{-} \rightarrow M^{-}(g)$ (for electron gain)

at temperature, T is

$$\Delta_r H\ (T) = \Delta_r H\ (0) + \int_0^T \Delta_r C_p^{\vee} dT$$

The value of C_p for each species in the above reaction is 5/2 R (C_V = 3/2R)

So, $\Delta_r C_p$ = + 5/2 R (for ionization)

$\Delta_r C_p$ = – 5/2 R (for electron gain)

Therefore,

$\Delta_r H$ (ionization enthalpy)

= E_0 (ionization energy) + 5/2 RT

$\Delta_r H$ (electron gain enthalpy)

= – A(electron affinity) – 5/2 RT

5. $Na^{+}(g) + Cl^{-}(g$
The sequence of steps is shown in Fig. 6.9, and is known as a Born-Haber cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero.

Applying Hess's law, we get,

$$\Delta_{lattice}H^{\vee} = 411$$

$$\Delta_{lattice}H^{\vee} = +7$$

for $NaCl(s) \rightarrow Na$

Internal energy is smaller by 2RT (because Δn_g = 2) and is equal to + 783 kJ mol^{-1}.

Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

$$\Delta_{sol}H^{\vee} = \Delta_{lattic}$$

For one mole of NaCl(s),
lattice enthalpy = + 788 kJ mol^{-1}
and $\Delta_{hyd}H$ = – 784 kJ mol^{-1}(from the literature)

$\Delta_{sol}H$ = + 788 kJ mol^{-1} – 784 kJ mol^{-1}
= + 4 kJ mol^{-1}

The dissolution of NaCl(s) is accompanied by very little heat change.

6.6 SPONTANEITY

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes ? What determines the direction of a spontaneous change ? In this section, we shall establish some criterion for these processes whether these will take place or not.

Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many

years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means *'having the potential to proceed without the assistance of external agency'*. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows:

A spontaneous process is an irreversible process and may only be reversed by some external agency.

(a) Is decrease in enthalpy a criterion for spontaneity ?

If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)\ ; \quad \Delta_r H = -46.1\ \text{kJ mol}^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl\ (g)\ ; \quad \Delta_r H = -92.32\ \text{kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)\ ; \quad \Delta_r H = -285.8\ \text{kJ mol}^{-1}$$

The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 6.10(a).

Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far !

Now let us examine the following reactions:

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g); \quad \Delta_r H = +33.2\ \text{kJ mol}^{-1}$$

Fig. 6.10 (a) *Enthalpy diagram for exothermic reactions*

$$C(\text{graphite, s}) + 2\ S(l) \rightarrow CS_2(l); \quad \Delta_r H = +128.5\ \text{kJ mol}^{-1}$$

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 6.10(b).

Fig. 6.10 (b) *Enthalpy diagram for endothermic reactions*

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(b) Entropy and spontaneity

Then, what drives the spontaneous process in a given direction ? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is

isolated from the surroundings as shown in Fig. 6.11.

Fig. 6.11 *Diffusion of two gases*

The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig. 6.11 (a)]. When the partition is withdrawn [Fig.6.11(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete.

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change !

At this point, we introduce another thermodynamic function, **entropy** denoted as *S*. The above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus **heat (q) has randomising influence** on the system. Can we then equate ΔS with q ? Wait ! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, **temperature is the measure of average chaotic motion of particles in the system**. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher

temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \quad (6.18)$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{syst} \quad (6.19)$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Problem 6.9

Predict in which of the following, entropy increases/decreases :

(i) A liquid crystallizes into a solid.

(ii) Temperature of a crystalline solid is raised from 0 K to 115 K.

(iii) 2NaHCC

(iv) $H_2(g) \rightarrow 2H($

Solution

(i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0 K, the contituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Problem 6.10

For oxidation of iron,

$4Fe(s) + 3O_2($

entropy change is – 549.4 $JK^{-1}mol^{-1}$at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H$ for this reaction is $-1648 \quad 10^3$ J mol^{-1})

Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{total}\left(\Delta S_{sys} + \right.$. For calculating ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H}{T}$$

$$= -\frac{(-1648 \times 1}{29}$$

$$= 5530\ JK^{-1}m$$

Thus, total entropy change for this reaction

$\Delta_r S_{total} = 5530\,J$

$= 4980.6\,JK^{-}$

This shows that the above reaction is spontaneous.

(c) Gibbs energy and spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, G, as

$$G \quad H \quad TS \qquad (6.20)$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{sys} = \Delta H_{sys} \cdot$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sy}$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \qquad (6.21)$$

Thus, Gibbs energy change = enthalpy change – temperature entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S$ = (K) (J/K) = J.

Now let us consider how ΔG is related to reaction spontaneity.

We know,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{sur}}{T}$$

$$\Delta S_{total} = \Delta S_{sys}$$

Rearranging the above equation:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontanious process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Rightarrow -\left(\Delta H_{sys} - T\right.$$

Using equation 6.21, the above equation can be written as

$$-\Delta G > 0$$

$$\Delta G = \Delta H - T\Delta \qquad (6.22)$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non spontaneous.

Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH. This can happen in two ways;

(a) The positive entropy change of the system can be 'small' in which case T must be large.
(b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 6.4 summarises the effect of temperature on spontaneity of reactions.

6.7 GIBBS ENERGY CHANGE AND EQUILIBRIUM

We have seen how a knowledge of the sign and magnitude of the free energy change of a chemical reaction allows:

(i) Prediction of the spontaneity of the chemical reaction.

(ii) Prediction of the useful work that could be extracted from it.

So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions.

'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium

A + B C + I ; is

$\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G + RT \ln K$$

or $\Delta_r G = -RT \ln K$

or $\Delta_r G = -2.303\, RT \log K$ (6.23)

We also know that

$$\Delta_r G^{\vee} = \Delta_r H^{\vee} - \quad (6.24)$$

For strongly endothermic reactions, the value of $\Delta_r H$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H$ is large and negative, and $\Delta_r G$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\Delta_r G$ also depends upon $\Delta_r S$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\Delta_r S$ is positive or negative.

Table 6.4 Effect of Temperature on Spontaneity of Reactions

$\Delta_r H$	$\Delta_r S$	$\Delta_r G$	Description*
–	+	–	Reaction spontaneous at all temperature
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

* *The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

Using equation (6.24),

(i) It is possible to obtain an estimate of ΔG^{V} from the measurement of ΔH^{V} and ΔS^{V}, and then calculate K at any temperature for economic yields of the products.

(ii) If K is measured directly in the laboratory, value of ΔG at any other temperature can be calculated.

Problem 6.11

Calculate $\Delta_r G$ for conversion of oxygen to ozone, $3/2\ O_2(g) \rightarrow O_3(g)$ at 298 K. if K_p for this conversion is $2.47 \quad 10^{-29}$.

Solution

We know $\Delta_r G = -2.303\ RT \log K_p$ and $R = 8.314\ JK^{-1}\ mol^{-1}$

Therefore, $\Delta_r G =$
$-2.303\ (8.314\ J\ K^{-1}\ mol^{-1})$
$(298\ K)\ (\log 2.47 \quad 10^{-29})$

$= 163000\ J\ mol^{-1}$

$= 163\ kJ\ mol^{-1}$.

Problem 6.12

Find out the value of equilibrium constant for the following reaction at 298 K.

$2NH_3(g) + CC$.

Standard Gibbs energy change, $\Delta_r G$ at the given temperature is $-13.6\ kJ\ mol^{-1}$.

Solution

We know, $\log K = \dfrac{-\Delta_r G^{V}}{2.303RT}$

$= \dfrac{(-13.6}{2.303(8.314}$

$= 2.38$

Hence K = antilog 2.38 = 2.4 $\quad 10^2$.

Problem 6.13

At 60 C, dinitrogen tetroxide is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution

$N_2O_4(g) \qquad 2NO_2(g)$

If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1-0.5}{1+0.5}\ ;\ x_{NO_2} = \frac{2\times 0.5}{1+0.5}$$

$$p_{N_2O_4} = \frac{0.5}{1.5}\times 1\ atm,\ p_{NO_2} = \frac{1}{1.5}\times 1\ atm.$$

The equilibrium constant K_p is given by

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{}{(1.5}$$

$= 1.33$ atm.

Since

$\Delta_r G = -RT \ln K_p$

$\Delta_r G = (-8.314\ JK^{-1}\ mol^{-1})\ (333\ K)$
$(2.303)\ (0.1239)$

$= -763.8\ kJ\ mol^{-1}$

SUMMARY

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the **first law of thermodynamics** via $\Delta U = q + w$. ΔU, change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $w = -p_{ex}\Delta V$, in case of expansion of gases. Under reversible process, we can put $p_{ex} = p$ for infinitesimal changes in the volume making $w_{rev} = -p\,dV$. In this condition, we can use gas equation, $pV = nRT$.

At constant volume, w = 0, then $\Delta U = q_V$, heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function **enthalpy**. Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f (a_i \Delta_f H)$$

and in gaseous state by

$\Delta_r H$ = Σ *bond enthalpies of the reactants* – Σ *bond enthalpies of the products*

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $\Delta U = 0$. We define another state function, S, **entropy** for this purpose. **Entropy** is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $\Delta U = 0$, $\Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation $\Delta S = \frac{q_{rev}}{T}$ for a reversible process. $\frac{q_{rev}}{T}$ is independent of path.

Chemical reactions are generally carried at constant pressure, so we define another state function **Gibbs energy**, G, which is related to entropy and enthalpy changes of the system by the equation:

$$\Delta_r G = \Delta_r H - T\,\Delta_r S$$

For a spontaneous change, $\Delta G_{sys} < 0$ and at equilibrium, $\Delta G_{sys} = 0$.

Standard Gibbs energy change is related to equilibrium constant by

$$\Delta_r G^{\circ} = -RT \ln K.$$

K can be calculated from this equation, if we know $\Delta_r G^{\circ}$ which can be found from $\Delta_r G^{\circ} = \Delta_r H^{\circ} - T$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.

EXERCISES

6.1 Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only.

6.2 For the process to occur under adiabatic conditions, the correct condition is:

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) $q = 0$

(iv) $w = 0$

6.3 The enthalpies of all elements in their standard states are:

(i) unity

(ii) zero

(iii) < 0

(iv) different for each element

6.4 ΔU of combustion of methane is – X kJ mol^{-1}. The value of ΔH is

(i) $= \Delta U$

(ii) $> \Delta U$

(iii) $< \Delta U$

(iv) $= 0$

6.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ mol^{-1} –393.5 kJ mol^{-1}, and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be

(i) –74.8 kJ mol^{-1} (ii) –52.27 kJ mol^{-1}

(iii) +74.8 kJ mol^{-1} (iv) +52.26 kJ mol^{-1}.

6.6 A reaction, A + B → C + D + q is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(v) possible at any temperature

6.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

6.8 The reaction of cyanamide, NH_2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.

$$NH_2CN(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$$

6.9 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35 C to 55 C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

6.10 Calculate the enthalpy change on freezing of 1.0 mol of water at10.0 C to ice at –10.0 C. $\Delta_{fus}H$ = 6.03 kJ mol^{-1} at 0 C.

C_p [H_2O(l)] = 75.3 J mol^{-1} K^{-1}

C_p [H_2O(s)] = 36.8 J mol^{-1} K^{-1}

6.11 Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

6.12 Enthalpies of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) are –110, – 393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of Δ_rH for the reaction:

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

6.13 Given

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; Δ_rH = –92.4 kJ mol^{-1}

What is the standard enthalpy of formation of NH_3 gas?

6.14 Calculate the standard enthalpy of formation of CH_3OH(l) from the following data:

$CH_3OH(l) + \frac{3}{2} O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; Δ_rH = –726 kJ mol^{-1}

$C(g) + O_2(g) \rightarrow CO_2(g)$; Δ_cH = –393 kJ mol^{-1}

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; Δ_fH = –286 kJ mol^{-1}.

6.15 Calculate the enthalpy change for the process

$CCl_4(g) \rightarrow C(g) + 4\ Cl(g)$

and calculate bond enthalpy of C – Cl in CCl_4(g).

$\Delta_{vap}H$ (CCl_4) = 30.5 kJ mol^{-1}.

Δ_fH (CCl_4) = –135.5 kJ mol^{-1}.

Δ_aH (C) = 715.0 kJ mol^{-1}, where Δ_aH is enthalpy of atomisation

Δ_aH (Cl_2) = 242 kJ mol^{-1}

6.16 For an isolated system, ΔU = 0, what will be ΔS ?

6.17 For the reaction at 298 K,

$2A + B \rightarrow C$

ΔH = 400 kJ mol^{-1} and ΔS = 0.2 kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

6.18 For the reaction,

$2\ Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

6.19 For the reaction

$2\ A(g) + B(g) \rightarrow 2D(g)$

ΔU = –10.5 kJ and ΔS = –44.1 JK^{-1}.

Calculate ΔG for the reaction, and predict whether the reaction may occur spontaneously.

6.20 The equilibrium constant for a reaction is 10. What will be the value of ΔG ? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

6.21 Comment on the thermodynamic stability of NO(g), given

$$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g) \quad ; \quad \Delta_r H = 90 \text{ kJ mol}^{-1}$$

$$NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g) \quad : \quad \Delta_r H = -74 \text{ kJ mol}^{-1}$$

6.22 Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H = -286$ kJ mol^{-1}.

UNIT 7

EQUILIBRIUM

Objectives

After studying this unit you will be able to

- identify dynamic nature of equilibrium involved in physical and chemical processes;
- state the law of equilibrium;
- explain characteristics of equilibria involved in physical and chemical processes;
- write expressions for equilibrium constants;
- establish a relationship between K_p and K_c;
- explain various factors that affect the equilibrium state of a reaction;
- classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts;
- classify acids and bases as weak or strong in terms of their ionization constants;
- explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion;
- describe pH scale for representing hydrogen ion concentration;
- explain ionisation of water and its duel role as acid and base;
- describe ionic product (K_w) and pK_w *for water;*
- appreciate use of buffer solutions;
- calculate solubility product constant.

Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving O_2 molecules and the protein hemoglobin play a crucial role in the transport and delivery of O_2 from our lungs to our muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO.

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an *equilibrium* in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached **equilibrium state** at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at *equilibrium*, the rate of evaporation is equal to the rate of condensation. It may be represented by

$$H_2O\,(l) \rightleftharpoons H_2O\,(vap)$$

The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the **dynamic equilibrium** and the rates of the forward and

reverse reactions become equal. It is due to this dynamic equilibrium stage that there is no change in the concentrations of various species in the reaction mixture. Based on the extent to which the reactions proceed, the state of **chemical equilibrium** in a chemical reaction may be classified in three groups.

(i) The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.

(ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.

(iii) The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as **ionic equilibrium**.

7.1 EQUILIBRIUM IN PHYSICAL PROCESSES

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are **phase transformation processes**, *e.g.*,

solid	liquid
liquid	gas
solid	gas

7.1.1 Solid-Liquid Equilibrium

Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.

It is obvious that ice and water are in equilibrium only at particular temperature and pressure. *For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.* The system here is in dynamic equilibrium and we can infer the following:

(i) Both the opposing processes occur simultaneously.

(ii) Both the processes occur at the same rate so that the amount of ice and water remains constant.

7.1.2 Liquid-Vapour Equilibrium

This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 7.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water

Fig.7.1 *Measuring equilibrium vapour pressure of water at a constant temperature*

molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained i.e.,

rate of evaporation= rate of condensation

$$H_2O(l) \rightleftharpoons H_2O\ (vap)$$

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point.

If we expose three watch glasses containing separately 1mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system.

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100 C in a closed vessel. The boiling point of water is 100 C at 1.013 bar pressure. For any pure liquid at atmospheric pressure (1.013 bar) the temperature at which the liquid and vapours are at equilibrium is called boiling point of the liquid. It depends on the atmospheric pressure. Boiling point of a liquid depends on the altitude of the place; at high altitude the boiling point decreases.

7.1.3 Solid – Vapour Equilibrium

Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$$I_2(solid) \rightleftharpoons I_2\ (vapour)$$

Other examples showing this kind of equilibrium are,

$$Camphor\ (solid) \rightleftharpoons Camphor\ (vapour)$$

$$NH_4Cl\ (solid) \rightleftharpoons NH_4Cl\ (vapour)$$

7.1.4 Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in liquids

We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution:

Sugar (solution) Sugar (solid), and

the rate of dissolution of sugar = rate of crystallisation of sugar.

Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

Gases in liquids

When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e.,

CO_2(gas) CO_2(in solution)

This equilibrium is governed by Henry's law, **which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.** This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'. It can be generalised that:

(i) For solid liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.

(ii) For liquid vapour equilibrium, the vapour pressure is constant at a given temperature.

(iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.

(iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 7.1

Table 7.1 Some Features of Physical Equilibria

Process	Conclusion
Liquid Vapour H_2O (l) H_2O (g)	P_{H_2O} constant at given temperature
Solid Liquid H_2O (s) H_2O (l)	Melting point is fixed at constant pressure
Solute(s) Solute (solution) Sugar(s) Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) Gas (aq) CO_2(g) CO_2(aq)	[gas(aq)]/[gas(g)] is constant at a given temperature $[CO_2(aq)]/[CO_2(g)]$ is constant at a given temperature

7.1.5 General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.

(iii) All measurable properties of the system remain constant.

(iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 7.1 lists such quantities.

(v) The magnitude of such quantities at any stage indicates the extent to which the reaction has proceeded before reaching equilibrium.

7.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,

$$A + B \quad C + D$$

With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 7.2). This leads to a decrease in the rate of forward reaction and an increase in he rate of the reverse reaction,

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium.

Fig. 7.2 *Attainment of chemical equilibrium.*

Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 7.4 (page 191) shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using D_2 (deuterium) in place of H_2. The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3. After equilibrium is attained, these two mixtures

Dynamic Equilibrium – A Student's Activity

Equilibrium whether in a physical or in a chemical system, is always of dynamic nature. This can be demonstrated by the use of radioactive isotopes. This is not feasible in a school laboratory. However this concept can be easily comprehended by performing the following activity. The activity can be performed in a group of 5 or 6 students.

Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and keep second cylinder (number 2) empty.

Put one tube in cylinder 1 and second in cylinder 2. Immerse one tube in cylinder 1, close its upper tip with a finger and transfer the coloured water contained in its lower portion to cylinder 2. Using second tube, kept in 2nd cylinder, transfer the coloured water in a similar manner from cylinder 2 to cylinder 1. In this way keep on transferring coloured water using the two glass tubes from cylinder 1 to 2 and from 2 to 1 till you notice that the level of coloured water in both the cylinders becomes constant.

If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process of transfer, which continues even after the constancy of level, is indicative of dynamic nature of the process. If we repeat the experiment taking two tubes of different diameters we find that at equilibrium the level of coloured water in two cylinders is different. How far diameters are responsible for change in levels in two cylinders? Empty cylinder (2) is an indicator of no product in it at the beginning.

Fig.7.3 *Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.*

Fig 7.4 *Depiction of equilibrium for the reaction*

$N_2(g) + 3H_2($

(H_2, N_2, NH_3 and D_2, N_2, ND_3) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and dihydrogen and its deutrated forms (H_2, HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

Use of isotope (deuterium) in the formation of ammonia clearly indicates that **chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.**

Equilibrium can be attained from both sides, whether we start reaction by taking, $H_2(g)$ and $N_2(g)$ and get $NH_3(g)$ or by taking $NH_3(g)$ and decomposing it into $N_2(g)$ and $H_2(g)$.

$N_2(g) + 3H_2(g)$ $2NH_3(g)$

$2NH_3(g)$ $N_2(g) + 3H_2(g)$

Similarly let us consider the reaction, $H_2(g) + I_2(g)$ $2HI(g)$. If we start with equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 7.5). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached (Fig.7.5). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

Fig.7.5 *Chemical equilibrium in the reaction* $H_2(g) + I_2(g)$ $2HI(g)$ *can be attained from either direction*

7.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations?

What factors can be exploited to alter the composition of an equilibrium mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as H_2, NH_3, CaO etc.

To answer these questions, let us consider a general reversible reaction:

$$A + B \quad C + D$$

where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following **equilibrium equation,**

$$K_c = \frac{[C][D]}{[A][B]} \qquad (7.1)$$

where K_c is the *equilibrium constant* and the expression on the right side is called the *equilibrium constant expression*.

The equilibrium equation is also known as the *law of mass action* because in the early days of chemistry, concentration was called "active mass". In order to appreciate their work better, let us consider reaction between gaseous H_2 and I_2 carried out in a sealed vessel at 731K.

$$\underset{1\ \text{mol}}{H_2(g)} + \underset{1\ \text{mol}}{I_2(g)} \quad \underset{2\ \text{mol}}{2HI(g)}$$

Six sets of experiments with varying initial conditions were performed, starting with only gaseous H_2 and I_2 in a sealed reaction vessel in first four experiments (1, 2, 3 and 4) and only HI in other two experiments (5 and 6). Experiment 1, 2, 3 and 4 were performed taking different concentrations of H_2 and / or I_2, and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are given in Table 7.2.

It is evident from the experiments 1, 2, 3 and 4 that number of moles of dihydrogen reacted = number of moles of iodine reacted = ½ (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$$[H_2(g)]_{eq} = [I_2(g)]_{eq}$$

Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$$[HI(g)]_{eq} / [H_2(g)]_{eq}\,[I_2(g)]_{eq}$$

It can be seen from Table 7.3 that if we put the equilibrium concentrations of the reactants and products, the above expression

Table 7.2 Initial and Equilibrium Concentrations of H_2, I_2 and HI

Experiment number	Initial concentration/mol L^{-1}			Equilibrium concentration/mol L^{-1}		
	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

Table 7.3 Expression Involving the Equilibrium Concentration of Reactants
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Experiments Number	$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$	$\frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

is far from constant. However, if we consider the expression,

$$[HI(g)]^2_{eq} / [H_2(g)]_{eq} [I_2(g)]_{eq}$$

we find that this expression gives constant value (as shown in Table 7.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction $H_2(g) + I_2(g)$ $2HI(g)$, following equation 7.1, the equilibrium constant K_c is written as,

$$K_c = [HI(g)]^2_{eq} / [H_2(g)]_{eq} [I_2(g)]_{eq} \quad (7.2)$$

Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. We, therefore, write,

$$K_c = [HI(g)]^2 / [H_2(g)] [I_2(g)] \quad (7.3)$$

The subscript '*c*' indicates that K_c is expressed in concentrations of mol L^{-1}.

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

The equilibrium constant for a general reaction,

$$aA + bB \quad cC + dD$$

is expressed as,

$$K_c = [C]^c[D]^d / [A]^a[B]^b \quad (7.4)$$

where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,

$4NH_3(g) + 5O_2(g)$ $4NO(g) + 6H_2O(g)$ is written as

$$K_c = [NO]^4[H_2O]^6 / [NH_3]^4 [O_2]^5$$

Molar concentration of different species is indicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored.

Let us write equilibrium constant for the reaction, $H_2(g) + I_2(g)$ $2HI(g)$ (7.5)

as, $K_c = [HI]^2 / [H_2] [I_2] = x$ (7.6)

The equilibrium constant for the reverse reaction, $2HI(g)$ $H_2(g) + I_2(g)$, at the same temperature is,

$$K'_c = [H_2] [I_2] / [HI]^2 = 1/ x = 1 / K_c \quad (7.7)$$

Thus, $K'_c = 1 / K_c$ (7.8)

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (7.5) is written as,

$$\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \quad HI(g) \quad (7.9)$$

the equilibrium constant for the above reaction is given by

$$K''_c = [HI] / [H_2]^{1/2}[I_2]^{1/2} = \{[HI]^2 / [H_2][I_2]\}^{1/2} = x^{1/2} = K_c^{1/2} \quad (7.10)$$

On multiplying the equation (7.5) by n, we get

$$nH_2(g) + nI_2(g) \quad 2nHI(g) \qquad (7.11)$$

Therefore, equilibrium constant for the reaction is equal to K_c^n. These findings are summarised in Table 7.4. It should be noted that because the equilibrium constants K_c and K_c' have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant.

Table 7.4 Relations between Equilibrium Constants for a General Reaction and its Multiples.

Chemical equation	Equilibrium constant
a A + b B c C + D	K
c C + d D a A + b B	$K_c' = (1/K_c)$
na A + nb B ncC + ndD	$K_c'' = (K_c^n)$

Problem 7.1

The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \quad 10^{-2}$M. $[H_2] = 3.0 \quad 10^{-2}$ M and $[NH_3] = 1.2 \quad 10^{-2}$M. Calculate equilibrium constant.

Solution

The equilibrium constant for the reaction,

$N_2(g) + 3H_2(g) \quad 2NH_3(g)$ can be written as,

$$K_c = \frac{[NH_3]}{[N_2(g)]}$$

$$= \frac{(1.2\times}{(1.5\times10^{-2})}$$

$$= 0.106 \quad 10^4 = 1.06 \quad 10^3$$

Problem 7.2

At equilibrium, the concentrations of N_2=3.0 $\quad 10^{-3}$M, O_2 = 4.2 $\quad 10^{-3}$M and NO= 2.8 $\quad 10^{-3}$M in a sealed vessel at 800K. What will be K_c for the reaction

$$N_2(g) + O_2(g) \quad 2NO(g)$$

Solution

For the reaction equilibrium constant, K_c can be written as,

$$K_c = \frac{[NO]^2}{[N_2][O_2}$$

$$= \frac{(2.8\times}{(3.0\times10^{-3}N}$$

$$= 0.622$$

7.4 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2(g) + 3H_2(g) \quad 2NH_3(g)$, reactants and products are in the homogeneous phase. Similarly, for the reactions,

$$CH_3COOC_2H_5\,(aq) + H_2O\,(l) \quad CH_3COOH\,(aq) + C_2H_5OH\,(aq)$$

and, $Fe^{3+}\,(aq) + SCN\,(aq) \quad Fe(SCN)^{2+}\,(aq)$

all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

7.4.1 Equilibrium Constant in Gaseous Systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$pV = nRT$$

$$\Rightarrow \quad p = \frac{n}{V}RT$$

Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and

T is the temperature in Kelvin

Therefore,

n/V is concentration expressed in mol/m^3

If concentration c, is in mol/L or mol/dm^3, and p is in bar then

$p = cRT$,

We can also write p = [gas]RT.

Here, R= 0.0831 bar litre/mol K

At constant temperature, the pressure of the gas is proportional to its concentration i.e.,

$p \propto$ [gas]

For reaction in equilibrium

$H_2(g) + I_2(g) \quad 2HI(g)$

We can write either

$$K_c = \frac{[HI(}{[H_2(g)]}$$

$$\text{or } K_c = \frac{(p_I}{(p_{H_2})} \qquad (7.12)$$

Further, sinc

Therefore,

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2}}$$

$$= \frac{[HI(g)]^2}{[H_2(g)][I_2} \qquad (7.13)$$

In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction

$N_2(g) + 3H_2(g) \quad 2NH_3(g)$

$$K_p = \frac{(p_{NH_3})}{(p_{N_2})(p_I}$$

$$= \frac{[NH_3(}{[N_2(g)]RT.}$$

$$= \frac{[NH_3(g)]^2[}{[N_2(g)][H_2}$$

$$\text{or } K_p = K_c(R \qquad (7.14)$$

Similarly, for a general reaction

a A + b B c C + d D

$$K_p = \frac{(p_C^c)(p_D^d}{(p_A^a)(p_B^b}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(R'$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(R' \qquad (7.15)$$

where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation.

(It is necessary that while calculating the value of K_p, pressure should be expressed in bar as standard state is 1bar). We have known from Unit 1,

1pascal, Pa=1Nm ^{2}, and 1bar = 10^5 Pa

K_p values for a few selected reactions at different temperatures are given in Table 7.5

Table 7.5 Equilibrium Constants, K_p for a Few Selected Reactions

Reaction	Temperature/K	K_p
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	298	4.0×10^{24}
	500	2.5×10^{10}
	700	3.0×10^4
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700

Problem 7.3

PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3, 1.59M Cl_2 and 1.41 M PCl_5.

Calculate K_c for the reaction,

$$PCl_5 \quad PCl_3 + Cl_2$$

Solution

The equilibrium constant K_c for the above reaction can be written as,

$$K_c = \frac{[PCl_3][C}{[PCl_5]}$$

Problem 7.4

The value of K_c = 4.24 at 800K for the reaction,

$$CO\ (g) + H_2O\ (g) \quad CO_2\ (g) + H_2\ (g)$$

Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K, if only CO and H_2O are present initially at concentrations of 0.10M each.

Solution

For the reaction,

$$CO\ (g) + H_2O\ (g) \quad CO_2\ (g) + H_2\ (g)$$

Initial concentration:

0.1M 0.1M 0 0

Let x mole of each of the product be formed.

At equilibrium:

(0.1-x) M (0.1-x) M x M x M

where x is the amount of CO_2 and H_2 at equilibrium.

Hence, equilibrium constant can be written as,

$K_c = x^2/(0.1-x)^2 = 4.24$

$x^2 = 4.24(0.01 + x^2-0.2x)$

$x^2 = 0.0424 + 4.24x^2-0.848x$

$3.24x^2 - 0.848x + 0.0424 = 0$

a = 3.24, b = – 0.848, c = 0.0424

(for quadratic equation $ax^2 + bx + c = 0$,

$$x = \frac{\left(-b \pm \sqrt{b^2}\right.}{2a}$$

$x = 0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)}/(3.24\ 2)$

$x = (0.848 \pm 0.4118)/\ 6.48$

$x_1 = (0.848 - 0.4118)/6.48 = 0.067$

$x_2 = (0.848 + 0.4118)/6.48 = 0.194$

the value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

Hence the equilibrium concentrations are,

$[CO_2] = [H_2] = x = 0.067$ M

$[CO] = [H_2O] = 0.1 - 0.067 = 0.033$ M

Problem 7.5

For the equilibrium,

$$2NOCl(g) \quad 2NO(g) + Cl_2(g)$$

the value of the equilibrium constant, K_c is 3.75 10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Solution

We know that,

$K_p = K_c(RT)^{\Delta n}$

For the above reaction,

$\Delta n = (2+1) - 2 = 1$

$K_p = 3.75\ 10^{-6}\ (0.0831\ 1069)$

$K_p = 0.033$

7.5 HETEROGENEOUS EQUILIBRIA

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$$H_2O(l) \quad H_2O(g)$$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,

$$Ca(OH)_2\ (s) + (aq) \quad Ca^{2+}\ (aq) + 2OH^-(aq)$$

is a heterogeneous equilibrium.

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then [X(s)] and [X(l)] are constant, whatever the amount of 'X' is taken. Contrary

to this, [X(g)] and [X(aq)] will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.

$$CaCO_3(s) \overset{\Delta}{} CaO(s) + CO_2(g) \qquad (7.16)$$

On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{[CaO(s)}{[CaC}$$

Since $[CaCO_3(s)]$ and [CaO(s)] are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K_c = [CO_2(g)] \qquad (7.17)$$

$$\text{or } K_p = p_{CO_2} \qquad (7.18)$$

Units of Equilibrium Constant

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

For the reactions,

$H_2(g) + I_2(g) \quad 2HI$, K_c and K_p have no unit.

$N_2O_4(g) \quad 2NO_2(g)$, K_c has unit mol/L and K_p has unit bar

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1bar. Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number. Standard state (c_0) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both K_p and K_c are dimensionless quantities but have different numerical values due to different standard states.

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2 in equilibrium with CaO(s) and $CaCO_3(s)$. Experimentally it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $CaCO_3(s)$ and CaO(s), is 2.0 10^5 Pa. Therefore, equilibrium constant at 1100K for the above reaction is:

$$K_p = p_{CO_2} = 2$$

Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),

$$Ni(s) + 4\,CO(g) \quad Ni(CO)_4(g),$$

the equilibrium constant is written as

$$K_c = \frac{[Ni(CO)}{[CO]^4}$$

It must be remembered that in heterogeneous equilibrium pure solids or liquids must be present (however small it may be) for the equilibrium to exist, but their concentrations or partial pressure do not appear in the expression of the equilibrium constant. In the reaction,

$$Ag_2O(s) + 2HNO_3(aq) \quad 2AgNO_3(aq) + H_2O(l)$$

$$K_c = \frac{[AgNO_3}{[HNO_3]}$$

Problem 7.6

The value of K_p for the reaction,

$CO_2(g) + C(s) \quad 2CO(g)$

is 3.0 at 1000 K. If initially $p_{CO_2} = 0.48$ bar and $p_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2.

Solution

For the reaction,

let 'x' be the amount of CO_2 reacted, then

	$CO_2(g)$ +	$C(s)$	$2CO(g)$
Initial pressure:	0.48 bar		0

At equilibrium:

(0.48 – x)bar 2x bar

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

$K_p = (2x)^2/(0.48 - x) = 3$

$4x^2 = 3(0.48 - x)$

$4x^2 = 1.44 - x$

$4x^2 + 3x - 1.44 = 0$

a = 4, b = 3, c = –1.44

$$x = \frac{\left(-b \pm \sqrt{b^2}\right.}{2a}$$

$= [-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}]/2 \quad 4$

$= (-3 \pm 5.66)/8$

$= (-3 + 5.66)/8$ (as value of x cannot be negative hence we neglect that value)

x = 2.66/8 = 0.33

The equilibrium partial pressures are,

$p_{CO} = 2x = 2 \quad 0.33 = 0.66$ bar

$p_{CO_2} = 0.48 - x = 0.48 - 0.33 = 0.15$ bar

7.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows:

1. Equilibrium constant is applicable only when concentrations of the reactants and products have attained their equilibrium state.
2. The value of equilibrium constant is independent of initial concentrations of the reactants and products.
3. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
4. The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
5. The equilibrium constant *K* for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Let us consider applications of equilibrium constant to:

- predict the extent of a reaction on the basis of its magnitude,
- predict the direction of the reaction, and
- calculate equilibrium concentrations.

7.6.1 Predicting the Extent of a Reaction

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium does not give any information about the *rate* at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of *K* is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants, i.e., if K_c is very large, the reaction proceeds nearly to completion. Consider the following examples:

(a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant, $K_c = 2.4 \quad 10^{47}$.

(b) $H_2(g) + Cl_2(g) \quad 2HCl(g)$ at 300K has $K_c = 4.0 \quad 10^{31}$.

(c) $H_2(g) + Br_2(g) \quad 2HBr\ (g)$ at 300 K, $K_c = 5.4 \quad 10^{18}$

- If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely. Consider the following examples:

(a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, $K_c = 4.1 \quad 10^{48}$

(b) $N_2(g) + O_2(g) \quad 2NO(g)$, at 298 K has $K_c = 4.8 \quad 10^{-31}$.

- If K_c is in the range of 10^{-3} to 10^{3}, appreciable concentrations of both reactants and products are present. Consider the following examples:

(a) For reaction of H_2 with I_2 to give HI, $K_c = 57.0$ at 700K.

(b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \quad 10^{-3}$ at 25 C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.

These generarlisations are illustrated in Fig. 7.6

Fig.7.6 *Dependence of extent of reaction on K_c*

7.6.2 Predicting the Direction of the Reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient *Q***. The reaction quotient, Q (Q_c with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values. For a general reaction:

$$a\,A + b\,B \quad c\,C + d\,D \qquad (7.19)$$

$$Q_c = [C]^c[D]^d / [A]^a[B]^b \qquad (7.20)$$

Then,

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).

If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Consider the gaseous reaction of H_2 with I_2,

$H_2(g) + I_2(g) \quad 2HI(g)$; $K_c = 57.0$ at 700 K.

Suppose we have molar concentrations $[H_2]_t$=0.10M, $[I_2]_t$ = 0.20 M and $[HI]_t$ = 0.40 M. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

Thus, the reaction quotient, Q_c at this stage of the reaction is given by,

$$Q_c = [HI]_t^{\,2} / [H_2]_t\,[I_2]_t = (0.40)^2 / (0.10)\,(0.20) = 8.0$$

Now, in this case, Q_c (8.0) does not equal K_c(57.0), so the mixture of $H_2(g)$, $I_2(g)$ and HI(g) is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more HI(g) and their concentrations will decrease till $Q_c = K_c$.

The reaction quotient, Q_c is useful in predicting the direction of reaction by comparing the values of Q_c and K_c.

Thus, we can make the following generalisations concerning the direction of the reaction (Fig. 7.7) :

Fig. 7.7 *Predicting the direction of the reaction*

- If $Q_c < K_c$, net reaction goes from left to right
- If $Q_c > K_c$, net reaction goes from right to left.
- If $Q_c = K_c$, no net reaction occurs.

Problem 7.7

The value of K_c for the reaction

$2A \quad B + C$ is $2 \quad 10^{-3}$. At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \quad 10^{-4}$ M. In which direction the reaction will proceed?

Solution

For the reaction the reaction quotient Q_c is given by,

$Q_c = [B][C]/[A]^2$

as [A] = [B] = [C] = 3 10^{-4}M

$Q_c = (3 \quad 10^{-4})(3 \quad 10^{-4}) / (3 \quad 10^{-4})^2 = 1$

as $Q_c > K_c$ so the reaction will proceed in the reverse direction.

7.6.3 Calculating Equilibrium Concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

(a) the initial concentration,
(b) the change in concentration on going to equilibrium, and
(c) the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

Problem 7.8

13.8g of N_2O_4 was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium

N_2O_4 (g) $2NO_2$ (g)

The total pressure at equilbrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressure at equilibrium.

Solution

We know $pV = nRT$

Total volume (V) = 1 L

Molecular mass of N_2O_4 = 92 g

Number of moles of the gas (n) = 13.8g/92 g = 0.15

Gas constant (R) = 0.083 bar L $mol^{-1}K^{-1}$

Temperature (T) = 400 K

$pV = nRT$

$p \quad 1L = 0.15 \text{ mol} \quad 0.083 \text{ bar L mol}^{-1}\text{K}^{-1} \quad 400 \text{ K}$

p = 4.98 bar

	N_2O_4	$2NO_2$
Initial pressure:	4.98 bar	0
At equilibrium:	(4.98 – x) bar	2x bar

Hence,

p_{total} at equilibrium = $p_{N_2O_4} + p_{NO_2}$

9.15 = (4.98 – x) + 2x

9.15 = 4.98 + x

x = 9.15 – 4.98 = 4.17 bar

Partial pressures at equilibrium are,

$p_{N_2O_4}$ = 4.98 – 4.17 = 0.81bar

p_{NO_2} = 2x = 2 4.17 = 8.34 bar

$K_p = \left(p_{NO_2}\right)^2$,

$= (8.34)^2/0.81 = 85.87$

$K_p = K_c(RT)^{\Delta n}$

$85.87 = K_c(0.083 \quad 400)^1$

$K_c = 2.586 = 2.6$

Problem 7.9

3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of the mixture at equilibrium. K_c= 1.80

Solution

	PCl_5	PCl_3 +	Cl_2
Initial concentration:	3.0	0	0

Let x mol of PCl_5 be dissociated,
At equilibrium:

(3-x) x x

$K_c = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/(3 - x)$

$x^2 + 1.8x - 5.4 = 0$

$x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]/2$

$x = [-1.8 \pm \sqrt{3.24 + 21.6}]/2$

$x = [-1.8 \pm 4.98]/2$

$x = [-1.8 + 4.98]/2 = 1.59$

$[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

7.7 RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT *K*, REACTION QUOTIENT *Q* AND GIBBS ENERGY *G*

The value of K_c for a reaction does not depend on the rate of the reaction. However, as you have studied in Unit 6, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, ΔG. If,

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG, the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\Delta G = \Delta G \quad + RT \ln Q \qquad (7.21)$$

where, G is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the equation (7.21) becomes,

$$\Delta G = \Delta G \quad + RT \ln K = 0$$

$$\Delta G \quad = - RT \ln K \qquad (7.22)$$

$$\ln K = - \Delta G \quad / RT$$

Taking antilog of both sides, we get,

$$K = e^{\Delta G^V / RT} \qquad (7.23)$$

Hence, using the equation (7.23), the reaction spontaneity can be interpreted in terms of the value of ΔG .

- If $\Delta G < 0$, then $-\Delta G / RT$ is positive, and $e^{\Delta G^V / RT} > 1$, making $K > 1$, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.
- If $\Delta G > 0$, then $-\Delta G / RT$ is negative, and $e^{\Delta G^V / RT} < 1$, that is , $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

Problem 7.10

The value of ΔG for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K.

Solution

ΔG = 13.8 kJ/mol = 13.8 10^3J/mol

Also, ΔG = – RT lnK_c

Hence, ln K_c = –13.8 10^3J/mol
(8.314 J mol ^{1}K ^{1} 298 K)

ln K_c = – 5.569

$K_c = e^{-5.569}$

K_c = 3.81 10^{-3}

Problem 7.11

Hydrolysis of sucrose gives,

Sucrose + H_2O Glucose + Fructose

Equilibrium constant K_c for the reaction is 2 10^{13} at 300K. Calculate ΔG at 300K.

Solution

ΔG = – RT lnK_c

ΔG = – 8.314J mol^{-1}K^{-1}
300K ln(2 10^{13})

ΔG = – 7.64 10^4 J mol^{-1}

7.8 FACTORS AFFECTING EQUILIBRIA

One of the principal goals of chemical synthesis is to maximise the conversion of the reactants

to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2, the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilizers.

Equilibrium constant, K_c is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and *make a qualitative prediction* about the effect of a change in conditions on equilibrium we use ***Le Chatelier's principle***. It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.** *This is applicable to all physical and chemical equilibria.*

We shall now be discussing factors which can influence the equilibrium.

7.8.1 Effect of Concentration Change

In general, when equilibrium is disturbed by the addition/removal of any reactant/products, Le Chatelier's principle predicts that:

- The concentration stress of an *added* reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a *removed* reactant/product is relieved by net reaction in the direction that *replenishes* the removed substance.

or in other words,

"*When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes*".

Let us take the reaction,

$$H_2(g) + I_2(g) \quad 2HI(g)$$

If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed, i.e., more of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.7.8). This is in accordance with the Le Chatelier's principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.

Fig. 7.8 *Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \quad 2HI(g)$*

The same point can be explained in terms of the reaction quotient, Q_c,

$$Q_c = [HI]^2 / [H_2][I_2]$$

Addition of hydrogen at equilibrium results in value of Q_c being less than K_c. Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

Effect of Concentration – An experiment

This can be demonstrated by the following reaction:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq) \quad (7.24)$$

yellow colourless deep red

$$K_c = \frac{[Fe(S}{[Fe^{3+}(a} \quad (7.25)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocynate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. The intensity of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^- ions. For example, oxalic acid ($H_2C_2O_4$), reacts with Fe^{3+} ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of free $Fe^{3+}(aq)$. In accordance with the Le Chatelier's principle, the concentration stress of removed Fe^{3+} is relieved by dissociation of $[Fe(SCN)]^{2+}$ to replenish the Fe^{3+} ions. Because the concentration of $[Fe(SCN)]^{2+}$ decreases, the intensity of red colour decreases.

Addition of aq. $HgCl_2$ also decreases red colour because Hg^{2+} reacts with SCN^- ions to form stable complex ion $[Hg(SCN)_4]^{2-}$. Removal of free SCN^- (aq) shifts the equilibrium in equation (7.24) from right to left to replenish SCN^- ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

7.8.2 Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.

Consider the reaction,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4 + H_2O$). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to pV = constant). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Q_c. Let [CO], $[H_2]$, $[CH_4]$ and $[H_2O]$ be the molar concentrations at equilibrium for methanation reaction. When

volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value.

$$Q_c = \frac{[CH_4(g)]}{[CO(g)]}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

In reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

7.8.3 Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

7.8.4 Effect of Temperature Change

Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c. However, when a change in temperature occurs, the value of equilibrium constant, K_c is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

Production of ammonia according to the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) ;$$
$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

Effect of Temperature – An experiment

Effect of temperature on equilibrium can be demonstrated by taking NO_2 gas (brown in colour) which dimerises into N_2O_4 gas (colourless).

$$2NO_2(g) \rightleftharpoons N_2O_4(g); \Delta H = -57.2 \text{ kJ mol}^{-1}$$

NO_2 gas prepared by addition of Cu turnings to conc. HNO_3 is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freezing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 7.9). Both the test tubes are placed in beaker 2 for 8-10 minutes. After this one is placed in beaker 1 and the other in beaker 3. The effect of temperature on direction of reaction is depicted very well in this experiment. At low temperatures in beaker 1, the forward reaction of formation of N_2O_4 is preferred, as reaction is exothermic, and thus, intensity of brown colour due to NO_2 decreases. While in beaker 3, high temperature favours the reverse reaction of

Fig. 7.9 *Effect of temperature on equilibrium for the reaction,* $2NO_2(g) \rightleftharpoons N_2O_4(g)$

formation of NO_2 and thus, the brown colour intensifies.

Effect of temperature can also be seen in an endothermic reaction,

$$[Co(H_2O)_6]^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

pink colourless blue

At room temperature, the equilibrium mixture is blue due to $[CoCl_4]^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $[Co(H_2O)_6]^{3+}$.

7.8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Let us consider the formation of NH_3 from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.

German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of NH_3 is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of NH_3 can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of NH_3 using catalyst are around 500 C and 200 atm.

Similarly, in manufacture of sulphuric acid by *contact process*,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad K_c = 1.7 \quad 10^{26}$$

though the value of K is suggestive of reaction going to completion, but practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V_2O_5) is used as catalyst to increase the rate of the reaction.

Note: If a reaction has an exceedingly small K, a catalyst would be of little help.

7.9 IONIC EQUILIBRIUM IN SOLUTION

Under the effect of change of concentration on the direction of equilibrium, you have incidently come across with the following equilibrium which involves ions:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called *electrolytes* while the other do not and are thus, referred to as *non electrolytes*. Faraday further classified electrolytes into *strong* and *weak* electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and protons. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted that in weak electrolytes, equilibrium is

established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

7.10 ACIDS, BASES AND SALTS

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word "acid" has been derived from a latin word "*acidus*" meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give *salts*. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.7.10). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules.

Fig.7.10 *Dissolution of sodium chloride in water. Na^+ and Cl ions are stablised by their hydration with polar water molecules.*

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent

Michael Faraday (1791–1867)

Faraday was born near London into a family of very limited means. At the age of 14 he was an apprentice to a kind bookbinder who allowed Faraday to read the books he was binding. Through a fortunate chance he became laboratory assistant to Davy, and during 1813-4, Faraday accompanied him to the Continent. During this trip he gained much from the experience of coming into contact with many of the leading scientists of the time. In 1825, he succeeded Davy as Director of the Royal Institution laboratories, and in 1833 he also became the first Fullerian Professor of Chemistry. Faraday's first important work was on analytical chemistry. After 1821 much of his work was on electricity and magnetism and different electromagnetic phenomena. His ideas have led to the establishment of modern field theory. He discovered his two laws of electrolysis in 1834. Faraday was a very modest and kind hearted person. He declined all honours and avoided scientific controversies. He preferred to work alone and never had any assistant. He disseminated science in a variety of ways including his Friday evening discourses, which he founded at the Royal Institution. He has been very famous for his Christmas lecture on the 'Chemical History of a Candle'. He published nearly 450 scientific papers.

molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably.

7.10.1 Arrhenius Concept of Acids and Bases

According to Arrhenius theory, *acids are substances that dissociates in water to give hydrogen ions H^+(aq) and bases are substances that produce hydroxyl ions* OH (aq). The ionization of an acid HX (aq) can be represented by the following equations:

$$HX\,(aq) \rightarrow H^+(aq) + X^-\,(aq)$$

or

$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$$

A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give *trigonal pyramidal* **hydronium ion**, H_3O^+ {[H (H_2O)]$^+$} (see box). In this chapter we shall use H^+(aq) and H_3O^+(aq) interchangeably to mean the same i.e., a hydrated proton.

Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH(aq) \rightarrow M^+(aq) + OH\,(aq)$$

The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

Hydronium and Hydroxyl Ions

Hydrogen ion by itself is a bare proton with very small size (~10^{-15} m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+. This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.

7.10.2 The Brönsted-Lowry Acids and Bases

The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, *acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+*. In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:

adds proton

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base acid conjugate acid conjugate base

loses proton

The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and

Svante Arrhenius (1859-1927)

Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH . In this case, NH_4^+ acts as a Bronsted acid while OH acted as a Brönsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, OH is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3. If Brönsted acid is a strong acid then **its conjugate base is a weak base and *vice-versa*.** It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H_2O molecule which acts as a base.

adds proton

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

acid base conjugate acid conjugate base

loses proton

It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl is a conjugate base of HCl and HCl is the conjugate acid of base Cl . Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Problem 7.12

What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3 ?

Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F , HSO_4 and CO_3^{2-} respectively.

Problem 7.13

Write the conjugate acids for the following Brönsted bases: NH_2 , NH_3 and $HCOO^-$.

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

Problem 7.14

The species: H_2O, HCO_3, HSO_4 and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Solution

The answer is given in the following Table:

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH
HCO_3	H_2CO_3	CO_3^{2-}
HSO_4	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2

7.10.3 Lewis Acids and Bases

G.N. Lewis in 1923 defined an *acid as a species which accepts electron pair and base which donates an electron pair*. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3.

BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$

Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH etc. which can donate a pair of electrons, can act as Lewis bases.

Problem 7.15

Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO (b)F (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:OH^-$).

(b) Flouride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

(d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

7.11 IONIZATION OF ACIDS AND BASES

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH . According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

acid base conjugate acid conjugate base

In section 7.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+, and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base

because **the stronger acid donates a proton to the stronger base**.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., **strong acids have very weak conjugate bases.** Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4, Cl, Br , I , NO_3 and HSO_4, which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the *weak acids have very strong conjugate bases*. For example, NH_2, O^{2-} and H are very good proton acceptors and thus, much stronger bases than H_2O.

Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In) forms.

$$\underset{\substack{\text{acid}\\\text{indicator}\\\text{colour A}}}{HIn(aq)} + H_2O(l) \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}\\\text{colourB}}}{In\ (aq)}$$

Such compounds are useful as indicators in acid-base titrations, and finding out H^+ ion concentration.

7.11.1 The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 7.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{OH^-(aq)}$$

The dissociation constant is represented by,

$$K = [H_3O^+]\,[OH\ ]\ /\ [H_2O] \qquad (7.26)$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[H_2O]$ is incorporated within the equilibrium constant to give a new constant, K_w, which is called the **ionic product of water**.

$$K_w = [H^+][OH\ ] \qquad (7.27)$$

The concentration of H^+ has been found out experimentally as 1.0 10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH ions, the concentration of hydroxyl ions, $[OH\ ] = [H^+] = 1.0\ \ 10^{-7}$ M. Thus, the value of K_w at 298K,

$$K_w = [H_3O^+][OH\ ] = (1\ \ 10^{-7})^2 = 1\ \ 10^{-14}\ M^2 \qquad (7.28)$$

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as,

$[H_2O] = (1000\ g\ /L)(1\ mol/18.0\ g) = 55.55$ M.

Therefore, the ratio of dissociated water to that of undissociated water can be given as:

10^{-7} / (55.55) = 1.8 10^{9} or ~ 2 in 10^{9} (thus, equilibrium lies mainly towards undissociated water)

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations:

Acidic: $[H_3O^+] > [OH\ ]$

Neutral: $[H_3O^+] = [OH\ ]$

Basic : $[H_3O^+] < [OH\ ]$

7.11.2 The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity $\left(a_{H^+}\right)$ of hydrogen

ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H^+) is equal in magnitude to molarity represented by $[H^+]$. It should be noted that activity has no units and is defined as:

$$a_{H^+} = [H^+] / \text{mol L}^{-1}$$

From the definition of pH, the following can be written,

$$pH = -\log a_{H+} = -\log \{[H^+] / \text{mol L}^{-1}\}$$

Thus, an acidic solution of HCl (10^{2} M) will have a pH = 2. Similarly, a basic solution of NaOH having $[OH^-] = 10^{4}$ M and $[H_3O^+] = 10^{10}$ M will have a pH = 10. At 25 C, pure water has a concentration of hydrogen ions, $[H^+] = 10^{7}$ M. Hence, the pH of pure water is given as:

$$pH = -\log(10^{7}) = 7$$

Acidic solutions possess a concentration of hydrogen ions, $[H^+] > 10^{-7}$ M, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ M. thus, we can summarise that

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

Now again, consider the equation (7.28) at 298 K

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

Taking negative logarithm on both sides of equation, we obtain

$$-\log K_w = -\log \{[H_3O^+][OH^-]\}$$
$$= -\log [H_3O^+] - \log [OH^-]$$
$$= -\log 10^{-14}$$

$$pK_w = pH + pOH = 14 \qquad (7.29)$$

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 7.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper.

Fig.7.11 *pH-paper with four strips that may have different colours at the same* pH

For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision. pH meters of the size of a writing pen are now available in the market. The pH of some very common substances are given in Table 7.5 (page 212).

Problem 7.16

The concentration of hydrogen ion in a sample of soft drink is 3.8 10^{-3}M. what is its pH ?

Solution

$$pH = -\log[3.8 \quad 10^{-3}]$$
$$= -\{\log[3.8] + \log[10^{-3}]\}$$
$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

Problem 7.17

Calculate pH of a 1.0 10^{8} M solution of HCl.

Table 7.5 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~–1.0
Human Saliva	6.4		

Solution

$2H_2O\ (l) \quad H_3O^+\ (aq) + OH\ (aq)$

$K_w = [OH\ ][H_3O^+]$

$= 10^{-14}$

Let, x = [OH] = $[H_3O^+]$ from H_2O. The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$HCl(aq) + H_2O(l) \quad H_3O^+\ (aq) + Cl\ (aq)$,

and (ii) from ionization of H_2O. In these very dilute solutions, both sources of H_3O^+ must be considered:

$[H_3O^+] = 10^{\ 8} + x$

$K_w = (10^{\ 8} + x)(x) = 10^{\ 14}$

or $x^2 + 10^{\ 8}x - 10^{-14} = 0$

$[OH\ ] = x = 9.5 \quad 10^{\ 8}$

So, pOH = 7.02 and pH = 6.98

7.11.3 Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:

$HX(aq) + H_2O(l) \quad H_3O^+(aq) + X\ (aq)$

Initial concentration (M)

c 0 0

Let α be the extent of ionization

Change (M)

-cα +cα +cα

Equilibrium concentration (M)

c-cα cα cα

Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

$K_a = c^2\alpha^2 / c(1-\alpha) = c\alpha^2 / 1-\alpha$

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$K_a = [H^+][X\ ] / [HX]$ (7.30)

At a given temperature *T*, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a, the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

The values of the ionization constants of some selected weak acids are given in Table 7.6.

Table 7.6 The Ionization Constants of Some Selected Weak Acids (at 298K)

Acid	Ionization Constant, K_a
Hydrofluoric Acid (HF)	$3.5 \quad 10^{-4}$
Nitrous Acid (HNO_2)	$4.5 \quad 10^{-4}$
Formic Acid (HCOOH)	$1.8 \quad 10^{-4}$
Niacin (C_5H_4NCOOH)	$1.5 \quad 10^{-5}$
Acetic Acid (CH_3COOH)	$1.74 \quad 10^{-5}$
Benzoic Acid (C_6H_5COOH)	$6.5 \quad 10^{-5}$
Hypochlorous Acid (HCIO)	$3.0 \quad 10^{-8}$
Hydrocyanic Acid (HCN)	$4.9 \quad 10^{-10}$
Phenol (C_6H_5OH)	$1.3 \quad 10^{-10}$

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w, it has been extended to other species and

quantities. Thus, we have:

$$pK_a = -\log (K_a) \quad (7.31)$$

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids / bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.

Step 7. Calculate pH = – log[H_3O^+]

The above mentioned methodology has been elucidated in the following examples.

Problem 7.18

The ionization constant of HF is 3.2 10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) HF + H_2O H_3O^+ + F

K_a = 3.2 10^{-4}

2) H_2O + H_2O H_3O^+ + OH

K_w = 1.0 10^{-14}

As $K_a >> K_w$, [1] is the principle reaction.

	HF +	H_2O	H_3O^+ +	F
Initial concentration (M)	0.02		0	0
Change (M)	–0.02α		+0.02α	+0.02α
Equilibrium concentration (M)	0.02 – 0.02 α		0.02 α	0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$K_a = (0.02\alpha)^2 / (0.02 - 0.02\alpha)$

$= 0.02\ \alpha^2 / (1 - \alpha) = 3.2 \quad 10^{-4}$

We obtain the following quadratic equation:

$\alpha^2 + 1.6 \quad 10^{-2}\alpha - 1.6 \quad 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

α = + 0.12 and – 0.12

The negative root is not acceptable and hence,

α = 0.12

This means that the degree of ionization, α = 0.12, then equilibrium concentrations of other species viz., HF, F and H_3O^+ are given by:

$[H_3O^+] = [F\ ] = c\alpha = 0.02 \quad 0.12$

$= 2.4 \quad 10^{-3}$ M

$[HF] = c(1 - \alpha) = 0.02\ (1 - 0.12)$

$= 17.6 \quad 10^{-3}$ M

$pH = -\log[H^+] = -\log(2.4 \quad 10^{-3}) = 2.62$

Problem 7.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+,

A and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution

$$pH = -\log [H^+]$$

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50}$

$= 3.16 \quad 10^{-5}$

$[H^+] = [A\ ] = 3.16 \quad 10^{-5}$

Thus, $K_a = [H^+][A^-] / [HA]$

$[HA]_{eqlbm} = 0.1 - (3.16 \quad 10^{-5}) \quad 0.1$

$K_a = (3.16 \quad 10^{-5})^2 / 0.1 = 1.0 \quad 10^{-8}$

$pK_a = -\log(10^{-8}) = 8$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

$$= [HA]_{dissociated}/[HA]_{initial} \quad 100\% \qquad (7.32)$$

Problem 7.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is $2.5 \quad 10^{-5}$. Determine the percent dissociation of HOCl.

Solution

$HOCl(aq) + H_2O\ (l) \quad H_3O^+(aq) + ClO^-(aq)$

Initial concentration (M)		
0.08	0	0
Change to reach equilibrium concentration (M)		
– x	+ x	+x
equilibrium concentartion (M)		
0.08 – x	x	x

$K_a = \{[H_3O^+][ClO^-] / [HOCl]\}$

$= x^2 / (0.08 - x)$

As $x << 0.08$, therefore $0.08 - x \quad 0.08$

$x^2 / 0.08 = 2.5 \quad 10^{-5}$

$x^2 = 2.0 \quad 10^{-6}$, thus, $x = 1.41 \quad 10^{-3}$

$[H^+] = 1.41 \quad 10^{-3}$ M.

Therefore,

Percent dissociation

$= \{[HOCl]_{dissociated} / [HOCl]_{undissociated}\} \quad 100$

$= 1.41 \quad 10^{-3} / 0.08 = 1.76\ \%.$

$pH = -\log(1.41 \quad 10^{-3}) = 2.85.$

7.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$$MOH(aq) \quad M^+(aq) + OH\ (aq)$$

In a weak base there is partial ionization of MOH into M^+ and OH , the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$$K_b = [M^+][OH\ ] / [MOH] \qquad (7.33)$$

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$$K_b = (c\alpha)^2 / c\ (1-\alpha) = c\alpha^2 / (1-\alpha)$$

The values of the ionization constants of some selected weak bases, K_b are given in Table 7.7.

Table 7.7 The Values of the Ionization Constant of Some Weak Bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	$5.4 \quad 10^{-4}$
Triethylamine, $(C_2H_5)_3N$	$6.45 \quad 10^{-5}$
Ammonia, NH_3 or NH_4OH	$1.77 \quad 10^{-5}$
Quinine, (A plant product)	$1.10 \quad 10^{-6}$
Pyridine, C_5H_5N	$1.77 \quad 10^{-9}$
Aniline, $C_6H_5NH_2$	$4.27 \quad 10^{-10}$
Urea, $CO\ (NH_2)_2$	$1.3 \quad 10^{-14}$

Many organic compounds like *amines* are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and

nicotine all behave as very weak bases due to their very small K_b. Ammonia produces OH^- in aqueous solution:

$$NH_3(aq) + H_2O(l) \quad NH_4^+(aq) + OH\ (aq)$$

The pH scale for the hydrogen ion concentration has been extended to get:

$$pK_b = -\log (K_b) \qquad (7.34)$$

Problem 7.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

$$NH_2NH_2 + H_2O \quad NH_2NH_3^+ + OH$$

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$[H^+]$ = antilog (–pH)

= antilog (–9.7) = 1.67 10^{-10}

$[OH^-] = K_w / [H^+] = 1 \quad 10^{-14} / 1.67 \quad 10^{-10}$
$= 5.98 \quad 10^{-5}$

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

$K_b = [NH_2NH_3^+][OH\ ] / [NH_2NH_2]$

$= (5.98 \quad 10^{-5})^2 / 0.004 = 8.96 \quad 10^{-7}$

$pK_b = -\log K_b = -\log(8.96 \quad 10^{-7}) = 6.04.$

Problem 7.22

Calculate the pH of solution formed on mixing 0.2M NH_4Cl and 0.1M NH_3. The pOH of ammonia solution is 4.75.

Solution

$$NH_3 + H_2O \quad NH_4^+ + OH$$

The ionization constant of NH_3,

K_b = antilog ($-pK_b$) i.e.

$K_b = 10^{-4.75} = 1.77 \quad 10^{-5}$ M

	NH_3 +	H_2O	NH_4^+ +	OH^-
Initial concentration (M)	0.10		0.20	0
Change to reach equilibrium (M)	–x		+x	+x
At equilibrium (M)	0.10 – x		0.20 + x	x

$K_b = [NH_4^+][OH^-] / [NH_3]$

$= (0.20 + x)(x) / (0.1 - x) = 1.77 \quad 10^{-5}$

As K_b is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,

$[OH\ ] = x = 0.88 \quad 10^{-5}$

Therefore, $[H^+] = 1.12 \quad 10^{-9}$

pH = – log$[H^+]$ = 8.95.

7.11.5 Relation between K_a and K_b

As seen earlier in this chapter, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of NH_4^+ and NH_3 we see,

$$NH_4^+(aq) + H_2O(l) \quad H_3O^+(aq) + NH_3(aq)$$

$$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \quad 10^{-10}$$

$$NH_3(aq) + H_2O(l) \quad NH_4^+(aq) + OH\ (aq)$$

$$K_b = [NH_4^+][OH\ ] / NH_3 = 1.8 \quad 10^{-5}$$

$$\text{Net: } 2\,H_2O(l) \quad H_3O^+(aq) + OH\ (aq)$$

$$K_w = [H_3O^+][OH\ ] = 1.0 \quad 10^{-14}\ M$$

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added. Thus,

$K_a \quad K_b = \{[H_3O^+][NH_3] / [NH_4^+]\} \quad \{[NH_4^+]\ [OH\ ] / [NH_3]\}$

$= [H_3O^+][OH\ ] = K_w$

$= (5.6x10^{-10}) \quad (1.8 \quad 10^{-5}) = 1.0 \quad 10^{-14}$ M

This can be extended to make a generalisation. **The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:**

$$K_{NET} = K_1 \quad K_2 \quad \ldots\ldots \qquad (3.35)$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \quad K_b = K_w \qquad (7.36)$$

Knowing one, the other can be obtained. It should be noted that a *strong acid will have a weak conjugate base and vice versa.*

Alternatively, the above expression $K_w = K_a \quad K_b$, can also be obtained by considering the base-dissociation equilibrium reaction:

$$B(aq) + H_2O(l) \quad BH^+(aq) + OH\ (aq)$$

$$K_b = [BH^+][OH\ ] / [B]$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get:

$$K_b = [BH^+][OH\ ][H^+] / [B][H^+]$$

$$= \{[\ OH\ ][H^+]\}\{[BH^+] / [B][H^+]\}$$

$$= K_w / K_a$$

or $K_a \quad K_b = K_w$

It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:

$$pK_a + pK_b = pK_w = 14 \text{ (at 298K)}$$

Problem 7.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 7.7. Also, calculate the ionic constant of the conjugate acid of ammonia.

Solution

The ionization of NH_3 in water is represented by equation:

$$NH_3 + H_2O \quad NH_4^+ + OH$$

We use equation (7.33) to calculate hydroxyl ion concentration,

$$[OH\ ] = c\ \alpha = 0.05\ \alpha$$

$$K_b = 0.05\ \alpha^2 / (1 - \alpha)$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$$K_b = c\ \alpha^2 \text{ or } \alpha = \sqrt{(1.77 \quad 10^{-5} / 0.05)}$$

$$= 0.018.$$

$$[OH\ ] = c\ \alpha = 0.05 \quad 0.018 = 9.4 \quad 10^{-4}M.$$

$$[H^+] = K_w / [OH\ ] = 10^{-14} / (9.4 \quad 10^{-4})$$

$$= 1.06 \quad 10^{-11}$$

$$pH = -\log(1.06 \quad 10^{-11}) = 10.97.$$

Now, using the relation for conjugate acid-base pair,

$$K_a \quad K_b = K_w$$

using the value of K_b of NH_3 from Table 7.7.

We can determine the concentration of conjugate acid NH_4^+

$$K_a = K_w / K_b = 10^{-14} / 1.77 \quad 10^{-5}$$

$$= 5.64 \quad 10^{-10}.$$

7.11.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a *dibasic acid* H_2X are represented by the equations:

$$H_2X(aq) \quad H^+(aq) + HX\ (aq)$$

$$HX\ (aq) \quad H^+(aq) + X^2\ (aq)$$

And the corresponding equilibrium constants are given below:

$$K_{a_1} = \{[H^+][HX^-]\} / [H_2X] \text{ and}$$

$K_{a_2} = \{[H^+][X^{2-}]\} / [HX^-]$

Here, K_{a_1} and K_{a_2} are called the first and second ionization constants respectively of the acid H_2X. Similarly, for tribasic acids like H_3PO_4 we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 7.8.

Table 7.8 The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

It can be seen that higher order ionization constants (K_{a_2}, K_{a_3}) are smaller than the lower order ionization constant (K_{a_1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-. Similarly, it is more difficult to remove a proton from a doubly charged HPO_4^{2-} anion as compared to $H_2PO_4^-$.

Polyprotic acid solutions contain a mixture of acids like H_2A, HA^- and A^{2-} in case of a diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2A, and H_3O^+ in the solution comes mainly from the first dissociation step.

7.11.7 Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.

But it should be noted that while comparing elements in the same *group* of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

$$\xrightarrow[\text{HF << HCl << HBr << HI}]{\text{Size increases}}$$

$$\xrightarrow[\text{Acid strength increases}]{}$$

Similarly, H_2S is stronger acid than H_2O.

But, when we discuss elements in the same *row* of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

$$\xrightarrow[\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}]{\text{Electronegativity of A increases}}$$

$$\xrightarrow[\text{Acid strength increases}]{}$$

7.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$\text{or } HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$$

$$K_a = [H^+][Ac^-] / [HAc]$$

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example of

common ion effect. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 7.8.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

$$HAc(aq) \quad H^+(aq) + Ac^-(aq)$$

Initial concentration (M)

0.05 0 0.05

Let x be the extent of ionization of acetic acid.

Change in concentration (M)

–x +x +x

Equilibrium concentration (M)

0.05-x x 0.05+x

Therefore,

$K_a = [H^+][Ac^-]/[HAc] = \{(0.05+x)(x)\}/(0.05-x)$

As K_a is small for a very weak acid, x<<0.05.

Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus,

$1.8 \quad 10^{-5} = (x)(0.05 + x) / (0.05 - x)$

$= x(0.05) / (0.05) = x = [H^+] = 1.8 \quad 10^{-5}M$

$pH = -\log(1.8 \quad 10^{-5}) = 4.74$

Problem 7.24

Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia, $K_b = 1.77 \quad 10^{-5}$

Solution

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$K_b = [NH_4^+][OH^-] / [NH_3] = 1.77 \quad 10^{-5}$

Before neutralization,

$[NH_4^+] = [OH^-] = x$

$[NH_3] = 0.10 - x \quad 0.10$

$x^2 / 0.10 = 1.77 \quad 10^{-5}$

Thus, $x = 1.33 \quad 10^{-3} = [OH^-]$

Therefore, $[H^+] = K_w / [OH^-] = 10^{-14} / (1.33 \quad 10^{-3}) = 7.51 \quad 10^{-12}$

$pH = -\log(7.5 \quad 10^{-12}) = 11.12$

On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of NH_3), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+.

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

2.5 2.5 0 0

At equilibrium

0 0 2.5 2.5

The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of uneutralised NH_3 molecules. This NH_3 exists in the following equilibrium:

$$NH_4OH \quad NH_4^+ + OH^-$$

0.033M – y y y

where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains 2.5 m mol NH_4^+ ions (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$[NH_4^+] = 0.033 + y$

As y is small, $[NH_4OH] \quad 0.033$ M and $[NH_4^+] \quad 0.033$M.

We know,

$K_b = [NH_4^+][OH^-] / [NH_4OH]$

$= y(0.033)/(0.033) = 1.77 \quad 10^{-5}$ M

Thus, $y = 1.77 \quad 10^{-5} = [OH^-]$

$[H^+] = 10^{-14} / 1.77 \quad 10^{-5} = 0.56 \quad 10^{-9}$

Hence, pH = 9.24

7.11.9 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed

on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., Cl , Br , NO_3, ClO_4 etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

(i) salts of weak acid and strong base e.g., CH_3COONa.

(ii) salts of strong acid and weak base e.g., NH_4Cl, and

(iii) salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions

$$CH_3COO^-(aq) + H_2O(l) \quad CH_3COOH(aq) + OH^-(aq)$$

Acetic acid being a weak acid ($K_a = 1.8 \quad 10^{-5}$) remains mainly unionised in solution. This results in increase of OH^- ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl\ (aq)$$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$$NH_4^+(aq) + H_2O$$

Ammonium hydroxide is a weak base ($K_b = 1.77 \quad 10^{-5}$) and therefore remains almost unionised in solution. This results in increased of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

CH_3COOH and NH_4OH, also remain into partially dissociated form:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH$$

$$H_2O \rightleftharpoons H^+ + OH$$

Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$$pH = 7 + ½ (pK_a - pK_b) \qquad (7.38)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Problem 7.25

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Solution

$$pH = 7 + ½ [pK_a - pK_b]$$
$$= 7 + ½ [4.76 - 4.75]$$
$$= 7 + ½ [0.01] = 7 + 0.005 = 7.005$$

7.12 BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer solutions

of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

7.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed as insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule , for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former. Each salt has its characteristic solubility which depends on temperature. We classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M<Solubility< 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution.

7.13.1 Solubility Product Constant

Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the undisolved solid and the ions in a saturated solution can be represented by the equation:

$$BaSO_4(s) \underset{\text{in water}}{\overset{\text{Saturated Solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4^{2-}(aq),$$

The equilibrium constant is given by the equation:

$$K = \{[Ba^{2+}][SO_4^{2-}]\} / [BaSO_4]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[BaSO_4] = [Ba^{2+}][SO_4^{2-}] \qquad (7.39)$$

We call K_{sp} the *solubility product constant* or simply *solubility product*. The experimental value of K_{sp} in above equation at 298K is $1.1 \quad 10^{-10}$. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then

$$1.1 \quad 10^{-10} = (S)(S) = S^2$$

or $$S = 1.05 \quad 10^{-5}.$$

Thus, molar solubility of barium sulphate will be equal to $1.05 \quad 10^{-5}$ mol L^{-1}.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula $(Zr^{4+})_3(PO_4^{3-})_4$. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$$[Zr^{4+}] = 3S \text{ and } [PO_4^{3-}] = 4S$$

$$\text{and } K_{sp} = (3S)^3 (4S)^4 = 6912 (S)^7$$

$$\text{or } S = \{K_{sp} / (3^3 \quad 4^4)\}^{1/7} = (K_{sp} / 6912)^{1/7}$$

A solid salt of the general formula $M_x^{p+} X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation:

$M_xX_y(s) \quad xM^{p+}(aq) + yX^{q-}(aq)$

(where $x \quad p^+ = y \quad q^-$)

And its solubility product constant is given by:

$$K_{sp} = [M^{p+}]^x[X^{q-}]^y = (xS)^x(yS)^y \qquad (7.40)$$
$$= x^x \cdot y^y \cdot S^{(x+y)}$$

$$S^{(x+y)} = K_{sp} / x^x \cdot y^y$$

$$S = (K_{sp} / x^x \cdot y^y)^{1/x+y} \qquad (7.41)$$

The term K_{sp} in equation is given by Q_{sp} (section 7.6.2) when the concentration of one or more species is not the concentration under equilibrium. Obviously under equilibrium conditions $K_{sp} = Q_{sp}$ but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298K are given in Table 7.9.

Problem 7.26

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \quad 10^{-23}$.

Solution

$A_2X_3 \rightarrow 2A^{3+} + 3X^{2-}$

$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = 1.1 \quad 10^{-23}$

If S = solubility of A_2X_3, then

$[A^{3+}] = 2S; \; [X^{2-}] = 3S$

therefore, $K_{sp} = (2S)^2(3S)^3 = 108S^5$

$= 1.1 \quad 10^{-23}$

thus, $S^5 = 1 \quad 10^{-25}$

$S = 1.0 \quad 10^{-5}$ mol/L.

Problem 7.27

The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are $2.0 \quad 10^{-15}$ and $6 \quad 0^{-17}$ respectively. Which salt is more soluble? Explain.

Solution

$AgCN \quad Ag^+ + CN$

Table 7.9 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298K.

Name of the Salt	Formula	K_{sp}
Silver Bromide	$AgBr$	5.0×10^{-13}
Silver Carbonate	Ag_2CO_3	8.1×10^{-12}
Silver Chromate	Ag_2CrO_4	1.1×10^{-12}
Silver Chloride	$AgCl$	1.8×10^{-10}
Silver Iodide	AgI	8.3×10^{-17}
Silver Sulphate	Ag_2SO_4	1.4×10^{-5}
Aluminium Hydroxide	$Al(OH)_3$	1.3×10^{-33}
Barium Chromate	$BaCrO_4$	1.2×10^{-10}
Barium Fluoride	BaF_2	1.0×10^{-6}
Barium Sulphate	$BaSO_4$	1.1×10^{-10}
Calcium Carbonate	$CaCO_3$	2.8×10^{-9}
Calcium Fluoride	CaF_2	5.3×10^{-9}
Calcium Hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium Oxalate	CaC_2O_4	4.0×10^{-9}
Calcium Sulphate	$CaSO_4$	9.1×10^{-6}
Cadmium Hydroxide	$Cd(OH)_2$	2.5×10^{-14}
Cadmium Sulphide	CdS	8.0×10^{-27}
Chromic Hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Cuprous Bromide	$CuBr$	5.3×10^{-9}
Cupric Carbonate	$CuCO_3$	1.4×10^{-10}
Cuprous Chloride	$CuCl$	1.7×10^{-6}
Cupric Hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Cuprous Iodide	CuI	1.1×10^{-12}
Cupric Sulphide	CuS	6.3×10^{-36}
Ferrous Carbonate	$FeCO_3$	3.2×10^{-11}
Ferrous Hydroxide	$Fe(OH)_2$	8.0×10^{-16}
Ferric Hydroxide	$Fe(OH)_3$	1.0×10^{-38}
Ferrous Sulphide	FeS	6.3×10^{-18}
Mercurous Bromide	Hg_2Br_2	5.6×10^{-23}
Mercurous Chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous Iodide	Hg_2I_2	4.5×10^{-29}
Mercurous Sulphate	Hg_2SO_4	7.4×10^{-7}
Mercuric Sulphide	HgS	4.0×10^{-53}
Magnesium Carbonate	$MgCO_3$	3.5×10^{-8}
Magnesium Fluoride	MgF_2	6.5×10^{-9}
Magnesium Hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Magnesium Oxalate	MgC_2O_4	7.0×10^{-7}
Manganese Carbonate	$MnCO_3$	1.8×10^{-11}
Manganese Sulphide	MnS	2.5×10^{-13}
Nickel Hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel Sulphide	NiS	4.7×10^{-5}
Lead Bromide	$PbBr_2$	4.0×10^{-5}
Lead Carbonate	$PbCO_3$	7.4×10^{-14}
Lead Chloride	$PbCl_2$	1.6×10^{-5}
Lead Fluoride	PbF_2	7.7×10^{-8}
Lead Hydroxide	$Pb(OH)_2$	1.2×10^{-15}
Lead Iodide	PbI_2	7.1×10^{-9}
Lead Sulphate	$PbSO_4$	1.6×10^{-8}
Lead Sulphide	PbS	8.0×10^{-28}
Stannous Hydroxide	$Sn(OH)_2$	1.4×10^{-28}
Stannous Sulphide	SnS	1.0×10^{-25}
Strontium Carbonate	$SrCO_3$	1.1×10^{-10}
Strontium Fluoride	SrF_2	2.5×10^{-9}
Strontium Sulphate	$SrSO_4$	3.2×10^{-7}
Thallous Bromide	$TlBr$	3.4×10^{-6}
Thallous Chloride	$TlCl$	1.7×10^{-4}
Thallous Iodide	TlI	6.5×10^{-8}
Zinc Carbonate	$ZnCO_3$	1.4×10^{-11}
Zinc Hydroxide	$Zn(OH)_2$	1.0×10^{-15}
Zinc Sulphide	ZnS	1.6×10^{-24}

$K_{sp} = [Ag^+][CN^-] = 6 \quad 10^{-17}$

$Ni(OH)_2 \quad Ni^{2+} + 2OH^-$

$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \quad 10^{-15}$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$S_1^2 = 6 \quad 10^{-17}$, $S_1 = 7.8 \quad 10^{-9}$

$(S_2)(2S_2)^2 = 2 \quad 10^{-15}$, $S_2 = 0.58 \quad 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

7.13.2 Common Ion Effect on Solubility of Ionic Salts

It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$. This is applicable even to soluble salts like sodium chloride except that due to higher concentrations of the ions, we use their activities instead of their molarities in the expression for Q_{sp}. Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations.

Problem 7.28

Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. The ionic product of $Ni(OH)_2$ is $2.0 \quad 10^{-15}$.

Solution

Let the solubility of $Ni(OH)_2$ be equal to S. Dissolution of S mol/L of $Ni(OH)_2$ provides S mol/L of Ni^{2+} and 2S mol/L of OH , but the total concentration of OH = (0.10 + 2S) mol/L because the solution already contains 0.10 mol/L of OH^- from NaOH.

$K_{sp} = 2.0 \quad 10^{-15} = [Ni^{2+}]\,[OH\ ]^2$

$= (S)\,(0.10 + 2S)^2$

As K_{sp} is small, $2S << 0.10$,

thus, $(0.10 + 2S) \approx 0.10$

Hence,

$2.0 \quad 10^{-15} = S\,(0.10)^2$

$S = 2.0 \quad 10^{-13}$ M $= [Ni^{2+}]$

The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$. We have to satisfy two equilibria simultaneously i.e.,

$K_{sp} = [M^+]\,[X^-]$,

$HX(aq) \quad H^+$

$$K_a = \frac{[H^+(aq)}{[HX}$$

$[X\ ] / [HX] = K_a / [H^+]$

Taking inverse of both side and adding 1 we get

$$\frac{[HX]}{[X]} + 1 = \frac{[H^-}{K_a}$$

$$\frac{[HX] + [H^-]}{[X^-]} =$$

Now, again taking inverse, we get

$[X\ ] / \{[X\ ] + [HX]\} = f = K_a / (K_a + [H^+])$ and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then

$K_{sp} = [S]\,[f\,S] = S^2\,\{K_a / (K_a + [H^+])\}$ and

$S = \{K_{sp}([H^+] + K_a) / K_a\}^{1/2}$ (7.42)

Thus solubility S increases with increase in $[H^+]$ or decrease in pH.

SUMMARY

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal. **Equilibrium constant**, K_c is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient.

For reaction, $a\,A + b\,B \rightleftharpoons c\,C + d\,D$

$$K_c = [C]^c[D]^d/[A]^a[B]^b$$

Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant. For a gaseous reaction equilibrium constant is expressed as K_p and is written by replacing concentration terms by partial pressures in K_c expression. The direction of reaction can be predicted by reaction quotient Q_c which is equal to K_c at equilibrium. **Le Chatelier's principle** states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. **Catalyst** does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa.

All substances that conduct electricity in aqueous solutions are called **electrolytes**. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the **dissociation or ionization of electrolytes** in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to **Arrhenius, acids** give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. **Brönsted-Lowry** on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a **conjugate pair of acid-base** differs only by one proton. **Lewis** further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration and common ion are discussed. The **pH scale** ($pH = -\log[H^+]$) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities ($pOH = -\log[OH^-]$) ; $pK_a = -\log[K_a]$; $pK_b = -\log[K_b]$; and $pK_w = -\log[K_w]$ etc.). The ionization of water has been considered and we note that the equation: $pH + pOH = pK_w$ is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution.The definition of **buffer solutions**, and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as **solubility product constant** (K_{sp}). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed.

SUGGESTED ACTIVITIES FOR STUDENTS REGARDING THIS UNIT

(a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available.
(b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these are formed from strong/weak acids and bases.
(c) They may prepare some buffer solutions by mixing the solutions of sodium acetate and acetic acid and determine their pH using pH paper.
(d) They may be provided with different indicators to observe their colours in solutions of varying pH.
(e) They may perform some acid-base titrations using indicators.
(f) They may observe common ion effect on the solubility of sparingly soluble salts.
(g) If pH meter is available in their school, they may measure the pH with it and compare the results obtained with that of the pH paper.

EXERCISES

7.1 A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

a) What is the initial effect of the change on vapour pressure?

b) How do rates of evaporation and condensation change initially?

c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

7.2 What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2]$= 0.60M, $[O_2]$ = 0.82M and $[SO_3]$ = 1.90M ?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

7.3 At a certain temperature and total pressure of 10^5Pa, iodine vapour contains 40% by volume of I atoms

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_p for the equilibrium.

7.4 Write the expression for the equilibrium constant, K_c for each of the following reactions:

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

7.5 Find out the value of K_c for each of the following equilibria from the value of K_p:

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; K_p= 1.8 10^{-2} at 500 K

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; K_p= 167 at 1073 K

7.6 For the following equilibrium, K_c= 6.3 10^{14} at 1000 K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction?

7.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

7.8 Reaction between N_2 and O_2 takes place as follows:

$$2N_2\,(g) + O_2\,(g) \quad 2N_2O\,(g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \quad 10^{-37}$, determine the composition of equilibrium mixture.

7.9 Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO\,(g) + Br_2\,(g) \quad 2NOBr\,(g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

7.10 At 450K, $K_p = 2.0 \quad 10^{10}$/bar for the given reaction at equilibrium.

$$2SO_2(g) + O_2(g) \quad 2SO_3\,(g)$$

What is K_c at this temperature ?

7.11 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium ?

$$2HI\,(g) \quad H_2\,(g) + I_2\,(g)$$

7.12 A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_2\,(g) + 3H_2\,(g) \quad 2NH_3\,(g)$ is $1.7 \quad 10^2$. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

7.13 The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4\,[O_2}{[NO]^4\,[H_2O}$$

Write the balanced chemical equation corresponding to this expression.

7.14 One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O\,(g) + CO\,(g) \quad H_2\,(g) + CO_2\,(g)$$

Calculate the equilibrium constant for the reaction.

7.15 At 700 K, equilibrium constant for the reaction:

$$H_2\,(g) + I_2\,(g) \quad 2HI\,(g)$$

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

7.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?

$2ICl\,(g) \quad I_2\,(g) + Cl_2\,(g)$; $K_c = 0.14$

7.17 K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)$$

7.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction (note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

7.19 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5 10^{-1} mol L^{-1}. If value of K_c is 8.3 10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2(g)$$

7.20 One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

$$FeO\,(s) + CO\,(g) \rightleftharpoons Fe\,(s) + CO_2\,(g); \quad K_p = 0.265 \text{ atm at } 1050K$$

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: p_{CO}= 1.4 atm and p_{CO_2} = 0.80 atm?

7.21 Equilibrium constant, K_c for the reaction

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \text{ at 500 K is 0.061}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

7.22 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl\,(g) \rightleftharpoons Br_2\,(g) + Cl_2\,(g)$$

for which K_c= 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3 10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

7.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with soild carbon has 90.55% CO by mass

$$C\,(s) + CO_2\,(g) \rightleftharpoons 2CO\,(g)$$

Calculate K_c for this reaction at the above temperature.

7.24 Calculate a) ΔG and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K

$$NO\,(g) + ½\,O_2\,(g) \rightleftharpoons NO_2\,(g)$$

where

$\Delta_f G\ (NO_2)$ = 52.0 kJ/mol

$\Delta_f G$ (NO) = 87.0 kJ/mol

$\Delta_f G$ (O_2) = 0 kJ/mol

7.25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a) PCl_5 (g) PCl_3 (g) + Cl_2 (g)

(b) CaO (s) + CO_2 (g) $CaCO_3$ (s)

(c) 3Fe (s) + $4H_2O$ (g) Fe_3O_4 (s) + $4H_2$ (g)

7.26 Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

(i) $COCl_2$ (g) CO (g) + Cl_2 (g)

(ii) CH_4 (g) + $2S_2$ (g) CS_2 (g) + $2H_2S$ (g)

(iii) CO_2 (g) + C (s) 2CO (g)

(iv) $2H_2$ (g) + CO (g) CH_3OH (g)

(v) $CaCO_3$ (s) CaO (s) + CO_2 (g)

(vi) 4 NH_3 (g) + $5O_2$ (g) 4NO (g) + $6H_2O$(g)

7.27 The equilibrium constant for the following reaction is 1.6 10^5 at 1024K

H_2(g) + Br_2(g) 2HBr(g)

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

7.28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

CH_4 (g) + H_2O (g) CO (g) + $3H_2$ (g)

(a) Write as expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by

(i) increasing the pressure

(ii) increasing the temperature

(iii) using a catalyst ?

7.29 Describe the effect of :

a) addition of H_2
b) addition of CH_3OH
c) removal of CO
d) removal of CH_3OH

on the equilibrium of the reaction:

$2H_2$(g) + CO (g) CH_3OH (g)

7.30 At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3 10^{-3}. If decomposition is depicted as,

PCl_5 (g) PCl_3 (g) + Cl_2 (g) $\Delta_r H$ = 124.0 kJ mol^{-1}

a) write an expression for K_c for the reaction.

b) what is the value of K_c for the reverse reaction at the same temperature ?

c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

7.31 Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$$CO\ (g) + H_2O\ (g) \quad CO_2\ (g) + H_2\ (g)$$

If a reaction vessel at 400 C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? K_p= 10.1 at 400 C

7.32 Predict which of the following reaction will have appreciable concentration of reactants and products:

a) $Cl_2\ (g) \quad 2Cl\ (g) \quad K_c = 5 \quad 10^{-39}$

b) $Cl_2\ (g) + 2NO\ (g) \quad 2NOCl\ (g)\ K_c = 3.7 \quad 10^{8}$

c) $Cl_2\ (g) + 2NO_2\ (g) \quad 2NO_2Cl\ (g) \quad K_c = 1.8$

7.33 The value of K_c for the reaction $3O_2\ (g) \quad 2O_3\ (g)$ is $2.0 \quad 10^{-50}$ at 25 C. If the equilibrium concentration of O_2 in air at 25 C is $1.6 \quad 10^{-2}$, what is the concentration of O_3?

7.34 The reaction, $CO(g) + 3H_2(g) \quad CH_4(g) + H_2O(g)$

is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

7.35 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}

7.36 Which of the followings are Lewis acids? H_2O, BF_3, H^+, and NH_4^+

7.37 What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO_3?

7.38 Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

7.39 The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

7.40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3 .

7.41 The concentration of hydrogen ion in a sample of soft drink is $3.8 \quad 10^{-3}$ M. what is its pH?

7.42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

7.43 The ionization constant of HF, HCOOH and HCN at 298K are $6.8 \quad 10^{-4}$, $1.8 \quad 10^{-4}$ and $4.8 \quad 10^{-9}$ respectively. Calculate the ionization constants of the corresponding conjugate base.

7.44 The ionization constant of phenol is $1.0 \quad 10^{-10}$. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

7.45 The first ionization constant of H_2S is $9.1 \quad 10^{-8}$. Calculate the concentration of HS^- ion in its 0.1M solution. How will this concentration be affected if the solution

is 0.1M in HCl also ? If the second dissociation constant of H_2S is 1.2 10^{-13}, calculate the concentration of S^{2-} under both conditions.

7.46 The ionization constant of acetic acid is 1.74 10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

7.47 It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

7.48 Assuming complete dissociation, calculate the pH of the following solutions:

(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

7.49 Calculate the pH of the following solutions:

a) 2 g of TlOH dissolved in water to give 2 litre of solution.

b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

d) 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

7.50 The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

7.51 The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

7.52 What is the pH of 0.001M aniline solution ? The ionization constant of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

7.53 Calculate the degree of ionization of 0.05M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01M (b) 0.1M in HCl ?

7.54 The ionization constant of dimethylamine is 5.4 10^{-4}. Calculate its degree of ionization in its 0.02M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M in NaOH?

7.55 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a) Human muscle-fluid, 6.83 (b) Human stomach fluid, 1.2

(c) Human blood, 7.38 (d) Human saliva, 6.4.

7.56 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

7.57 If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

7.58 The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

7.59 The ionization constant of propanoic acid is 1.32 10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

7.60 The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

7.61 The ionization constant of nitrous acid is 4.5 10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

7.62 A 0.02M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

7.63 Predict if the solutions of the following salts are neutral, acidic or basic:

NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

7.64 The ionization constant of chloroacetic acid is $1.35 \quad 10^{-3}$. What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

7.65 Ionic product of water at 310 K is $2.7 \quad 10^{-14}$. What is the pH of neutral water at this temperature?

7.66 Calculate the pH of the resultant mixtures:

a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

7.67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9. Determine also the molarities of individual ions.

7.68 The solubility product constant of Ag_2CrO_4 and AgBr are $1.1 \quad 10^{-12}$ and $5.0 \quad 10^{-13}$ respectively. Calculate the ratio of the molarities of their saturated solutions.

7.69 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \quad 10^{-8}$).

7.70 The ionization constant of benzoic acid is $6.46 \quad 10^{-5}$ and K_{sp} for silver benzoate is $2.5 \quad 10^{-13}$. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

7.71 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \quad 10^{-18}$).

7.72 What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is $9.1 \quad 10^{-6}$).

7.73 The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is $1.0 \quad 10^{-19}$M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

Answer to Some Selected Problems

UNIT 1

1.17 ~ 15 10^{-4} g , 1.25 10^{-4} *m*

1.18 (i) 4.8×10^{-3} (ii) 2.34×10^{-5} (iii) 8.008×10^{-3} (iv) 5.000×10^{-2}
(v) 6.0012×10^{-0}

1.19 (i) 2 (ii) 3 (iii) 4 (iv) 3
(v) 4 (vi) 5

1.20 (i) 34.2 (ii) 10.4 (iii) 0.0460 (iv) 2810

1.21 (a) law of multiple proportion (b) (i) Ans : (10^6 mm, 10^{15} pm)
(ii) Ans : (10^6 kg, 10^9 ng)
(iii) Ans : (10^{-3} L, 10^{-3} dm^3)

1.22 6.00×10^{-1} m =0.600 m

1.23 (i) B is limiting (ii) A is limiting
(iii) Stoichiometric mixture –No (iv) B is limiting
(v) A is limiting

1.24 (i) 2571 g (ii) 428.5g
(iii) Hydrogen will remain unreacted; 571.5 g

1.26 Ten volumes

1.27 (i) 2.87×10^{-11}pm (ii) 1.515×10^{-5} s (iii) 2.5365×10^{-2}kg

1.30 1.99265×10^{-23}g

1.31 (i) 3 (ii) 4 (iii) 4

1.32 39.948 g mol^{-1}

1.33 (i) 3.131 10^{-25} atoms (ii) 13 atoms (iii) 7.8286 10^{-24} atoms

1.34 Empirical formula CH, molar mass 22.0 g mol^{-1}, molecular formula C_2H_2

1.35 0.94 g $CaCO_3$

1.36 8.40 g HCl

UNIT 2

2.1 (i) 1.099 10^{27} electrons (ii) 5.48 10^{7} kg, 9.65 10^{4}C

2.2 (i) 6.022 10^{24}electrons
(ii) (a) 2.4088 10^{21} neutrons (b) 4.0347 10^{6} kg
(iii) (a) 1.2044 10^{22} protons (b) 2.015 10^{5} kg

2.3 7,6: 8,8: 12,12: 30,26: 50, 38

2.4 (i) Cl (ii) U (iii) Be

2.5 5.17 10^{14} s^{1}, 1.72 $10^{6}$$m^{1}$

2.6 (i) 1.988 10^{18} J (ii) 3.98 10^{15} J

2.7 $6.0 \quad 10^{2}$ m, $5.0 \quad 10^{9}$ s ^{1} and 16.66 m ^{1}

2.8 $2.012 \quad 10^{16}$ photons

2.9 (i) $4.97 \quad 10^{19}$ J (3.10 eV); (ii) 0.97 eV (iii) $5.84 \quad 10^{5}$ m s ^{1}

2.10 494 kJ mol ^{1}

2.11 $7.18 \quad 10^{19}$s ^{1}

2.12 $4.41 \quad 10^{14}$s ^{1}, $2.91 \quad 10^{19}$J

2.13 486 nm

2.14 $8.72 \quad 10^{20}$J

2.15 15 emmission lines

2.16 (i) $8.72 \quad 10^{20}$J (ii) 1.3225 nm

2.17 $1.523 \quad 10^{6}$ m ^{1}

2.18 $2.08 \quad 10^{11}$ ergs, 956 Å

2.19 3647Å

2.20 $3.55 \quad 10^{11}$m

2.21 8967Å

2.22 Na^{+}, Mg^{2+}, Ca^{2+}; Ar, S^{2} and K^{+}

2.23 (i) (a) $1s^2$ (b) $1s^2\ 2s^2\ 2p^6$; (c) $1s^22s^22p^6$ (d) $1s^22s^22p^6$

2.24 n = 5

2.25 n = 3; l = 2; m_l = –2, –1, 0, +1, +2 (any one value)

2.26 (i) 29 protons

2.27 1, 2, 15

2.28 (i)

l	m_l
0	0
1	–1,0,+1
2	–2,–1,0,+1,+2

(ii) l = 2; m_1=–2, –1,0,+1,+2

(iii) 2s, 2p

2.29 (a) 1s, (b) 3p, (c) 4d and (d) 4f

2.30 (a), (c) and (e) are not possible

2.31 (a) 16 electrons (b) 2 electrons

2.33 n = 2 to n = 1

2.34 $8.72 \quad 10^{18}$J

2.35 $1.33 \quad 10^{9}$

2.36 6 nm

2.37 (a) $1.3 \quad 10^{4}$ pm (b) $1.23 \quad 10^{6}$

2.38 1563

2.39 8

2.40 More number of K–particles will pass as the nucleus of the lighter atoms is small, smaller number of K–particles will be deflected as a number of positve charges is less than on the lighter nuclei.

2.41 For a given element the number of prontons is the same for the isotopes, whereas the mass number can be different for the given atomic number.

2.42 $^{81}_{35}Br$

2.43 $^{37}_{17}Cl^{-1}$

2.44 $^{56}_{26}Fe^{3+}$

2.45 Cosmic rays < X–rays < amber colour < microwave < FM

2.46 3.3 10^{7} J

2.47 (a) 4.87 10^{14} s^{1} (b) 9.0 10^{9} m (c) 32.27 10^{20} J
(d) 6.2 10^{18}

2.48 10

2.49 8.828 10^{10} J

2.50 3.46 10^{22} J

2.51 (a) 652 nm (b) 4.598 10^{14} s^{1}
(c) 3.97 10^{13} J, 9.33 10^{8} ms^{1}

2.53 4.3 eV

2.54 7.6 10^{3} eV

2.55 infrared, 5

2.56 453 pm

2.57 400 pm

2.58 9.89 ms^{1}

2.59 332 pm

2.60 1.51 10^{27} m

2.61 Can not be defined as the actual magnitude is smaller than uncertainity.

2.62 (v) < (ii) = (iv) < (vi) = (iii) < (i)

2.63 4*p*

2.64 (i) 2*s* (ii) 4*d* (iii) 3*p*

2.65 Si

2.66 (a) 3 (b) 2 (c) 6
(d) 4 (e) zero

2.67 16

UNIT 5

5.1 2.5 bar

5.2 0.8 bar

5.4 70 g/mol

5.5 $M_B = 4M_A$

5.6 202.5 mL

5.7 8.314 10^{4} Pa

5.8 1.8 bar

5.9 3g/dm^3

5.10 1247.7 g

5.11 3/5

5.12 50 K

5.13 4.2154 10^{23} electrons

5.14 1.90956 10^6 year

5.15 56.025 bar

5.16 3811.1 kg

5.17 5.05 L

5.18 40 g mol ^{1}

5.19 0.8 bar

UNIT 6

6.1 (ii)

6.2 (iii)

6.3 (ii)

6.4 (iii)

6.5 (i)

6.6 (iv)

6.7 q = + 701 J
w = – 394 J, since work is done by the system
ΔU = 307 J

6.8 – 741.5 kJ

6.9 1.09 kJ

6.10 $\Delta H = -5.65$ kJ mol^{-1}

6.11 – 315 kJ

6.12 $\Delta_r H = -778$ kJ

6.13 – 46.2 kJ mol^{-1}

6.14 – 239 kJ mol^{-1}

6.15 327 kJ mol^{-1}

6.16 $\Delta S > 0$

6.17 200 K

6.18 ΔH is negative (bond energy is released) and ΔS is negative (There is less randomness among the molecules than among the atoms)

6.19 0.164 kJ, the reaction is not spontaneous.

6.20 –55.27 kJ mol^{-1}

6.21 NO(g) is unstable, but NO_2(g) is formed.

6.22 q_{surr} = + 286 kJ mol^{-1}
ΔS_{surr} = 959.73 J K^{-1}

UNIT 7

7.2 12.237 $molL^{-1}$

7.3 2.67 x 10^4

7.5 (i) 4.4 10^{-4} (ii) 1.90

7.6 1.59 10^{-15}

7.8 $[N_2]$ = 0.0482 $molL^{-1}$, $[O_2]$ = 0.0933 $molL^{-1}$, $[N_2O]$ = 6.6 10^{-21} $molL^{-1}$

7.9 0.0355mol of NO and 0.0178mol of Br_2

7.10 7.47 10^{11} M^{-1}

7.11 4.0

7.12 Q_c = 2.97 10^3. No, reaction is not at equilibrium.

7.14 0.44

7.15 0.068 $molL^{-1}$ each of H_2 and I_2

7.16 $[I_2] = [Cl_2]$ = 0.21 M, [ICl] = 0.36 M

7.17 $[C_2H_6]_{eq}$ = 3.62 atm

7.18 (i) $[CH_3COOC_2H_5][H_2O]$ / $[CH_3COOH][C_2H_5OH]$
(ii) 22.9 (iii) value of Q_c is less than K_c therefore equilibrium is not attained.

7.19 0.02$molL^{-1}$ for both.

7.20 $[P_{CO}]$ = 1.739atm, $[P_{CO2}]$ = 0.461atm.

7.21 No, the reaction proceeds to form more products.

7.22 3 10^{-4} $molL^{-1}$

7.23 14.0

7.24 a) – 35.0kJ, b) 1.365 10^6

7.27 $[P_{H2}]_{eq} = [P_{Br2}]_{eq}$ = 2.5 10^{-2}bar, $[P_{HBr}]$ = 10.0 bar

7.30 b) 120.48

7.31 $[H_2]_{eq}$ = 0.96 bar

7.33 2.86 10^{-28} M

7.34 5.85x10^{-2}

7.35 NO_2^-, HCN, ClO_4, HF, H_2O, HCO_3^-, HS^-

7.36 BF_3, H^+, NH_4^+

7.37 F^-, HSO_4^-, CO_3^{2-}

7.38 NH_3, NH_4^+, HCOOH

7.41 2.42

7.42 1.7 x 10^{-4}M

7.43 F^-= 1.5 x 10^{-11}, $HCOO^-$= 5.6 10^{-11}, CN^-= 2.08 x 10^{-6}

7.44 [phenate ion]= 2.2 10^{-6}, pH= 5.65, á= 4.47 10^{-5}. pH of 0.01M sodium phenate solution= 9.30.

7.45 $[HS^-]$= 9.54 x 10^{-5}, in 0.1M HCl $[HS^-]$ = 9.1 10^{-8}M, $[S^{2-}]$= 1.2 10^{-13}M, in 0.1M HCl $[S^{2-}]$= 1.09 10^{-19}M

7.46 $[Ac^-]$= 0.00093, pH= 3.03

7.47 $[A^-]$ = 7.08 x10^{-5}M, K_a= 5.08 10^{-7}, pK_a= 6.29

7.48 a) 2.52 b) 11.70 c) 2.70 d) 11.30

7.49 a) 11.65 b) 12.21 c) 12.57 c) 1.87

7.50 pH = 1.88, pK_a = 2.70

7.51 K_b = 1.6 10^{-6}, pK_b = 5.8

7.52 α = 6.53 10^{-4}, K_a = 2.34 10^{-5}

7.53 a) 0.0018 b) 0.00018

7.54 α = 0.0054

7.55 a) 1.48 10^{-7}M, b) 0.063 c) 4.17 10^{-8}M d) 3.98 10^{-7}

7.56 a) 1.5 10^{-7}M, b) 10^{-5}M, c) 6.31 10^{-5}M d) 6.31 10^{-3}M

7.57 $[K^+] = [OH^-]$ = 0.05M, $[H^+]$ = 2.0 10^{-13}M

7.58 $[Sr^{2+}] = 0.1581M$, $[OH^-] = 0.3162M$, pH = 13.50

7.59 $\alpha = 1.63 \quad 10^{-2}$, pH = 3.09. In presence of 0.01M HCl, $\alpha = 1.32 \quad 10^{-3}$

7.60 $K_a = 2.09 \quad 10^{-4}$ and degree of ionization = 0.0457

7.61 pH = 7.97. Degree of hydrolysis = $2.36 \quad 10^{-5}$

7.62 $K_b = 1.5 \quad 10^{-9}$

7.63 NaCl, KBr solutions are neutral, NaCN, $NaNO_2$ and KF solutions are basic and NH_4NO_3 solution is acidic.

7.64 (a) pH of acid solution= 1.94 (b) its salt solution= 2.87

7.65 pH = 6.78

7.66 a) 11.2 b) 7.00 c) 3.00

7.67 Silver chromate S= $0.65 \quad 10^{-4}M$; Molarity of $Ag^+ = 1.30 \times 10^{-4}M$

Molarity of $CrO_4^{2-} = 0.65 \quad 10^{-4}M$; Barium Chromate S = $1.1 \quad 10^{-5}M$; Molarity of Ba^{2+} and CrO_4^{2-} each is $1.1 \quad 10^{-5}M$; Ferric Hydroxide S = $1.39 \quad 10^{-10}M$;

Molarity of $Fe^{3+} = 1.39 \quad 10^{-10}M$; Molarity of $[OH^-] = 4.17 \quad 10^{-10}M$

Lead Chloride S = $1.59 \quad 10^{-2}M$; Molarity of $Pb^{2+} = 1.59 \quad 10^{-2}M$

Molarity of $Cl^- = 3.18 \quad 10^{-2}M$; Mercurous Iodide S = $2.24 \quad 10^{-10}M$;

Molarity of $Hg_2^{2+} = 2.24 \quad 10^{-10}M$ and molarity of $I^- = 4.48 \quad 10^{-10}M$

7.68 Silver chromate is more soluble and the ratio of their molarities = 91.9

7.69 No precipitate

7.70 Silver benzoate is 3.317 times more soluble at lower pH

7.71 The highest molarity for the solution is $2.5 \quad 10^{-9}M$

7.72 2.46 litre of water

7.73 Precipitation will take place in cadmium chloride solution

Appendix I

Definitions of the SI Base Units

Metre (m): The metre is the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second (17th CGPM, 1983).

Kilogram (kg): The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram (3rd CGPM, 1901).

Second (s): The second is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom (13th CGPM, 1967).

Ampere (A): The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to $2 \quad 10^{7}$ Newton per metre of length (9th CGPM, 1948).

Kelvin (K): The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water (13th CGPM, 1967).

Mole (mol): The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles (14th CGPM, 1971).

Candela (cd): The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \quad 10^{12}$ hertz and that has a radiant intensity in that direction of (1/683) watt per steradian (16th CGPM, 1979).

(The symbols listed here are internationally agreed and should not be changed in other languages or scripts).

Appendix II

Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half life.

Appendix III

A. Specific and Molar Heat Capacities for Some Substances at 298 K and one Atmospheric Pressure

Substance	Specific Heat Capacity (J/g)	Molar Heat Capacity (J/mol)
air	0.720	20.8
water (liquid)	4.184	75.4
ammonia (gas)	2.06	35.1
hydrogen chloride	0.797	29.1
hydrogen bromide	0.360	29.1
ammonia (liquid)	4.70	79.9
ethyl alcohol (liquid)	2.46	113.16
ethylene glycol (liquid)	2.42	152.52
water (solid)	2.06	37.08
carbon tetrachloride (liquid)	0.861	132.59
chlorofluorocarbon (CCl_2F_2)	0.5980	72.35
ozone	0.817	39.2
neon	1.03	20.7
chlorine	0.477	33.8
bromine	0.473	75.6
iron	0.460	25.1
copper	0.385	24.7
aluminium	0.902	24.35
gold	0.128	25.2
graphite	0.720	8.65

B. Molar Heat Capacities for Some Gases (J/mol)

Gas	C_p	C_v	$C_p - C_v$	C_p / C_v
Monatomic*				
helium	20.9	12.8	8.28	1.63
argon	20.8	12.5	8.33	1.66
iodine	20.9	12.6	8.37	1.66
mercury	20.8	12.5	8.33	1.66
Diatomic†				
hydrogen	28.6	20.2	8.33	1.41
oxygen	29.1	20.8	8.33	1.39
nitrogen	29.0	20.7	8.30	1.40
hydrogen chloride	29.6	21.0	8.60	1.39
carbon monoxide	29.0	21.0	8.00	1.41
Triatomic†				
nitrous oxide	39.0	30.5	8.50	1.28
carbon dioxide	37.5	29.0	8.50	1.29
Polyatomic†				
ethane	53.2	44.6	8.60	1.19

*Translational kinetic energy only.
†Translational, vibrational and rotational energy.

Appendix IV

Physical Constants

Quantity	Symbol	Traditional Units	SI Units
Acceleration of gravity	g	980.6 cm/s	9.806 m/s
Atomic mass unit (1/12 the mass of ^{12}C atom)	amu or u	1.6606×10^{24} g	1.6606×10^{27} kg
Avogadro constant	N_A	6.022×10^{23} particles/mol	6.022×10^{23} particles/mol
Bohr radius	a_o	0.52918 Å 5.2918×10^{9} cm	5.2918×10^{11} m
Boltzmann constant	k	1.3807×10^{16} erg/K	1.3807×10^{23} J/K
Charge-to-mass ratio of electron	e/m	1.7588×10^{8} coulomb/g	1.7588×10^{11} C/kg
Electronic charge	e	1.60219×10^{19} coulomb 4.8033×10^{19} esu	1.60219×10^{19} C
Electron rest mass	m_e	9.10952×10^{28} g 0.00054859 u	9.10952×10^{31} kg
Faraday constant	F	96,487 coulombs/eq 23.06 kcal/volt. eq	96,487 C/mol e 96,487 J/V.mol e
Gas constant	R	$0.8206 \frac{\text{L atm}}{\text{m l}}$ $1.987 \frac{\text{al}}{\text{m l}}$	$8.3145 \frac{\text{a dm}^3}{\text{m l}}$ 8.3145 J/mol.K
Molar volume (STP)	V_m	22.710981 L/mol	22.710981×10^{3} m^3/mol 22.710981 dm^3/mol
Neutron rest mass	m_n	1.67495×10^{24} g 1.008665 u	1.67495×10^{27} kg
Planck constant	h	6.6262×10^{27} ergs	6.6262×10^{34} J s
Proton rest mass	m_p	1.6726×10^{24} g 1.007277 u	1.6726×10^{27} kg
Rydberg constant	R_∞	3.289×10^{15} cycles/s 2.1799×10^{11} erg	1.0974×10^{7} m^{1} 2.1799×10^{18} J
Speed of light (in a vacuum)	c	2.9979×10^{10} cm/s (186,281 miles/second)	2.9979×10^{8} m/s

π = 3.1416 2.303 R = 4.576 cal/mol K = 19.15 J/mol K

e = 2.71828 2.303 RT (at 25 C) = 1364 cal/mol = 5709 J/mol

ln X = 2.303 log X

Appendix V

Some Useful Conversion Factors

Common Unit of Mass and Weight
1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram
1 kilogram = 1000 grams = 2.205 pounds
1 gram = 10 decigrams = 100 centigrams
= 1000 milligrams
1 gram = 6.022×10^{23} atomic mass units or u
1 atomic mass unit = 1.6606×10^{-24} gram
1 metric tonne = 1000 kilograms
= 2205 pounds

Common Unit of Volume
1 quart = 0.9463 litre
1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre
1 millilitre = 1 cubic centimetre = 0.001 litre
= 1.056×10^{-3} quart
1 cubic foot = 28.316 litres = 29.902 quarts
= 7.475 gallons

Common Units of Energy
1 joule = 1×10^7 ergs

1 thermochemical calorie**
= 4.184 joules
= 4.184×10^7 ergs
= 4.129×10^{-2} litre atmospheres
= 2.612×10^{19} electron volts
1 ergs = 1×10^{-7} joule = 2.3901×10^{-8} calorie
1 electron volt = 1.6022×10^{-19} joule
= 1.6022×10^{-12} erg
= 96.487 kJ/mol†
1 litre atmosphere = 24.217 calories
= 101.32 joules
= 1.0132×10^9 ergs
1 British thermal unit = 1055.06 joules
= 1.05506×10^{10} ergs
= 252.2 calories

Common Units of Length
1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres
1 yard = 36 inches = 0.9144 metre
1 metre = 100 centimetres = 39.37 inches
= 3.281 feet
= 1.094 yards
1 kilometre = 1000 metres = 1094 yards
= 0.6215 mile
1 Angstrom = 1.0×10^{-8} centimetre
= 0.10 nanometre
= 1.0×10^{-10} metre
= 3.937×10^{-9} inch

Common Units of Force* and Pressure

1 atmosphere = 760 millimetres of mercury
= 1.013×10^5 pascals
= 14.70 pounds per square inch
1 bar = 10^5 pascals
1 torr = 1 millimetre of mercury
1 pascal = 1 kg/ms^2 = 1 N/m^2

Temperature
SI Base Unit: Kelvin (K)

K = 273.15 C
K = C + 273.15
F = 1.8(C) + 32

$$°C = \frac{°F - 32}{1.8}$$

* Force: 1 newton (N) = 1 kg m/s^2, i.e.,the force that, when applied for 1 second, gives a 1 kilogram mass a velocity of 1 metre per second.
** The amount of heat required to raise the temperature of one gram of water from 14.5^{0}C to 15.5^{0}C.
† Note that the other units are per particle and must be multiplied by 6.022×10^{23} to be strictly comparable.

Appendix VI

Thermodynamic Data at 298 K

INORGANIC SUBSTANCES

Substance	Enthalpy of formation, $\Delta_f H^J$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^J$/ (kJ mol^{-1})	Entropy,* S^J/(J K^{-1} mol^{-1})
Aluminium			
Al(s)	0	0	28.33
Al^{3+}(aq)	–524.7	–481.2	–321.7
Al_2O_3(s)	–1675.7	–1582.3	50.92
$Al(OH)_3$(s)	–1276	—	—
$AlCl_3$(s)	–704.2	–628.8	110.67
Antimony			
SbH_3(g)	145.11	147.75	232.78
$SbCl_3$(g)	–313.8	–301.2	337.80
$SbCl_5$(g)	–394.34	–334.29	401.94
Arsenic			
As(s), gray	0	0	35.1
As_2S_3(s)	–169.0	–168.6	163.6
AsO_4^{3-}(aq)	–888.14	–648.41	–162.8
Barium			
Ba(s)	0	0	62.8
Ba^{2+}(aq)	–537.64	–560.77	9.6
BaO(s)	–553.5	–525.1	70.42
$BaCO_3$(s)	–1216.3	–1137.6	112.1
$BaCO_3$(aq)	–1214.78	–1088.59	–47.3
Boron			
B(s)	0	0	5.86
B_2O_3(s)	–1272.8	–1193.7	53.97
BF_3(g)	–1137.0	–1120.3	254.12
Bromine			
Br_2(l)	0	0	152.23
Br_2(g)	30.91	3.11	245.46
Br(g)	111.88	82.40	175.02
Br^-(aq)	–121.55	–103.96	82.4
HBr(g)	–36.40	–53.45	198.70
BrF_3(g)	–255.60	–229.43	292.53
Calcium			
Ca(s)	0	0	41.42
Ca(g)	178.2	144.3	154.88
Ca^{2+}(aq)	–542.83	–553.58	–53.1

(continued)

Substance	Enthalpy of formation, $\Delta_f H^J$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^J$/ (kJ mol^{-1})	Entropy,* S^J/(J K^{-1} mol^{-1})
Calcium (continued)			
CaO(s)	–635.09	–604.03	39.75
$Ca(OH)_2$(s)	–986.09	–898.49	83.39
$Ca(OH)_2$(aq)	–1002.82	–868.07	–74.5
$CaCO_3$(s), calcite	–1206.92	–1128.8	92.9
$CaCO_3$(s), aragonite	–1207.1	–1127.8	88.7
$CaCO_3$(aq)	–1219.97	–1081.39	–110.0
CaF_2(s)	–1219.6	–1167.3	68.87
CaF_2(aq)	–1208.09	–1111.15	–80.8
$CaCl_2$(s)	–795.8	–748.1	104.6
$CaCl_2$(aq)	–877.1	–816.0	59.8
$CaBr_2$(s)	–682.8	–663.6	130
CaC_2(s)	–59.8	–64.9	69.96
CaS(s)	–482.4	–477.4	56.5
$CaSO_4$(s)	–1434.11	–1321.79	106.7
$CaSO_4$(aq)	–1452.10	–1298.10	–33.1
*Carbon***			
C(s), graphite	0	0	5.740
C(s), diamond	1.895	2.900	2.377
C(g)	716.68	671.26	158.10
CO(g)	–110.53	–137.17	197.67
CO_2(g)	–393.51	–394.36	213.74
CO_3^{2-}(aq)	–677.14	–527.81	–56.9
CCl_4(l)	–135.44	–65.21	216.40
CS_2(l)	89.70	65.27	151.34
HCN(g)	135.1	124.7	201.78
HCN(l)	108.87	124.97	112.84
Cerium			
Ce(s)	0	0	72.0
Ce^{3+}(aq)	–696.2	–672.0	–205
Ce^{4+}(aq)	–537.2	–503.8	–301
Chlorine			
Cl_2(g)	0	0	223.07
Cl(g)	121.68	105.68	165.20
Cl^-(aq)	–167.16	–131.23	56.5
HCl(g)	–92.31	–95.30	186.91
HCl(aq)	–167.16	–131.23	56.5
Copper			
Cu(s)	0	0	33.15
Cu^+(aq)	71.67	49.98	40.6
Cu^{2+}(aq)	64.77	65.49	–99.6
Cu_2O(aq)	–168.6	–146.0	93.14
CuO(s)	–157.3	–129.7	42.63
$CuSO_4$(s)	–771.36	–661.8	109
$CuSO_4.5H_2O$(s)	–2279.7	–1879.7	300.4

** For organic compounds, a separate table is provided in continuation.

(continued)

Substance	Enthalpy of formation, $\Delta_f H^J$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^J$/ (kJ mol^{-1})	Entropy,* S^J/(J K^{-1} mol^{-1})
Deuterium			
$D_2(g)$	0	0	144.96
$D_2O(g)$	–249.20	–234.54	198.34
$D_2O(l)$	–294.60	–243.44	75.94
Fluorine			
$F_2(g)$	0	0	202.78
$F^-(aq)$	–332.63	–278.79	–13.8
HF(g)	–271.1	–273.2	173.78
HF(aq)	–332.63	–278.79	–13.8
Hydrogen (see also Deuterium)			
$H_2(g)$	0	0	130.68
H(g)	217.97	203.25	114.71
$H^+(aq)$	0	0	0
$H_2O(l)$	–285.83	–237.13	69.91
$H_2O(g)$	–241.82	–228.57	188.83
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(aq)$	–191.17	–134.03	143.9
Iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.44	19.33	260.69
$I^-(aq)$	–55.19	–51.57	111.3
HI(g)	26.48	1.70	206.59
Iron			
Fe(s)	0	0	27.28
$Fe^{2+}(aq)$	–89.1	–78.90	–137.7
$Fe^{3+}(aq)$	–48.5	–4.7	–315.9
$Fe_3O_4(s)$, magnetite	–1118.4	–1015.4	146.4
$Fe_2O_3(s)$, haematite	–824.2	–742.2	87.40
FeS(s,α)	–100.0	–100.4	60.29
FeS(aq)	—	6.9	—
$FeS_2(s)$	–178.2	–166.9	52.93
Lead			
Pb(s)	0	0	64.81
$Pb^{2+}(aq)$	–1.7	–24.43	10.5
$PbO_2(s)$	–277.4	–217.33	68.6
$PbSO_4(s)$	–919.94	–813.14	148.57
$PbBr_2(s)$	–278.7	–261.92	161.5
$PbBr_2(aq)$	–244.8	–232.34	175.3
Magnesium			
Mg(s)	0	0	32.68
Mg(g)	147.70	113.10	148.65
$Mg^{2+}(aq)$	–466.85	–454.8	–138.1
MgO(s)	–601.70	–569.43	26.94
$MgCO_3(s)$	–1095.8	–1012.1	65.7
$MgBr_2(s)$	–524.3	–503.8	117.2

(continued)

Substance	Enthalpy of formation, $\Delta_f H^\circ$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^\circ$/ (kJ mol^{-1})	Entropy,* S°/(J K^{-1} mol^{-1})
Mercury			
Hg(1)	0	0	76.02
Hg(g)	61.32	31.82	174.96
HgO(s)	–90.83	–58.54	70.29
Hg_2Cl_2(s)	–265.22	–210.75	192.5
Nitrogen			
N_2(g)	0	0	191.61
NO(g)	90.25	86.55	210.76
N_2O(g)	82.05	104.20	219.85
NO_2(g)	33.18	51.31	240.06
N_2O_4(g)	9.16	97.89	304.29
HNO_3(1)	–174.10	–80.71	155.60
HNO_3(aq)	–207.36	–111.25	146.4
NO_3^- (aq)	–205.0	–108.74	146.4
NH_3(g)	–46.11	–16.45	192.45
NH_3(aq)	–80.29	–26.50	111.3
NH_4^+ (aq)	–132.51	–79.31	113.4
NH_2OH(s)	–114.2	—	—
HN_3(g)	294.1	328.1	238.97
N_2H_4(1)	50.63	149.34	121.21
NH_4NO_3(s)	–365.56	–183.87	151.08
NH_4Cl(s)	–314.43	–202.87	94.6
NH_4ClO_4(s)	–295.31	–88.75	186.2
Oxygen			
O_2(g)	0	0	205.14
O_3(g)	142.7	163.2	238.93
OH^-(aq)	–229.99	–157.24	–10.75
Phosphorus			
P(s), white	0	0	41.09
P_4(g)	58.91	24.44	279.98
PH_3(g)	5.4	13.4	210.23
P_4O_{10}(s)	–2984.0	–2697.0	228.86
H_3PO_3(aq)	–964.8	—	—
H_3PO_4(1)	–1266.9	—	—
H_3PO_4(aq)	–1277.4	–1018.7	—
PCl_3(1)	–319.7	–272.3	217.18
PCl_3(g)	–287.0	–267.8	311.78
PCl_5(g)	–374.9	–305.0	364.6
Potassium			
K(s)	0	0	64.18
K(g)	89.24	60.59	160.34
K^+(aq)	–252.38	–283.27	102.5
KOH(s)	–424.76	–379.08	78.9
KOH(aq)	–482.37	–440.50	91.6
KF(s)	–567.27	–537.75	66.57

(continued)

Substance	Enthalpy of formation, $\Delta_f H^J$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^J$/ (kJ mol^{-1})	Entropy,* S^J/(J K^{-1} mol^{-1})
Potassium (continued)			
KCl(s)	–436.75	–409.14	82.59
KBr(s)	–393.80	–380.66	95.90
KI(s)	–327.90	–324.89	106.32
$KClO_3$(s)	–397.73	–296.25	143.1
$KClO_4$(s)	–432.75	–303.09	151.0
K_2S(s)	–380.7	–364.0	105
K_2S(aq)	–471.5	–480.7	190.4
Silicon			
Si(s)	0	0	18.83
SiO_2(s,α)	–910.94	–856.64	41.84
Silver			
Ag(s)	0	0	42.55
Ag^+(aq)	105.58	77.11	72.68
Ag_2O(s)	–31.05	–11.20	121.3
AgBr(s)	–100.37	–96.90	107.1
AgBr(aq)	–15.98	–26.86	155.2
AgCl(s)	–127.07	–109.79	96.2
AgCl(aq)	–61.58	–54.12	129.3
AgI(s)	–61.84	–66.19	115.5
AgI(aq)	50.38	25.52	184.1
$AgNO_3$(s)	–124.39	–33.41	140.92
Sodium			
Na(s)	0	0	51.21
Na(g)	107.32	76.76	153.71
Na^+(aq)	–240.12	–261.91	59.0
NaOH(s)	–425.61	–379.49	64.46
NaOH(aq)	–470.11	–419.15	48.1
NaCl(s)	–411.15	–384.14	72.13
NaCl(aq)	–407.3	–393.1	115.5
NaBr(s)	–361.06	–348.98	86.82
NaI(s)	–287.78	–286.06	98.53
$NaHCO_3$(s)	–947.7	–851.9	102.1
Na_2CO_3(s)	–1130.9	–1047.7	136.0
Sulphur			
S(s), rhombic	0	0	31.80
S(s), monoclinic	0.33	0.1	32.6
S^{2-}(aq)	33.1	85.8	–14.6
SO_2(g)	–296.83	–300.19	248.22
SO_3(g)	–395.72	–371.06	256.76
H_2SO_4(l)	–813.99	–690.00	156.90
H_2SO_4(aq)	–909.27	–744.53	20.1
SO_4^{2-}(aq)	–909.27	–744.53	20.1
H_2S(g)	–20.63	–33.56	205.79
H_2S(aq)	–39.7	–27.83	121
SF_6(g)	–1209	–1105.3	291.82

(continued)

Substance	Enthalpy of formation, $\Delta_f H^J$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^J$/ (kJ mol^{-1})	Entropy,* S^J/(J K^{-1} mol^{-1})
Tin			
Sn(s), white	0	0	51.55
Sn(s), gray	–2.09	0.13	44.14
SnO(s)	–285.8	–256.9	56.5
SnO_2(s)	–580.7	–519.6	52.3
Zinc			
Zn(s)	0	0	41.63
Zn^{2+}(aq)	–153.89	–147.06	–112.1
ZnO(s)	–348.28	–318.30	43.64
Zn(g)	+130.73	+95.14	160.93

*The entropies of individual ions in solution are determined by setting the entropy of H^+ in water equal to 0 and then defining the entropies of all other ions relative to this value; hence a negative entropy is one that is lower than the entropy of H^+ in water.

ORGANIC COMPOUNDS

Substance	Enthalpy of combustion, $\Delta_c H^J$/ (kJ mol^{-1})	Enthalpy of formation, $\Delta_f H^J$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^J$/ (kJ mol^{-1})	Entropy, S^J/(J K^{-1} mol^{-1})
Hydrocarbons				
CH_4(g), methane	–890	–74.81	–50.72	186.26
C_2H_2(g), ethyne (acetylene)	–1300	226.73	209.20	200.94
C_2H_4(g), ethene(ethylene)	–1411	52.26	68.15	219.56
C_2H_6(g), ethane	–1560	–84.68	–32.82	229.60
C_3H_6(g), propene (propylene)	–2058	20.42	62.78	266.6
C_3H_6(g), cyclopropane	–2091	53.30	104.45	237.4
C_3H_8(g), propane	–2220	–103.85	–23.49	270.2
C_4H_{10}(g), butane	–2878	–126.15	–17.03	310.1
C_5H_{12}(g), pentane	–3537	–146.44	–8.20	349
C_6H_6(l), benzene	–3268	49.0	124.3	173.3
C_6H_6(g)	–3302	—	—	—
C_7H_8(l), toluene	–3910	12.0	113.8	221.0
C_7H_8(g)	–3953	—	—	—
C_6H_{12}(l), cyclohexane	–3920	–156.4	26.7	204.4
C_6H_{12}(g),	–3953	—	—	—
C_8H_{18}(l), octane	–5471	–249.9	6.4	358
Alcohols and phenols				
CH_3OH(l), methanol	–726	–238.86	–166.27	126.8
CH_3OH(g)	–764	–200.66	–161.96	239.81
C_2H_5OH(l), ethanol	–1368	–277.69	–174.78	160.7
C_2H_5OH(g)	–1409	–235.10	–168.49	282.70
C_6H_5OH(s), phenol	–3054	–164.6	–50.42	144.0

(continued)

Substance	Enthalpy of combustion, $\Delta_c H^\circ$/ (kJ mol^{-1})	Enthalpy of formation, $\Delta_f H^\circ$/ (kJ mol^{-1})	Gibbs Energy of formation, $\Delta_f G^\circ$/ (kJ mol^{-1})	Entropy, S°/(J K^{-1} mol^{-1})
Carboxylic acid				
HCOOH(l), formic acid	–255	–424.72	–361.35	128.95
CH_3COOH(l), acetic acid	–875	–484.5	–389.9	159.8
CH_3COOH (aq)	—	–485.76	–396.64	86.6
$(COOH)_2$(s), oxalic acid	–254	–827.2	–697.9	120
C_6H_5COOH(s), benzoic acid	–3227	–385.1	–245.3	167.6
Aldehydes and ketones				
HCHO(g), methanal (formaldehyde)	–571	–108.57	–102.53	218.77
CH_3CHO(l), ethanal (acetaldehyde)	–1166	–192.30	–128.12	160.2
CH_3CHO(g)	–1192	–166.19	–128.86	250.3
CH_3COCH_3(l), propanone (acetone)	–1790	–248.1	–155.4	200
Sugars				
$C_6H_{12}O_6$(s), glucose	–2808	–1268	–910	212
$C_6H_{12}O_6$(aq)	—	—	–917	—
$C_6H_{12}O_6$(s), fructose	–2810	–1266	—	—
$C_{12}H_{22}O_{11}$(s), sucrose	–5645	–2222	–1545	360
Nitrogen compounds				
$CO(NH_2)_2$(s), urea	–632	–333.51	–197.33	104.60
$C_6H_5NH_2$(l), aniline	–3393	31.6	149.1	191.3
NH_2CH_2COOH(s), glycine	–969	–532.9	–373.4	103.51
CH_3NH_2(g), methylamine	–1085	–22.97	32.16	243.41

Appendix VII

Standard potentials at 298 K in electrochemical order

Reduction half-reaction	E°/V	Reduction half-reaction	E°/V
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0	$Cu^+ + e^- \longrightarrow Cu$	+0.52
$F_2 + 2e^- \longrightarrow 2F^-$	+2.87	$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07	$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$Ag^+ + e^- \longrightarrow Ag^+$	+1.98	$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81	$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Au^+ + e^- \longrightarrow Au$	+1.69	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67	$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.27
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63	$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3 + H_2O$	+0.17
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51	$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40	$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36	$2H^+ + 2e^- \longrightarrow H_2$	0.0 by definition
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33	$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.04
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24	$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	–0.08
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23	$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + 2H_2O$	+1.23	$In^+ + e^- \longrightarrow In$	–0.14
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23	$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20	$AgI + e^- \longrightarrow Ag + I^-$	–0.15
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09	$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.23
$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97	$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96	$Co^{2+} + 2e^- \longrightarrow Co$	–0.28
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92	$In^{3+} + 3e^- \longrightarrow In$	–0.34
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89	$Tl^+ + e^- \longrightarrow Tl$	–0.34
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86	$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	–0.36
$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80	$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37
$Ag^+ + e^- \longrightarrow Ag$	+0.80	$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79	$In^{2+} + e^- \longrightarrow In^+$	–0.40
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76	$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62	$In^{3+} + 2e^- \longrightarrow In^+$	–0.44
$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60	$S + 2e^- \longrightarrow S^{2-}$	–0.48
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56	$In^{3+} + e^- \longrightarrow In^{2+}$	–0.49
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54	$U^{4+} + e^- \longrightarrow U^{3+}$	–0.61
$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
		$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76

(continued)

Appendix continued

Reduction half-reaction	E^J/V	**Reduction half-reaction**	E^J/V
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	–0.81	$La^{3+} + 3e^- \longrightarrow La$	–2.52
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	–0.83	$Na^+ + e^- \longrightarrow Na$	–2.71
$Cr^{2+} + 2e^- \longrightarrow Cr$	–0.91	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18	$Sr^{2+} + 2e^- \longrightarrow Sr$	–2.89
$V^{2+} + 2e^- \longrightarrow V$	–1.19	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.91
$Ti^{2+} + 2e^- \longrightarrow Ti$	–1.63	$Ra^{2+} + 2e^- \longrightarrow Ra$	–2.92
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66	$Cs^+ + e^- \longrightarrow Cs$	–2.92
$U^{3+} + 3e^- \longrightarrow U$	–1.79	$Rb^+ + e^- \longrightarrow Rb$	–2.93
$Sc^{3+} + 3e^- \longrightarrow Sc$	–2.09	$K^+ + e^- \longrightarrow K$	–2.93
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36	$Li^+ + e^- \longrightarrow Li$	–3.05
$Ce^{3+} + 3e^- \longrightarrow Ce$	–2.48		

Textbook for Class XI

Chemistry

Part 1

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UNIT 8

REDOX REACTIONS

Objectives

After studying this unit you will be able to

- identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously;
- define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent);
- explain mechanism of redox reactions by electron transfer process;
- use the concept of oxidation number to identify oxidant and reductant in a reaction;
- classify redox reaction into combination (synthesis), decomposition, displacement and disproportionation reactions;
- suggest a comparative order among various reductants and oxidants;
- balance chemical equations using (i) oxidation number (ii) half reaction method;
- learn the concept of redox reactions in terms of electrode processes.

"Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems."

Chemistry deals with varieties of matter and change of one kind of matter into the other. Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is **Redox Reactions**. A number of phenomena, both physical as well as biological, are concerned with redox reactions. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like **Hydrogen Economy** (use of liquid hydrogen as fuel) and development of **'Ozone Hole'** have started figuring under redox phenomenon.

8.1 CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS

Originally, the term **oxidation** was used to describe the addition of oxygen to an element or a compound. Because of the presence of dioxygen in the atmosphere (~20%), many elements combine with it and this is the principal reason why they commonly occur on the earth in the form of their oxides. The following reactions represent oxidation processes according to the limited definition of oxidation:

$$2\,Mg\,(s) + O_2\,(g) \rightarrow 2\,MgO\,(s) \quad (8.1)$$

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g) \quad (8.2)$$

In reactions (8.1) and (8.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \qquad (8.3)$$

A careful examination of reaction (8.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.

$$2\,H_2S(g) + O_2\,(g) \rightarrow 2\,S\,(s) + 2\,H_2O\,(l) \qquad (8.4)$$

As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (8.1 to 8.4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. occurs according to the following reactions :

$$Mg\,(s) + F_2\,(g) \rightarrow MgF_2\,(s) \qquad (8.5)$$

$$Mg\,(s) + Cl_2\,(g) \rightarrow MgCl_2\,(s) \qquad (8.6)$$

$$Mg\,(s) + S\,(s) \rightarrow MgS\,(s) \qquad (8.7)$$

Incorporating the reactions (8.5 to 8.7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as oxidation. Thus the reaction :

$$2K_4\,[Fe(CN)_6](aq) + H_2O_2\,(aq) \rightarrow 2K_3[Fe(CN)_6](aq) + 2\,KOH\,(aq)$$

is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term **"oxidation"** is defined as the **addition of oxygen/electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.**

In the beginning, reduction was considered as removal of oxygen from a compound. However, the term **reduction** has been broadened these days to include **removal of oxygen/electronegative element from a substance or addition of hydrogen/ electropositive element to a substance.**

According to the definition given above, the following are the examples of reduction processes:

$$2\,HgO\,(s) \xrightarrow{\Delta} 2\,Hg\,(l) + O_2\,(g) \qquad (8.8)$$

(removal of oxygen from mercuric oxide)

$$2\,FeCl_3\,(aq) + H_2\,(g) \rightarrow 2\,FeCl_2\,(aq) + 2\,HCl(aq) \qquad (8.9)$$

(removal of electronegative element, chlorine from ferric chloride)

$$CH_2 = CH_2\,(g) + H_2\,(g) \rightarrow H_3C - CH_3\,(g) \qquad (8.10)$$

(addition of hydrogen)

$$2HgCl_2\,(aq) + SnCl_2\,(aq) \rightarrow Hg_2Cl_2\,(s) + SnCl_4\,(aq) \qquad (8.11)$$

(addition of mercury to mercuric chloride)

In reaction (8.11) simultaneous oxidation of stannous chloride to stannic chloride is also occurring because of the addition of electronegative element chlorine to it. It was soon realised that oxidation and reduction always occur simultaneously (as will be apparent by re-examining all the equations given above), hence, the word **"redox"** was coined for this class of chemical reactions.

Problem 8.1

In the reactions given below, identify the species undergoing oxidation and reduction:

(i) $H_2S\,(g) + Cl_2\,(g) \rightarrow 2\,HCl\,(g) + S\,(s)$

(ii) $3Fe_3O_4\,(s) + 8\,Al\,(s) \rightarrow 9\,Fe\,(s) + 4Al_2O_3\,(s)$

(iii) $2\,Na\,(s) + H_2\,(g) \rightarrow 2\,NaH\,(s)$

Solution

(i) H_2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed from S). Chlorine is reduced due to addition of hydrogen to it.

(ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide

(Fe_3O_4) is reduced because oxygen has been removed from it.

(iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced.

Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

8.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

We have already learnt that the reactions

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl\ (s) \quad (8.12)$$

$$2Na(s) + O_2(g) \rightarrow Na_2O(s) \quad (8.13)$$

$$2Na(s) + S(s) \rightarrow Na_2S(s) \quad (8.14)$$

are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine, oxygen and sulphur are reduced because to each of these, the electropositive element sodium has been added. From our knowledge of chemical bonding we also know that sodium chloride, sodium oxide and sodium sulphide are ionic compounds and perhaps better written as Na^+Cl^- (s), $(Na^+)_2O^{2-}$(s), and $(Na^+)_2\ S^{2-}$(s). Development of charges on the species produced suggests us to rewrite the reactions (8.12 to 8.14) in the following manner :

loss of $2e^-$

$$2Na(s) + Cl_2(g) \longrightarrow 2Na^+Cl^-(s)$$

gain of $2e^-$

loss of $2e^-$

$$2Na(s) + O_2\ (g) \longrightarrow (Na^+)_2O^{2-}(s)$$

gain of $2e^-$

loss of $2e^-$

$$2Na(s) + S(s) \longrightarrow (Na^+)_2S^{2-}(s)$$

gain of $2e^-$

For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and the other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride.

$$2\ Na(s) \rightarrow 2\ Na^+(g) + 2e^-$$

$$Cl_2(g) + 2e^- \rightarrow 2\ Cl^-(g)$$

Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction :

$$2\ Na(s) + Cl_2\ (g) \rightarrow 2\ Na^+\ Cl^-\ (s) \text{ or } 2\ NaCl\ (s)$$

Reactions 8.12 to 8.14 **suggest that half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions.** It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change. In reactions (8.12 to 8.14) sodium, which is oxidised, acts as **a reducing agent** because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine, oxygen and sulphur are reduced and act as oxidising agents because these accept electrons from sodium. To summarise, we may mention that

Oxidation : Loss of electron(s) by any species.

Reduction : Gain of electron(s) by any species.

Oxidising agent : Acceptor of electron(s).

Reducing agent : Donor of electron(s).

Problem 8.2 Justify that the reaction :

$2\ Na(s) + H_2(g) \rightarrow 2\ NaH\ (s)$ is a redox change.

Solution

Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na^+H^- (s), this suggests that one half reaction in this process is :

$$2\ Na\ (s) \rightarrow 2\ Na^+(g) + 2e^-$$

and the other half reaction is:

$H_2\,(g) + 2e^- \rightarrow 2\,H^-(g)$

This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.

8.2.1 Competitive Electron Transfer Reactions

Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 8.1, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of Zn^{2+} ions among the products can easily be judged when the blue colour of the solution due to Cu^{2+} has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing Zn^{2+} ions, appearance of white zinc sulphide, ZnS can be seen on making the solution alkaline with ammonia.

The reaction between metallic zinc and the aqueous solution of copper nitrate is :

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (8.15)$$

In reaction (8.15), zinc has lost electrons to form Zn^{2+} and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons, something must be reduced, accepting the electrons lost by zinc. Copper ion is reduced by gaining electrons from the zinc.

Reaction (8.15) may be rewritten as :

$$\underbrace{Zn(s)}_{\text{release of } 2e^-} + \underbrace{Cu^{2+}(aq)}_{\text{gain of } 2e^-} \longrightarrow Zn^{2+}(aq) + Cu(s)$$

At this stage we may investigate the state of equilibrium for the reaction represented by equation (8.15). For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of Cu^{2+} ions by passing H_2S gas through the solution to produce the black colour of cupric sulphide, CuS, does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of Cu^{2+} formed cannot be detected. We thus conclude that the state of equilibrium for the reaction (8.15) greatly favours the products over the reactants.

Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 8.2. The solution develops blue colour due to the formation of Cu^{2+} ions on account of the reaction:

$$\underbrace{Cu(s)}_{\text{release of } 2e^-} + \underbrace{2Ag^+(aq)}_{\text{gain of } 2e^-} \longrightarrow Cu^{2+}(aq) + 2Ag(s) \qquad (8.16)$$

Here, Cu(s) is oxidised to $Cu^{2+}(aq)$ and $Ag^+(aq)$ is reduced to Ag(s). Equilibrium greatly favours the products Cu^{2+} (aq) and Ag(s).

By way of contrast, let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs here is :

$$\underbrace{Co(s)}_{\text{release of } 2e^-} + \underbrace{Ni^{2+}(aq)}_{\text{gain of } 2e^-} \longrightarrow Co^{2+}(aq) + Ni(s) \qquad (8.17)$$

Fig. 8.1 *Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.*

Fig. 8.2 *Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.*

At equilibrium, chemical tests reveal that both $Ni^{2+}(aq)$ and $Co^{2+}(aq)$ are present at moderate concentrations. In this case, neither the reactants [Co(s) and $Ni^{2+}(aq)$] nor the products [$Co^{2+}(aq)$ and Ni (s)] are greatly favoured.

This competition for release of electrons incidently reminds us of the competition for release of protons among acids. The similarity suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order: Zn>Cu>Ag. We would love to make our list more vast and design a **metal activity series or electrochemical series**. The competition for electrons between various metals helps us to design a class of cells, named as Galvanic cells in which the chemical reactions become the source of electrical energy. We would study more about these cells in Class XII.

8.3 OXIDATION NUMBER

A less obvious example of electron transfer is realised when hydrogen combines with oxygen to form water by the reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad (8.18)$$

Though not simple in its approach, yet we can visualise the H atom as going from a neutral (zero) state in H_2 to a positive state in H_2O, the O atom goes from a zero state in O_2 to a dinegative state in H_2O. It is assumed that there is an electron transfer from H to O and consequently H_2 is oxidised and O_2 is reduced. However, as we shall see later, the charge transfer is only partial and is perhaps better described as an electron shift rather than a complete loss of electron by H and gain by O. What has been said here with respect to equation (8.18) may be true for a good number of other reactions involving covalent compounds. Two such examples of this class of the reactions are:

$$H_2(s) + Cl_2(g) \rightarrow 2HCl(g) \quad (8.19)$$

and,

$$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g) \quad (8.20)$$

In order to keep track of electron shifts in chemical reactions involving formation of covalent compounds, a more practical method of using **oxidation number** has been developed. In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electonegative atom. For example, we rewrite equations (8.18 to 8.20) to show charge on each of the atoms forming part of the reaction :

$$\overset{0}{2H_2}(g) + \overset{0}{O_2}(g) \rightarrow \overset{+1}{2H_2}\overset{-2}{O}(l) \quad (8.21)$$

$$\overset{0}{H_2}(s) + \overset{0}{Cl_2}(g) \rightarrow \overset{+1}{2H}\overset{-1}{Cl}(g) \quad (8.22)$$

$$\overset{-4}{C}\overset{+1}{H_4}(g) + \overset{0}{4Cl_2}(g) \rightarrow \overset{+4}{4C}\overset{-1}{Cl_4}(l) + \overset{+1}{4H}\overset{-1}{Cl}(g) \quad (8.23)$$

It may be emphasised that the assumption of electron transfer is made for book-keeping purpose only and it will become obvious at a later stage in this unit that it leads to the simple description of redox reactions.

Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that

electron in a covalent bond belongs entirely to more electronegative element.

It is not always possible to remember or make out easily in a compound/ion, which element is more electronegative than the other. Therefore, a set of rules has been formulated to determine the oxidation number of an element in a compound/ion. If two or more than two atoms of an element are present in the molecule/ion such as $Na_2S_2O_3/Cr_2O_7^{2-}$, the oxidation number of the atom of that element will then be the average of the oxidation number of all the atoms of that element. We may at this stage, state the rules for the calculation of oxidation number. These rules are:

1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H_2, O_2, Cl_2, O_3, P_4, S_8, Na, Mg, Al has the oxidation number zero.
2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion, +2, Fe^{3+} ion, +3, Cl^- ion, –1, O^{2-} ion, –2; and so on. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds is –2. However, we come across two kinds of exceptions here. One arises in the case of peroxides and superoxides, the compounds of oxygen in which oxygen atoms are directly linked to each other. While in peroxides (e.g., H_2O_2, Na_2O_2), each oxygen atom is assigned an oxidation number of –1, in superoxides (e.g., KO_2, RbO_2) each oxygen atom is assigned an oxidation number of –(½). The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of +2 and +1, respectively. The number assigned to oxygen will depend upon the bonding state of oxygen but this number would now be a positive figure only.
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and CaH_2, its oxidation number is –1.
5. In all its compounds, fluorine has an oxidation number of –1. Other halogens (Cl, Br, and I) also have an oxidation number of –1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.
6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion. Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion, $(CO_3)^{2-}$ must equal –2.

By the application of above rules, we can find out the oxidation number of the desired element in a molecule or in an ion. It is clear that the metallic elements have positive oxidation number and nonmetallic elements have positive or negative oxidation number. The atoms of transition elements usually display several positive oxidation states. The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the long form of periodic table) for the other groups. Thus, it implies that the highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table. In the third period, the highest value of oxidation number changes from 1 to 7 as indicated below in the compounds of the elements.

A term that is often used interchangeably with the oxidation number is the **oxidation state.** Thus in CO_2, the oxidation state of carbon is +4, that is also its oxidation number and similarly the oxidation state as well as oxidation number of oxygen is – 2. This implies that the oxidation number denotes the oxidation state of an element in a compound.

Group	1	2	13	14	15	16	17
Element	Na	Mg	Al	Si	P	S	Cl
Compound	NaCl	$MgSO_4$	AlF_3	$SiCl_4$	P_4O_{10}	SF_6	$HClO_4$
Highest oxidation number state of the group element	+1	+2	+3	+4	+5	+6	+7

The oxidation number state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as **Stock notation.** According to this, the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl_3. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl_2 and Sn(IV)Cl_4. This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised form or reduced form. Thus, Hg_2(I)Cl_2 is the reduced form of Hg(II) Cl_2.

Problem 8.3

Using Stock notation, represent the following compounds :$HAuCl_4$, Tl_2O, FeO, Fe_2O_3, CuI, CuO, MnO and MnO_2.

Solution

By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows:

$HAuCl_4$ → Au has 3
Tl_2O → Tl has 1
FeO → Fe has 2
Fe_2O_3 → Fe has 3
CuI → Cu has 1
CuO → Cu has 2
MnO → Mn has 2
MnO_2 → Mn has 4

Therefore, these compounds may be represented as:

HAu(III)Cl_4, Tl_2(I)O, Fe(II)O, Fe_2(III)O_3, Cu(I)I, Cu(II)O, Mn(II)O, Mn(IV)O_2.

The idea of oxidation number has been invariably applied to define oxidation, reduction, oxidising agent (oxidant), reducing agent (reductant) and the redox reaction. To summarise, we may say that:

Oxidation: An increase in the oxidation number of the element in the given substance.

Reduction: A decrease in the oxidation number of the element in the given substance.

Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as **oxidants** also.

Reducing agent: A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as **reductants**.

Redox reactions: Reactions which involve change in oxidation number of the interacting species.

Problem 8.4

Justify that the reaction:

$$2Cu_2O(s) + Cu_2S(s) \rightarrow 6Cu(s) + SO_2(g)$$

is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant and which acts as a reductant.

Solution

Let us assign oxidation number to each of the species in the reaction under examination. This results into:

$$\overset{+1\ -2}{2Cu_2O(s)} + \overset{+1\ -2}{Cu_2S(s)} \rightarrow \overset{0}{6Cu(s)} + \overset{+4\ -2}{SO_2}$$

We therefore, conclude that in this reaction *copper is reduced* from +1 state to zero oxidation state and *sulphur is oxidised* from –2 state to +4 state. The above reaction is thus a *redox reaction.*

Further, Cu_2O helps sulphur in Cu_2S to increase its oxidation number, therefore, Cu(I) is an oxidant; and sulphur of Cu_2S helps copper both in Cu_2S itself and Cu_2O to decrease its oxidation number; therefore, sulphur of Cu_2S is reductant.

8.3.1 Types of Redox Reactions

1. Combination reactions

A combination reaction may be denoted in the manner:

$$A + B \rightarrow C$$

Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions. Some important examples of this category are:

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4\ -2}{CO_2}(g) \quad (8.24)$$

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2\ -3}{Mg_3N_2}(s) \quad (8.25)$$

$$\overset{-4\ +1}{CH_4}(g) + \overset{0}{2O_2}(g) \xrightarrow{\Delta} \overset{+4\ -2}{CO_2}(g) + \overset{+1\ -2}{2H_2O}(l)$$

2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are:

$$\overset{+1\ -2}{2H_2O}(l) \xrightarrow{\Delta} \overset{0}{2H_2}(g) + \overset{0}{O_2}(g) \quad (8.26)$$

$$\overset{+1\ -1}{2NaH}(s) \xrightarrow{\Delta} \overset{0}{2Na}(s) + \overset{0}{H_2}(g) \quad (8.27)$$

$$\overset{+1\ +5\ -2}{2KClO_3}(s) \xrightarrow{\Delta} \overset{+1\ -1}{2KCl}(s) + \overset{0}{3O_2}(g) \quad (8.28)$$

It may carefully be noted that there is no change in the oxidation number of hydrogen in methane under combination reactions and that of potassium in potassium chlorate in reaction (8.28). This may also be noted here that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.

$$\overset{+2\ +4\ -2}{CaCO_3}(s) \xrightarrow{\Delta} \overset{+2\ -2}{CaO}(s) + \overset{+4\ -2}{CO_2}(g)$$

3. Displacement reactions

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:

$$X + YZ \rightarrow XZ + Y$$

Displacement reactions fit into two categories: metal displacement and non-metal displacement.

(a) Metal displacement: A metal in a compound can be displaced by another metal in the uncombined state. We have already discussed about this class of the reactions under section 8.2.1. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are:

$$\overset{+2\ +4\ -2}{CuSO_4}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2\ +4\ -2}{ZnSO_4}(aq) \quad (8.29)$$

$$\overset{+5\ -2}{V_2O_5}(s) + \overset{0}{5Ca}(s) \xrightarrow{\Delta} \overset{0}{2V}(s) + \overset{+2\ -2}{5CaO}(s) \quad (8.30)$$

$$\overset{+4\ -1}{TiCl_4}(l) + \overset{0}{2Mg}(s) \xrightarrow{\Delta} \overset{0}{Ti}(s) + \overset{+2\ -1}{2\ MgCl_2}(s) \quad (8.31)$$

$$\overset{+3\ -2}{Cr_2O_3}(s) + \overset{0}{2\ Al}(s) \xrightarrow{\Delta} \overset{+3\ -2}{Al_2O_3}(s) + \overset{0}{2Cr}(s) \quad (8.32)$$

In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

(b) Non-metal displacement: The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.

$$\overset{0}{2Na(s)} + \overset{+1\ -2}{2H_2O(l)} \rightarrow \overset{+1\ -2\ +1}{2NaOH(aq)} + \overset{0}{H_2(g)} \quad (8.33)$$

$$\overset{0}{Ca(s)} + \overset{+1\ -2}{2H_2O(l)} \rightarrow \overset{+2\ -2\ +1}{Ca(OH)_2\ (aq)} + \overset{0}{H_2(g)} \quad (8.34)$$

Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:

$$\overset{0}{Mg(s)} + \overset{+1\ -2}{2H_2O(l)} \xrightarrow{\Delta} \overset{+2\ -2\ +1}{Mg(OH)_2(s)} + \overset{0}{H_2(g)} \quad (8.35)$$

$$\overset{0}{2Fe(s)} + \overset{+1\ -2}{3H_2O(l)} \xrightarrow{\Delta} \overset{+3\ -2}{Fe_2O_3(s)} + \overset{0}{3H_2(g)} \quad (8.36)$$

Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are:

$$\overset{0}{Zn(s)} + \overset{+1\ -1}{2HCl(aq)} \rightarrow \overset{+2\ -1}{ZnCl_2\ (aq)} + \overset{0}{H_2\ (g)} \quad (8.37)$$

$$\overset{0}{Mg\ (s)} + \overset{+1\ -1}{2HCl\ (aq)} \rightarrow \overset{+2\ -1}{MgCl_2\ (aq)} + \overset{0}{H_2\ (g)} \quad (8.38)$$

$$\overset{0}{Fe(s)} + \overset{+1\ -1}{2HCl(aq)} \rightarrow \overset{+2\ -1}{FeCl_2(aq)} + \overset{0}{H_2(g)} \quad (8.39)$$

Reactions (8.37 to 8.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.

In section (8.2.1) we have already discussed that the metals – zinc (Zn), copper (Cu) and silver (Ag) through tendency to lose electrons show their reducing activity in the order Zn> Cu>Ag. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :

$$\overset{+1\ -2}{2H_2O\ (l)} + \overset{0}{2F_2\ (g)} \rightarrow \overset{+1\ -1}{4HF(aq)} + \overset{0}{O_2(g)} \quad (8.40)$$

It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:

$$\overset{0}{Cl_2\ (g)} + \overset{+1\ -1}{2KBr\ (aq)} \rightarrow \overset{+1\ -1}{2\ KCl\ (aq)} + \overset{0}{Br_2\ (l)} \quad (8.41)$$

$$\overset{0}{Cl_2\ (g)} + \overset{+1-1}{2KI\ (aq)} \rightarrow \overset{+1\ -1}{2\ KCl\ (aq)} + \overset{0}{I_2\ (s)} \quad (8.42)$$

As Br_2 and I_2 are coloured and dissolve in CCl_4, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:

$$\overset{0}{Cl_2\ (g)} + \overset{-1}{2Br^-\ (aq)} \rightarrow \overset{-1}{2Cl^-\ (aq)} + \overset{0}{Br_2\ (l)} \quad (8.41a)$$

$$\overset{0}{Cl_2\ (g)} + \overset{-1}{2I^-\ (aq)} \rightarrow \overset{-1}{2Cl^-\ (aq)} + \overset{0}{I_2\ (s)} \quad (8.42b)$$

Reactions (8.41) and (8.42) form the basis of identifying Br^- and I^- in the laboratory through the test popularly known as 'Layer Test'. It may not be out of place to mention here that bromine likewise can displace iodide ion in solution:

$$\overset{0}{Br_2\ (l)} + \overset{-1}{2I^-\ (aq)} \rightarrow \overset{-1}{2Br^-\ (aq)} + \overset{0}{I_2\ (s)} \quad (8.43)$$

The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

$$2X^- \rightarrow X_2 + 2e^- \quad (8.44)$$

here X denotes a halogen element. Whereas chemical means are available to oxidise Cl^-, Br^- and I^-, as fluorine is the strongest oxidising

agent; there is no way to convert F^- ions to F_2 by chemical means. The only way to achieve F_2 from F^- is to oxidise electrolytically, the details of which you will study at a later stage.

4. Disproportionation reactions

Disproportionation reactions are a special type of redox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experiences disproportionation.

$$2\overset{+1\ -1}{H_2O_2}(aq) \rightarrow 2\overset{+1\ -2}{H_2O}(l) + \overset{0}{O_2}(g) \quad (8.45)$$

Here the oxygen of peroxide, which is present in –1 state, is converted to zero oxidation state in O_2 and decreases to –2 oxidation state in H_2O.

Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :

$$\overset{0}{P_4}(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow \overset{-3}{PH_3}(g) + 3\overset{+1}{H_2PO_2^-}(aq) \quad (8.46)$$

$$\overset{0}{S_8}(s) + 12\ OH^-(aq) \rightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2O_3^{2-}}(aq) + 6H_2O(l) \quad (8.47)$$

$$\overset{0}{Cl_2}(g) + 2\ OH^-(aq) \rightarrow \overset{+1}{ClO^-}(aq) + \overset{-1}{Cl^-}(aq) + H_2O(l) \quad (8.48)$$

The reaction (8.48) describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds.

It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (8.48), fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows:

$$2\ F_2(g) + 2OH^-(aq) \rightarrow 2\ F^-(aq) + OF_2(g) + H_2O(l) \quad (8.49)$$

(It is to be noted with care that fluorine in reaction (8.49) will undoubtedly attack water to produce some oxygen also). This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show a disproportionation tendency.

Problem 8.5

Which of the following species, do not show disproportionation reaction and why ?

ClO^-, ClO_2^-, ClO_3^- and ClO_4^-

Also write reaction for each of the species that disproportionates.

Solution

Among the oxoanions of chlorine listed above, ClO_4^- does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is, +7. The disproportionation reactions for the other three oxoanions of chlorine are as follows:

$$3\overset{+1}{ClO^-} \rightarrow 2\overset{-1}{Cl^-} + \overset{+5}{ClO_3^-}$$

$$6\ \overset{+3}{ClO_2^-} \xrightarrow{h\nu} 4\overset{+5}{ClO_3^-} + 2\overset{-1}{Cl^-}$$

$$4\overset{+5}{ClO_3^-} \rightarrow \overset{-1}{Cl^-} + 3\ \overset{+7}{ClO_4^-}$$

Problem 8.6

Suggest a scheme of classification of the following redox reactions

(a) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$

(b) $2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 2\ NO_2\ (g) + ½\ O_2\ (g)$

(c) $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2\ (g)$

(d) $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-\ (aq) + H_2O(l)$

Solution

In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen and oxygen; therefore, this is an example of combination redox reactions. The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorised under decomposition redox reaction. In reaction (c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of NO_2 (+4 state) into NO_2^- (+3 state) and NO_3^- (+5 state). Therefore reaction (d) is an example of disproportionation redox reaction.

The Paradox of Fractional Oxidation Number

Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:

C_3O_2 [where oxidation number of carbon is (4/3)],

Br_3O_8 [where oxidation number of bromine is (16/3)]

and $Na_2S_4O_6$ (where oxidation number of sulphur is 2.5).

We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations:

Structure of C_3O_2 (carbon suboxide)

Structure of Br_3O_8 (tribromooctaoxide)

Structure of $S_4O_6^{2-}$ (tetrathionate ion)

The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each, whereas the third one is present in zero oxidation state and the average is 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon. Likewise in Br_3O_8, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is 16/3. In the same fashion, in the species $S_4O_6^{2-}$, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of sulphurs of the $S_4O_6^{2-}$ is 2.5, whereas the reality being + 5,0,0 and +5 oxidation number respectively for each sulphur.

We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only. In reality (revealed by structures only), the element in that particular species is present in more than one whole number oxidation states. Fe_3O_4, Mn_3O_4, Pb_3O_4 are some of the other examples of the compounds, which are mixed oxides, where we come across with fractional oxidation states of the metal atom. However, the oxidation states may be in fraction as in O_2^+ and O_2^- where it is +½ and –½ respectively.

Problem 8.7

Why do the following reactions proceed differently?

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$ and

$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

Solution

Pb_3O_4 is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO_2. In PbO_2, lead is present in +4 oxidation state, whereas the stable oxidation state of lead in PbO is +2. PbO_2 thus can act as an oxidant (oxidising agent) and, therefore, can oxidise Cl^- ion of HCl into chlorine. We may also keep in mind that PbO is a basic oxide. Therefore, the reaction

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$

can be splitted into two reactions namely:

$2PbO + 4HCl \rightarrow 2PbCl_2 + 2H_2O$ (acid-base reaction)

$\overset{+4}{PbO_2} + 4\overset{-1}{HCl} \rightarrow \overset{+2}{PbCl_2} + \overset{0}{Cl_2} + 2H_2O$ (redox reaction)

Since HNO_3 itself is an oxidising agent therefore, it is unlikely that the reaction may occur between PbO_2 and HNO_3. However, the acid-base reaction occurs between PbO and HNO_3 as:

$2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O$

It is the passive nature of PbO_2 against HNO_3 that makes the reaction different from the one that follows with HCl.

8.3.2 Balancing of Redox Reactions

Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them.

(a) Oxidation Number Method: In writing equations for oxidation-reduction reactions, just as for other reactions, the compositions and formulas must be known for the substances that react and for the products that are formed. The oxidation number method is now best illustrated in the following steps:

Step 1: Write the correct formula for each reactant and product.

Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction.

Step 3: Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable coefficients so that these become equal. (If you realise that two substances are reduced and nothing is oxidised or vice-versa, something is wrong. Either the formulas of reactants or products are wrong or the oxidation numbers have not been assigned properly).

Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.

Step 5 : Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

Let us now explain the steps involved in the method with the help of a few problems given below:

Problem 8.8

Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite, Na_2SO_3, in an acid solution to give chromium(III) ion and the sulphate ion.

Solution

Step 1: The skeletal ionic equation is:

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Step 2: Assign oxidation numbers for Cr and S

$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + \overset{+4\ -2}{SO_3^{2-}}(aq) \rightarrow \overset{+3}{Cr}(aq) + \overset{+6\ -2}{SO_4^{2-}}(aq)$$

This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make them equal:

$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + 3\overset{+4\ -2}{SO_3^{2-}}(aq) \rightarrow 2\overset{+3}{Cr^{3+}}(aq) + 3\overset{+6\ -2}{SO_4^{2-}}(aq)$$

Step 4: As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add $8H^+$ on the left to make ionic charges equal

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., $4H_2O$) on the right to achieve balanced redox change.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$

Problem 8.9

Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

Solution

Step 1 : The skeletal ionic equation is :

$$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$$

Step 2 : Assign oxidation numbers for Mn and Br

$$\overset{+7}{MnO_4^-}(aq) + \overset{-1}{Br^-}(aq) \rightarrow \overset{+4}{MnO_2}(s) + \overset{+5}{BrO_3^-}(aq)$$

this indicates that permanganate ion is the oxidant and bromide ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.

$$2\overset{+7}{MnO_4^-}(aq) + \overset{-1}{Br^-}(aq) \rightarrow 2\overset{+4}{MnO_2}(s) + \overset{+5}{BrO_3^-}(aq)$$

Step 4: As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add 2 OH^- ions on the right to make ionic charges equal.

$$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

Step 5: Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one H_2O molecule) on the left side to achieve balanced redox change.

$$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

(b) Half Reaction Method: In this method, the two half equations are balanced separately and then added together to give balanced equation.

Suppose we are to balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium, wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr^{3+} ions. The following steps are involved in this task.

Step 1: Produce unbalanced equation for the reaction in ionic form :

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq) \quad (8.50)$$

Step 2: Separate the equation into half-reactions:

$$\text{Oxidation half : } \overset{+2}{Fe^{2+}}(aq) \rightarrow \overset{+3}{Fe^{3+}}(aq) \quad (8.51)$$

$$\text{Reduction half : } \overset{+6\ -2}{Cr_2O_7^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq) \quad (8.52)$$

Step 3: Balance the atoms other than O and H in each half reaction individually. Here the oxidation half reaction is already balanced with respect to Fe atoms. For the reduction half reaction, we multiply the Cr^{3+} by 2 to balance Cr atoms.

$$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) \quad (8.53)$$

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.

Thus, we get :

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 7H_2O\ (l) \quad (8.54)$$

Step 5: Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.

The oxidation half reaction is thus rewritten to balance the charge:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \quad (8.55)$$

Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O\ (l) \quad (8.56)$$

To equalise the number of electrons in both the half reactions, we multiply the oxidation half reaction by 6 and write as :

$$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^- \quad (8.57)$$

Step 6: We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation as :

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l) \quad (8.58)$$

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to number of atoms and the charges.

For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each H^+ ion, add an equal number of OH^- ions to both sides of the equation. Where H^+ and OH^- appear on the same side of the equation, combine these to give H_2O.

Problem 8.10

Permanganate(VII) ion, MnO_4^- in basic solution oxidises iodide ion, I^- to produce molecular iodine (I_2) and manganese (IV) oxide (MnO_2). Write a balanced ionic equation to represent this redox reaction.

Solution

Step 1: First we write the skeletal ionic equation, which is

$$MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$$

Step 2: The two half-reactions are:

Oxidation half : $\overset{-1}{I^-}(aq) \rightarrow \overset{0}{I_2}(s)$

Reduction half: $\overset{+7}{MnO_4^-}(aq) \rightarrow \overset{+4}{MnO_2}(s)$

Step 3: To balance the I atoms in the oxidation half reaction, we rewrite it as:

$$2I^-(aq) \rightarrow I_2(s)$$

Step 4: To balance the O atoms in the reduction half reaction, we add two water molecules on the right:

$$MnO_4^-(aq) \rightarrow MnO_2(s) + 2\ H_2O\ (l)$$

To balance the H atoms, we add four H^+ ions on the left:

$$MnO_4^-(aq) + 4\ H^+(aq) \rightarrow MnO_2(s) + 2H_2O\ (l)$$

As the reaction takes place in a basic solution, therefore, for four H^+ ions, we add four OH^- ions to both sides of the equation:

$$MnO_4^-(aq) + 4H^+(aq) + 4OH^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l) + 4OH^-(aq)$$

Replacing the H^+ and OH^- ions with water, the resultant equation is:

$$MnO_4^-(aq) + 2H_2O\ (l) \rightarrow MnO_2(s) + 4\ OH^-(aq)$$

Step 5 : In this step we balance the charges of the two half-reactions in the manner depicted as:

$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$

$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$$

Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.

$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

$2\,MnO_4^-(aq) + 4H_2O(l) + 6e^- \rightarrow 2MnO_2(s) + 8OH^-(aq)$

Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

$6I^-(aq) + 2MnO_4^-(aq) + 4H_2O(l) \rightarrow 3I_2(s) + 2MnO_2(s) + 8\,OH^-(aq)$

Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

8.3.3 Redox Reactions as the Basis for Titrations

In acid-base systems we come across with a titration method for finding out the strength of one solution against the other using a pH sensitive indicator. Similarly, in redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below:

(i) In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, MnO_4^-. Here MnO_4^- acts as the self indicator. The visible end point in this case is achieved after the last of the reductant (Fe^{2+} or $C_2O_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as 10^{-6} mol dm^{-3} (10^{-6} mol L^{-1}). This ensures a minimal 'overshoot' in colour beyond the equivalence point, the point where the reductant and the oxidant are equal in terms of their mole stoichiometry.

(ii) If there is no dramatic auto-colour change (as with MnO_4^- titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

(iii) There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to oxidise I^- ions, say, for example, Cu(II):

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq) \quad (8.59)$$

This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions ($S_2O_3^{2-}$), which too is a redox reaction:

$$I_2(aq) + 2\,S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \quad (8.60)$$

I_2, though insoluble in water, remains in solution containing KI as KI_3.

On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

8.3.4 Limitations of Concept of Oxidation Number

As you have observed in the above discussion, the concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

8.4 REDOX REACTIONS AND ELECTRODE PROCESSES

The experiment corresponding to reaction (8.15), can also be observed if zinc rod is dipped in copper sulphate solution. The redox reaction takes place and during the reaction, zinc is oxidised to zinc ions and copper ions are reduced to metallic copper due to direct transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now we modify the experiment in such a manner that for the same redox reaction transfer of electrons takes place indirectly. This necessitates the separation of zinc metal from copper sulphate solution. We take copper sulphate solution in a beaker and put a copper strip or rod in it. We also take zinc sulphate

solution in another beaker and put a zinc rod or strip in it. Now reaction takes place in either of the beakers and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reactions. A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.

This is represented by separating the oxidised form from the reduced form by a vertical line or a slash representing an interface (e.g. solid/solution). For example in this experiment the two redox couples are represented as Zn^{2+}/Zn and Cu^{2+}/Cu. In both cases, oxidised form is put before the reduced form. Now we put the beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side (Fig. 8.3). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and a switch. The set-up as shown in Fig.8.3 is known as Daniell cell. When the switch is in the off position, no reaction takes place in either of the beakers and no current flows through the metallic wire. As soon as the switch is in the on position, we make the following observations:

Fig.8.3 *The set-up for Daniell cell. Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these reduce the copper ions. The circuit is completed inside the cell by the migration of ions through the salt bridge. It may be noted that the direction of current is opposite to the direction of electron flow.*

1. The transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current.
2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is a potential difference between the copper and zinc rods known as **electrodes** here.

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential**. By convention, the standard electrode potential ($E^{\ominus}$••of hydrogen electrode is 0.00 volts. The electrode potential value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative $E^{\ominus}$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive $E^{\ominus}$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. The standard electrode potentials are very important and we can get a lot of other useful information from them. The values of standard electrode potentials for some selected electrode processes (reduction reactions) are given in Table 8.1. You will learn more about electrode reactions and cells in Class XII.

Table 8.1 The Standard Electrode Potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s respectively.

Reaction (Oxidised form + ne^-	→ Reduced form)	$E^\ominus$ / V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2(s) + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-$	–0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	–2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Increasing strength of oxidising agent ↑

Increasing strength of reducing agent ↓

1. A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

SUMMARY

Redox reactions form an important class of reactions in which **oxidation** and **reduction** occur simultaneously. Three tier conceptualisation viz, classical, electronic and oxidation number, which is usually available in the texts, has been presented in detail. Oxidation, reduction, oxidising agent (**oxidant**) and reducing agent (**reductant**) have been viewed according to each conceptualisation. **Oxidation numbers** are assigned in accordance with a consistent set of rules. Oxidation number and ion-electron method both are useful means in writing equations for the redox reactions. Redox reactions are classified into four categories: combination, decomposition displacement and disproportionation reactions. The concept of **redox couple** and **electrode processes** is introduced here. The redox reactions find wide applications in the study of electrode processes and cells.

EXERCISES

8.1 Assign oxidation number to the underlined elements in each of the following species:

(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$ (c) $H_4\underline{P}_2O_7$ (d) $K_2\underline{Mn}O_4$

(e) $Ca\underline{O}_2$ (f) $Na\underline{B}H_4$ (g) $H_2\underline{S}_2O_7$ (h) $KAl(\underline{S}O_4)_2.12\ H_2O$

8.2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?

(a) $K\underline{I}_3$ (b) $H_2\underline{S}_4O_6$ (c) $\underline{Fe}_3O_4$ (d) $\underline{C}H_3\underline{C}H_2OH$ (e) $\underline{C}H_3\underline{C}OOH$

8.3 Justify that the following reactions are redox reactions:

(a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(c) $4BCl_3(g) + 3LiAlH_4(s) \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3\ AlCl_3\ (s)$

(d) $2K(s) + F_2(g) \rightarrow 2K^+F^-\ (s)$

(e) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

8.4 Fluorine reacts with ice and results in the change:

$H_2O(s) + F_2(g) \rightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

8.5 Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest structure of these compounds. Count for the fallacy.

8.6 Write formulas for the following compounds:

(a) Mercury(II) chloride (b) Nickel(II) sulphate

(c) Tin(IV) oxide (d) Thallium(I) sulphate

(e) Iron(III) sulphate (f) Chromium(III) oxide

8.7 Suggest a list of the substances where carbon can exhibit oxidation states from –4 to +4 and nitrogen from –3 to +5.

8.8 While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why ?

8.9 Consider the reactions:

(a) $6\ CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as :

(a) $6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$

(b) $O_3(g) + H_2O_2(l) \rightarrow H_2O(l) + O_2(g) + O_2(g)$

Also suggest a technique to investigate the path of the above (a) and (b) redox reactions.

8.10 The compound AgF_2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ?

8.11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

8.12 How do you count for the following observations ?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction.

(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why ?

8.13 Identify the substance oxidised reduced, oxidising agent and reducing agent for each of the following reactions:

(a) $2AgBr(s) + C_6H_6O_2(aq) \rightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$

(b) $HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_2O(l)$

(c) $HCHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow Cu_2O(s) + HCOO^-(aq) + 3H_2O(l)$

(d) $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

(e) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

8.14 Consider the reactions :

$2S_2O_3^{2-}(aq) + I_2(s) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

$S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$

Why does the same reductant, thiosulphate react differently with iodine and bromine ?

8.15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

8.16 Why does the following reaction occur ?

$XeO_6^{4-}(aq) + 2F^-(aq) + 6H^+(aq) \rightarrow XeO_3(g) + F_2(g) + 3H_2O(l)$

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction.

8.17 Consider the reactions:

(a) $H_3PO_2(aq) + 4AgNO_3(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 4Ag(s) + 4HNO_3(aq)$

(b) $H_3PO_2(aq) + 2CuSO_4(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 2Cu(s) + H_2SO_4(aq)$

(c) $C_6H_5CHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow C_6H_5COO^-(aq) + 2Ag(s) + 4NH_3(aq) + 2H_2O(l)$

(d) $C_6H_5CHO(l) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow$ No change observed.

What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions ?

8.18 Balance the following redox reactions by ion – electron method :

(a) $MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$ (in basic medium)

(b) $MnO_4^-(aq) + SO_2(g) \rightarrow Mn^{2+}(aq) + HSO_4^-(aq)$ (in acidic solution)

(c) $H_2O_2(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + H_2O(l)$ (in acidic solution)

(d) $Cr_2O_7^{2-} + SO_2(g) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (in acidic solution)

8.19 Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.

(a) $P_4(s) + OH^-(aq) \rightarrow PH_3(g) + HPO_2^-(aq)$

(b) $N_2H_4(l) + ClO_3^-(aq) \rightarrow NO(g) + Cl^-(g)$

(c) $Cl_2O_7(g) + H_2O_2(aq) \rightarrow ClO_2^-(aq) + O_2(g) + H^+$

8.20 What sorts of informations can you draw from the following reaction ?

$(CN)_2(g) + 2OH^-(aq) \rightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$

8.21 The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2, and H^+ ion. Write a balanced ionic equation for the reaction.

8.22 Consider the elements :

Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only postive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states.

(d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

8.23 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

8.24 Refer to the periodic table given in your book and now answer the following questions:

(a) Select the possible non metals that can show disproportionation reaction.

(b) Select three metals that can show disproportionation reaction.

8.25 In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g. of ammonia and 20.00 g of oxygen ?

8.26 Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible:

(a) $Fe^{3+}(aq)$ and $I^-(aq)$

(b) $Ag^+(aq)$ and $Cu(s)$

(c) $Fe^{3+}(aq)$ and $Cu(s)$

(d) $Ag(s)$ and $Fe^{3+}(aq)$

(e) $Br_2(aq)$ and $Fe^{2+}(aq)$.

8.27 Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes

(ii) An aqueous solution $AgNO_3$ with platinum electrodes

(iii) A dilute solution of H_2SO_4 with platinum electrodes

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

8.28 Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

8.29 Given the standard electrode potentials,

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,

$Hg^{2+}/Hg = 0.79V$

$Mg^{2+}/Mg = -2.37V$. $Cr^{3+}/Cr = -0.74V$

arrange these metals in their increasing order of reducing power.

8.30 Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place, Further show:

(i) which of the electrode is negatively charged,

(ii) the carriers of the current in the cell, and

(iii) individual reaction at each electrode.

UNIT 9

HYDROGEN

Objectives

After studying this unit, you will be able to

- present informed opinions on the position of hydrogen in the periodic table;
- identify the modes of occurrence and preparation of dihydrogen on a small and commercial scale; describe isotopes of hydrogen;
- explain how different elements combine with hydrogen to form ionic, molecular and non-stoichiometric compounds;
- describe how an understanding of its properties can lead to the production of useful substances, and new technologies;
- understand the structure of water and use the knowledge for explaining physical and chemical properties;
- explain how environmental water quality depends on a variety of dissolved substances; difference between 'hard' and 'soft' water and learn about water softening;
- acquire the knowledge about heavy water and its importance;
- understand the structure of hydrogen peroxide, learn its preparatory methods and properties leading to the manufacture of useful chemicals and cleaning of environment;
- understand and use certain terms e.g., electron-deficient, electron-precise, electron-rich, hydrogen economy, hydrogenation etc.

"Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy."

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic (H_2) molecule and is called dihydrogen. It forms more compounds than any other element. Do you know that the global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance as you will learn in this unit.

9.1 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations.

Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration (ns^1) of alkali metals , which belong to the first group of the periodic table. On the other hand, like halogens (with ns^2np^5 configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uninegative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not

possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more with halogens, $\Delta_i H$ of Li is 520 kJ mol^{-1}, F is 1680 kJ mol^{-1} and that of H is 1312 kJ mol^{-1}. Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

Inspite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus (H^+) of ~1.5×10^{-3} pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200pm. As a consequence, H^+ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table (Unit 3).

9.2 DIHYDROGEN, H_2

9.2.1 Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

9.2.2 Isotopes of Hydrogen

Hydrogen has three isotopes: **protium**, ^1_1H, **deuterium**, ^2_1H or D and **tritium**, ^3_1H or T. Can you guess how these isotopes differ from each other ? These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 10^{18} atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy β^- particles ($t_{1/2}$, 12.33 years).

Table 9.1 Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point/ K	20.39	23.67	25.0
Density / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion/kJ mol^{-1}	0.117	0.197	-
Enthalpy of vaporization/kJ mol^{-1}	0.904	1.226	-
Enthalpy of bond dissociation/kJ mol^{-1} at 298.2K	435.88	443.35	-
Internuclear distance/pm	74.14	74.14	-
Ionization enthalpy/kJ mol^{-1}	1312	-	-
Electron gain enthalpy/kJ mol^{-1}	–73	-	-
Covalent radius/pm	37	-	-
Ionic radius(H^-)/pm	208		

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation (Table 9.1). However, in physical properties these isotopes differ considerably due to their large mass differences.

9.3 PREPARATION OF DIHYDROGEN, H_2

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

9.3.1 Laboratory Preparation of Dihydrogen

(i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

9.3.2 Commercial Production of Dihydrogen

The commonly used processes are outlined below:

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(l) \xrightarrow[\text{Traces of acid / base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) High purity (>99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are:

at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

at cathode: $2H_2O\ (l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The overall reaction is

$$2Na^+\ (aq) + 2Cl^-(aq) + 2H_2O(l)$$
$$\downarrow$$
$$Cl_2(g) + H_2(g) + 2Na^+\ (aq) + 2OH^-(aq)$$

(iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270K} nCO + (3n+1)H_2$$

e.g.,

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270K} CO(g) + 3H_2(g)$$

The mixture of CO and H_2 is called *water gas*. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called *synthesis gas or* **'syngas'**. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called *'coal gasification'*.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$$CO(g) + H_2O(g) \xrightarrow[\text{catalyst}]{673K} CO_2(g) + H_2(g)$$

This is called *water-gas shift reaction*. Carbon dioxide is removed by scrubbing with sodium arsenite solution.

Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

9.4 PROPERTIES OF DIHYDROGEN

9.4.1 Physical Properties

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties alongwith those of deuterium are given in Table 9.1.

9.4.2 Chemical Properties

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact ? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the

high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give H^+, (ii) gain of an electron to form H^-, and (iii) sharing electrons to form a single covalent bond.

The chemistry of dihydrogen can be illustrated by the following reactions:

Reaction with halogens: It reacts with halogens, X_2 to give hydrogen halides, HX,

$$H_2(g) + X_2(g) \rightarrow 2HX(g) \quad (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

Reaction with dioxygen: It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(l); \quad \Delta H^\ominus = -285.9 \text{ kJ mol}^{-1}$$

Reaction with dinitrogen: With dinitrogen it forms ammonia.

$$3H_2(g) + N_2(g) \xrightarrow[\text{Fe}]{673K, 200 atm} 2NH_3(g); \quad \Delta H^\ominus = -92.6 \text{ kJ mol}^{-1}$$

This is the method for the manufacture of ammonia by the Haber process.

Reactions with metals: With many metals it combines at high a temperature to yield the corresponding hydrides (section 9.5)

$$H_2(g) + 2M(g) \rightarrow 2MH(s);$$

where M is an alkali metal

Reactions with metal ions and metal oxides: It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}(aq) \rightarrow Pd(s) + 2H^+(aq)$$

$$yH_2(g) + M_xO_y(s) \rightarrow xM(s) + yH_2O(l)$$

Reactions with organic compounds: It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

(i) Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$$H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$$

Problem 9.1

Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide

Solution

(i) Dihydrogen reduces chlorine into chloride (Cl^-) ion and itself gets oxidised to H^+ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.

(ii) Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, Na^+H^-.

(iii) Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to H_2O, which is a covalent molecule.

9.4.3 Uses of Dihydrogen

- The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.
- It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(l)$$

- It is widely used for the manufacture of metal hydrides (section 9.5)
- It is used for the preparation of hydrogen chloride, a highly useful chemical.

- In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- It is used as a rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

9.5 HYDRIDES

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as EH_x (e.g., MgH_2) or E_mH_n (e.g., B_2H_6).

The hydrides are classified into three categories :

(i) Ionic or saline or saltlike hydrides
(ii) Covalent or molecular hydrides
(iii) Metallic or non-stoichiometric hydrides

9.5.1 Ionic or Saline Hydrides

These are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH, BeH_2 and MgH_2. In fact BeH_2 and MgH_2 are polymeric in structure. The ionic hydrides are crystalline, non-volatile and non-conducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H^- ion.

$$2H^-(\text{melt}) \xrightarrow{\text{anode}} H_2(g) + 2e^-$$

Saline hydrides react violently with water producing dihydrogen gas.

$$NaH(s) + H_2O(aq) \rightarrow NaOH(aq) + H_2(g)$$

Lithium hydride is rather unreactive at moderate temperatures with O_2 or Cl_2. It is, therefore, used in the synthesis of other useful hydrides, e.g.,

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

9.5.2 Covalent or Molecular Hydride

Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar examples are CH_4, NH_3, H_2O and HF. For convenience hydrogen compounds of non-metals have also been considered as hydrides. Being covalent, they are volatile compounds.

Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :
(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. In fact all elements of group 13 will form electron-deficient compounds. What do you expect from their behaviour? They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH_4) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH_3 has 1- lone pair, H_2O – 2 and HF –3 lone pairs). What do you expect from the behaviour of such compounds ? They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

Problem 9.2

Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members ? Give reasons.

Solution

On the basis of molecular masses of NH_3, H_2O and HF, their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points NH_3, H_2O and HF will be higher than the hydrides of their subsequent group members.

9.5.3 Metallic or Non-stoichiometric (or Interstitial) Hydrides

These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

Problem 9.3

Can phosphorus with outer electronic configuration $3s^2 3p^3$ form PH_5 ?

Solution

Although phosphorus exhibits +3 and +5 oxidation states, it cannot form PH_5. Besides some other considerations, high $\Delta_a H$ value of dihydrogen and $\Delta_{eg} H$ value of hydrogen do not favour to exhibit the highest oxidation state of P, and consequently the formation of PH_5.

9.6 WATER

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table 9.2

Table 9.2 Estimated World Water Supply

Source	% of Total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

9.6.1 Physical Properties of Water

It is a colourless and tasteless liquid. Its physical properties are given in Table 9.3 along with the physical properties of heavy water.

The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H_2S and H_2Se. In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

Table 9.3 Physical Properties of H_2O and D_2O

Property	H_2O	D_2O
Molecular mass (g mol^{-1})	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/kJ mol^{-1}	–285.9	–294.6
Enthalpy of vaporisation (373K)/kJ mol^{-1}	40.66	41.61
Enthalpy of fusion/kJ mol^{-1}	6.01	-
Temp of max. density/K	276.98	284.2
Density (298K)/g cm^{-3}	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant/$C^2/N.m^2$	78.39	78.06
Electrical conductivity (293K/ohm^{-1} cm^{-1})	5.7×10^{-8}	-

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

9.6.2 Structure of Water

In the gas phase water is a bent molecule with a bond angle of 104.5°, and O–H bond length of 95.7 pm as shown in Fig 9.1(a). It is a highly polar molecule, (Fig 9.1(b)). Its orbital overlap picture is shown in Fig. 9.1(c). In the liquid phase water molecules are associated together by hydrogen bonds.

H_2O molecule

Fig. 9.1 *(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.*

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

9.6.3 Structure of Ice

Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. 9.2. Examination of ice crystals with

Fig. 9.2 *The structure of ice*

X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.

Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.

9.6.4 Chemical Properties of Water

Water reacts with a large number of substances. Some of the important reactions are given below.

(1) Amphoteric Nature: It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with NH_3 and a base with H_2S.

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

$$H_2O(l) + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

The auto-protolysis (self-ionization) of water takes place as follows :

$$\underset{\substack{\text{acid-1}\\\text{(acid)}}}{H_2O(l)} + \underset{\substack{\text{base-2}\\\text{(base)}}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{acid-2}\\\text{(conjugate acid)}}}{H_3O^+(aq)} + \underset{\substack{\text{base-1}\\\text{(conjugate base)}}}{OH^-(aq)}$$

(2) Redox Reactions Involving Water: Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$$

Thus, it is a great source of dihydrogen.

Water is oxidised to O_2 during photosynthesis.

$$6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$$

With fluorine also it is oxidised to O_2.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

(3) Hydrolysis Reaction: Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$$

$$N^{3-}(s) + 3H_2O(l) \rightarrow NH_3(g) + 3OH^-(aq)$$

(4) Hydrates Formation: From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,

$$\left[Cr(H_2O)_6\right]^{3+} 3Cl^-$$

(ii) interstitial water e.g., $BaCl_2.2H_2O$

(iii) hydrogen-bonded water e.g.,

$\left[Cu(H_2O)_4\right]^{2+} SO_4^{2-}.H_2O$ in $CuSO_4.5H_2O$,

Problem 9.4

How many hydrogen-bonded water molecule(s) are associated in $CuSO_4.5H_2O$?

Solution

Only one water molecule, which is outside the brackets (coordination sphere), is hydrogen-bonded. The other four molecules of water are coordinated.

9.6.5 Hard and Soft Water

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water **'hard'**. **Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow$$

$$(C_{17}H_{35}COO)_2 M \downarrow + 2Na^+(aq); \text{ M is Ca / Mg}$$

It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The

hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

9.6.6 Temporary Hardness

Temporary hardness is due to the presence of magnesium and calcium hydrogen-carbonates. It can be removed by :

(i) Boiling: During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. It is because of high solubility product of $Mg(OH)_2$ as compared to that of $MgCO_3$, that $Mg(OH)_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

(ii) Clark's method: In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

9.6.7 Permanent Hardness

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

(i) Treatment with washing soda (sodium carbonate): Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl \quad (M = Mg, Ca)$$

$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$$

(ii) Calgon's method: Sodium hexameta-phosphate ($Na_6P_6O_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

$$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-} \quad (M = Mg, Ca)$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$

The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

(iii) Ion-exchange method: This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$$2NaZ(s) + M^{2+}(aq) \rightarrow MZ_2(s) + 2Na^+(aq) \quad (M = Mg, Ca)$$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$$MZ_2(s) + 2NaCl(aq) \rightarrow 2NaZ(s) + MCl_2(aq)$$

(iv) Synthetic resins method: Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with - SO_3H group and are water insoluble. Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl. The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft. Here R is resin anion.

$$2RNa(s) + M^{2+}(aq) \rightarrow R_2M(s) + 2Na^+(aq)$$

The resin can be regenerated by adding aqueous NaCl solution.

Pure de-mineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the H^+ form) and an anion-exchange (in the OH^- form) resins:

$$2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$$

In this cation exchange process, H^+ exchanges for Na^+, Ca^{2+}, Mg^{2+} and other cations present in water. This process results in proton release and thus makes the water acidic. In the anion exchange process:

$$RNH_2(s) + H_2O(l) \rightleftharpoons RNH_3^+.OH^-(s)$$

$$RNH_3^+.OH^-(s) + X^-(aq) \rightleftharpoons RNH_3^+.X^-(s) + OH^-(aq)$$

OH^- exchanges for anions like Cl^-, HCO_3^-, SO_4^{2-} etc. present in water. OH^- ions, thus, liberated neutralise the H^+ ions set free in the cation exchange.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.

9.7 HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

9.7.1 Preparation

It can be prepared by the following methods.

(i) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$$

(ii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.

$$2HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H(aq) \xrightarrow{\text{Hydrolysis}} 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$$

This method is now used for the laboratory preparation of D_2O_2.

$$K_2S_2O_8(s) + 2D_2O(l) \rightarrow 2KDSO_4(aq) + D_2O_2(l)$$

(iii) Industrially it is prepared by the auto-oxidation of 2-alklylanthraquinols.

$$2-\text{ethylanthraquinol} \underset{H_2/Pd}{\overset{O_2(air)}{\rightleftharpoons}} H_2O_2 + (\text{oxidised product})$$

In this case 1% H_2O_2 is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2.

9.7.2 Physical Properties

In the pure state H_2O_2 is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table 9.4.

H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K). A 30% solution of H_2O_2 is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H_2O_2 solution will give 100 V of oxygen at STP. Commercially, it is marketed as 10 V, which means it contains 3% H_2O_2.

Problem 9.4

Calculate the strength of 10 volume solution of hydrogen peroxide.

Solution

10 volume solution of H_2O_2 means that 1L of this H_2O_2 will give 10 L of oxygen at STP

$$2H_2O_2(l) \rightarrow O_2(g) + H_2O(l)$$

2×34 g 22.4 L at STP
68 g

22.4 L of O_2 at STP is produced from H_2O_2 = 68 g

10 L of O_2 at STP is produced from

$$H_2O_2 = \frac{68 \times 10}{22.4} g = 30.36 g$$

Therefore, strength of H_2O_2 in 10 volume H_2O_2 = 30.36 g/L

Table 9.4 Physical Properties of Hydrogen Peroxide

Melting point/K	272.4	Density (liquid at 298 K)/g cm^{-3}	1.44
Boiling point(exrapolated)/K	423	Viscosity (290K)/centipoise	1.25
Vapour pressure(298K)/mmHg	1.9	Dielectric constant (298K)/$C^2/N\ m^2$	70.7
Density (solid at 268.5K)/g cm^{-3}	1.64	Electrical conductivity (298K)/$\Omega^{-1}\ cm^{-1}$	5.1×10^{-8}

9.7.3 Structure

Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig 9.3

Fig. 9.3 *(a) H_2O_2 structure in gas phase, dihedral angle is 111.5°. (b) H_2O_2 structure in solid phase at 110K, dihedral angle is 90.2°.*

9.7.4 Chemical Properties

It acts as an oxidising as well as reducing agent in both acidic and alkaline media. Simple reactions are described below.

(i) Oxidising action in acidic medium

$$2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

$$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$$

(ii) Reducing action in acidic medium

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

$$HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$$

(iii) Oxidising action in basic medium

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$$

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$$

(iv) Reducing action in basic medium

$$I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$$

$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

9.7.5 Storage

H_2O_2 decomposes slowly on exposure to light.

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

9.7.6 Uses

Its wide scale use has led to tremendous increase in the industrial production of H_2O_2. Some of the uses are listed below:

(i) In daily life it is used as a hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.

(ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.

(iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.

(iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.

(v) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

9.8 HEAVY WATER, D_2O

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. Its physical properties are given in Table 9.3. It is used for the preparation of other deuterium compounds, for example:

$$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \rightarrow D_2SO_4$$

$$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$$

9.9 DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same

amounts in mole, mass and volume, are shown in Table 9.3.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen). This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like $NaNi_5$, Ti–TiH_2, Mg–MgH_2 etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view **Hydrogen Economy** is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

Table 9.3 The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume

Energy released on combustion in kJ state)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid)	LPG	CH_4 gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

SUMMARY

Hydrogen is the lightest atom with only one electron. Loss of this electron results in an elementary particle, the proton. Thus, it is unique in character. It has three isotopes, namely : **protium** (^1_1H), **deuterium** (D or ^2_1H) and **tritium** (T or ^3_1H). Amongst these three, only tritium is radioactive. Inspite of its resemblance both with alkali metals and halogens, it occupies a separate position in the periodic table because of its unique properties.

Hydrogen is the most abundant element in the universe. In the free state it is almost not found in the earth's atmosphere. However, in the combined state, it is the third most abundant element on the earth's surface.

Dihydrogen on the industrial scale is prepared by the **water-gas shift** reaction from petrochemicals. It is obtained as a byproduct by the electrolysis of brine.

The H–H **bond dissociation enthalpy** of dihydrogen (435.88 kJ mol^{-1}) is the highest for a single bond between two atoms of any elements. This property is made use of in the atomic hydrogen torch which generates a temperature of ~4000K and is ideal for welding of high melting metals.

Though dihydrogen is rather inactive at room temperature because of very high negative dissociation enthalpy, it combines with almost all the elements under appropriate conditions to form **hydrides.** All the type of hydrides can be classified into three categories: ionic or saline hydrides, covalent or molecular hydrides and metallic or non-stoichiometric hydrides. Alkali metal hydrides are good reagents for preparing other hydride compounds. Molecular hydrides (e.g., B_2H_6, CH_4, NH_3, H_2O) are of great importance in day-to-day life. Metallic hydrides are useful for ultrapurification of dihydrogen and as dihydrogen storage media.

Among the other chemical reactions of dihydrogen, **reducing reactions** leading to the formation hydrogen halides, water, ammonia, methanol, vanaspati ghee, etc. are of great importance. In metallurgical process, it is used to reduce metal oxides. In space programmes, it is used as a rocket fuel. In fact, it has promising potential for use as a non-polluting fuel of the near future **(Hydrogen Economy)**.

Water is the most common and abundantly available substance. It is of a great chemical and biological significance. The ease with which water is transformed from liquid to solid and to gaseous state allows it to play a vital role in the **biosphere.** The water molecule is highly polar in nature due to its bent structure. This property leads to hydrogen bonding which is the maximum in ice and least in water vapour. The polar nature of water makes it: (a) a very good solvent for ionic and partially ionic compounds; (b) to act as an amphoteric (acid as well as base) substance; and (c) to form hydrates of different types. Its property to dissolve many salts, particularly in large quantity, makes it hard and hazardous for industrial use. Both temporary and permanent **hardness** can be removed by the use of zeolites, and synthetic ion-exchangers.

Heavy water, D_2O is another important compound which is manufactured by the electrolytic enrichment of normal water. It is essentially used as a moderator in nuclear reactors.

Hydrogen peroxide, H_2O_2 has an interesting non-polar structure and is widely used as an industrial bleach and in pharmaceutical and pollution control treatment of industrial and domestic effluents.

EXERCISES

9.1 Justify the position of hydrogen in the periodic table on the basis of its electronic configuration.

9.2 Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

9.3 Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions?

9.4 How can the production of dihydrogen, obtained from 'coal gasification', be increased?

9.5 Describe the bulk preparation of dihydrogen by electrolytic method. What is the role of an electrolyte in this process ?

9.6 Complete the following reactions:

(i) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta}$

(ii) $CO(g) + H_2(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iii) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{catalyst}]{\Delta}$

(iv) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}}$

9.7 Discuss the consequences of high enthalpy of H–H bond in terms of chemical reactivity of dihydrogen.

9.8 What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.

9.9 What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions?

9.10 Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as 'Lewis' acid or base? Justify your answer.

9.11 What do you understand by the term "non-stoichiometric hydrides"? Do you expect this type of the hydrides to be formed by alkali metals? Justify your answer.

9.12 How do you expect the metallic hydrides to be useful for hydrogen storage? Explain.

9.13 How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes ? Explain.

9.14 Among NH_3, H_2O and HF, which would you expect to have highest magnitude of hydrogen bonding and why?

9.15 Saline hydrides are known to react with water violently producing fire. Can CO_2, a well known fire extinguisher, be used in this case? Explain.

9.16 Arrange the following

(i) CaH_2, BeH_2 and TiH_2 in order of increasing electrical conductance.

(ii) LiH, NaH and CsH in order of increasing ionic character.

(iii) H–H, D–D and F–F in order of increasing bond dissociation enthalpy.

(iv) NaH, MgH_2 and H_2O in order of increasing reducing property.

9.17 Compare the structures of H_2O and H_2O_2.

9.18 What do you understand by the term 'auto-protolysis' of water? What is its significance?

9.19 Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction, which species are oxidised/reduced.

9.20 Complete the following chemical reactions.

(i) $PbS(s) + H_2O_2(aq) \rightarrow$

(ii) $MnO_4^-(aq) + H_2O_2(aq) \rightarrow$

(iii) $CaO(s) + H_2O(g) \rightarrow$

(v) $AlCl_3(g) + H_2O(l) \rightarrow$

(vi) $Ca_3N_2(s) + H_2O(l) \rightarrow$

Classify the above into (a) hydrolysis, (b) redox and (c) hydration reactions.

9.21 Describe the structure of the common form of ice.

9.22 What causes the temporary and permanent hardness of water ?

9.23 Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

9.24 Write chemical reactions to show the amphoteric nature of water.

9.25 Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

9.26 What is meant by 'demineralised' water and how can it be obtained ?

9.27 Is demineralised or distilled water useful for drinking purposes? If not, how can it be made useful?

9.28 Describe the usefulness of water in biosphere and biological systems.

9.29 What properties of water make it useful as a solvent? What types of compound can it (i) dissolve, and (ii) hydrolyse ?

9.30 Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purposes?

9.31 What is the difference between the terms 'hydrolysis' and 'hydration' ?

9.32 How can saline hydrides remove traces of water from organic compounds?

9.33 What do you expect the nature of hydrides is, if formed by elements of atomic numbers 15, 19, 23 and 44 with dihydrogen? Compare their behaviour towards water.

9.34 Do you expect different products in solution when aluminium(III) chloride and potassium chloride treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water? Write equations wherever necessary.

9.35 How does H_2O_2 behave as a bleaching agent?

9.36 What do you understand by the terms:

(i) hydrogen economy (ii) hydrogenation (iii) 'syngas' (iv) water-gas shift reaction (v) fuel-cell ?

UNIT 10

THE *s* -BLOCK ELEMENTS

Objectives

After studying this unit, you will be able to

- describe the general characteristics of the alkali metals and their compounds;
- explain the general characteristics of the alkaline earth metals and their compounds;
- describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement;
- appreciate the biological significance of sodium, potassium, magnesium and calcium.

"The first element of alkali and alkaline earth metals differs in many respects from the other members of the group"

The *s*-block elements of the Periodic Table are those in which the last electron enters the outermost *s*-orbital. As the *s*-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals*. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust*.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances (Table 10.1). Francium is highly radioactive; its longest-lived isotope ^{223}Fr has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10^{-10} per cent of igneous rocks† (Table 10.2, page 299).

The general electronic configuration of *s*-block elements is [noble gas]ns^1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

** The thin, rocky outer layer of the Earth is crust. † A type of rock formed from magma (molten rock) that has cooled and hardened.*

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

10.1 GROUP 1 ELEMENTS: ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

10.1.1 Electronic Configuration

All the alkali metals have one valence electron, ns^1 (Table 10.1) outside the noble gas core. The loosely held *s*-electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent M^+ ions. Hence they are never found in free state in nature.

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or [Xe] $6s^1$
Francium	Fr	[Rn]$7s^1$

10.1.2 Atomic and Ionic Radii

The alkali metal atoms have the largest sizes in a particular period of the periodic table. With increase in atomic number, the atom becomes larger. The monovalent ions (M^+) are smaller than the parent atom. The atomic and ionic radii of alkali metals increase on moving down the group i.e., they increase in size while going from Li to Cs.

10.1.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$

10.1.5 Physical Properties

All the alkali metals are silvery white, soft and light metals. Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium. The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below:

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy. These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron.

Table 10.1 Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius / pm	152	186	227	248	265	–
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p / K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^{\ominus}$ / V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	~ 10^{-18} *

**ppm (part per million), ** percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle*

This property makes caesium and potassium useful as electrodes in photoelectric cells.

10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

(i) Reactivity towards air: The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K, Rb, Cs.

$$4\,Li + O_2 \rightarrow 2\,Li_2O \text{ (oxide)}$$

$$2\,Na + O_2 \rightarrow Na_2O_2 \text{ (peroxide)}$$

$$M + O_2 \rightarrow MO_2 \text{ (superoxide)}$$

(M = K, Rb, Cs)

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N as well. Because of their high reactivity towards air and water, they are normally kept in kerosene oil.

Problem 10.1

What is the oxidation state of K in KO_2?

Solution

The superoxide species is represented as O_2^-; since the compound is neutral, therefore, the oxidation state of potassium is +1.

(ii) Reactivity towards water: The alkali metals react with water to form hydroxide and dihydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$
(M = an alkali metal)

It may be noted that although lithium has most negative $E^\ominus$ value (Table 10.1), its reaction with water is less vigorous than that of sodium which has the least negative $E^\ominus$ value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) Reactivity towards dihydrogen: The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

$$2M + H_2 \rightarrow 2M^+H^-$$

(iv) Reactivity towards halogens : The alkali metals readily react vigorously with halogens to form ionic halides, M^+X^-. However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The Li^+ ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) Reducing nature: The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful (Table 10.1). The standard electrode potential ($E^\ominus$) which measures the reducing power represents the overall change :

$M(s) \rightarrow M(g)$ sublimation enthalpy

$M(g) \rightarrow M^+(g) + e^-$ ionization enthalpy

$M^+(g) + H_2O \rightarrow M^+(aq)$ hydration enthalpy

With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative $E^\ominus$ value and its high reducing power.

Problem 10.2

The $E^\ominus$ for Cl_2/Cl^- is +1.36, for I_2/I^- is + 0.53, for Ag^+/Ag is +0.79, Na^+/Na is –2.71 and for Li^+/Li is – 3.04. Arrange the following ionic species in decreasing order of reducing strength:

I^-, Ag, Cl^-, Li, Na

Solution

The order is Li > Na > I^- > Ag > Cl^-

(vi) Solutions in liquid ammonia: The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

$$M^+_{(am)} + e^- + NH_3(l) \rightarrow MNH_{2(am)} + \tfrac{1}{2}H_2(g)$$

(where 'am' denotes solution in ammonia.)

In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

10.1.7 Uses

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions. Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make $PbEt_4$ and $PbMe_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has

a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (and some superoxide NaO_2) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

Problem 10.3

Why is KO_2 paramagnetic ?

Solution

The superoxide O_2^- is paramagnetic because of one unpaired electron in π^*2p molecular orbital.

The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

10.2.2 Halides

The alkali metal halides, MX, (X=F,Cl,Br,I) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^\ominus$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta_f H^\ominus$ for chlorides, bromides and iodides. For a given metal $\Delta_f H^\ominus$ always becomes less negative from fluoride to iodide.

The melting and boiling points always follow the trend: fluoride > chloride > bromide > iodide. All these halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of CsI is due to smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol, acetone and ethylacetate; LiCl is soluble in pyridine also.

10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid, H_2CO_3 ($OC(OH)_2$; sulphuric acid, H_2SO_4 ($O_2S(OH)_2$). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable. Their carbonates (M_2CO_3) and in most cases the hydrogencarbonates ($MHCO_3$) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydorgencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2. Its hydrogencarbonate does not exist as a solid.

10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

10.3.1 Points of Difference between Lithium and other Alkali Metals

(i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

(iii) LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(iv) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.

(v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.

(vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \rightarrow 2\,Li_2O + 4\,NO_2 + O_2$$

$$2\,NaNO_3 \rightarrow 2\,NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li^+ = 76 pm, Mg^{2+} = 72 pm. The main points of similarity are:

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO_2. Solid hydrogencarbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol.

(vi) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl{\cdot}2H_2O$ and $MgCl_2{\cdot}8H_2O$.

10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below:

Sodium Carbonate (Washing Soda), $Na_2CO_3{\cdot}10H_2O$

Sodium carbonate is generally prepared by Solvay Process. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed. The equations for the complete process may be written as :

$$2\,NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2\,CO_3$$

$$(NH_4)_2\,CO_3 + H_2O + CO_2 \rightarrow 2\,NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $Ca(OH)_2$. Calcium chloride is obtained as a by-product.

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow 2\,NH_3 + CaCl_2 + H_2O$$

It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties : Sodium carbonate is a white crystalline solid which exists as a decahydrate, $Na_2CO_3 \cdot 10H_2O$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow{375K} Na_2CO_3 \cdot H_2O + 9H_2O$$

$$Na_2CO_3 \cdot H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$$

Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

Uses:

(i) It is used in water softening, laundering and cleaning.

(ii) It is used in the manufacture of glass, soap, borax and caustic soda.

(iii) It is used in paper, paints and textile industries.

(iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$ are impurities because they are deliquescent (absorb moisture easily from the atmosphere). To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

(i) It is used as a common salt or table salt for domestic purpose.

(ii) It is used for the preparation of Na_2O_2, NaOH and Na_2CO_3.

Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

$$\text{Cathode}: Na^+ + e^- \xrightarrow{Hg} Na - \text{amalgam}$$

$$\text{Anode}: Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

The amalgam is treated with water to give sodium hydroxide and hydrogen gas.

$$2Na\text{-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3.

Uses: It is used in (i) the manufacture of soap, paper, artificial silk and a number of chemicals, (ii) in petroleum refining, (iii) in the purification of bauxite, (iv) in the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and (vi) as a laboratory reagent.

Sodium Hydrogencarbonate (Baking Soda), $NaHCO_3$

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2\,NaHCO_3$$

Sodium hydrogencarbonate is a mild antiseptic for skin infections. It is used in fire extinguishers.

10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 $mmolL^{-1}$, whereas the potassium level is only 5 $mmolL^{-1}$ within the red blood cells. These concentrations change to 10 $mmolL^{-1}$ (Na^+) and 105 $mmolL^{-1}$ (K^+). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table 10.2.

10.6.1 Electronic Configuration

These elements have two electrons in the *s*-orbital of the valence shell (Table 10.2). Their general electronic configuration may be represented as [noble gas] ns^2. Like alkali metals, the compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe]$6s^2$
Radium	Ra	[Rn]$7s^2$

10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the

Table 10.2 Atomic and Physical Properties of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electron configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I) / kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II) /kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy (kJ/mol)	– 2494	– 1921	–1577	– 1443	– 1305	–
Metallic radius / pm	112	160	197	215	222	–
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p / K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential $E^{\ominus}$ / V for (M^{2+}/ M)	–1.97	–2.36	–2.84	–2.89	– 2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390 *	10^{-6}*

**ppm (part per million); ** percentage by weight*

corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

10.6.3 Ionization Enthalpies

The alkaline earth metals have low ionization enthalpies due to fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases (Table 10.2). The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding Group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that the second ionisation enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2.6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

10.6.5 Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic. Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium,

strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry. The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) Reactivity towards air and water: Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

(ii) Reactivity towards the halogens: All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

$$M + X_2 \rightarrow MX_2 \; (X = F, Cl, Br, 1)$$

Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2, and $BeCl_2$ is conveniently made from the oxide.

$$BeO + C + Cl_2 \xrightleftharpoons{600-800K} BeCl_2 + CO$$

(iii) Reactivity towards hydrogen: All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2.

BeH_2, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

(iv) Reactivity towards acids: The alkaline earth metals readily react with acids liberating dihydrogen.

$$M + 2HCl \rightarrow MCl_2 + H_2$$

(v) Reducing nature: Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials (Table 10.2). However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal.

(vi) Solutions in liquid ammonia: Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.

$$M + (x+y)NH_3 \rightarrow \left[M(NH_3)_X\right]^{2+} + 2\left[e(NH_3)_Y\right]^-$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

10.6.7 Uses

Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes. Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes. Radium salts are used in radiotherapy, for example, in the treatment of cancer.

10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The dipositive oxidation state (M^{2+}) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

(i) Oxides and Hydroxides: The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

$$Be(OH)_2 + 2OH^- \rightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

$$Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$$

(ii) Halides: Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:

In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, $MgCl_2 \cdot 8H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) Salts of Oxoacids: The alkaline earth metals also form salts of oxoacids. Some of these are :

Carbonates: Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2. The thermal stability increases with increasing cationic size.

Sulphates: The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates: The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

(M = Be, Mg, Ca, Sr, Ba)

Problem 10.4

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Solution

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Problem 10.5

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

(i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.

(iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

10.8.1 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

(iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.

10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

***Calcium Oxide or Quick Lime*, CaO**

It is prepared on a commercial scale by heating limestone ($CaCO_3$) in a rotary kiln at 1070-1270 K.

$$CaCO_3 \xrightleftharpoons{\text{heat}} CaO + CO_2$$

The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$CaO + CO_2 \rightarrow CaCO_3$$

The addition of limited amount of water breaks the lump of lime. This process is called *slaking of lime*. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

Uses:

(i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.

(ii) It is used in the manufacture of sodium carbonate from caustic soda.

(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + \underset{\text{Bleaching powder}}{Ca(OCl)_2} + 2H_2O$$

Uses:

(i) It is used in the preparation of mortar, a building material.

(ii) It is used in white wash due to its disinfectant nature.

(iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

Calcium Carbonate, $CaCO_3$

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$CaCO_3 \xrightarrow{1200\,K} CaO + CO_2$$

It reacts with dilute acid to liberate carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

Uses:

It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated $CaCO_3$ is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

Calcium Sulphate (Plaster of Paris), $CaSO_4 \cdot \frac{1}{2} H_2O$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immoblising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

Cement: Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is : CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe_2O_3, 1-2% and SO_3, 1-2%. For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.

Setting of Cement: When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses: Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

10.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL^{-1}. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

SUMMARY

The ***s*-Block** of the periodic table constitutes **Group1** (alkali metals) and **Group 2** (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one *s*-electron and the alkaline earth metals by two *s*-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive **(M^+)** and dipositve **(M^{2+})** ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic numbers. The **atomic** and **ionic** sizes increase and the **ionization enthalpies** decrease systematically down the group. Somewhat similar trends are observed among the properties of the alkaline earth metals.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the **'diagonal relationship'** in the periodic table. As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate. Sodium hydroxide is manufactured by **Castner-Kellner** process and sodium carbonate by **Solvay** process.

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate **(Plaster of Paris),** calcium carbonate (limestone) and cement. **Portland cement** is an important constructional material. It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important **biological functions** such as maintenance of ion balance and nerve impulse conduction.

EXERCISES

10.1 What are the common physical and chemical features of alkali metals ?

10.2 Discuss the general characteristics and gradation in properties of alkaline earth metals.

10.3 Why are alkali metals not found in nature ?

10.4 Find out the oxidation state of sodium in Na_2O_2.

10.5 Explain why is sodium less reactive than potassium.

10.6 Compare the alkali metals and alkaline earth metals with respect to (i) ionisation enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides.

10.7 In what ways lithium shows similarities to magnesium in its chemical behaviour?

10.8 Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

10.9 Why are potassium and caesium, rather than lithium used in photoelectric cells?

10.10 When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.

10.11 Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so. Why ?

10.12 Discuss the various reactions that occur in the Solvay process.

10.13 Potassium carbonate cannot be prepared by Solvay process. Why ?

10.14 Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

10.15 Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals. (a) Nitrates (b) Carbonates (c) Sulphates.

10.16 Starting with sodium chloride how would you proceed to prepare (i) sodium metal (ii) sodium hydroxide (iii) sodium peroxide (iv) sodium carbonate ?

10.17 What happens when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated ?

10.18 Describe two important uses of each of the following : (i) caustic soda (ii) sodium carbonate (iii) quicklime.

10.19 Draw the structure of (i) $BeCl_2$ (vapour) (ii) $BeCl_2$ (solid).

10.20 The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

10.21 Describe the importance of the following : (i) limestone (ii) cement (iii) plaster of paris.

10.22 Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?

10.23 Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone ?

10.24 Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

10.25 What happens when

(i) sodium metal is dropped in water ?

(ii) sodium metal is heated in free supply of air ?

(iii) sodium peroxide dissolves in water ?

10.26 Comment on each of the following observations:

(a) The mobilities of the alkali metal ions in aqueous solution are $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(b) Lithium is the only alkali metal to form a nitride directly.

(c) $E^{\ominus}$ for $M^{2+}(aq) + 2e^- \rightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant.

10.27 State as to why

(a) a solution of Na_2CO_3 is alkaline ?

(b) alkali metals are prepared by electrolysis of their fused chlorides ?

(c) sodium is found to be more useful than potassium ?

10.28 Write balanced equations for reactions between

(a) Na_2O_2 and water

(b) KO_2 and water

(c) Na_2O and CO_2.

10.29 How would you explain the following observations?

(i) BeO is almost insoluble but $BeSO_4$ in soluble in water,

(ii) BaO is soluble but $BaSO_4$ is insoluble in water,

(iii) LiI is more soluble than KI in ethanol.

10.30 Which of the alkali metal is having least melting point ?

(a) Na (b) K (c) Rb (d) Cs

10.31 Which one of the following alkali metals gives hydrated salts ?

(a) Li (b) Na (c) K (d) Cs

10.32 Which one of the alkaline earth metal carbonates is thermally the most stable ?

(a) $MgCO_3$ (b) $CaCO_3$ (c) $SrCO_3$ (d) $BaCO_3$

UNIT 11

THE *p* -BLOCK ELEMENTS

Objectives

After studying this unit, you will be able to

- appreciate the general trends in the chemistry of *p*-block elements;
- describe the trends in physical and chemical properties of group 13 and 14 elements;
- explain anomalous behaviour of boron and carbon;
- describe allotropic forms of carbon;
- know the chemistry of some important compounds of boron, carbon and silicon;
- list the important uses of group 13 and 14 elements and their compounds.

"The variation in properties of the p-block elements due to the influence of d and f electrons in the inner core of the heavier elements makes their chemistry interesting"

In *p*-block elements the last electron enters the outermost *p* orbital. As we know that the number of *p* orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of *p* orbitals is six. Consequently there are six groups of *p*–block elements in the periodic table numbering from 13 to 18. Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups. Their valence shell **electronic configuration is** ns^2np^{1-6} (except for He). The **inner core** of the electronic configuration may, however, differ. The difference in inner core of elements greatly influences their physical properties (such as atomic and ionic radii, ionisation enthalpy, etc.) as well as chemical properties. Consequently, a lot of variation in properties of elements in a group of *p*-block is observed. The *maximum oxidation state* shown by a *p*-block element is equal to the total number of valence electrons (*i.e.*, the sum of the *s*- and *p*-electrons). Clearly, the number of possible oxidation states increases towards the right of the periodic table. In addition to this so called *group oxidation state*, *p*-block elements may show other oxidation states which normally, but not necessarily, differ from the total number of valence electrons by unit of two. The important oxidation states exhibited by *p*-block elements are shown in Table 11.1. In boron, carbon and nitrogen families the group oxidation state is the most stable state for the lighter elements in the group. However, the oxidation state two unit less than the group oxidation state becomes progressively more stable for the heavier elements in each group. The occurrences of oxidation states two unit less than the group oxidation states are sometime attributed to the '**inert pair effect**'.

Table 11.1 General Electronic Configuration and Oxidation States of *p*-Block Elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, – 4	+3, – 3	+4, +2, –2	+5, + 3, +1, –1	+6, +4, +2

The relative stabilities of these two oxidation states – group oxidation state and two unit less than the group oxidation state – may vary from group to group and will be discussed at appropriate places.

It is interesting to note that the *non-metals* and *metalloids* exist only in the *p*-block of the periodic table. The non-metallic character of elements decreases down the group. In fact the heaviest element in each *p*-block group is the most metallic in nature. This change from non-metallic to metallic character brings diversity in the chemistry of these elements depending on the group to which they belong.

In general, non-metals have higher ionisation enthalpies and higher electronegativities than the metals. Hence, in contrast to metals which readily form cations, non-metals readily form anions. The compounds formed by highly reactive non-metals with highly reactive metals are generally ionic because of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. The change of non-metallic to metallic character can be best illustrated by the nature of oxides they form. The non-metal oxides are acidic or neutral whereas metal oxides are basic in nature.

The first member of p-block differs from the remaining members of their corresponding group in two major respects. First is the size and all other properties which depend on size. Thus, the lightest *p*-block elements show the same kind of differences as the lightest *s*-block elements, lithium and beryllium. The second important difference, which applies only to the *p*-block elements, arises from the effect of *d*-orbitals in the valence shell of heavier elements (starting from the third period onwards) and their lack in second period elements. The second period elements of *p*-groups starting from boron are restricted to a maximum covalence of four (using 2*s* and three 2*p* orbitals). In contrast, the third period elements of *p*-groups with the electronic configuration $3s^23p^n$ have the vacant 3*d* orbitals lying between the 3*p* and the 4*s* levels of energy. Using these *d*-orbitals the third period elements can expand their covalence above four. For example, while boron forms only $[BF_4]^-$, aluminium gives $[AlF_6]^{3-}$ ion. The presence of these *d*-orbitals influences the chemistry of the heavier elements in a number of other ways. The combined effect of size and availability of *d* orbitals considerably influences the ability of these elements to form π bonds. The first member of a group differs from the heavier members in its ability to form $p\pi$ - $p\pi$ multiple bonds to itself (e.g., C=C, C≡C,

N≡N) and to other second row elements (e.g., C=O, C=N, C≡N, N=O). This type of π - bonding is not particularly strong for the heavier *p*-block elements. The heavier elements do form π bonds but this involves *d* orbitals ($d\pi - p\pi$ or $d\pi - d\pi$). As the *d* orbitals are of higher energy than the *p* orbitals, they contribute less to the overall stability of molecules than does $p\pi$ - $p\pi$ bonding of the second row elements. However, the coordination number in species of heavier elements may be higher than for the first element in the same oxidation state. For example, in +5 oxidation state both N and P form oxoanions : NO_3^- (three-coordination with π – bond involving one nitrogen *p*-orbital) and PO_4^{3-} (four-coordination involving *s*, *p* and *d* orbitals contributing to the π – bond). In this unit we will study the chemistry of group 13 and 14 elements of the periodic table.

11.1 GROUP 13 ELEMENTS: THE BORON FAMILY

This group elements show a wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character.

Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$. In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan). The abundance of boron in earth crust is less than 0.0001% by mass. There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%). Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, $Al_2O_3 . 2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium. In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu. Gallium, indium and thallium are less abundant elements in nature.

The atomic, physical and chemical properties of these elements are discussed below.

11.1.1 Electronic Configuration

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 *d*-electrons, and thallium has noble gas plus 14 *f*- electrons plus 10 *d*-electrons cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

11.1.2 Atomic Radii

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen. Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect (Unit 2) for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

11.1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of *d*- and *f*-electrons ,which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties.

11.1.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases

marginally (Table 11.2). This is because of the discrepancies in atomic size of the elements.

11.1.5 Physical Properties

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity. It is worthwhile to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

11.1.6 Chemical Properties

Oxidation state and trends in chemical reactivity

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal. However, down the group, due to poor shielding effect of intervening *d* and *f* orbitals, the increased effective nuclear charge holds *ns* electrons tightly (responsible for *inter pair effect*) and thereby, restricting their participation in bonding. As a result of this, only *p*-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: Al<Ga<In<Tl. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character. The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

In trivalent state, the number of electrons around the central atom in a molecule

Table 11.2 Atomic and Physical Properties of Group 13 Elements

Property		Element				
		Boron B	Aluminium Al	Gallium Ga	Indium In	Thallium Tl
Atomic number		5	13	31	49	81
Atomic mass(g mol^{-1})		10.81	26.98	69.72	114.82	204.38
Electronic		$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10} 4s^2 4p^1$	$[Kr]4d^{10} 5s^2 5p^1$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
Atomic radius/pm[a]		(85)	143	135	167	170
Ionic radius M^{3+}/pm[b]		(27)	53.5	62.0	80.0	88.5
Ionic radius M^+/pm		-	-	120	140	150
Ionization enthalpy (kJ mol^{-1})	$\Delta_i H_1$	801	577	579	558	589
	$\Delta_i H_2$	2427	1816	1979	1820	1971
	$\Delta_i H_3$	3659	2744	2962	2704	2877
Electronegativity[c]		2.0	1.5	1.6	1.7	1.8
Density /g cm^{-3} at 298 K		2.35	2.70	5.90	7.31	11.85
Melting point / K		2453	933	303	430	576
Boiling point / K		3923	2740	2676	2353	1730
$E^{\ominus}$/ V for (M^{3+}/M)		-	–1.66	–0.56	–0.34	+1.26
$E^{\ominus}$ / V for (M^+/M)		-	+0.55	-0.79(acid) –1.39(alkali)	–0.18	–0.34

[a]*Metallic radius,* [b] *6-coordination,* [c] *Pauling scale,*

of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$.

Planar Tetrahedral

$AlCl_3$ achieves stability by forming a dimer

Tetrahedral

In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $\left[M(OH)_4\right]^-$ species; the hybridisation state of element M is sp^3. Aluminium chloride in acidified aqueous solution forms octahedral $\left[Al(H_2O)_6\right]^{3+}$ ion. In this complex ion, the $3d$ orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

Problem 11.1

Standard electrode potential values, $E^\ominus$ for Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Solution

Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make Al^{3+}(aq) ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidising agent also. Thus Tl^+ is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$$

$$2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$$

(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2Al(s) + 6HCl\ (aq) \rightarrow 2Al^{3+}\ (aq) + 6Cl^-\ (aq) + 3H_2\ (g)$$

However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.

Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$$2Al\ (s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2\ Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$$

Sodium tetrahydroxoaluminate(III)

(iii) Reactivity towards halogens

These elements react with halogens to form trihalides (except TlI_3).

$$2E(s) + 3\ X_2\ (g) \rightarrow 2EX_3\ (s) \qquad (X = F, Cl, Br, I)$$

Problem 11.2

White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Solution

Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

11.2 IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.

The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$F_3B + :NH_3 \rightarrow F_3B \leftarrow NH_3$$

It is due to the absence of *d* orbitals that the maximum covalence of B is 4. Since the *d* orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (*e.g.*, $AlCl_3$) are dimerised through halogen bridging (*e.g.*, Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

Problem 11.3

Boron is unable to form BF_6^{3-} ion. Explain.

Solution

Due to non-availability of *d* orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

11.3 SOME IMPORTANT COMPOUNDS OF BORON

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

11.3.1 Borax

It is the most important compound of boron. It is a white crystalline solid of formula $Na_2B_4O_7 \cdot 10H_2O$. In fact it contains the tetranuclear units $\left[B_4O_5(OH)_4\right]^{2-}$ and correct formula; therefore, is $Na_2[B_4O_5(OH)_4].8H_2O$. Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + \underset{\text{Orthoboric acid}}{4H_3BO_3}$$

On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{Na_2B_4O_7} \xrightarrow{\Delta} 2NaBO_2 + \underset{\text{Boric anhydride}}{B_2O_3}$$

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

11.3.2 Orthoboric acid

Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It has a layer structure in which planar BO_3 units are

joined by hydrogen bonds as shown in Fig. 11.1.

Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

On heating, orthoboric acid above 370K forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3.

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

Fig. 11. 1 *Structure of boric acid; the dotted lines represent hydrogen bonds*

Problem 11.4

Why is boric acid considered as a weak acid?

Solution

Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

11.3.3 Diborane, B_2H_6

The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3\ LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

Diborane is a colourless, highly toxic gas with a b.p. of 180 K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O; \quad \Delta_c H^\ominus = -1976\ kJ\ mol^{-1}$$

Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolysed by water to give boric acid.

$$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $BH_3{\cdot}L$

$$B_2H_6 + 2\ NMe_3 \rightarrow 2BH_3{\cdot}NMe_3$$

$$B_2H_6 + 2\ CO \rightarrow 2BH_3{\cdot}CO$$

Reaction of ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^+\ [BH_4]^-$; further heating gives borazine, $B_3N_3H_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.

$$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{Heat} 2B_3N_3H_6 + 12H_2$$

The structure of diborane is shown in Fig.11.2(a). The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three

Fig.11.2(a) *The structure of diborane, B_2H_6*

centre–two electron bonds shown in Fig.11.2 (b).

Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[BH_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetra-hydridoborates, also known as ***borohydrides***, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

$$2MH + B_2H_6 \rightarrow 2\ M^+\ [BH_4]^- \qquad (M = Li \text{ or } Na)$$

Fig.11.2(b) *Bonding in diborane. Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.*

Both $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

11.4 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications. Boron fibres are used in making bullet-proof vest and light composite material for aircraft. The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods. The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass. Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

Aluminium is a bright silvery-white metal, with high tensile strength. It has a high electrical and thermal conductivity. On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper. Aluminium is used extensively in industry and every day life. It forms alloys with Cu, Mn, Mg, Si and Zn. Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry. The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

11.5 GROUP 14 ELEMENTS: THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Carbon is the seventeenth most abundant element by mass in the earth's crust. It is widely distributed in nature in free as well as in the combined state. In elemental state it is available as coal, graphite and diamond; however, in combined state it is present as metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air. One can emphatically say that carbon is the most versatile element in the world. Its combination with other elements such as dihydrogen, dioxygen, chlorine and sulphur provides an astonishing array of materials ranging from living tissues to drugs and plastics. Organic chemistry is devoted to carbon containing compounds. It is an essential constituent of all living organisms. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement.

Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS.

Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

The important atomic and physical properties of the group 14 elements along with their electronic configuration are given in Table 11.2 Some of the atomic, physical and chemical properties are discussed below:

11.5.1 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2. The inner core of the electronic configuration of elements in this group also differs.

11.5.2 Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled *d* and *f* orbitals in heavier members.

11.5.3 Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening *d* and *f* orbitals and increase in size of the atom.

11.5.4 Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

11.5.5 Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid,

Table 11.3 Atomic and Physical Properties of Group 14 Elements

Property		Element				
		Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic Number		6	14	32	50	82
Atomic mass (g mol^{-1})		12.01	28.09	72.60	118.71	207.2
Electronic configuration		$[He]2s^22p^2$	$[Ne]3s^23p^2$	$[Ar]3d^{10}4s^24p^2$	$[Kr]4d^{10}5s^25p^2$	$[Xe]4f^{14}5d6s^26p^2$
Covalent radius/pm[a]		77	118	122	140	146
Ionic radius M^{4+}/pm[b]		–	40	53	69	78
Ionic radius M^{2+}/pm[b]		–	–	73	118	119
Ionization enthalpy/ kJ mol^{-1}	$\Delta_i H_1$	1086	786	761	708	715
	$\Delta_i H_2$	2352	1577	1537	1411	1450
	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082
Electronegativity[c]		2.5	1.8	1.8	1.8	1.9
Density[d]/g cm^{-3}		3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point/K		4373	1693	1218	505	600
Boiling point/K		–	3550	3123	2896	2024
Electrical resistivity/ ohm cm (293 K)		10^{14}–10^{16}	50	50	10^{-5}	2×10^{-5}

[a] for M^{IV} oxidation state; [b] 6–coordination; [c] Pauling scale; [d] 293 K; [e] for diamond; for graphite, density is 2.22; [f] β-form (stable at room temperature)

whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

11.5.6 Chemical Properties

Oxidation states and trends in chemical reactivity

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge<Sn<Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state. Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent). Lead compounds in +2 state are stable and in +4 state are strong oxidising agents. In tetravalent state the number of electrons around the central atom in a molecule (*e.g.*, carbon in CCl_4) is eight. Being *electron precise* molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of *d* orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-}, $[GeCl_6]^{2-}$, $[Sn(OH)_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2.

(i) Reactivity towards oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides, *i.e.*, monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Problem 11.5

Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

Solution

(i) carbon (ii) lead
(iii) silicon and germanium

(ii) Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

$$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature. PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2. Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2, whereas PbX_2 is more than PbX_4. Except CCl_4, other tetrachlorides are easily hydrolysed by water because the central atom can

accommodate the lone pair of electrons from oxygen atom of water molecule in *d* orbital.

Hydrolysis can be understood by taking the example of $SiCl_4$. It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si, finally leading to the formation of $Si(OH)_4$ as shown below :

Silicic acid

Problem 11. 6

$[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

Solution

The main reasons are :

(i) six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

(ii) interaction between lone pair of chloride ion and Si^{4+} is not very strong.

11.6 IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of *d* orbitals.

In carbon, only *s* and *p* orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of *d* orbitals.

Carbon also has unique ability to form $p\pi-p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: C=C, C ≡ C, C = O, C = S, and C ≡ N. Heavier elements do not form $p\pi-p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C >> Si > Ge ≈ Sn. Lead does not show catenation.

Bond	Bond enthalpy / kJ mol $^{-1}$
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

Due to property of catenation and $p\pi-p\pi$ bond formation, carbon is able to show allotropic forms.

11.7 ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

11.7.1 Diamond

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three-dimensional network of carbon atoms. In this

Fig. 11.3 *The structure of diamond*

Fig 11.4 *The structure of graphite*

structure (Fig. 11.3) directional covalent bonds are present throughout the lattice.

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

Problem 11.7

Diamond is covalent, yet it has high melting point. Why ?

Solution

Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

11.7.2 Graphite

Graphite has layered structure (Fig. 11.4). Layers are held by van der Waals forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

11.7.3 Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene** (Fig. 11.5).

It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in

molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.

Fig.11.5 *The structure of C_{60}, Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).*

It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^{\ominus}$ of graphite is taken as zero. $\Delta_f H^{\ominus}$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

11.7.4 Uses of Carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

11.8 SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

Oxides of Carbon

Two important oxides of carbon are carbon monoxide, CO and carbon dioxide, CO_2.

11.8.1 Carbon Monoxide

Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K

$$HCOOH \xrightarrow[\text{conc.}H_2SO_4]{373K} H_2O + CO$$

On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as **water gas** or **synthesis gas**.

$$C(s) + H_2O(g) \xrightarrow{473\text{–}1273K} \underset{\text{Water gas}}{CO(g) + H_2(g)}$$

When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas**.

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} \underset{\text{Producer gas}}{2CO(g) + 4N_2(g)}$$

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

Carbon monoxide is a colourless, odourless and almost water insoluble gas. It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of

CO is used in the extraction of many metals from their oxides ores.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

In CO molecule, there are one sigma and two π bonds between carbon and oxygen, :C ≡ O: . Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**. The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

11.8.2 Carbon Dioxide

It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

In the laboratory it is conveniently prepared by the action of dilute HCl on calcium carbonate.

$$CaCO_3(s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O(l)$$

On commercial scale it is obtained by heating limestone.

It is a colourless and odourless gas. Its low solubility in water makes it of immense bio-chemical and geo-chemical importance. With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorphyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

By this process plants make food for themselves as well as for animals and human beings. Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food. Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

In CO_2 molecule carbon atom undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in $p\pi - p\pi$ bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:

Resonance structures of carbon dioxide

11.8.3 Silicon Dioxide, SiO_2

95% of the earth's crust is made up of silica and silicates. Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature. Silicon dioxide is a covalent, three-dimensional

network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms as shown in diagram (Fig 11.6). Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternate silicon and oxygen atoms.

Fig. 11.6 *Three dimensional structure of SiO_2*

Silica in its normal form is almost non-reactive because of very high Si—O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. However, it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

11.8.4 Silicones

They are a group of organosilicon polymers, which have $\{R_2SiO\}$ as a repeating unit. The starting materials for the manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$, where R is alkyl or aryl group. When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K various types of methyl substituted chlorosilane of formula $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl with small amount of Me_4Si are formed. Hydrolysis of dimethyl-dichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain polymers.

Silicone

The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below :

Silicone

Silicones being surrounded by non-polar alkyl groups are water repelling in nature. They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals. They have wide applications. They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Problem: 11.8

What are silicones ?

Solution

Simple silicones consist of $\left(\begin{matrix} | \\ Si - O \\ | \end{matrix} \right)_n$ chains in which alkyl or phenyl groups occupy the remaining bonding positions on each silicon. They are hydrophobic (water repellant) in nature.

11.8.5 Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-} (Fig.11.7) in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. In silicates either the discrete unit is present or a number of such units are joined together via corners by sharing 1,2,3 or 4 oxygen atoms per silicate units. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures. Negative charge on silicate structure is

Fig. 11.7 *(a) Tetrahedral structure of SiO_4^{4-} anion; (b) Representation of SiO_4^{4-} unit*

neutralized by positively charged metal ions. If all the four corners are shared with other tetrahedral units, three-dimensional network is formed.

Two important man-made silicates are glass and cement.

11.8.6 Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.

SUMMARY

***p*-Block** of the periodic table is unique in terms of having all types of elements – **metals, non-metals** and **metalloids**. There are six groups of *p*-block elements in the periodic table numbering from 13 to 18. Their valence shell electronic configuration is ns^2np^{1-6} (except for He). Differences in the **inner core** of their electronic configuration greatly influence their physical and chemical properties. As a consequence of this, a lot of variation in properties among these elements is observed. In addition to the *group oxidation state*, these elements show other oxidation states differing from the total number of valence electrons by unit of two. While the group oxidation state is the most stable for the lighter elements of the group, lower oxidation states become progressively more stable for the heavier elements. The combined effect of size and availability of *d* orbitals considerably

influences the ability of these elements to form π-bonds. While the lighter elements form $p\pi$–$p\pi$ bonds, the heavier ones form $d\pi$–$p\pi$ or $d\pi$–$d\pi$ bonds. Absence of *d* orbital in second period elements limits their maximum covalence to 4 while heavier ones can exceed this limit.

Boron is a typical non-metal and the other members are metals. The availability of 3 valence electrons ($2s^2 2p^1$) for covalent bond formation using four orbitals ($2s$, $2p_x$, $2p_y$ and $2p_z$) leads to the so called **electron deficiency** in boron compounds. This deficiency makes them good electron acceptor and thus boron compounds behave as **Lewis acids**. Boron forms covalent molecular compounds with dihydrogen as boranes, the simplest of which is **diborane**, B_2H_6. Diborane contains two bridging hydrogen atoms between two boron atoms; these bridge bonds are considered to be **three-centre two-electron bonds**. The important compounds of boron with dioxygen are **boric acid** and **borax**. Boric acid, $B(OH)_3$ is a weak monobasic acid; it acts as a Lewis acid by accepting electrons from hydroxyl ion. Borax is a white crystalline solid of formula $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$. The **borax bead test** gives characteristic colours of transition metals.

Aluminium exhibits +3 oxidation state. With heavier elements +1 oxidation state gets progressively stabilised on going down the group. This is a consequence of the so called **inert pair effect**.

Carbon is a typical non-metal forming covalent bonds employing all its four valence electrons ($2s^2 2p^2$). It shows the property of **catenation**, the ability to form chains or rings, not only with C–C single bonds but also with multiple bonds (C=C or C≡C). The tendency to catenation decreases as C>>Si>Ge $\simeq$ Sn > Pb. Carbon provides one of the best examples of **allotropy**. Three important allotropes of carbon are **diamond**, **graphite** and **fullerenes**. The members of the carbon family mainly exhibit +4 and +2 oxidation states; compouds in +4 oxidation states are generally covalent in nature. The tendency to show +2 oxidation state increases among heavier elements. Lead in +2 state is stable whereas in +4 oxidation state it is a strong oxidising agent. Carbon also exhibits negative oxidation states. It forms two important oxides: CO and CO_2. Carbon monoxide is neutral whereas CO_2 is acidic in nature. Carbon monoxide having lone pair of electrons on C forms metal **carbonyls**. It is deadly poisonous due to higher stability of its **haemoglobin complex** as compared to that of oxyhaemoglobin complex. Carbon dioxide as such is not toxic. However, increased content of CO_2 in atmosphere due to combustion of fossil fuels and decomposition of limestone is feared to cause increase in '**green house effect**'. This, in turn, raises the temperature of the atmosphere and causes serious complications. **Silica**, **silicates** and **silicones** are important class of compounds and find applications in industry and technology.

EXERCISES

11.1 Discuss the pattern of variation in the oxidation states of
(i) B to Tl and (ii) C to Pb.

11.2 How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

11.3 Why does boron triflouride behave as a Lewis acid ?

11.4 Consider the compounds, BCl_3 and CCl_4. How will they behave with water ? Justify.

11.5 Is boric acid a protic acid ? Explain.

11.6 Explain what happens when boric acid is heated .

11.7 Describe the shapes of BF_3 and BH_4^-. Assign the hybridisation of boron in these species.

11.8 Write reactions to justify amphoteric nature of aluminium.

11.9 What are electron deficient compounds ? Are BCl_3 and $SiCl_4$ electron deficient species ? Explain.

11.10 Write the resonance structures of CO_3^{2-} and HCO_3^- .

11.11 What is the state of hybridisation of carbon in (a) CO_3^{2-} (b) diamond (c) graphite?

11.12 Explain the difference in properties of diamond and graphite on the basis of their structures.

11.13 Rationalise the given statements and give chemical reactions :

- Lead(II) chloride reacts with Cl_2 to give $PbCl_4$.
- Lead(IV) chloride is highly unstable towards heat.
- Lead is known not to form an iodide, PbI_4.

11.14 Suggest reasons why the B–F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ.

11.15 If B–Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment.

11.16 Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

11.17 Suggest a reason as to why CO is poisonous.

11.18 How is excessive content of CO_2 responsible for global warming ?

11.19 Explain structures of diborane and boric acid.

11.20 What happens when

(a) Borax is heated strongly,

(b) Boric acid is added to water,

(c) Aluminium is treated with dilute NaOH,

(d) BF_3 is reacted with ammonia ?

11.21 Explain the following reactions

(a) Silicon is heated with methyl chloride at high temperature in the presence of copper;

(b) Silicon dioxide is treated with hydrogen fluoride;

(c) CO is heated with ZnO;

(d) Hydrated alumina is treated with aqueous NaOH solution.

11.22 Give reasons :

(i) Conc. HNO_3 can be transported in aluminium container.

(ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.

(iii) Graphite is used as lubricant.

(iv) Diamond is used as an abrasive.

(v) Aluminium alloys are used to make aircraft body.

(vi) Aluminium utensils should not be kept in water overnight.

(vii) Aluminium wire is used to make transmission cables.

11.23 Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon ?

11.24 How would you explain the lower atomic radius of Ga as compared to Al ?

11.25 What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

11.26 (a) Classify following oxides as neutral, acidic, basic or amphoteric:

CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3

(b) Write suitable chemical equations to show their nature.

11.27 In some of the reactions thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

11.28 When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.

11.29 What do you understand by (a) inert pair effect (b) allotropy and (c) catenation?

11.30 A certain salt X, gives the following results.

(i) Its aqueous solution is alkaline to litmus.

(ii) It swells up to a glassy material Y on strong heating.

(iii) When conc. H_2SO_4 is added to a hot solution of X,white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and Z.

11.31 Write balanced equations for:

(i) $BF_3 + LiH \rightarrow$

(ii) $B_2H_6 + H_2O \rightarrow$

(iii) $NaH + B_2H_6 \rightarrow$

(iv) $H_3BO_3 \xrightarrow{\Delta}$

(v) $Al + NaOH \rightarrow$

(vi) $B_2H_6 + NH_3 \rightarrow$

11.32. Give one method for industrial preparation and one for laboratory preparation of CO and CO_2 each.

11.33 An aqueous solution of borax is

(a) neutral (b) amphoteric

(c) basic (d) acidic

11.34 Boric acid is polymeric due to

(a) its acidic nature (b) the presence of hydrogen bonds

(c) its monobasic nature (d) its geometry

11.35 The type of hybridisation of boron in diborane is

(a) *sp* (b) sp^2 (c) sp^3 (d) dsp^2

11.36 Thermodynamically the most stable form of carbon is

(a) diamond (b) graphite

(c) fullerenes (d) coal

11.37 Elements of group 14

(a) exhibit oxidation state of +4 only

(b) exhibit oxidation state of +2 and +4

(c) form M^{2-} and M^{4+} ion

(d) form M^{2+} and M^{4+} ions

11.38 If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

UNIT 12

ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Objectives

After studying this unit, you will be able to

- understand reasons for tetravalence of carbon and shapes of organic molecules;
- write structures of organic molecules in various ways;
- classify the organic compounds;
- name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;
- understand the concept of organic reaction mechanism;
- explain the influence of electronic displacements on structure and reactivity of organic compounds;
- recognise the types of organic reactions;
- learn the techniques of purification of organic compounds;
- write the chemical reactions involved in the qualitative analysis of organic compounds;
- understand the principles involved in quantitative analysis of organic compounds.

In the previous unit you have learnt that the element carbon has the unique property called **catenation** due to which it forms covalent bonds with other carbon atoms. It also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens. The resulting compounds are studied under a separate branch of chemistry called **organic chemistry**. This unit incorporates some basic principles and techniques of analysis required for understanding the formation and properties of organic compounds.

12.1 GENERAL INTRODUCTION

Organic compounds are vital for sustaining life on earth and include complex molecules like genetic information bearing deoxyribonucleic acid (DNA) and proteins that constitute essential compounds of our blood, muscles and skin. Organic chemicals appear in materials like clothing, fuels, polymers, dyes and medicines. These are some of the important areas of application of these compounds.

Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in a laboratory.

The development of electronic theory of covalent bonding ushered organic chemistry into its modern shape.

12.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

12.2.1 The Shapes of Carbon Compounds

The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of organic compounds. You have already learnt theories of valency and molecular structure in Unit 4. Also, you already know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of *s* and *p* orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp^3, sp^2 and *sp* hybrid orbitals by carbon atoms in the respective molecules.

Hybridisation influences the bond length and bond enthalpy (strength) in organic compounds. The *sp* hybrid orbital contains more *s* character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp^3 hybrid orbital. The sp^2 hybrid orbital is intermediate in *s* character between *sp* and sp^3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation affects the electronegativity of carbon. The greater the *s* character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having an *sp* hybrid orbital with 50% *s* character is more electronegative than that possessing sp^2 or sp^3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later units.

12.2.2 Some Characteristic Features of π Bonds

In a π (pi) bond formation, parallel orientation of the two *p* orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in $H_2C{=}CH_2$ molecule all the atoms must be in the same plane. The *p* orbitals are mutually parallel and both the *p* orbitals are perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to other interferes with maximum overlap of *p* orbitals and, therefore, such rotation about carbon-carbon double bond (C=C) is restricted. The electron charge cloud of the π bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, π bonds provide the most reactive centres in the molecules containing multiple bonds.

Problem 12.1

How many σ and π bonds are present in each of the following molecules?

(a) $HC{\equiv}CCH{=}CHCH_3$ (b) $CH_2{=}C{=}CHCH_3$

Solution

(a) σ_{C-C}: 4; σ_{C-H} : 6; $\pi_{C=C}$:1; π C≡C:2

(b) σ_{C-C}: 3; σ_{C-H}: 6; $\pi_{C=C}$: 2.

Problem 12.2

What is the type of hybridisation of each carbon in the following compounds?

(a) CH_3Cl, (b) $(CH_3)_2CO$, (c) CH_3CN,

(d) $HCONH_2$, (e) $CH_3CH{=}CHCN$

Solution

(a) sp^3, (b) sp^3, sp^2, (c) sp^3, *sp*, (d) sp^2, (e) sp^3, sp^2, sp^2, *sp*

Problem 12.3

Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

(a) $H_2C{=}O$, (b) CH_3F, (c) $HC{\equiv}N$.

Solution

(a) sp^2 hybridised carbon, trigonal planar; (b) sp^3 hybridised carbon, tetrahedral; (c) *sp* hybridised carbon, linear.

12.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

12.3.1 Complete, Condensed and Bond-line Structural Formulas

Structures of organic compounds are represented in several ways. The *Lewis structure* or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (–). Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond. Lone-pairs of electrons on heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulas. Such structural representations are called *complete structural formulas*.

Ethane

Ethene

Ethyne *Methanol*

These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a *condensed structural formula*. Thus, ethane, ethene, ethyne and methanol can be written as:

CH_3CH_3	$H_2C{=}CH_2$	$HC{\equiv}CH$	CH_3OH
Ethane	*Ethene*	*Ethyne*	*Methanol*

Similarly, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ can be further condensed to $CH_3(CH_2)_6CH_3$. For further simplification, organic chemists use another way of representing the structures, in which only lines are used. In this *bond-line structural* representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a *zig-zag* fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl ($-CH_3$) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Some of the examples are represented as follows:

(i) 3-Methyloctane can be represented in various forms as:

(a) $CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_2CH_3$

(b)

(c)

(ii) Various ways of representing 2-bromo butane are:

(a) $CH_3CHBrCH_2CH_3$ (b)

(c)

In cyclic compounds, the bond-line formulas may be given as follows:

Cyclopropane

Cyclopentane

chlorocyclohexane

Problem 12.4

Expand each of the following condensed formulas into their complete structural formulas.

(a) $CH_3CH_2COCH_2CH_3$

(b) $CH_3CH{=}CH(CH_2)_3CH_3$

Solution

(a)

(b)

Problem 12.5

For each of the following compounds, write a condensed formula and also their bond-line formula.

(a) $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$

(b) $N{\equiv}C{-}CH(OH){-}C{\equiv}N$

Solution

Condensed formula:

(a) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$

(b) $HOCH(CN)_2$

Bond-line formula:

(a)

(b)

Problem 12.6

Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen

(a)

(b)

(c)

(d)

Solution

(a)

(b)

(c)

(d)

12.3.2 Three-Dimensional Representation of Organic Molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid (◄) and dashed (····||||) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—). 3-D representation of methane molecule on paper has been shown in Fig. 12.1.

Fig. 12.1 *Wedge-and-dash representation of* CH_4

Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) *Framework model*, (2) *Ball-and-stick model*, and (3) *Space filling model*. In the *framework model* only the bonds connecting the atoms of a molecule and not the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of atoms. In the *ball-and-stick model*, both the atoms and the bonds are shown. Balls represent atoms and the stick denotes a bond. Compounds containing C=C (e.g., ethene) can best be represented by using springs in place of sticks. These models are referred to as *ball-and-spring model*. The *space-filling model* emphasises the relative size of each atom based on its van der Waals radius. Bonds are not shown in this model. It conveys the volume occupied by each atom in the molecule. In addition to these models, computer graphics can also be used for molecular modelling.

Framework model

Ball and stick model

Space filling model

Fig. 12.2

12.4 CLASSIFICATION OF ORGANIC COMPOUNDS

The existing large number of organic compounds and their ever-increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows:

- Organic compounds
  - Acyclic or Open chain compounds (I)
  - Cyclic or Closed chain or Ring compounds (II)
    - Homocyclic or Carbocyclic compounds
      - Alicyclic compounds
      - Aromatic compounds
        - Benzenoid compounds
        - Non-benzenoid compounds
    - Heterocyclic compounds

I. *Acyclic or open chain compounds*

These compounds are also called as **aliphatic** compounds and consist of straight or branched chain compounds, for example:

Ethane

Isobutane

Acetaldehyde

Acetic acid

II *Alicyclic or closed chain or ring compounds*

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocylic). Some examples of this type of compounds are:

Cyclopropane

Cyclohexane

Cyclohexene

Tetrahydrofuran

These exhibit some of the properties similar to those of aliphatic compounds.

Aromatic compounds

Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 13. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic comounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

Benzenoid aromatic compounds

Benzene

Aniline

Naphthalene

Non-benzenoid compound

Tropolone

Heterocyclic aromatic compounds

Furan Thiophene Pyridine

Organic compounds can also be classified on the basis of functional groups, into *families* or *homologous series*.

Functional Group

The functional group may be defined as an atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH) etc.

Homologous Series

A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called *homologues*. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a $-CH_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.

12.5 NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry)** system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is *formica*. These names are traditional and are considered as *trivial* or *common names*. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 12.1.

Table 12.1 Common or Trivial Names of Some Organic Compounds

Compound	Common name
CH_4	Methane
$H_3CCH_2CH_2CH_3$	*n*-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol
HCHO	Formaldehyde
$(H_3C)_2CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

12.5.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.

By further using *prefixes* and *suffixes*, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is *alkane*. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond.

12.5.2 IUPAC Nomenclature of Alkanes

***Straight chain hydrocarbons*:** The names of such compounds are based on their chain structure, and end with suffix '*-ane*' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 12.2. The alkanes in Table 12.2 differ from each other by merely the number of $-CH_2$ groups in the chain. They are homologues of alkane series.

Table 12.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

***Branched chain hydrocarbons*:** In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:

(a) (b)

In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH_4 becomes $-CH_3$ and is called *methyl group*. An alkyl group is named by substituting '*yl*' for '*ane*' in the corresponding alkane. Some alkyl groups are listed in Table 12.3.

Table 12.3 Some Alkyl Groups

Alkane		Alkyl group	
Molecular formula	**Name of alkane**	**Structural formula**	**Name of alkyl group**
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.

Common branched groups have specific trivial names. For example, the propyl groups can either be *n*-propyl group or isopropyl group. The branched butyl groups are called *sec*-butyl, isobutyl and *tert*-butyl group. We also encounter the structural unit, $-CH_2C(CH_3)_3$, which is called neopentyl group.

Nomenclature of branched chain alkanes: We encounter a number of branched chain alkanes. The rules for naming them are given below.

1. First of all, the **longest carbon chain in the molecule is identified**. In the example (I) given below, the longest chain has nine carbons and it is considered as the *parent* or *root* chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons.

I

II

2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. **The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.** Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).

3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.]

4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:

2,4-Dimethylpentane

2,2,4-Trimethylpentane

3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the **lower number is given to the one coming first in the alphabetical listing**. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.

6. The branched alkyl groups can be named by following the above mentioned procedures. However, the **carbon atom of the branch that attaches to the root alkane** is numbered 1 as exemplified below.

1,3-Dimethylbutyl-

The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' **in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes *sec-* and *tert-* are not** considered to be the part of the fundamental name. The use of *iso* and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multi-substituted compounds, the following rules may aso be remembered:

- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.

5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

5-sec-Butyl-4-isopropyldecane

5-(2,2-Dimethylpropyl)nonane

***Cyclic Compounds*:** A saturated monocyclic compound is named by prefixing '*cyclo*' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.

Cyclopentane

1-Methyl-3-propylcyclohexane

3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

Problem 12.7

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

(a)

2,5,6- Trimethyloctane
[and not 3,4,7-Trimethyloctane]

(b)

3-Ethyl-5-methylheptane
[and not 5-Ethyl-3-methylheptane]

Solution

(a) Lowest locant number, 2,5,6 is lower than 3,5,7, (b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

12.5.3 Nomenclature of Organic Compounds having Functional Group(s)

A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of

chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$ — all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 12.4.

First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. **The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain**. By using the suffix as given in Table 12.4, the name of the compound is arrived at.

In the case of polyfunctional compounds, one of the functional groups is chosen as the *principal functional group* and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. **The order of decreasing priority for some functional groups is:**

-COOH, $-SO_3H$, -COOR (R=alkyl group), COCl, $-CONH_2$, -CN,-HC=O, >C=O, -OH, $-NH_2$, >C=C<, -C≡C- .

The –R, C_6H_5-, halogens (F, Cl, Br, I), $-NO_2$, alkoxy (–OR) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone since the keto group is preferred to the hydroxyl group.

For example, $HOCH_2(CH_2)_3CH_2COCH_3$ will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan -7-ol. Similarly, $BrCH_2CH{=}CH_2$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $CH_2(OH)CH_2(OH)$ is named as ethane–1,2–diol. However, the ending – ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, $CH_2{=}CH{-}CH{=}CH_2$ is named as buta–1,3–diene.

Problem 12.8

Write the IUPAC names of the compounds i-iv from their given structures.

(i)
```
 1    2    3    4    5    6    7    8
CH3–CH2–CH–CH2–CH2–CH –CH2–CH3
         |              |
         OH             CH3
```

Solution

- The functional group present is an alcohol (OH). Hence the suffix is '-ol'.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.
  Hence, the systematic name of this compound is 6-Methyloctan-3-ol.

(ii)
```
                O        O
                ||       ||
CH3–CH2–C–CH2–C–CH3
6    5    4  3    2  1
```

Solution

The functional group present is ketone (>C=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

(iii)
```
          O
          ||
CH3–C–CH2–CH2–CH2–COOH
6    5  4    3    2    1
```

Table 12.4 Some Functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	>C=C<	-	-ene	But-1-ene, $CH_2{=}CHCH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne, $CH{\equiv}CCH_2CH_3$
Arenes	-	-	-	Benzene,
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	>C=O	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	-C≡N	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ions	$-COO^-$	-	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2^-\ Na^+$
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, >NH,>N-	amino-	-amine	Butan -2-amine , $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitros	$-NO_2$	nitro	-	1-Nitrobutane, $CH_3(CH_2)_3NO_2$

Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of – COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid.

(iv) $\underset{6}{CH}\equiv\underset{5}{C}-\underset{4}{CH}=\underset{3}{CH}-\underset{2}{CH}=\underset{1}{CH_2}$

Solution

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3-dien-5-yne.

Problem 12.9

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxy-heptanal.

Solution

(i) 'hexane' indicates the presence of 6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is $CH_3CH_2CH_2CH_2CH(Cl)CH_3$.

(ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is

$CH_2{=}CHCH_2CH\ (OH)CH_3$.

(iii) Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO_2 is prefixed functional group therefore double bond gets preference over $-NO_2$ group:

I II

(iv) '1-ol' means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown in (II):

I II

(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: $CH_3CH(OH)CH_2CH_2CH_2CH_2CHO$. Carbon atom of –CHO group is included while numbering the carbon chain.

12.5.4 Nomenclature of Substituted Benzene Compounds

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.

Methylbenzene (Toluene)

Methoxybenzene (Anisole)

Aminobenzene (Aniline)

Nitrobenzene

Bromobenzene

If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.For example, the compound(b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.

(a)

1,2-Dibromo-benzene

(b)

1,3-Dibromo-benzene

(c)

1,4-Dibromo-benzene

In the trivial system of nomenclature the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1,2- ;1,3- and 1,4- respectively. Thus, 1,3-dibromobenzene (b) is named as *m*-dibromobenzene (*meta* is abbreviated as *m*-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as *ortho* (or just *o*-) and *para* (or just *p*-)-dibromobenzene, respectively.

For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.

1-Chloro-2,4-dinitrobenzene
(not 4-chloro,1,3-dinitrobenzene)

2-Chloro-1-methyl-4-nitrobenzene
(not 4-methyl-5-chloro-nitrobenzene)

2-Chloro-4-methylanisole

4-Ethyl-2-methylaniline

3,4-Dimethylphenol

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is *phenyl* (C_6H_5-, also abbreviated as Ph).

Problem 12.10

Write the structural formula of:
(a) *o*-Ethylanisole, (b) *p*-Nitroaniline,
(c) 2,3 - Dibromo -1 - phenylpentane,
(d) 4-Ethyl-1-fluoro-2-nitrobenzene.

Solution

(a)

(b)

(c)

(d)

12.6 ISOMERISM

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

12.6.1 Structural Isomerism

Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

(i) Chain isomerism: When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:

$CH_3CH_2CH_2CH_2CH_3$
Pentane

$CH_3-CH(CH_3)CH_2CH_3$
Isopentane
(2-Methylbutane)

$CH_3-C(CH_3)_2-CH_3$
Neopentane
(2,2-Dimethylpropane)

(ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:

$CH_3CH_2CH_2OH$
Propan-1-ol

$CH_3-CH(OH)-CH_3$
Propan-2-ol

(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone:

Propanone

Propanal

(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

12.6.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as *geometrical* and optical *isomerism*.

12.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s)

The general reaction is depicted as follows :

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called *substrate*.

In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. **A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.** The knowledge of reaction mechanism helps in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

In the following sections, we shall learn some of the principles that explain how these reactions take place.

12.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) ***heterolytic cleavage***, or by (ii) ***homolytic cleavage.***

In ***heterolytic cleavage***, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $\overset{+}{C}H_3$ and Br^- as shown below.

A species having a carbon atom possessing sextext of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion)*. The $\overset{+}{C}H_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: $CH_3\overset{+}{C}H_2$ (ethyl cation, a primary carbocation), $(CH_3)_2\overset{+}{C}H$ (isopropyl cation, a secondary carbocation), and $(CH_3)_3\overset{+}{C}$ (*tert*-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 12.7.5 and 12.7.9. The observed order of carbocation stability is: $\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $\overset{+}{C}H_3$ may be considered as being derived from the overlap of three equivalent C(sp^2) hybridised orbitals

with 1*s* orbital of each of the three hydrogen atoms. Each bond may be represented as C(sp^2)–H(1*s*) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. (Fig. 12.3).

Fig. 12.3 *Shape of methyl cation*

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without

$$CH_3 - Z \longrightarrow H_3C^{-}: + Z^{+}$$

electron pair, the methyl anion $\left(H_3C^{-}:\right)$ is formed. Such a carbon species carrying a negative charge on carbon atom is called *carbanion*. Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic** or **heteropolar** or just polar reactions.

In ***homolytic cleavage***, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook:) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be shown as:

$$R - X \xrightarrow{\text{Heat or Light}} \underset{\substack{\text{Alkyl}\\ \text{free radical}}}{\dot{R}} + \dot{X}$$

Alkyl radicals are classified as *primary*, *secondary*, or *tertiary*. Alkyl radical stability increases as we proceed from primary to tertiary:

$$\underset{\substack{\text{Methyl}\\ \text{free}\\ \text{radical}}}{\dot{C}H_3} < \underset{\substack{\text{Ethyl}\\ \text{free}\\ \text{radical}}}{\dot{C}H_2CH_3} < \underset{\substack{\text{Isopropyl}\\ \text{free}\\ \text{radical}}}{\dot{C}H(CH_3)_2} < \underset{\substack{\text{Tert-butyl}\\ \text{free}\\ \text{radical}}}{\dot{C}(CH_3)_3},$$

Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar* reactions.

12.7.2 Nucleophiles and Electrophiles

A reagent that brings an electron pair is called a **nucleophile** (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**. A reagent that takes away an electron pair is called **electrophile** (E^+) i.e., electron seeking and the reaction is called **electrophilic**.

During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the electrophile that is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate. Thus, the electrophiles receive electron pair from nucleophile when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R_3C:^-$). Neutral molecules such as $H_2\ddot{O}:$, $R_3N:$, $R_2\ddot{N}H$ etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ($\overset{+}{C}H_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R_3C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated

on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

Problem 12.11

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(a) $CH_3–SCH_3$, (b) $CH_3–CN$, (c) $CH_3–Cu$

Solution

(a) $CH_3 — SCH_3 \longrightarrow \overset{+}{C}H_3 + \overset{-}{S}CH_3$

(b) $CH_3 — CN \longrightarrow \overset{+}{C}H_3 + \overset{-}{C}N$

(c) $CH_3 — Cu \longrightarrow \overset{-}{C}H_3 + \overset{+}{C}u$

Problem 12.12

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

HS^-, BF_3, $C_2H_5O^-$, $(CH_3)_3N:$,

$\overset{+}{C}l$, $CH_3\overset{+}{C}=O$, $H_2N:^-$, $\overset{+}{N}O_2$

Solution

Nucleophiles: HS^-, $C_2H_5O^-$, $(CH_3)_3N:$, $H_2N:^-$

These species have unshared pair of electrons, which can be donated and shared with an electrophile.

Electrophiles: BF_3, $\overset{+}{C}l$, $CH_3-\overset{+}{C}=O$, $\overset{+}{N}O_2$.

Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

Problem 12.13

Identify electrophilic centre in the following: $CH_3CH=O$, CH_3CN, CH_3I.

Solution

Among $CH_3H\overset{*}{C}=O$, $H_3C\overset{*}{C}\equiv N$, and $H_3\overset{*}{C}–I$, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

12.7.3 Electron Movement in Organic Reactions

The movement of electrons in organic reactions can be shown by curved-arrow notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron may move.

Presentation of shifting of electron pair is given below :

(i) $=Y— \longleftrightarrow —Y=$ from π bond to adjacent bond position

(ii) $=\ddot{Y}— \longleftrightarrow —\ddot{Y}—$ from π bond to adjacent atom

(iii) $—\ddot{Y}— \longleftrightarrow —Y=$ from atom to adjacent bond position

Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows:

12.7.4 Electron Displacement Effects in Covalent Bonds

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule

when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements.

12.7.5 Inductive Effect

When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Let us consider cholorethane (CH_3CH_2Cl) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge (δ^+) and the chlorine some negative charge (δ^-). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol δ (delta) and the shift of electron density is shown by an arrow that points from δ^+ to δ^- end of the polar bond.

$$\underset{2}{\overset{\delta\delta^+}{CH_3}} \longrightarrow \underset{1}{\overset{\delta^+}{CH_2}} \longrightarrow \overset{\delta^-}{Cl}$$

In turn carbon-1, which has developed partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta^+$) develops on carbon-2 also, where $\delta\delta^+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of σ-bond caused by the polarisation of adjacent σ-bond is referred to as the **inductive effect**. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as *electron-withdrawing* or *electron donating* groups relative to hydrogen. Halogens and many other groups such as nitro (- NO_2), cyano (- CN), carboxy (- COOH), ester (-COOR), aryloxy (-OAr, e.g. – OC_6H_5), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (–CH_3) and ethyl (–CH_2–CH_3) are usually considered as electron donating groups.

Problem 12.14

Which bond is more polar in the following pairs of molecules: (a) H_3C-H, H_3C-Br (b) H_3C-NH_2, H_3C-OH (c) H_3C-OH, H_3C-SH

Solution

(a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

Problem 12.15

In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?

Solution

Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

12.7.6 Resonance Structure

There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene. Its cyclic structure containing alternating C–C single and C=C double bonds shown is inadequate for explaining its characteristic properties.

Benzene

As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, as determined experimentally benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single(154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.

Therefore, according to the resonance theory (Unit 4) the actual structure of benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called *resonance structures.* **The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.** They contribute to the actual structure in proportion to their stability.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures.

However, it is known that the two N–O bonds of nitromethane are of the same length (intermediate between a N–O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the ***resonance stabilisation energy*** or simply the ***resonance energy***. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others.

Problem 12.16

Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

Solution

First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.

Problem 12.17

Write resonance structures of CH_2=CH–CHO. Indicate relative stability of the contributing structures.

Solution

Stability: I > II > III

[I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable].

Problem 12.18

Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.

Solution

The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

12.7.7 Resonance Effect

The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated as R or M effect.

(i) Positive Resonance Effect (+R effect)

In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as :

(ii) Negative Resonance Effect (- R effect)

This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as :

The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

+R effect: – halogen, –OH, –OR, –OCOR, $–NH_2$, –NHR, $–NR_2$, –NHCOR,

– R effect: – COOH, –CHO, >C=O, – CN, $–NO_2$

The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the π-electrons are delocalised and the system develops polarity.

12.7.8 Electromeric Effect (E effect)

It is a temporary effect. The organic compounds having a **multiple bond** (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (↷). There are two distinct types of electromeric effect.

(i) Positive Eelctromeric Effect (+E effect) In this effect the π–electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :

(ii) Negative Electromeric Effect (–E effect) In this effect the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:

When inductive and electromeric effects operate in opposite directions, the electomeric effect predominates.

12.7.9 Hyperconjugation

Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p* orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared *p* orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of $CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty *p* orbital. One of the C-H bonds of the methyl group can align in the plane of this empty *p* orbital and the electrons constituting the C-H bond in plane with this *p* orbital can then be delocalised into the empty *p* orbital as depicted in Fig. 12.4 (a).

Fig. 12.4(a) *Orbital diagram showing hyperconjugation in ethyl cation*

This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.

In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations :

Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 12.4(b).

Fig. 12.4(b) *Orbital diagram showing hyperconjugation in propene*

There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance.

The hyperconjugation may also be regarded as no bond resonance.

Problem 12.19

Explain why $(CH_3)_3\overset{+}{C}$ is more stable than $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$ is the least stable cation.

Solution

Hyperconjugation interaction in $(CH_3)_3\overset{+}{C}$ is greater than in $CH_3\overset{+}{C}H_2$ as the $(CH_3)_3\overset{+}{C}$ has nine C-H bonds. In $\overset{+}{C}H_3$, vacant *p* orbital is perpendicular to the plane in which C-H bonds lie; hence cannot overlap with it. Thus, $\overset{+}{C}H_3$ lacks hyperconjugative stability.

12.7.10 Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

(i) Substitution reactions
(ii) Addition reactions
(iii) Elimination reactions
(iv) Rearrangement reactions

You will be studying these reactions in Unit 13 and later in class XII.

12.8 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows :

(i) Sublimation
(ii) Crystallisation
(iii) Distillation
(iv) Differential extraction and
(v) Chromatography

Finally, the purity of a compound is ascertained by determining its melting or boiling point. Most of the pure compounds have sharp melting points and boiling points. New methods of checking the purity of an organic compound are based on different types of chromatographic and spectroscopic techniques.

12.8.1 Sublimation

You have learnt earlier that on heating, some solid substances change from solid to vapour state without passing through liquid state. The purification technique based on the above principle is known as sublimation and is used to separate sublimable compounds from non-sublimable impurities.

12.8.2 Crystallisation

This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents. Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal. Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities.

12.8.3 Distillation

This important method is used to separate (i) volatile liquids from nonvolatile impurities and (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p 334 K) and aniline (b.p. 457 K) are easily separated by the technique of distillation (Fig 12.5). The liquid mixture is

Fig.12.5 *Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.*

taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately.

Fractional Distillation: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask (Fig.12.6).

Fig.12.6 *Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.*

Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the time the vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig.12.7. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporises. The vapours thus become richer in low boiling component. The vapours of low boiling component ascend to the top of the column. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vaporisation unit in the fractionating column is called a ***theoretical plate.*** Commercially, columns with hundreds of plates are available.

Fig.12.7 *Different types of fractionating columns.*

One of the technological applications of fractional distillation is to separate different fractions of ***crude oil in petroleum industry.***

Distillation under reduced pressure: This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump (Fig.12.8). Glycerol can be separated from **spent-lye in soap industry** by using this technique.

Steam Distillation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. $p = p_1 + p_2$. Since p_1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point.

Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture (Fig.12.9).

12.8.4 Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking

Fig.12.8 *Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.*

Fig.12.9 *Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.*

it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separatory funnel as shown in Fig. 12.10. If the organic compound is less

Fig.12.10 *Differential extraction. Extraction of compound takes place based on difference in solubility*

soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of ***continuous extraction*** is employed in such cases. In this technique same solvent is repeatedly used for extraction of the compound.

12.8.5 Chromatography

Chromatography is an important technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds. The name chromatography is based on the Greek word *chroma*, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the mobile phase.

Based on the principle involved, chromatography is classified into different categories. Two of these are:

(a) Adsorption chromatography, and
(b) Partition chromatography.

***a) Adsorption Chromatography*:** Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

(a) Column chromatography, and
(b) Thin layer chromatography.

Column Chromatography: Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end (Fig. 12.11). The mixture adsorbed on

Fig.12.11 *Column chromatography. Different stages of separation of components of a mixture.*

adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column (Fig.12.11).

Thin Layer Chromatography: Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as *thin layer chromatography plate or chromaplate*. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the eluant (Fig. 12.12a). As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor** i.e. **$R_f$value** (Fig.12.12 b).

Fig.12.12 (a) *Thin layer chromatography. Chromatogram being developed.*

Fig.12.12 (b) *Developed chromatogram.*

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds, which are invisible to the eye but fluoresce, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution (Fig.12.12b).

Partition Chromatography: Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents (Fig. 12.13). This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either

Fig.12.13 *Paper chromatography. Chromatography paper in two different shapes.*

under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

12.9 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

12.9.1 Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$\underset{\text{White}}{5H_2O + CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$$

12.9.2 Detection of Other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by **"Lassaigne's test"**. The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} Na\,X$$

(X = Cl, Br or I)

C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

(A) Test for Nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

(B) Test for Sulphur

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$S^{2-} + Pb^{2+} \longrightarrow \underset{\text{Black}}{PbS}$$

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a

violet colour further indicates the presence of sulphur.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$$

In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

$$Na + C + N + S \longrightarrow NaSCN$$

$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}$$

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

(C) Test for Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$$X^- + Ag^+ \longrightarrow AgX$$

X represents a halogen – Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

(D) Test for Phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow$$

$$\underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

12.10 QUANTITATIVE ANALYSIS

The percentage composition of elements present in an organic compound is determined by the methods based on the following principles:

12.10.1 Carbon and Hydrogen

Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

$$C_xH_y + (x + y/4)\,O_2 \longrightarrow x\,CO_2 + (y/2)\,H_2O$$

The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series (Fig.12.14). The

Fig.12.14 *Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.*

increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m_1 and m_2 g respectively;

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

Problem 12.20

On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Solution

$$\text{Percentage of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95\%$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58\%$$

12.10.2 Nitrogen

There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

(i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x + y/2)\ CuO \longrightarrow x\ CO_2 + y/2\ H_2O + z/2\ N_2 + (2x + y/2)\ Cu$$

Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig.12.15).

Fig.12.15 *Dumas method. The organic compound yields nitrogen gas on heating it with copper(II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.*

Let the mass of organic compound = m g
Volume of nitrogen collected = V_1 mL
Room temperature = T_1K

$$\text{Volume of nitrogen at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1}$$

(Let it be V mL)

Where p_1 and V_1 are the pressure and volume of nitrogen, p_1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of p_1 is obtained by the relation;

p_1= Atmospheric pressure – Aqueous tension

22400 mL N_2 at STP weighs 28 g.

$$V \text{ mL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

Problem 12.21

In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15 mm)

Solution

Volume of nitrogen collected at 300K and 715mm pressure is 50 mL
Actual pressure = 715-15 =700 mm

$$\text{Volume of nitrogen at STP} = \frac{273 \times 700 \times 50}{300 \times 760}$$
$$= 41.9 \text{ mL}$$

22,400 mL of N_2 at STP weighs = 28 g

$$41.9 \text{ mL of nitrogen weighs} = \frac{28 \times 41.9}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22400 \times 0.3}$$
$$= 17.46\%$$

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate (Fig. 12.16). The resulting acid mixture is then heated with excess of sodium

Fig.12.16 *Kjeldahl method. Nitrogen-containing compound is treated with concentrated H_2SO_4 to get ammonium sulphate which liberates ammonia on treating with NaOH; ammonia is absorbed in known volume of standard acid.*

hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

$$\text{Organic compound} + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Let the mass of organic compound taken = m g
Volume of H2SO4 of molarity, M,
taken = V mL

Volume of NaOH of molarity, M, used for titration of excess of H_2SO_4 = V_1 mL

V_1mL of NaOH of molarity M

= V_1 /2 mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused = $(V - V_1/2)$ mL

$(V - V_1/2)$ mL of H_2SO_4 of molarity M

= $2(V-V_1/2)$ mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains 17g NH_3 or 14 g of N

$2(V-V_1/2)$ mL of NH_3 solution of molarity M contains:

$$\frac{14 \times M \times 2(V - V_1/2)}{1000} \text{ g N}$$

$$\text{Percentage of N} = \frac{14 \times M \times 2(V\text{-}V_1/2)}{1000} \times \frac{100}{m}$$

$$= \frac{1.4 \times M \times 2(V\text{-}V_1/2)}{m}$$

Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

Problem 12.22

During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

Solution

1 M of 10 mL H_2SO_4=1M of 20 mL NH_3
1000 mL of 1M ammonia contains 14 g nitrogen
20 mL of 1M ammonia contains $\frac{14 \times 20}{1000}$ g nitrogen

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

12.10.3 Halogens

Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, (Fig.12.17) in a furnace. Carbon and hydrogen

Fig. 12.17 *Carius method. Halogen containing organic compound is heated with fuming nitric acid in the presence of silver nitrate.*

present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

Let the mass of organic compound taken = m g

Mass of AgX formed = m_1 g

1 mol of AgX contains 1 mol of X

Mass of halogen in m_1g of AgX

$$= \frac{\text{atomic mass of X} \times m_1 \text{g}}{\text{molecular mass of AgX}}$$

Percentage of halogen

$$= \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$$

Problem 12.23

In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Solution

Molar mass of AgBr = 108 + 80 = 188 g mol^{-1}

188 g AgBr contains 80 g bromine

0.12 g AgBr contains $\frac{80 \times 0.12}{188}$ g bromine

$$\text{Percentage of bromine} = \frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04\%$$

12.10.4 Sulphur

A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution in water. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.

Let the mass of organic compound taken = m g

and the mass of barium sulphate formed = m_1g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

m_1 g $BaSO_4$ contains $\frac{32 \times m_1}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Problem 12.24

In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Solution

Molecular mass of $BaSO_4$ = 137+32+64 = 233 g

233 g $BaSO_4$ contains 32 g sulphur

0.4813 g $BaSO_4$ contains $\frac{32 \times 0.4813}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10\%$$

12.10.5 Phosphorus

A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ by adding magnesia mixture which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken = m g and mass of ammonium phospho molydate = m_1g

Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877 g

$$\text{Percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m}\%$$

If phosphorus is estimated as $Mg_2P_2O_7$,

$$\text{Percentage of phosphorus} = \frac{62 \times m_1 \times 100}{222 \times m}\%$$

where, 222 u is the molar mass of $Mg_2P_2O_7$, m, the mass of organic compound taken, m_1, the mass of $Mg_2P_2O_7$ formed and 62, the mass of two phosphorus atoms present in the compound $Mg_2P_2O_7$.

12.10.6 Oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:

A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{other gaseous products}$$

$$2C + O_2 \xrightarrow{1373\,K} 2CO$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

The percentage of oxygen can be derived from the amount of carbon dioxide or iodine produced.

Let the mass of organic compound taken = m g

Mass of carbon dioxide = m_1 g

44 g carbon dioxide = 32 g oxygen

m_1 g carbon dioxide contains $\frac{32 \times m_1}{44}$ g O_2

$$\text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{44 \times m}\ \%$$

Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as CHN *elemental analyser*. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book.

SUMMARY

In this unit, we have learnt some basic concepts in structure and reactivity of organic compounds, which are formed due to covalent bonding. The nature of the covalent bonding in organic compounds can be described in terms of **orbitals hybridisation** concept, according to which carbon can have sp^3, sp^2 and sp hybridised orbitals. The sp^3, sp^2 and sp hybridised carbons are found in compounds like methane, ethene and ethyne respectively. The tetrahedral shape of methane, planar shape of ethene and linear shape of ethyne can be understood on the basis of this concept. A sp^3 hybrid orbital can overlap with 1*s* orbital of hydrogen to give a carbon - hydrogen (C–H) single bond (sigma, σ bond). Overlap of a sp^2 orbital of one carbon with sp^2 orbital of another results in the formation of a carbon–carbon σ bond. The unhybridised *p* orbitals on two adjacent carbons can undergo lateral (side-by-side) overlap to give a pi (π) bond. Organic compounds can be represented by various structural formulas. The three dimensional representation of organic compounds on paper can be drawn by **wedge** and **dash** formula.

Organic compounds can be classified on the basis of their structure or the functional groups they contain. A **functional group** is an atom or group of atoms bonded together in a unique fashion and which determines the physical and chemical properties of the compounds. The naming of the organic compounds is carried out by following a set of rules laid down by the International Union of Pure and Applied Chemistry (**IUPAC**). In IUPAC nomenclature, the names are correlated with the structure in such a way that the reader can deduce the structure from the name.

Organic reaction mechanism concepts are based on the structure of the substrate molecule, fission of a covalent bond, the attacking reagents the electron displacement effects and the conditions of the reaction. These organic reactions involve breaking and making of covalent bonds. A covalent bond may be cleaved in **heterolytic** or **homolytic** fashion. A heterolytic cleavage yields **carbocations** or **carbanions**, while a homolytic cleavage gives **free radicals** as reactive intermediate. Reactions proceeding through heterolytic cleavage involve the complimentary pairs of reactive species. These are electron pair donor known as **nucleophile** and an electron pair acceptor known as **electrophile**. The **inductive**, **resonance**, **electromeric** and **hyperconjugation effects** may help in the polarisation of a bond making certain carbon atom or other atom positions as places of low or high electron densities.

Organic reactions can be broadly classified into following types; **substitution, addition, elimination** and **rearrangement** reactions.

Purification, qualitative and quantitative analysis of organic compounds are carried out for determining their structures. The methods of purification namely : sublimation, distillation and differential extraction are based on the difference in one or more physical properties. **Chromatography** is a useful technique of separation, identification and purification of compounds. It is classified into two categories : adsorption and partition chromatography. Adsorption chromatography is based on differential adsorption of various components of a mixture on an adsorbent. Partition chromatography involves continuous partitioning of the components of a mixture between stationary and mobile phases. After getting the compound in a pure form, its qualitative analysis is carried out for detection of elements present in it. Nitrogen, sulphur, halogens and phosphorus are detected by **Lassaigne's test**. Carbon and hydrogen are estimated by determining the amounts of carbon dioxide and water produced. Nitrogen is estimated by **Dumas** or **Kjeldahl's** method and halogens by **Carius** method. Sulphur and phosphorus are estimated by oxidising them to sulphuric and phosphoric acids respectively. The percentage of oxygen is usually determined by difference between the total percentage (100) and the sum of percentages of all other elements present.

EXERCISES

12.1 What are hybridisation states of each carbon atom in the following compounds ?
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6

12.2 Indicate the σ and π bonds in the following molecules :
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2=C=CH_2$, CH_3NO_2, $HCONHCH_3$

12.3 Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethyl butanal, Heptan-4-one.

12.4 Give the IUPAC names of the following compounds :

(a)

(b)

(c)

(d)

(e)

(f) Cl_2CHCH_2OH

12.5 Which of the following represents the correct IUPAC name for the compounds concerned ? (a) 2,2-Dimethylpentane or 2-Dimethylpentane (b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane (c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane (d) But-3-yn-1-ol or But-4-ol-1-yne.

12.6 Draw formulas for the first five members of each homologous series beginning with the following compounds. (a) H–COOH (b) CH_3COCH_3 (c) $H–CH=CH_2$

12.7 Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :

(a) 2,2,4-Trimethylpentane

(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid

(c) Hexanedial

12.8 Identify the functional groups in the following compounds

(a)

(b)

(c)

12.9 Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why ?

12.10 Explain why alkyl groups act as electron donors when attached to a π system.

12.11 Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(a) C_6H_5OH (b) $C_6H_5NO_2$ (c) $CH_3CH=CHCHO$ (d) $C_6H_5–CHO$ (e) $C_6H_5–\overset{+}{C}H_2$

(f) $CH_3CH=CH\overset{+}{C}H_2$

12.12 What are electrophiles and nucleophiles ? Explain with examples.

12.13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

(a) $CH_3COOH + \mathbf{HO^-} \rightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + \mathbf{\bar{C}N} \rightarrow (CH_3)_2C(CN)(OH)$

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \rightarrow C_6H_5COCH_3$

12.14 Classify the following reactions in one of the reaction type studied in this unit.

(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH$

(b) $(CH_3)_2C=CH_2 + HCl \rightarrow (CH_3)_2ClC$

(c) $CH_3CH_2Br + HO^- \rightarrow CH_2=CH_2 + H_2C$

(d) $(CH_3)_3C-CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH$

12.15 What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors ?

(a)

(b)

(c)

12.16 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(a) $CH_3O - OCH_3 \rightarrow CH_3\dot{O} + \dot{O}CH_3$

(b)

(c)

(d)

12.17 Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

12.18 Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation (b) Distillation (c) Chromatography

12.19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

12.20 What is the difference between distillation, distillation under reduced pressure and steam distillation ?

12.21 Discuss the chemistry of Lassaigne's test.

12.22 Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.

12.23 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

12.24 Explain the principle of paper chromatography.

12.25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

12.26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

12.27 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

12.28 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation ?

12.29 Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

12.30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

12.31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

12.32 An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

12.33 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

12.34 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

12.35 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

12.36 In the organic compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the pair of hydridised orbitals involved in the formation of: $C_2 - C_3$ bond is:

(a) $sp - sp^2$ (b) $sp - sp^3$ (c) $sp^2 - sp^3$ (d) $sp^3 - sp^3$

12.37 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

12.38 Which of the following carbocation is most stable ?

(a) $(CH_3)_3C.\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C}$ (c) $CH_3CH_2\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}H\,CH_2CH_3$

12.39 The best and latest technique for isolation, purification and separation of organic compounds is:

(a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography

12.40 The reaction:

$CH_3CH_2I + KOH(aq) \rightarrow CH_3CH_2OH + KI$

is classified as :

(a) electrophilic substitution (b) nucleophilic substitution

(c) elimination (d) addition

UNIT 13

HYDROCARBONS

Objectives

After studying this unit, you will be able to

- name hydrocarbons according to IUPAC system of nomenclature;
- recognise and write structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons;
- learn about various methods of preparation of hydrocarbons;
- distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;
- draw and differentiate between various conformations of ethane;
- appreciate the role of hydrocarbons as sources of energy and for other industrial applications;
- predict the formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism;
- comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitution reactions of benzene;
- predict the directive influence of substituents in monosubstituted benzene ring;
- learn about carcinogenicity and toxicity.

"Hydrocarbons are the important sources of energy."

The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

13.1 CLASSIFICATION

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated

(ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes as you have already studied in Unit 12. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed.

13.2 ALKANES

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane (CH_4) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you get? You get C_2H_6. This hydrocarbon with molecular formula C_2H_6 is known as ethane. Thus you can consider C_2H_6 as derived from CH_4 by replacing one hydrogen atom by $-CH_3$ group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by $-CH_3$ group. The next molecules will be C_3H_8, C_4H_{10} ...

These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (*latin : parum*, little; *affinis*, affinity). Can you think of the general formula for alkane family or **homologous series**? The general formula for alkanes is C_nH_{2n+2}, where n stands for number of carbon atoms and 2n+2 for number of hydrogen atoms in the molecule. Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 13.1) which is multiplanar, in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5°.

Fig. 13.1 *Structure of methane*

In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 12). You have already read that C–C and C–H σ bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1*s* orbitals of hydrogen atoms.

13.2.1 Nomenclature and Isomerism

You have already read about nomenclature of different classes of organic compounds in Unit 12. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C_4H_{10}. Four carbon atoms of C_4H_{10} can be joined either in a continuous chain or with a branched chain in the following two ways :

I

Butane (*n*- butane), (b.p. 273 K)

II

2-Methylpropane (isobutane)
(b.p.261 K)

In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C_5H_{12}? They can be arranged in three ways as shown in structures III–V

III

Pentane (*n*-pentane)
(b.p. 309 K)

IV

2-Methylbutane (isopentane)
(b.p. 301 K)

V

2,2-Dimethylpropane (neopentane)
(b.p. 282.5 K)

Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as **structural isomers**. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as **chain isomers**. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

Problem 13.1

Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

Solution

(i) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

n-Hexane

(ii) $CH_3 - CH(CH_3) - CH_2 - CH_2 - CH_3$

2-Methylpentane

(iii) $CH_3 - CH_2 - CH(CH_3) - CH_2 - CH_3$

3-Methylpentane

(iv) $CH_3 - CH(CH_3) - CH(CH_3) - CH_3$

2,3-Dimethylbutane

(v) $CH_3 - C(CH_3)_2 - CH_2 - CH_3$

2,2 - Dimethylbutane

Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1°, 2°, 3° and 4° carbon atoms in structures I

to V ? If you go on constructing structures for higher alkanes, you will be getting still larger number of isomers. C_6H_{14} has got five isomers and C_7H_{16} has nine. As many as 75 isomers are possible for $C_{10}H_{22}$.

In structures II, IV and V, you observed that $-CH_3$ group is attached to carbon atom numbered as 2. You will come across groups like $-CH_3$, $-C_2H_5$, $-C_3H_7$ etc. attached to carbon atoms in alkanes or other classes of compounds. These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom. General formula for alkyl groups is C_nH_{2n+1} (Unit 12).

Let us recall the general rules for nomenclature already discussed in Unit 12. Nomenclature of substituted alkanes can further be understood by considering the following problem:

Problem 13.2

Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of –OH groups at different carbons of the chain.

Solution

Structures of – C_5H_{11} group	**Corresponding alcohols**
(i) $CH_3-CH_2-CH_2-CH_2-CH_2-$	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$ Pentan-1-ol
(ii) $CH_3-\underset{\vert}{CH}-CH_2-CH_2-CH_3$	$CH_3-\underset{\vert\,OH}{CH}-CH_2-CH_2-CH_3$ Pentan-2-ol
(iii) $CH_3-CH_2-\underset{\vert}{CH}-CH_2-CH_2$	$CH_3-CH_2-\underset{\vert\,OH}{CH}-CH_2-CH_3$ Pentan-3-ol
(iv) $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-CH_2-$	$CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-CH_2-OH$ 3-Methylbutan-1-ol
(v) $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-$	$CH_3-CH_2-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-OH$ 2-Methylbutan-1-ol
(vi) $CH_3-\overset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}-CH_2-CH_3$	$CH_3-\overset{CH_3}{\overset{\vert}{\underset{\vert\,OH}{C}}}-CH_2-CH_3$ 2-Methylbutan-2-ol
(vii) $CH_3-\overset{CH_3}{\overset{\vert}{\underset{\vert\,CH_3}{C}}}-CH_2-$	$CH_3-\overset{CH_3}{\overset{\vert}{\underset{\vert\,CH_3}{C}}}-CH_2OH$ 2,2- Dimethylpropan-1-ol

Table 13.1 Nomenclature of a Few Organic Compounds

Structure and IUPAC Name	Remarks
(a) (4 – Ethyl – 2 – methylhexane)	Lowest sum and alphabetical arrangement
(b) (3,3-Diethyl-5-isopropyl-4-methyloctane)	Lowest sum and alphabetical arrangement
(c) 5-*sec*– Butyl-4-isopropyldecane	*sec* is not considered while arranging alphabetically; isopropyl is taken as one word
(d) 5-(2,2– Dimethylpropyl)nonane	Further numbering to the substituents of the side chain
(e) 3–Ethyl–5–methylheptane	Alphabetical priority order

Problem 13.3

Write IUPAC names of the following compounds :

(i) $(CH_3)_3\,C\,CH_2C(CH_3)_3$

(ii) $(CH_3)_2\,C(C_2H_5)_2$

(iii) tetra – *tert*-butylmethane

Solution

(i) 2, 2, 4, 4-Tetramethylpentane

(ii) 3, 3-Dimethylpentane

(iii) 3,3-Di-*tert*-butyl -2, 2, 4, 4 - tetramethylpentane

If it is important to write the correct IUPAC name for a given structure, it is equally important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2, 2–dimethylpentane in the following steps :

i) Draw the chain of five carbon atoms: C – C – C – C – C

ii) Give number to carbon atoms: $C^1 – C^2 – C^3 – C^4 – C^5$

iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2

iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms :

Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems.

Problem 13.4

Write structural formulas of the following compounds :

(i) 3, 4, 4, 5–Tetramethylheptane

(ii) 2,5-Dimethyhexane

Solution

(i)

(ii)

Problem 13.5

Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names.

(i) 2-Ethylpentane

(ii) 5-Ethyl – 3-methylheptane

Solution

(i)

Longest chain is of six carbon atoms and not that of five. Hence, correct name is 3-Methylhexane.

(ii)

Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane.

13.2.2 Preparation

Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods :

1. From unsaturated hydrocarbons

Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called **hydrogenation**. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen – hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3-CH_3} \quad (13.1)$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3} \quad (13.2)$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H} + 2H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3} \quad (13.3)$$

2. From alkyl halides

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

$$\underset{\text{Chloromethane}}{CH_3-Cl} + H_2 \xrightarrow{Zn,\ H^+} \underset{\text{Methane}}{CH_4} + HCl \quad (13.4)$$

$$C_2H_5-Cl + H_2 \xrightarrow{Zn,\ H^+} C_2H_6 + HCl$$

Chloroethane Ethane (13.5)

$$CH_3CH_2CH_2Cl + H_2 \xrightarrow{Zn, H^+} CH_3CH_2CH_3 + HCl$$

1-Chloropropane Propane (13.6)

ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction** and is used for the preparation of higher alkanes containing even number of carbon atoms.

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} CH_3-CH_3 + 2NaBr$$

Bromomethane Ethane (13.7)

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5-C_2H_5$$

Bromoethane n-Butane (13.8)

What will happen if two different alkyl halides are taken?

3. From carboxylic acids

i) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as **decarboxylation**.

$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Sodium ethanoate

Problem 13.6

Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction.

Solution

Butanoic acid,

$$CH_3CH_2CH_2COO^-Na^+ + NaOH \xrightarrow{CaO} CH_3CH_2CH_3 + Na_2CO_3$$

ii) ***Kolbe's electrolytic method*** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

$$2CH_3COO^-Na^+ + 2H_2O$$

Sodium acetate

$$\downarrow \text{Electrolysis}$$

$$CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH \quad (13.9)$$

The reaction is supposed to follow the following path :

i) $$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + 2Na^+$$

At anode:

$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\cdot\cdot}{\dot{O}}: \longrightarrow 2\dot{C}H_3 + 2CO_2\uparrow$$

Acetate ion Acetate free radical Methyl free radical

iii) $$H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3\uparrow$$

iv) **At cathode :**

$$H_2O + e^- \rightarrow {}^-OH + \dot{H}$$

$$2\dot{H} \rightarrow H_2\uparrow$$

Methane cannot be prepared by this method. Why?

13.2.3 Properties

Physical properties

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak van der Waals forces. Due to the weak forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do you think about solubility of alkanes in water based upon non-polar nature of alkanes? Petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. On the basis of this observation, what do you think about the nature of the greasy substance? You are correct if you say that grease (mixture of higher

alkanes) is non-polar and, hence, hydrophobic in nature. It is generally observed that in relation to solubility of substances in solvents, polar substances are soluble in polar solvents, whereas the non-polar ones in non-polar solvents *i.e., like dissolves like*.

Boiling point (b.p.) of different alkanes are given in Table 13.2 from which it is clear that there is a steady increase in boiling point with increase in molecular mass. This is due to the fact that the intermolecular van der Waals forces increase with increase of the molecular size or the surface area of the molecule.

You can make an interesting observation by having a look on the boiling points of three isomeric pentanes viz., (pentane, 2-methylbutane and 2,2-dimethylpropane). It is observed (Table 13.2) that pentane having a continuous chain of five carbon atoms has the highest boiling point (309.1K) whereas 2,2 – dimethylpropane boils at 282.5K. With increase in number of branched chains, the molecule attains the shape of a sphere. This results in smaller area of contact and therefore weak intermolecular forces between spherical molecules, which are overcome at relatively lower temperatures.

Chemical properties

As already mentioned, alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they undergo the following reactions under certain conditions.

1. Substitution reactions

One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. **Halogenation** takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atoms of alkanes are substituted are known as *substitution reactions*. As an example, chlorination of methane is given below:

Halogenation

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl \quad (13.10)$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl \quad (13.11)$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane}}{CHCl_3} + HCl \quad (13.12)$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl \quad (13.13)$$

Table 13.2 Variation of Melting Point and Boiling Point in Alkanes

Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.7	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.1	243.3
$C_{20}H_{42}$	Eicosane	282	615.0	236.2

$$CH_3\text{-}CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-CH_2Cl + HCl$$

Chloroethane (13.14)

It is found that the rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is : $3° > 2° > 1°$. Fluorination is too violent to be controlled. Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO_3 or HNO_3.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \quad (13.15)$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O \quad (13.16)$$

Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely initiation, propagation and termination as given below:

Mechanism

(i) *Initiation* : The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl–Cl bond is weaker than the C–C and C–H bond and hence, is easiest to break.

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \dot{Cl} + \dot{Cl}$$

Chlorine free radicals

(ii) *Propagation* : Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

$$\text{(a)}\ CH_4 + \dot{Cl} \xrightarrow{h\nu} \dot{C}H_3 + H-Cl$$

The methyl radical thus obtained attacks the second molecule of chlorine to form CH_3-Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

$$\text{(b)}\ \dot{C}H_3 + Cl-Cl \xrightarrow{h\nu} CH_3-Cl + \dot{C}l$$

Chlorine free radical

The chlorine and methyl free radicals generated above repeat steps (a) and (b) respectively and thereby setup a chain of reactions. The propagation steps (a) and (b) are those which directly give principal products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly haloginated products are formed.

$$CH_3Cl + \dot{Cl} \rightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl-Cl \rightarrow CH_2Cl_2 + \dot{Cl}$$

(iii)Termination: The reaction stops after some time due to consumption of reactants and / or due to the following side reactions :

The possible chain terminating steps are :

(a) $\dot{Cl} + \dot{Cl} \rightarrow Cl-Cl$

(b) $H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C-CH_3$

(c) $H_3\dot{C} + \dot{Cl} \rightarrow H_3C-Cl$

Though in (c), CH_3-Cl, the one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane.

2. Combustion

Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta_c H^\ominus = -890\ \text{kJ mol}^{-1} \quad (13.17)$$

$$C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \quad \Delta_c H^\ominus = -2875.84\ \text{kJ mol}^{-1} \quad (13.18)$$

The general combustion equation for any alkane is :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)\,H_2O \quad (13.19)$$

Due to the evolution of large amount of heat during combustion, alkanes are used as fuels.

During incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.

$$CH_4(g)+O_2(g)\xrightarrow[\text{combustion}]{\text{Incomplete}}C(s)+2H_2O(l) \quad (13.20)$$

3. Controlled oxidation

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

(i) $$2CH_4+O_2\xrightarrow{Cu/523K/100atm}\underset{\text{Methanol}}{2CH_3OH} \quad (13.21)$$

(ii) $$CH_4 + O_2\xrightarrow[\Delta]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O \quad (13.22)$$

(iii) $$2CH_3CH_3+3O_2\xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O \quad (13.23)$$

(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.

$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH} \xrightarrow[\text{Oxidation}]{KMnO_4} \underset{\text{2-Methylpropan-2-ol}}{(CH_3)_3COH} \quad (13.24)$$

4. Isomerisation

n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions.

$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\text{Anhy. } AlCl_3/HCl}$$

$$\underset{\text{2-Methylpentane}}{CH_3\underset{\underset{CH_3}{|}}{CH}-(CH_2)_2-CH_3} + \underset{\text{3-Methylpentane}}{CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3} \quad (13.25)$$

5. Aromatization

n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get **dehydrogenated** and cyclised to benzene and its homologues. This reaction is known as *aromatization* or *reforming*.

(13.26)

Toluene (C_7H_8) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ?

6. Reaction with steam

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas

$$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2 \quad (13.27)$$

7. Pyrolysis

Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called *pyrolysis* or *cracking*.

$$C_6H_{14} \xrightarrow{773K} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases} \quad (13.28)$$

Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene.

$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973K]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{other products} \quad (13.29)$$

13.2.4 Conformations

Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis. This permits free rotation about C–C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol^{-1} due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

Conformations of ethane : Ethane molecule (C_2H_6) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers** (conformers). Thus there are infinite number of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called **eclipsed** conformation and the other in which hydrogens are as far apart as possible is known as the **staggered** conformation. Any other intermediate conformation is called a **skew** conformation.It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by **Sawhorse** and **Newman projections**.

1. Sawhorse projections

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 13.2.

(i) Eclipsed (ii) Staggered

Fig. 13.2 *Sawhorse projections of ethane*

2. Newman projections

In this projection, the molecule is viewed at the C–C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig. 13.3.

(i) Eclipsed (ii) Staggered

Fig. 13.3 *Newman's projections of ethane*

Relative stability of conformations: As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called **torsional strain**. Magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called **dihedral angle** or **torsional angle**. Of all the conformations of ethane, the *staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain.* Thus it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol^{-1} through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

13.3 ALKENES

Alkenes are unsaturated hydrocarbons containing at least one double bond. What should be the general formula of alkenes? If there is one double bond between two carbon atoms in alkenes, they must possess two hydrogen atoms less than alkanes. Hence, general formula for alkenes is C_nH_{2n}. Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene (C_2H_4) was found to form an oily liquid on reaction with chlorine.

13.3.1 Structure of Double Bond

Carbon-carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol^{-1}) due to head-on overlapping of sp^2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about 284 kJ mol^{-1}) obtained by lateral or sideways overlapping of the two 2*p* orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm). You have already read that the pi (π) bond is a weaker bond due to poor sideways overlapping between the two 2*p* orbitals. Thus, the presence of the pi (π) bond makes alkenes behave as sources of loosely held mobile electrons. Therefore, alkenes are easily attacked by reagents or compounds which are in search of electrons. Such reagents are called **electrophilic reagents**. The presence of weaker π-bond makes alkenes unstable molecules in comparison to alkanes and thus, alkenes can be changed into single bond compounds by combining with the electrophilic reagents. Strength of the double bond (bond enthalpy, 681 kJ mol^{-1}) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy, 348 kJ mol^{-1}). Orbital diagrams of ethene molecule are shown in Figs. 13.4 and 13.5.

Fig. 13.4 *Orbital picture of ethene depicting σ bonds only*

13.3.2 Nomenclature

For nomenclature of alkenes in IUPAC system, the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to the double bond. The suffix '*ene*' replaces '*ane*'

Fig. 13.5 *Orbital picture of ethene showing formation of (a) π-bond, (b) π-cloud and (c) bond angles and bond lengths*

of alkanes. It may be remembered that first member of alkene series is: CH_2 (replacing n by 1 in C_nH_{2n}) known as methene but has a very short life. As already mentioned, first stable member of alkene series is C_2H_4 known as ethylene (common) or ethene (IUPAC). IUPAC names of a few members of alkenes are given below :

Structure	**IUPAC name**
$CH_3 - CH = CH_2$	Propene
$CH_3 - CH_2 - CH = CH_2$	But – 1 - ene
$CH_3 - CH = CH - CH_3$	But-2-ene
$CH_2 = CH - CH = CH_2$	Buta – 1,3 - diene
$CH_2 = C(CH_3) - CH_3$	2-Methylprop-1-ene
$CH_2 = CH - CH(CH_3) - CH_3$	3-Methylbut-1-ene

Problem 13.7

Write IUPAC names of the following compounds:

(i) $(CH_3)_2CH - CH = CH - CH_2 - CH = CH - CH(C_2H_5)$

(ii)

(iii) $CH_2 = C(CH_2CH_2CH_3)_2$

(iv) $CH_3CH_2CH_2CH_2 - CH = CH - C(CH_2CH_3) - CH_2 - CH(CH_3) - CH_3$

Solution

(i) 2,8-Dimethyl-3, 6-decadiene;

(ii) 1,3,5,7 Octatetraene;

(iii) 2-*n*-Propylpent-1-ene;

(iv) 4-Ethyl-2,6-dimethyl-dec-4-ene;

Problem 13.8

Calculate number of sigma (σ) and pi (π) bonds in the above structures (i-iv).

Solution

σ bonds : 33, π bonds : 2

σ bonds : 7, π bonds : 4

σ bonds : 23, π bond : 1

σ bonds : 41, π bond : 1

13.3.3 Isomerism

Alkenes show both structural isomerism and geometrical isomerism.

Structural isomerism : As in alkanes, ethene (C_2H_4) and propene (C_3H_6) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing C_4H_8 as molecular formula can be written in the following three ways:

I. $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_3$

But-1-ene

(C_4H_8)

II. $\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$

But-2-ene

(C_4H_8)

III. $\overset{1}{CH_2} = \overset{2}{C} - \overset{3}{CH_3}$
$\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad CH_3$

2-Methyprop-1-ene

(C_4H_8)

Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

Problem 13.9

Write structures and IUPAC names of different structural isomers of alkenes corresponding to C_5H_{10}.

Solution

(a) $CH_2 = CH - CH_2 - CH_2 - CH_3$

Pent-1-ene

(b) $CH_3 - CH{=}CH - CH_2 - CH_3$

Pent-2-ene

(c) $CH_3 - C = CH - CH_3$
$\quad\quad\quad |$
$\quad\quad CH_3$

2-Methylbut-2-ene

(d) $CH_3 - CH - CH = CH_2$
$\quad\quad\quad |$
$\quad\quad CH_3$

3-Methylbut-1-ene

(e) $CH_2 = C - CH_2 - CH_3$
$\quad\quad\quad |$
$\quad\quad CH_3$

2-Methylbut-1-ene

Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining with two atoms or groups. If the two atoms or groups attached to each carbon atom are different, they can be represented by YX C = C XY like structure. YX C = C XY can be represented in space in the following two ways :

(a) (b)

In (a), the two identical atoms *i.e.*, both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) i.e. disposition of atoms or groups in space in the two arrangements is different. Therefore, they are **stereoisomers**. They would have the same geometry if atoms or groups around C=C bond can be rotated but rotation around C=C bond is not free. It is restricted. For understanding this concept, take two pieces of strong cardboards and join them with the help of two nails. Hold one cardboard in your one hand and try to rotate the other. Can you really rotate the other cardboard ? The answer is no. The rotation is restricted. This illustrates that the restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called **geometrical isomers**. The isomer of the type (a), in which two identical atoms or groups lie on the same side of the double bond is called ***cis* isomer** and the other isomer of the type (b), in which identical atoms or groups lie on the opposite sides of the double bond is called ***trans* isomer** . Thus *cis* and *trans* isomers have the same structure but have different configuration (arrangement of atoms or groups in space). Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc. Geometrical or *cis-trans* isomers of but-2-ene are represented below :

cis-But-2-ene (b.p. 277 K) *trans*-But-2-ene (b.p. 274 K)

Cis form of alkene is found to be more polar than the *trans* form. For example, dipole moment of *cis*-but-2-ene is 0.33 Debye, whereas, dipole moment of the *trans* form is almost zero or it can be said that

trans-but-2-ene is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in the *trans*-but-2-ene, the two methyl groups are in opposite directions, Threfore, dipole moments of C-CH_3 bonds cancel, thus making the *trans* form non-polar.

cis-But-2-ene (μ = 0.33D) *trans*-But-2-ene (μ = 0)

In the case of solids, it is observed that the *trans* isomer has higher melting point than the *cis* form.

Geometrical or *cis-trans* isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW

Problem 13.10

Draw *cis* and *trans* isomers of the following compounds. Also write their IUPAC names :

(i) CHCl = CHCl

(ii) $C_2H_5CCH_3 = CCH_3C_2H_5$

Solution

(i)

cis-1, 2-Dichloroethene *trans-1, 2-Dichloroethene*

(ii)

cis-3, 4-Dimethylhex-3-ene *trans-3, 4-Dimethylhex -3-ene*

Problem 13.11

Which of the following compounds will show *cis-trans* isomerism?

(i) $(CH_3)_2C = CH - C_2H_5$

(ii) $CH_2 = CBr_2$

(iii) $C_6H_5CH = CH - CH_3$

(iv) $CH_3CH = CCl\,CH_3$

Solution

(iii) and (iv). In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atom.

13.3.4 Preparation

1. ***From alkynes:*** Alkynes on partial reduction with calculated amount of dihydrogen in the presence of *palladised* charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst.* Alkenes thus obtained are having *cis* geometry. However, alkynes on reduction with sodium in liquid ammonia form *trans* alkenes.

i) $RC \equiv CR^1 + H_2 \xrightarrow{Pd/C}$

Alkyne *cis*-Alkene (13.30)

ii) $RC \equiv CR^1 + H_2 \xrightarrow{Na/liquid\ NH_3}$

Alkyne *trans*-Alkene (13.31)

iii) $CH \equiv CH + H_2 \xrightarrow{Pd/C} CH_2 = CH_2$ (13.32)

Ethyne Ethene

iv) $CH_3 - C \equiv CH + H_2 \xrightarrow{Pd/C} CH_3 - CH = CH_2$

Propyne Propene (13.33)

Will propene thus obtained show geometrical isomerism? Think for the reason in support of your answer.

2. ***From alkyl halides:*** Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol,

say, ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation** i.e., removal of halogen acid. This is example of **β-elimination reaction**, since hydrogen atom is eliminated from the β carbon atom (carbon atom next to the carbon to which halogen is attached).

(X = Cl, Br, I)

(13.34)

Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tert > secondary > primary.

3. ***From vicinal dihalides:*** Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as *vicinal dihalides*. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as **dehalogenation**.

$$CH_2Br-CH_2Br+Zn \longrightarrow CH_2=CH_2+ZnBr_2 \quad (13.35)$$

$$CH_3CHBr-CH_2Br+Zn \longrightarrow CH_3CH=CH_2+ZnBr_2 \quad (13.36)$$

4. ***From alcohols by acidic dehydration:*** You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by R–OH where, R is C_nH_{2n+1}. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as **acidic dehydration of alcohols**. This reaction is also the example of β-elimination reaction since –OH group takes out one hydrogen atom from the β-carbon atom.

Ethanol Ethene

(13.37)

13.3.5 Properties

Physical properties

Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size *i.e.*, every – CH_2 group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds.

Chemical properties

Alkenes are the rich source of loosely held pi (π) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below:

1. ***Addition of dihydrogen:*** Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 13.2.2)

2. ***Addition of halogens :*** Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under

normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.

(i) $CH_2 = CH_2 + Br - Br \xrightarrow{CCl_4} CH_2(Br) - CH_2(Br)$

Ethene — 1,2 Dibromoethane

(13.38)

(ii) $CH_3 - CH = CH_2 + Cl - Cl \longrightarrow CH_3 - CH(Cl) - CH_2(Cl)$

Propene — 1,2-Dichloropropane

(13.39)

3. *Addition of hydrogen halides:* Hydrogen halides (HCl, HBr,HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes

Addition reaction of HBr to symmetrical alkenes

Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.

$$CH_2 = CH_2 + H - Br \longrightarrow CH_3 - CH_2 - Br \quad (13.40)$$

$$CH_3 - CH = CH - CH_3 + HBr \longrightarrow CH_3 - CH_2 - CH(Br)CH_3$$

(13.41)

Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

How will H – Br add to propene ? The two possible products are I and II.

$$CH_3 - CH = CH_2 + H - Br \longrightarrow \begin{cases} \text{I } CH_3 - CH(Br) - CH_3 \text{ — 2-Bromopropane} \\ \text{II } CH_3 - CH_2 - CH_2 - Br \text{ — 1-Bromopropane} \end{cases}$$

(13.42)

Markovnikov, a Russian chemist made a generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called **Markovnikov rule.** The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I *i.e.,* 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction.

Mechanism

Hydrogen bromide provides an electrophile, H^+, which attacks the double bond to form carbocation as shown below :

$$\overset{3}{H_3C} - \overset{2}{CH} = \overset{1}{CH_2} + H - Br \xrightarrow{H^+}$$

$$H_3C - CH_2 - \overset{+}{C}H_2 + Br^- \qquad H_3C - \overset{+}{C}H - CH_3 + Br^-$$

(a) less stable primary carbocation — (b) more stable secondary carbocation

(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

(ii) The carbocation (b) is attacked by Br^- ion to form the product as follows :

$$Br^- \curvearrowright H_3C - \overset{+}{C}H - CH_3 \longrightarrow H_3C - CH(Br) - CH_3$$

2-Bromopropane (major product)

Anti Markovnikov addition or peroxide effect or Kharash effect

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and HI. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as *peroxide* or *Kharash* effect or addition reaction anti to Markovnikov rule.

$$CH_3-CH=CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-\underset{\underset{CH_2Br}{|}}{CH_2}$$

1-Bromopropane

(13.43)

Mechanism : Peroxide effect proceeds via free radical chain mechanism as given below:

(i)

$$\underset{\text{Benzoyl peroxide}}{C_6H_5-\overset{O}{\overset{||}{C}}-O-O-\overset{O}{\overset{||}{C}}-C_6H_5} \xrightarrow{\text{Homolysis}} 2C_6H_5-\overset{O}{\overset{||}{C}}-\underset{\cdot\cdot}{\dot{O}}: \rightarrow 2\dot{C}_6H_5 + 2CO_2$$

(ii) $\dot{C}_6H_5 + H-Br \xrightarrow{\text{Homolysis}} C_6H_6 + \dot{Br}$

(iii)

$$CH_3-CH=CH_2 + \dot{Br} \xrightarrow{\text{Homolysis}}$$

$$CH_3-\underset{\underset{Br}{|}}{CH}-\dot{C}H_2 \qquad CH_3-\dot{C}H-CH_2-Br$$

(a) (less stable primary free radical) (b) (more stable secondary free radical)

(iv) $CH_3-\dot{C}H-CH_2Br + H-Br \xrightarrow{\text{Homolysis}} CH_3-CH_2-CH_2Br + \dot{Br}$

(major product)

(v) $CH_3-\underset{\underset{Br}{|}}{CH}-\dot{C}H_2 + H-Br \xrightarrow{\text{Homolysis}} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + \dot{Br}$

(minor product)

The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger (430.5 kJ mol^{-1}) than H–Br bond (363.7 kJ mol^{-1}), is not cleaved by the free radical, whereas the H–I bond is weaker (296.8 kJ mol^{-1}) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

Problem 13.12

Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

(i) in the absence of peroxide and

(ii) in the presence of peroxide.

Solution

(i) $CH_2=CH-CH_2-CH_2-CH_2-CH_3 + H-Br \xrightarrow{\text{No Peroxide}} CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$

Hex-1-ene → 2-Bromohexane

(ii) $CH_2=CH-CH_2-CH_2-CH_2-CH_3 + H-Br \xrightarrow{\text{Peroxide}} \underset{\underset{Br}{|}}{CH_2}-CH_2-CH_2-CH_2-CH_2-CH_3$

1-Bromohexane

4. ***Addition of sulphuric acid*** : Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.

$CH_3 - CH_2 - O\,SO_2 - OH$ or $C_2H_5HSO_4$

Ethyl hydrogen sulphate

(13.44)

Propyl hydrogen sulphate

(13.45)

5. ***Addition of water :*** In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

2-Methylpropene 2-Methylpropan-2-ol

(13.46)

6. ***Oxidation:*** Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of $KMnO_4$ solution is used as a test for unsaturation.

Ethane-1, 2-diol (Glycol)

(13.47)

$CH_3CH(OH)CH_2OH$

Propane-1, 2-diol

(13.48)

b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental conditions

2-Methlypropene Propan-2-one

(13.49)

But-2-ene Ethanoic acid

(13.50)

7. ***Ozonolysis :*** Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H_2O to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.

Propene ozonide

Ethanal Methanal

(13.51)

2-Methylpropene Ozonide

Propan-2-one

(13.52)

8. ***Polymerisation:*** You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as **polymerisation.** The simple compounds from which polymers

are made are called **monomers**. Other alkenes also undergo polymerisation.

$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \underset{\text{Polythene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n} \quad (13.53)$$

$$n(CH_3-CH=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \underset{\text{Polypropene}}{-\!\!\left(\underset{\underset{CH_3}{|}}{CH}-CH_2\right)\!\!-_n} \quad (13.54)$$

Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern for all of us.

13.4 ALKYNES

Like alkenes, alkynes are also unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is C_nH_{2n-2}.

The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

13.4.1 Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing '*ane*' by the suffix '*yne*'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 13.2.

You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne – (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as **position isomers**. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula C_5H_8? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures :

	Structure	IUPAC name
I.	$\overset{1}{H}\overset{}{C}\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3$	Pent–1-yne
II.	$H_3\overset{1}{C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_3$	Pent–2-yne
III.	$H_3\overset{4}{C}-\overset{3}{C}H(CH_3)-\overset{2}{C}\equiv\overset{1}{C}H$	3-Methylbut–1-yne

Structures I and II are position isomers and structures I and III or II and III are chain isomers.

Problem 13.13

Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

Solution

5th member of alkyne has the molecular formula C_6H_{10}. The possible isomers are:

Table 13.2 Common and IUPAC Names of Alkynes (C_nH_{2n-2})

Value of n	Formula	Structure	Common name	IUPAC name
2	C_2H_2	H-C≡CH	Acetylene	Ethyne
3	C_3H_4	CH_3-C≡CH	Methylacetylene	Propyne
4	C_4H_6	CH_3CH_2-C≡CH	Ethylacetylene	But-1-yne
4	C_4H_6	CH_3-C≡C-CH_3	Dimethylacetylene	But-2-yne

(a) $HC \equiv C - CH_2 - CH_2 - CH_2 - CH_3$
Hex-1-yne

(b) $CH_3 - C \equiv C - CH_2 - CH_2 - CH_3$
Hex-2-yne

(c) $CH_3 - CH_2 - C \equiv C - CH_2 - CH_3$
Hex-3-yne

(d) $HC \equiv C - CH(CH_3) - CH_2 - CH_3$
3-Methylpent-1-yne

(e) $HC \equiv C - CH_2 - CH(CH_3) - CH_3$
4-Methylpent-1-yne

(f) $CH_3 - C \equiv C - CH(CH_3) - CH_3$
4-Methylpent-2-yne

(g) $HC \equiv C - C(CH_3)_2 - CH_3$
3,3-Dimethylbut-1-yne

Position and chain isomerism shown by different pairs.

13.4.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 13.6.

Each carbon atom of ethyne has two *sp* hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two *sp* hybridised orbitals of the two carbon atoms. The remaining *sp* hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the 1*s* orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised *p* orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2*p* orbitals of one carbon atom are parallel to the 2*p*

Fig. 13.6 *Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.*

orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one C–C σ bond, two C–H σ bonds and two C–C π bonds. The strength of C≡C bond (bond enthalpy 823 kJ mol^{-1}) is more than those of C=C bond (bond enthalpy 681 kJ mol^{-1}) and C–C bond (bond enthalpy 348 kJ mol^{-1}). The C≡C bond length is shorter (120 pm) than those of C=C (133 pm) and C–C (154 pm). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.

13.4.3 Preparation

1. *From calcium carbide:* On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \qquad (13.55)$$

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO \qquad (13.56)$$

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \qquad (13.57)$$

2. *From vicinal dihalides :* Vicinal dihalides on treatment with alcoholic *potassium hydroxide* undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.

13.4.4 Properties

Physical properties

Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass.

Chemical properties

Alkynes show acidic nature, addition reactions and polymerisation reactions as follows :

A. Acidic character of alkyne: Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. Why is it so ? Has it something to do with their structures and the hybridisation ? You have read that hydrogen atoms in ethyne are attached to the *sp* hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene and sp^3 hybridised carbons in ethane. Due to the maximum percentage of *s* character (50%), the *sp* hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the sp^2 hybridised orbitals of carbon in ethene and the sp^3 hybridised orbital of carbon in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that the hydrogen atoms attached to the triply bonded carbons are acidic but not all the hydrogen atoms of alkynes.

$$HC \equiv CH + Na \rightarrow \underset{\text{Monosodium ethynide}}{HC \equiv C^-Na^+} + \tfrac{1}{2}H_2 \qquad (13.59)$$

$$HC \equiv C^-Na^+ + Na \rightarrow \underset{\text{Disodium ethynide}}{Na^+C^- \equiv C^-Na^+} + \tfrac{1}{2}H_2 \qquad (13.60)$$

$$CH_3 - C \equiv C - H + Na^+NH_2^- \rightarrow \underset{\text{Sodium propynide}}{CH_3 - C \equiv C^-Na^+} + NH_3 \qquad (13.61)$$

These reactions are not shown by alkenes and alkanes, hence used for distinction between alkynes, alkenes and alkanes. What about the above reactions with but-1-yne and but-2-yne ? Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

i) $HC \equiv CH > H_2C = CH_2 > CH_3 - CH_3$

ii) $HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$

B. *Addition reactions*: Alkynes contain a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides etc.

Formation of the addition product takes place according to the following steps.

$$-C\equiv C- + H-Z \xrightarrow{H^+} -\overset{H}{\overset{|}{C}}=\overset{\oplus}{C}- + :\bar{Z} \longrightarrow -\overset{H}{\overset{|}{C}}=\overset{Z}{\overset{|}{C}}-$$

Vinylic cation

The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

(i) *Addition of dihydrogen*

$$HC\equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3 \quad (13.62)$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propene}}{[CH_3-CH=CH_2]}$$

$$\downarrow H_2$$

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \quad (13.63)$$

(ii) Addition of halogens

$$CH_3-C\equiv CH + Br-Br \longrightarrow \underset{\text{1,2-Dibromopropene}}{[CH_3CBr=CHBr]}$$

$$\downarrow Br_2$$

$$CH_3-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{CH}}}}$$

1,1,2,2-Tetrabromopropane (13.64)

Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

(iii) Addition of hydrogen halides

Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form *gem* dihalides (in which two halogens are attached to the same carbon atom)

$$H-C\equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2=CH-Br]} \longrightarrow \underset{CH_3}{\underset{|}{CHBr_2}}$$

1,1-Dibromoethane (13.65)

$$CH_3-C\equiv CH + H-Br \longrightarrow \underset{\text{2-Bromopropene}}{[CH_3-\underset{Br}{\underset{|}{C}}=CH_2]}$$

$$\downarrow$$

$$CH_3-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3$$

2,2-Dibromopropane (13.66)

(iv) Addition of water

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.

$$\underset{\text{Ethyne}}{HC\equiv CH} + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_2=\underset{OH}{\underset{|}{C}}-H$$

$$\downarrow \text{Isomerisation}$$

$$CH_3-\underset{O}{\underset{||}{C}}-H$$

Ethanal (13.67)

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_3-\underset{O-H}{\underset{|}{C}}=CH_2$$

$$\text{Isomerisation} \downarrow$$

$$CH_3-\underset{O}{\underset{||}{C}}-CH_3$$

Propanone (13.68)

(v) Polymerisation

(a) *Linear polymerisation*: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH – CH = CH) and can be represented as $-(CH=CH-CH=CH)_n-$ Under special conditions, this polymer conducts electricity.

Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

(b) ***Cyclic polymerisation:*** Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:

(13.69)

Problem 13.14

How will you convert ethanoic acid into benzene?

Solution

13.5 AROMATIC HYDROCARBON

These hydrocarbons are also known as '**arenes**'. Since most of them possess pleasant odour (*Greek; aroma meaning pleasant smelling*), the class of compounds was named as '*aromatic compounds*'. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated but in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. However, there are examples of aromatic hydrocarbons which do not contain a benzene ring but instead contain other highly unsaturated ring. Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**. Some examples of arenes are given below:

13.5.1 Nomenclature and Isomerism

The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 12. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the *ortho* (*o*–), the 1, 3 or 1, 5 *as meta* (*m*–) and the 1, 4 as *para* (*p*–) disubstituted compounds. A few examples of derivatives of benzene are given below:

Methylbenzene (Toluene) 1,2-Dimethylbenzene (*o*-Xylene)

Friedrich August Kekulé, a German chemist was born in 1829 at Darmsdt in Germany. He became Professor in 1856 and Fellow of Royal Society in 1875. He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865, he found an answer to the challenging problem of benzene structure by suggesting that these chains can close to form rings. He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure. He described the discovery of benzene structure later as:

FRIEDRICH AUGUST KEKULÉ (7th September 1829–13th July 1896)

"I was sitting writing at my text book, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows, sometimes more closely fitted together; all twisting and turning in snake like motion. But look! What was that? One of the snakes had seized hold of it's own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;.... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth but let us beware of making our dreams public before they have been approved by the waking mind."(1890).

One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes.

1,3 Dimethylbenzene (*m*-Xylene)

1,4-Dimethylbenzene (*p*-Xylene)

13.5.2 Structure of Benzene

Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene, C_6H_6, indicates a high degree of unsaturation. This molecular formula did not account for its relationship to corresponding alkanes, alkenes and alkynes which you have studied in earlier sections of this unit. What do you think about its possible structure? Due to its unique properties and unusual stability, it took several years to assign its structure. Benzene was found to be a stable molecule and found to form a triozonide which indicates the presence of three double bonds. Benzene was further found to produce one and only one monosubstituted derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekulé in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.

or

The Kekulé structure indicates the possibility of two isomeric 1, 2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other, they are attached to the singly bonded carbons.

However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.

Even with this modification, Kekulé structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance.

Resonance and stability of benzene

According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekulé are the main contributing structures. The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon as shown in (C). The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring.

(A) (B) (C)

The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining sp^2 hybrid orbital of each carbon atom overlaps with *s* orbital of a hydrogen atom to form six C—H sigma bonds. Each carbon atom is now left with one unhybridised *p* orbital perpendicular to the plane of the ring as shown below:

The unhybridised *p* orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of *p* orbitals of C_1–C_2, C_3 – C_4, C_5 – C_6 or C_2 – C_3, C_4 – C_5, C_6 – C_1 respectively as shown in the following figures.

Fig. 13.7 (a)

Fig. 13.7 (b)

Structures shown in Fig. 13.7(a) and (b) correspond to two Kekulé's structure with localised π bonds. The internuclear distance

between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the *p* orbital of each carbon atom to overlap with the *p* orbitals of adjacent carbon atoms [Fig. 13.7 (c)]. This can be represented in the form of two doughtnuts (rings) of electron clouds [Fig. 13.7 (d)], one above and one below the plane of the hexagonal ring as shown below:

or

(electron cloud)

Fig. 13.7 (c) ***Fig. 13.7 (d)***

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 13.6 (a) or (b). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

X-Ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A or B) been correct, two types of C—C bond lengths were expected. However, X-ray data indicates that all the six C—C bond lengths are of the same order (139 pm) which is intermediate between C— C single bond (154 pm) and C—C double bond (133 pm). Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

13.5.3 Aromaticity

Benzene was considered as parent 'aromatic' compound. Now, the name is applied to all the ring systems whether or not having benzene ring, possessing following characteristics.

(i) Planarity

(ii) Complete delocalisation of the π electrons in the ring

(iii) Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \ldots$).

This is often referred to as **Hückel Rule**.

Some examples of aromatic compounds are given below:

Benzene

Cyclopentadienyl anion

Cycloheptatrienyl cation

(n=1, 6π electrons)

Naphthalene

(n = 2, 10 π electrons)

Anthracene

Phenanthrene

(n =3, 14 π electrons)

13.5.4 Preparation of Benzene

Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods.

(i) ***Cyclic polymerisation of ethyne:*** (Section 13.4.4)

(ii) ***Decarboxylation of aromatic acids:*** Sodium salt of benzoic acid on heating with sodalime gives benzene.

(13.70)

(iii) ***Reduction of phenol:*** Phenol is reduced to benzene by passing its vapours over heated zinc dust

(13.71)

13.5.5 Properties

Physical properties

Aromatic hydrocarbons are non- polar molecules and are usually colourless liquids or solids with a characteristic aroma. You are also familiar with naphthalene balls which are used in toilets and for preservation of clothes because of unique smell of the compound and the moth repellent property. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents. They burn with sooty flame.

Chemical properties

Arenes are characterised by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

Electrophilic substitution reactions

The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel Craft's alkylation and acylation reactions in which attacking reagent is an electrophile (E^+)

(i) ***Nitration:*** A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).

Nitrobenzene

(13.72)

(ii) ***Halogenation:*** Arenes react with halogens in the presence of a Lewis acid like anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ to yield haloarenes.

Chlorobenzene

(13.73)

(iii) ***Sulphonation:*** The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum).

Benzene sulphonic acid

(13.74)

(iv) ***Friedel-Crafts alkylation reaction:*** When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed.

Toluene

(13.75)

Ethylbenzene

(13.76)

Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of *n*-propyl benzene?

(v) ***Friedel-Crafts acylation reaction:*** The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ($AlCl_3$) yields acyl benzene.

(13.77)

(13.78)

If excess of electrophilic reagent is used, further substitution reaction may take place in which other hydrogen atoms of benzene ring may also be successively replaced by the electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ in dark yields hexachlorobenzene (C_6Cl_6)

(13.79)

Mechanism of electrophilic substitution reactions:

According to experimental evidences, S_E (S = substitution; E = electrophilic) reactions are supposed to proceed via the following three steps:

(a) Generation of the eletrophile

(b) Formation of carbocation intermediate

(c) Removal of proton from the carbocation intermediate

(a) ***Generation of electrophile $E^{\oplus}$:*** During chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$, being a Lewis acid helps in generation of the elctrophile $Cl^{\oplus}$, $R^{\oplus}$, $RC^{\oplus}O$ (acylium ion) respectively by combining with the attacking reagent.

In the case of nitration, the electrophile, nitronium ion, $\overset{+}{N}O_2$ is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I

Step II

It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium.

(b) ***Formation of Carbocation (arenium ion):*** Attack of electrophile results in the formation of σ-complex or arenium ion in which one of the carbon is sp^3 hybridised.

sigma complex (arenium ion)

The arenium ion gets stabilised by resonance:

Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at sp^3 hybridised carbon.

(c) *Removal of proton:* To restore the aromatic character, σ -complex releases proton from sp^3 hybridised carbon on attack by $[AlCl_4]^-$ (in case of halogenation, alkylation and acylation) and $[HSO_4]^-$ (in case of nitration).

Addition reactions

Under vigorous conditions, *i.e.*, at high temperature and/ or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.

Cyclohexane

(13.80)

Under utra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride, $C_6H_6Cl_6$ which is also called gammaxane.

Benzene hexachloride, (BHC)

(13.81)

Combustion: When heated in air, benzene burns with sooty flame producing CO_2 and H_2O

$$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \qquad (13.82)$$

General combustion reaction for any hydrocarbon may be given by the following chemical equation:

$$C_xH_y + (x + \frac{y}{4})\,O_2 \rightarrow x\,CO_2 + \frac{y}{2}\,H_2O \qquad (13.83)$$

13.5.6 Directive influence of a functional group in monosubstituted benzene

When monosubstituted benzene is subjected to further substitution, three possible disubstituted products are not formed in equal amounts. Two types of behaviour are observed. Either *ortho and para* products or *meta* product are predominantly formed. It has also been observed that this behaviour depends on the nature of the substituent already present in the benzene ring and not on the nature of the entering group. This is known as directive influence of substituents. Reasons for *ortho/ para or meta* directive nature of groups are discussed below:

Ortho and para directing groups: The groups which direct the incoming group to *ortho* and *para* positions are called *ortho* and *para* directing groups. As an example, let us discuss the directive influence of phenolic (–OH) group. Phenol is resonance hybrid of following structures:

It is clear from the above resonating structures that the electron density is more on *o* – and *p* – positions. Hence, the substitution takes place mainly at these positions. However, it may be noted that –I effect of – OH group also operates due to which the electron density on *ortho* and *para* positions of the benzene ring is slightly reduced. But the overall electron density increases at these positions of the ring

due to resonance. Therefore, –OH group **activates** the benzene ring for the attack by an electrophile. Other examples of **activating** groups are $-NH_2$, –NHR, $-NHCOCH_3$, $-OCH_3$, $-CH_3$, $-C_2H_5$, etc.

In the case of aryl halides, halogens are moderately **deactivating**. Because of their strong – I effect, overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on *o*– and *p*– positions is greater than that at the *m*-position. Hence, they are also *o*– and *p*– directing groups.

Meta directing group: The groups which direct the incoming group to *meta* position are called *meta* directing groups. Some examples of *meta* directing groups are $-NO_2$, –CN, –CHO, –COR, –COOH, –COOR, $-SO_3H$, etc.

Let us take the example of nitro group. Nitro group reduces the electron density in the benzene ring due to its strong–I effect. Nitrobenzene is a resonance hybrid of the following structures.

In this case, the overall electron density on benzene ring decreases making further substitution difficult, therefore these groups are also called '**deactivating groups**'. The electron density on *o*– and *p*– position is comparatively less than that at *meta* position. Hence, the electrophile attacks on comparatively electron rich *meta* position resulting in *meta* substitution.

13.6 CARCINOGENICITY AND TOXICITY

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below (see box).

1,2-Benzanthracene

3-Methylcholanthrene

1,2-Benzpyrene

1,2,5,6-Dibenzanthracene

9,10-Dimethyl-1,2-benzanthracene

SUMMARY

Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major **sources of energy**. **Petrochemicals** are the prominent starting materials used for the manufacture of a large number of commercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas), the main sources of energy for domestic fuels and the automobile industry, are obtained from petroleum. Hydrocarbons are classified as **open chain saturated** (alkanes) and **unsaturated** (alkenes and alkynes), **cyclic** (alicyclic) and **aromatic**, according to their structure.

The important reactions of alkanes are **free radical substitution**, **combustion**, **oxidation** and **aromatization**. Alkenes and alkynes undergo addition reactions, which are mainly **electrophilic additions**. Aromatic hydrocarbons, despite having unsaturation, undergo mainly **electrophilic substitution** reactions. These undergo addition reactions only under special conditions.

Alkanes show conformational isomerism due to free rotation along the C–C sigma bonds. Out of **staggered** and the **eclipsed** conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit **geometrical (*cis-trans*) isomerism** due to restricted rotation around the carbon–carbon double bond.

Benzene and **benzenoid** compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Hückel $(4n+2)\pi$ electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the incoming group. Some of the polynuclear hydrocarbons having fused benzene ring system have carcinogenic property.

EXERCISES

13.1 How do you account for the formation of ethane during chlorination of methane ?

13.2 Write IUPAC names of the following compounds :

(a) $CH_3CH{=}C(CH_3)_2$ (b) $CH_2{=}CH\text{-}C{\equiv}C\text{-}CH_3$

(c)

(d) $-CH_2-CH_2-CH{=}CH_2$

(e)

(f) $CH_3(CH_2)_4\ CH(CH_2)_3CH_3$
$\qquad\qquad\qquad\qquad |$
$\qquad\qquad\qquad\quad CH_2-CH(CH_3)_2$

(g) $CH_3-CH=CH-CH_2-CH=CH-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH=CH_2$

13.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated :

(a) C_4H_8 (one double bond) (b) C_5H_8 (one triple bond)

13.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds :

(i) Pent-2-ene (ii) 3,4-Dimethyl-hept-3-ene

(iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene

13.5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.

13.6 An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.

13.7 Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?

13.8 Write chemical equations for combustion reaction of the following hydrocarbons:

(i) Butane (ii) Pentene

(iii) Hexyne (iv) Toluene

13.9 Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.p. and why?

13.10 Why is benzene extra ordinarily stable though it contains three double bonds?

13.11 What are the necessary conditions for any system to be aromatic?

13.12 Explain why the following systems are not aromatic?

(i)

(ii)

(iii)

13.13 How will you convert benzene into

(i) *p*-nitrobromobenzene (ii) *m*- nitrochlorobenzene

(iii) *p* - nitrotoluene (iv) acetophenone?

13.14 In the alkane $H_3C-CH_2-C(CH_3)_2-CH_2-CH(CH_3)_2$, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these.

13.15 What effect does branching of an alkane chain has on its boiling point?

13.16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

13.17 Write down the products of ozonolysis of 1,2-dimethylbenzene (*o*-xylene). How does the result support Kekulé structure for benzene?

13.18 Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

13.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

13.20 How would you convert the following compounds into benzene?

(i) Ethyne (ii) Ethene (iii) Hexane

13.21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

13.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+

(a) Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene

(b) Toluene, *p*-$H_3C-C_6H_4-NO_2$, *p*-$O_2N-C_6H_4-NO_2$.

13.23 Out of benzene, *m*–dinitrobenzene and toluene which will undergo nitration most easily and why?

13.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

13.25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

UNIT 14

ENVIRONMENTAL CHEMISTRY

Objectives

After studying this unit, you will be able to

- understand the meaning of environmental chemistry;
- define atmospheric pollution, list reasons for global warming. green house effect and acid rain;
- identify causes for ozone layer depletion and its effects;
- give reasons for water pollution and know about international standards for drinking water;
- describe causes of soil pollution;
- suggest and adopt strategies for control of environmental pollution;
- appreciate the importance of green chemistry in day to day life.

"The world has achieved brilliance without wisdom, power without conscience. Ours is a world of nuclear giants and ethical infants."

You have already studied about environment in your earlier classes. Environmental studies deal with the sum of all social, economical, biological, physical and chemical interrelations with our surroundings. In this unit the focus will be on environmental chemistry. Environmental chemistry deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment. Let us discuss some important aspects of environmental chemistry.

14.1 ENVIRONMENTAL POLLUTION

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance, which causes pollution, is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings. Do you know, an average human being requires nearly 12-15 times more air than the food. So, even small amounts of pollutants in the air become significant compared to similar levels present in the food. Pollutants can be degradable, like discarded vegetables which rapidly break down by natural processes. On the other hand, pollutants which are slowly degradable, remain in the environment in an unchanged form for many decades. For example, substances such as dichlorodiphenyltrichloroethane (DDT), plastic materials, heavy metals, many chemicals, nuclear wastes etc., once released into the environment are difficult to remove. These

pollutants cannot be degraded by natural processes and are harmful to living organisms. In the process of environmental pollution, pollutants originate from a source and get transported by air or water or are dumped into the soil by human beings.

14.2 ATMOSPHERIC POLLUTION

The atmosphere that surrounds the earth is not of the same thickness at all heights. There are concentric layers of air or regions and each layer has different density. The lowest region of atmosphere in which the human beings along with other organisms live is called **troposphere**. It extends up to the height of ~ 10 km from sea level. Above the troposphere, between 10 and 50 km above sea level lies **stratosphere**. Troposphere is a turbulent, dusty zone containing air, much water vapour and clouds. This is the region of strong air movement and cloud formation. The stratosphere, on the other hand, contains dinitrogen, dioxygen, ozone and little water vapour.

Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface and thereby protecting humans and other animals from its effect.

14.2.1 Tropospheric Pollution

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere:

1. Gaseous air pollutants: These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
2. Particulate pollutants: These are dust, mist, fumes, smoke, smog etc.

1. Gaseous air pollutants

(a) Oxides of Sulphur: Oxides of sulphur are produced when sulphur containing fossil fuel is burnt. The most common species, sulphur dioxide, is a gas that is poisonous to both animals and plants. It has been reported that even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings. Sulphur dioxide causes irritation to the eyes, resulting in tears and redness. High concentration of SO_2 leads to stiffness of flower buds which eventually fall off from plants. Uncatalysed oxidation of sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of sulphur dioxide to sulphur trioxide.

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3(g)$$

The reaction can also be promoted by ozone and hydrogen peroxide.

$$SO_2\,(g) + O_3\,(g) \rightarrow SO_3(g) + O_2\,(g)$$

$$SO_2(g) + H_2O_2(l) \rightarrow H_2SO_4(aq)$$

(b) Oxides of Nitrogen: Dinitrogen and dioxygen are the main constituents of air. These gases do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen. NO_2 is oxidised to nitrate ion, NO_3^- which is washed into soil, where it serves as a fertilizer. In an automobile engine, (at high temperature) when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:

$$N_2\,(g) + O_2\,(g) \xrightarrow{1483K} 2NO(g)$$

NO reacts instantly with oxygen to give NO_2

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

Rate of production of NO_2 is faster when nitric oxide reacts with ozone in the stratosphere.

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

The irritant red haze in the traffic and congested places is due to oxides of nitrogen. Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis. Nitrogen dioxide is a lung irritant that can lead to an acute respiratory disease in children. It is toxic to living tissues also. Nitrogen dioxide is also harmful to various textile fibres and metals.

(c) Hydrocarbons: Hydrocarbons are composed of hydrogen and carbon only and are formed by incomplete combustion of fuel used in automobiles. Hydrocarbons are carcinogenic, *i.e.*, they cause cancer. They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

(d) Oxides of Carbon

(i) Carbon monoxide: Carbon monoxide (CO) is one of the most serious air pollutants. It is a colourless and odourless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon. Carbon monoxide is mainly released into the air by automobile exhaust. Other sources, which produce CO, involve incomplete combustion of coal, firewood, petrol, etc. The number of vehicles has been increasing over the years all over the world. Many vehicles are poorly maintained and several have inadequate pollution control equipments resulting in the release of greater amount of carbon monoxide and other polluting gases. Do you know why carbon monoxide is poisonous? It binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3–4 per cent, the oxygen carrying capacity of blood is greatly reduced. This oxygen deficiency, results into headache, weak eyesight, nervousness and cardiovascular disorder. This is the reason why people are advised not to smoke. In pregnant women who have the habit of smoking the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

(ii) Carbon dioxide: Carbon dioxide (CO_2) is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacture of cement. It is also emitted during volcanic eruptions. Carbon dioxide gas is confined to troposphere only. Normally it forms about 0.03 per cent by volume of the atmosphere. With the increased use of fossil fuels, a large amount of carbon dioxide gets released into the atmosphere. Excess of CO_2 in the air is removed by green plants and this maintains an appropriate level of CO_2 in the atmosphere. Green plants require CO_2 for photosynthesis and they, in turn, emit oxygen, thus maintaining the delicate balance. As you know, deforestation and burning of fossil fuel increases the CO_2 level and disturb the balance in the atmosphere. The increased amount of CO_2 in the air is mainly responsible for global warming.

Global Warming and Greenhouse Effect

About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

We all know that in cold places flowers, vegetables and fruits are grown in glass covered areas called greenhouse. Do you know that we humans also live in a greenhouse? Of course, we are not surrounded by glass but a blanket of air called the atmosphere, which has kept the temperature on earth constant for centuries. But it is now undergoing change, though slowly. Just as the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called *natural greenhouse effect* because it maintains the temperature and makes the earth perfect for life. In a greenhouse, visible light passes through the transparent glass and heats up the soil and the plants. The warm soil and plants emit infrared radiations. Since glass is opaque to infrared (heat) radiations, it partly reflects and partly absorbs these radiations. This mechanism keeps the energy of the sun trapped in the greenhouse. Similarly, carbon dioxide molecules also trap heat as they are transparent to sunlight but not to the heat radiation. If the amount of

carbon dioxide crosses the delicate proportion of 0.03 per cent, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming.

Besides carbon dioxide, other greenhouse gases are methane, water vapour, nitrous oxide, CFCs and ozone. Methane is produced naturally when vegetation is burnt, digested or rotted in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels. Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning etc. CFCs are also damaging the ozone layer (Section 14.2.2). Nitrous oxide occurs naturally in the environment. In recent years, their quantities have increased significantly due to the use of chemical fertilizers and the burning of fossil fuels. If these trends continue, the average global temperature will increase to a level which may lead to melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

Think it Over

What can we do to reduce the rate of global warming?

If burning of fossil fuels, cutting down forests and trees add to greenhouse gases in the atmosphere, we must find ways to use these just efficiently and judiciously. One of the simple things which we can do to reduce global warming is to minimise the use of automobiles. Depending upon the situation, one can use bicycle, public transport system, or go for carpool. We should plant more trees to increase the green cover. Avoid burning of dry leaves, wood etc. It is illegal to smoke in public places and work places, because it is harmful not only for the one who is smoking but also for others, and therefore, we should avoid it. Many people do not understand the greenhouse effect and the global warming. We can help them by sharing the information that we have.

Acid rain

We are aware that normally rain water has a pH of 5.6 due to the presence of H^+ ions formed by the reaction of rain water with carbon

Fig. 14.1 *Acid deposition*

dioxide present in the atmosphere.

$$H_2O\,(l) + CO_2\,(g) \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

When the pH of the rain water drops below 5.6, it is called acid rain.

Acid rain refers to the ways in which acid from the atmosphere is deposited on the earth's surface. Oxides of nitrogen and sulphur which are acidic in nature can be blown by wind along with solid particles in the atmosphere and finally settle down either on the ground as dry deposition or in water, fog and snow as wet deposition. (Fig. 14.1)

Acid rain is a byproduct of a variety of human activities that emit the oxides of sulphur and nitrogen in the atmosphere. As mentioned earlier, burning of fossil fuels (which contain sulphur and nitrogenous matter) such as coal and oil in power stations and furnaces or petrol and diesel in motor engines produce sulphur dioxide and nitrogen oxides. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain, because polluted air usually contains particulate matter that catalyse the oxidation.

$$2SO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 2H_2SO_4\,(aq)$$

$$4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightarrow 4HNO_3\,(aq)$$

Ammonium salts are also formed and can be seen as an atmospheric haze (aerosol of fine particles). Aerosol particles of oxides or ammonium salts in rain drops result in wet-deposition. SO_2 is also absorbed directly on both solid and liquid ground surfaces and is thus deposited as dry-deposition.

Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth. It causes respiratory ailments in human beings and animals. When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem. It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water. Acid rain damages buildings and other structures made of stone or metal. The Taj Mahal in India has been affected by acid rain.

Activity 1

You can collect samples of water from nearby places and record their pH values. Discuss your results in the class. Let us discuss how we can help to reduce the formation of acid rain.

This can be done by reducing the emission of sulphur dioxide and nitrogen dioxide in the atmosphere. We should use less vehicles driven by fossil fuels; use less sulphur content fossil fuels for power plants and industries. We should use natural gas which is a better fuel than coal or use coal with less sulphur content. Catalytic converters must be used in cars to reduce the effect of exhaust fumes on the atmosphere. The main component of the converter is a ceramic honeycomb coated with precious metals — Pd, Pt and Rh. The exhaust gases containing unburnt fuel, CO and NO_x, when pass through the converter at 573 K, are converted into CO_2 and N_2. We can also reduce the acidity of the soil by adding powdered limestone to neutralise the acidity of the soil. Many people do not know of acid rain and its harmful effects. We can make them aware by passing on this information and save the Nature.

Taj Mahal and Acid Rain

The air around the city of Agra, where the Taj Mahal is located, contains fairly high levels of sulphur and nitrogen oxides. It is mainly due to a large number of industries and power plants around the area. Use of poor quality of coal, kerosene and firewood as fuel for domestic purposes add up to this problem. The resulting acid rain reacts with marble, $CaCO_3$ of Taj Mahal ($CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$) causing damage to this wonderful monument that has attracted people from around the world. As a result, the monument is being slowly disfigured and the marble is getting discoloured and lustreless. The Government of India announced an action plan in early 1995 to prevent the disfiguring of this historical monument. Mathura refinery has already taken suitable measures to check the emission of toxic gases.

This plan aims at clearing the air in the **'Taj Trapezium'**– an area that includes the towns of Agra, Firozabad, Mathura and Bharatpur. Under this plan more than 2000 polluting industries lying inside the trapezium would switch over to the use of natural gas or liquefied petroleum gas instead of coal or oil. A new natural gas pipeline would bring more than half a million cubic metres of natural gas a day to this area. People living in the city will also be encouraged to use liquefied petroleum gas in place of coal, kerosene or firewood. Vehicles plying on highways in the vicinity of Taj would be encouraged to use low sulphur content diesel.

2. Particulate Pollutants

Particulates pollutants are the minute solid particles or liquid droplets in air. These are present in vehicle emissions, smoke particles from fires, dust particles and ash from industries. Particulates in the atmosphere may be viable or non-viable. The viable particulates *e.g.*, bacteria, fungi, moulds, algae etc., are minute living organisms that are dispersed in the atmosphere. Human beings are allergic to some of the fungi found in air. They can also cause plant diseases.

Non-viable particulates may be classified according to their nature and size as follows:

(a) Smoke particulates consist of solid or mixture of solid and liquid particles formed during combustion of organic matter. Examples are cigarette smoke, smoke from burning of fossil fuel, garbage and dry leaves, oil smoke etc.

(b) Dust is composed of fine solid particles (over 1μm in diameter), produced during crushing, grinding and attribution of solid materials. Sand from sand blasting, saw dust from wood works, pulverized coal, cement and fly ash from factories, dust storms etc., are some typical examples of this type of particulate emission.

(c) Mists are produced by particles of spray liquids and by condensation of vapours in air. Examples are sulphuric acid mist and herbicides and insecticides that miss their targets and travel through air and form mists.

(d) Fumes are generally obtained by the condensation of vapours during sublimation, distillation, boiling and several other chemical reactions. Generally, organic solvents, metals and metallic oxides form fume particles.

The effect of particulate pollutants are largely dependent on the particle size. Air-borne particles such as dust, fumes, mist etc., are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to lodge in the nasal passage, whereas particles of about 1.0 micron enter into lungs easily.

Lead used to be a major air pollutant emitted by vehicles. Leaded petrol used to be the primary source of air-borne lead emission in Indian cities. This problem has now been overcome by using unleaded petrol in most of the cities in India. Lead interferes with the development and maturation of red blood cells.

Smog

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog:

(a) Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. Chemically it is a reducing mixture and so it is also called as reducing smog.

(b) Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories. Photochemical smog has high concentration of oxidising agents and is, therefore, called as oxidising smog.

Formation of photochemical smog

When fossil fuels are burnt, a variety of pollutants are emitted into the earth's

troposphere. Two of the pollutants that are emitted are hydrocarbons (unburnt fuels) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which NO is converted into nitrogen dioxide (NO_2). This NO_2 in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom (Fig. 14.2).

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g) \quad \text{(i)}$$

Oxygen atoms are very reactive and combine with the O_2 in air to produce ozone.

$$O(g) + O_2(g) \rightleftharpoons O_3(g) \quad \text{(ii)}$$

The ozone formed in the above reaction (ii) reacts rapidly with the NO(g) formed in the reaction (i) to regenerate NO_2. NO_2 is a brown gas and at sufficiently high levels can contribute to haze.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \quad \text{(iii)}$$

Ozone is a toxic gas and both NO_2 and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

$$3CH_4 + 2O_3 \rightarrow \underset{\text{Formaldehyde}}{3CH_2=O} + 3H_2O$$

$$\underset{\text{Acrolein}}{CH_2=CHCH=O} \qquad \underset{\text{Peroxyacetyl nitrate (PAN)}}{CH_3\underset{\underset{O}{\|}}{C}OONO_2}$$

Effects of photochemical smog

The common components of photochemical smog are ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Photochemical smog causes serious health problems. Both ozone and PAN act as powerful eye irritants. Ozone and nitric oxide irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing. Photochemical smog leads to cracking of rubber and extensive damage to plant life. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

Fig. 14.2 *Photochemical smog occurs where sunlight acts on vehicle pollutants.*

How can photochemical smog be controlled ?

Many techniques are used to control or reduce the formation of photochemical smog. If we control the primary precursors of photochemical smog, such as NO_2 and hydrocarbons, the secondary precursors such as ozone and PAN, the photochemical smog will automatically be reduced. Usually catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants e.g., Pinus, Juniparus, Quercus, Pyrus and Vitis can metabolise nitrogen oxide and therefore, their plantation could help in this matter.

14.2.2 Stratospheric Pollution

Formation and Breakdown of Ozone

The upper stratosphere consists of considerable amount of ozone (O_3), which protects us from the harmful ultraviolet (UV) radiations (λ 255 nm) coming from the sun. These radiations cause skin cancer (melanoma) in humans. Therefore, it is important to maintain the ozone shield.

Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O_2(g) \xrightarrow{UV} O(g) + O(g)$$

$$O(g) + O_2(g) \underset{}{\overset{UV}{\rightleftharpoons}} O_3(g)$$

Ozone is thermodynamically unstable and decomposes to molecular oxygen. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules. In recent years, there have been reports of the depletion of this protective ozone layer because of the presence of certain chemicals in the stratosphere. The main reason of ozone layer depletion is believed to be the release of chlorofluorocarbon compounds (CFCs), also known as freons. These compounds are nonreactive, non flammable, non toxic organic molecules and therefore used in refrigerators, air conditioners, in the production of plastic foam and by the electronic industry for cleaning computer parts etc. Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and eventually reach the stratosphere. In stratosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + F_2Cl(g) \quad \text{(i)}$$

The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

$$\dot{C}l(g) + O_3(g) \rightarrow Cl\dot{O}(g) + O_2(g) \quad \text{(ii)}$$

Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

$$Cl\dot{O}(g) + O(g) \rightarrow \dot{C}l(g) + O_2(g) \quad \text{(iii)}$$

The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer.

The Ozone Hole

In 1980s atmospheric scientists working in Antarctica reported about depletion of ozone layer commonly known as ozone hole over the South Pole. It was found that a unique set of conditions was responsible for the ozone hole. In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction iv) gets hydrolysed to form hypochlorous acid (reaction (vi)). It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.

$$Cl\dot{O}(g) + NO_2(g) \rightarrow ClONO_2(g) \quad \text{(iv)}$$

$$\dot{C}l(g) + CH_4(g) \rightarrow \dot{C}H_3(g) + HCl(g) \quad \text{(v)}$$

$$ClONO_2(g) + H_2O(g) \rightarrow HOCl(g) + HNO_3(g) \quad \text{(vi)}$$

$$ClONO_2(g) + HCl(g) \rightarrow Cl_2(g) + HNO_3(g) \quad \text{(vii)}$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl_2 are photolysed by sunlight, as given in reactions (viii) and (ix).

$$HOCl\,(g) \xrightarrow{h\nu} \dot{O}H\,(g) + \dot{C}l(g) \qquad \text{(viii)}$$

$$Cl_2\,(g) \xrightarrow{h\nu} 2\dot{C}l\,(g) \qquad \text{(ix)}$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion as described earlier.

Effects of Depletion of the Ozone Layer

With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc. It has also been reported that plant proteins get easily affected by UV radiations which leads to the harmful mutation of cells. It also increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil. Increase in UV radiations damage paints and fibres, causing them to fade faster.

14.3 WATER POLLUTION

Water is essential for life. Without water there would be no life. We usually take water as granted for its purity, but we must ensure the quality of water. Pollution of water originates from human activities. Through different paths, pollution reaches surface or ground water. Easily identified source or place of pollution is called as point source. e.g., municipal and industrial discharge pipes where pollutants enter the water-source. Non point sources of pollution are those where a source of pollution cannot be easily identified, e.g., agricultural run off (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns), etc. Table 14.1 lists the major water pollutants and their sources.

14.3.1 Causes of Water Pollution

(i) Pathogens: The most serious water pollutants are the disease causing agents called pathogens. Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contain bacteria such as *Escherichia coli* and *Streptococcus faecalis* which cause gastrointestinal diseases.

(ii) Organic wastes: The other major water pollutant is organic matter such as leaves, grass, trash etc. They pollute water as a consequence of run off. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable.

The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. The amount of oxygen that water can hold in the solution is limited. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million), whereas oxygen in air is about 200,000 ppm. That is why even a moderate amount of organic matter when decomposes in water can deplete the water of its dissolved oxygen. The concentration of

Table 14.1 Major Water Pollutants

Pollutant	Source
Micro-organisms	Domestic sewage
Organic wastes	Domestic sewage, animal excreta and waste, decaying animals and plants, discharge from food processing factories.
Plant nutrients	Chemcial fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Water used for cooling in industries

dissolved oxygen in water is very important for aquatic life . If the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited. Oxygen reaches water either through atmosphere or from the process of photosynthesis carried out by many aquatic green plants during day light. However, during night, photosynthesis stops but the plants continue to respire, resulting in reduction of dissolved oxygen. The dissolved oxygen is also used by microorganisms to oxidise organic matter.

If too much of organic matter is added to water, all the available oxygen is used up. This causes oxygen dependent aquatic life to die. Thus, anaerobic bacteria (which do not require oxygen) begin to break down the organic waste and produce chemicals that have a foul smell and are harmful to human health. Aerobic (oxygen requiring) bacteria degrade these organic wastes and keep the water depleted in dissolved oxygen.

Thus, the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called **Biochemical Oxygen Demand (BOD)**. The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

(iii) Chemical Pollutants: As we know that water is an excellent solvent, water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel etc constitute an important class of pollutants. All these metals are dangerous to humans because our body cannot excrete them. Over the time, it crosses the tolerance limit. These metals then can damage kidneys, central nervous system, liver etc. Acids (like sulphuric acid) from mine drainage and salts from many different sources including raw salt used to melt snow and ice in the colder climates (sodium and calcium chloride) are water soluble chemical pollutants.

The organic chemicals are another group of substances that are found in polluted water. Petroleum products pollute many sources of water e.g., major oil spills in oceans. Other organic substances with serious impacts are the pesticides that drift down from sprays or runoff from lands. Various industrial chemicals like polychlorinated biphenyls, (PCBs) which are used as cleansing solvent, detergents and fertilizers add to the list of water pollutants. PCBs are suspected to be carcinogenic. Nowadays most of the detergents available are biodegradable. However, their use can create other problems. The bacteria responsible for degrading biodegradable detergent feed on it and grow rapidly. While growing, they may use up all the oxygen dissolved in water. The lack of oxygen kills all other forms of aquatic life such as fish and plants. Fertilizers contain phosphates as additives. The addition of phosphates in water enhances algae growth. Such profuse growth of algae, covers the water surface and reduces the oxygen concentration in water. This leads to anaerobic conditions, commonly with accumulation of abnoxious decay and animal death. Thus, bloom-infested water inhibits the growth of other living organisms in the water body. This process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as ***Eutrophication***.

14.3.2 International Standards for Drinking Water

The International Standards for drinking water are given below and they must be followed.

Fluoride: For drinking purposes, water should be tested for fluoride ion concentration. Its deficiency in drinking water is harmful to man and causes diseases such as tooth decay etc. Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1 mg dm^{-3}. The F^- ions make the enamel on teeth much harder by converting hydroxyapatite, $[3(Ca_3(PO_4)_2.Ca(OH)_2]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[3(Ca_3(PO_4)_2.CaF_2]$.

However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth, as reported from some parts of Rajasthan.

Lead: Drinking water gets contaminated with lead when lead pipes are used for transportation of water. The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Other metals: The maximum concentration of some common metals recommended in drinking water are given in Table 14.2.

Table 14.2 Maximum Prescribed Concentration of Some Metals in Drinking Water.

Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

Activity 2

You can visit local water sources and observe if the river/lake/tank/pond are unpolluted/slightly polluted/ moderately polluted or severely polluted by looking at water or by checking pH of water. Document the name of the river and the nearby urban or industrial site from where the pollution is generated. Inform about this to Pollution Control Board's office set up by Government to measure pollution levels. Ensure that appropriate action is taken. You can write to the press also. Do not dump waste into a household or industrial drain which can enter directly to any water body, such as, river, pond, stream or lake. Use compost instead of chemical fertilizers in gardens. Avoid the use of pesticides like DDT, malathion etc., at home and try to use dried neem leaves to help keep insects away. Add a few crystals of potassium permanganate ($KMnO_4$) or bleaching powder to the water tank of your house.

14.4 SOIL POLLUTION

India being an agriculture based economy gives high priority to agriculture, fisheries and livestock development. The surplus production is stored by governmental and non-governmental organisations for the lean season. The food loss during the storage also needs special attention. Have you ever seen the damages caused to the crops, food items by insects, rodents, weeds and crop diseases etc? How can we protect them? You are acquainted with some insecticides and pesticides for protection of our crops. However, these insecticides, pesticides and herbicides cause soil pollution. Hence, there is a need for their judicious use.

14.4.1 Pesticides

Prior to World War II, many naturally occurring chemicals such as nicotine (by planting tobacco plants in the crop field), were used as pest controlling substance for major crops in agricultural practices.

During World War II, DDT was found to be of great use in the control of malaria and other insect-borne diseases. Therefore, after the war, DDT was put to use in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. However, due to adverse effects, its use has been banned in India.

Pesticides are basically synthetic toxic chemicals with ecological repercussions. The repeated use of the same or similar pesticides give rise to pests that are resistant to that

group of pesticides thus making the pesticides ineffective. Therefore, as insect resistance of DDT increased, other organic toxins such as Aldrin and Dieldrin were introduced in the market by pesticide industry. Most of the organic toxins are water insoluble and non-biodegradable. These high persistent toxins are, therefore, transferred from lower trophic level to higher trophic level through food chain (Fig.14.3). Over the time, the concentration of toxins in higher animals reach a level which causes serious metabolic and physiological disorders.

Fig. 14.3 *At each trophic level, the pollutant gets 10 times concentrated.*

In response to high persistence of chlorinated organic toxins, a new series of less persistent or more bio-degradable products called organo-phosphates and carbamates have been introduced in the market. But these chemicals are severe nerve toxins and hence more harmful to humans. As a result, there are reports of some pesticides related deaths of agricultural field workers. Insects have become resistant to these insecticides also. The insecticide industry is engaged in developing new groups of insecticides. But one has to think, is this the only solution to pest menace?

These days, the pesticide industry has shifted its attention to **herbicides** such as sodium chlorate ($NaClO_3$), sodium arsinite (Na_3AsO_3) and many others. During the first half of the last century, the shift from mechanical to chemical weed control had provided the industry with flourishing economic market. But one must remember that these are also not environment friendly.

Most herbicides are toxic to mammals but are not as persistent as organo-chlorides. These chemicals decompose in a few months. Like organo-chlorides, these too become concentrated in the food web. Some herbicides cause birth defects. Studies show that corn-fields sprayed with herbicides are more prone to insect attack and plant disease than fields that are weeded manually.

Pesticides and herbicides represent only a very small portion of widespread chemical pollution. A large number of other compounds that are used regularly in chemical and industrial processes for manufacturing activities are finally released in the atmosphere in one or other form.

14.5 INDUSTRIAL WASTE

Industrial solid wastes are also sorted out as biodegradable and non-degradable wastes. Biodegradable wastes are generated by cotton mills, food processing units, paper mills, and textile factories.

Non-biodegradable wastes are generated by thermal power plants which produce fly ash; integrated iron and steel plants which produce blast furnace slag and steel melting slag. Industries manufacturing aluminium, zinc and copper produce mud and tailings. Fertilizer industries produce gypsum. Hazardous wastes such as inflammables, composite explosives or highly reactive substances are produced by industries dealing in metals, chemicals, drugs, pharmaceuticals, dyes, pesticides, rubber goods etc.

The disposal of non-degradable industrial solid wastes, if not done by a proper and suitable method, may cause serious threat to the environment. New innovations have led to different uses of waste material. Nowadays, fly ash and slag from the steel industry are utilised by the cement industry. Large

quantities of toxic wastes are usually destroyed by controlled incineration, whereas small quantities are burnt along with factory garbage in open bins. Moreover, solid wastes if not managed effectively, affect the components of the environment.

Do you know about waste recycling?

- Fuel obtained from plastic waste has high octane rating. It contains no lead and is known as "green fuel".
- Due to recent developments made in chemical and textile industries, clothes will be made from recycled plastic waste. These will be available soon in the global textile market.
- In India, our cities and towns face endless hours of power cut. We can also see piles of rotting garbage here and there. There is a good news that we can get rid from both these problems simultaneously. Technology has now been developed to produce electricity from the garbage. A pilot plant has been set up, where after removing ferrous metals, plastic, glass, paper etc. from garbage, it is mixed with water. It is then cultured with bacterial species for producing methane, commonly known as biogas. The remaining product is used as manure and biogas is used to produce electricity.

14.6 STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

After studying air, water, soil and industrial waste pollution in this unit, by now you must have started feeling the need of controlling environmental pollution: How can you save your immediate environment? Think of the steps/activities, which you would like to undertake for controlling air, water, soil and industrial waste pollution in your neighbourhood. Here, an idea about the strategies for the management of waste is given.

14.6.1 Waste Management

Solid waste is not the only waste, which you see in your household garbage box. Besides household discards, there are medical, agricultural, industrial and mining wastes. The improper disposal of wastes is one of the major causes of environmental degradation. Therefore, the management of wastes is of utmost importance.

Collection and Disposal

Domestic wastes are collected in small bins, which are then transferred to community bins by private or municipal workers. From these community bins, these are collected and carried to the disposable site. At the site, garbage is sorted out and separated into biodegradable and non-biodegradable materials. Non-biodegradable materials such as plastic, glass, metal scraps etc. are sent for recycling. Biodegradable wastes are deposited in land fills and are converted into compost.

The waste if not collected in garbage bins, finds its way into the sewers. Some of it is eaten by cattle. Non-biodegradable wastes like polythene bag, metal scraps, etc. choke the sewers and cause inconvenience. Polythene bags, if swallowed by cattle can cost their lives also.

As a normal practice, therefore, all domestic wastes should be properly collected and disposed. The poor management causes health problems leading to epidemics due to contamination of ground water. It is specially hazardous for those who are in direct contact with the waste such as rag pickers and workers involved in waste disposal, as they are the ones who handle waste materials mostly without protective device such as gloves or water proof boots and gas masks. What can you do for them?

14.7 GREEN CHEMISTRY

14.7.1 Introduction

It is well known fact that self-sufficiency in food has been achieved in India since late 20th century by using fertilizers and pesticides and exploring improved methods of farming, good quality seeds, irrigation etc. But over-exploitation of soil and excessive use of fertilizers and pesticides have resulted in the deterioration of soil, water and air.

The solution of this problem does not lie in stopping the process of development that has been set in; but to discover methods, which would help in the reduction of deterioration of the environment. *Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment. The byproducts generated during a process, if not used gainfully, add to the environmental pollution. Such processes are not only environmental unfriendly but also cost-ineffective. The waste generation and its disposal both are economically unsound. Utilisation of existing knowledge base for reducing the chemical hazards along with the developmental activities is the foundation of green chemistry.* Have you perceived the idea of green chemistry ? It is well known that organic solvents such as benzene, toluene, carbon tetrachloride etc., are highly toxic. One should be careful while using them.

As you know, a chemical reaction involves reactants, attacking reagents and the medium in which the reaction takes place. Extent of any reaction depends upon physical parameters like temperature, pressure and use of catalyst. In a chemical reaction, if reactants are fully converted into useful environmental friendly products by using an environment friendly medium then there would be no chemical pollutants introduced in the environment.

During a synthesis, care must be taken to choose starting materials that can be converted into end products with yield approximately upto 100 per cent. This can be achieved by arriving at optimum conditions of synthesis. It may be worthwhile to carry out synthetic reactions in aqueous medium since water has high specific heat and low volatility. Water is cost effective, noninflammable and devoid of any carcinogenic effects.

Nobel goes to Green Chemists

Yves Chauvin

Robert H. Grubbs

Richard R. Schrock

Yves Chauvin, Institut Français du Pétrole, Rueil-Malmaison France, **Robert H. Grubbs** California Institute of Technology (Caltech), Pasadena, CA, USA and **Richard R. Schrock** Massachusetts Institute of Technology (MIT), Cambridge, MA, USA won the 2005 Nobel Prize in chemistry for work that reduces hazardous waste in creating new chemicals. The trio won the award for their development of the metathesis method in organic synthesis –a way to rearrange groups of atoms within molecules that the Royal Swedish Academy of Sciences likened to a dance in which couples change partners. The metathesis has tremendous commercial potential in the pharmaceuticals, biotechnology and food stuffs production industries. It is also used in the development of revolutionary environmentally-friendlier polymers.

This represents a great step forward for 'green chemistry', reducing potentially hazardous waste through smarter production. Metathesis is an example of how important application of basic science is for the benefit of man, society and the environment.

14.7.2 Green Chemistry in day-to-day Life

(i) Dry Cleaning of Clothes

Tetra chlroroethene ($Cl_2C{=}CCl_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. The process using this compound is now being replaced by a process, where liquefied carbondioxide, with a suitable detergent is used. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water.

These days hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundary, which gives better results and makes use of lesser amount of water.

(ii) Bleaching of Paper

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst, which promotes the bleaching action of hydrogen peroxide, is used.

(iii) Synthesis of Chemicals

Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with an yield of 90%.

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{Pd(II)/Cu(II)(in water)}]{\text{Catalyst}} CH_3CHO\,(90\%)$$

Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.

Think it Over

What is our responsibility as a human being to protect our environment?

Some concepts, if followed by an individual, contribute towards a better quality of our environment and human life. Always set up a compost tin in your garden or any other place in your home and use it to produce manure for your plants to reduce the use of fertilizers. Use a cloth bag and avoid asking for plastic carry bags when you buy groceries, vegetables or any other item. See that all newspapers, glass, aluminum and other items in your area are recycled. We might have to take little trouble to locate such dealers. We must realize that we do not have solutions for every problem but we can concentrate on issues, which we feel strongly about and can do some thing about. We should take care to put into practice whatever we preach. Always remember environment protection begins with us.

SUMMARY

Environmental chemistry plays a major role in environment. Chemical species present in the environment are either naturally occurring or generated by human activities. **Environmental pollution** is the effect of undesirable changes in the surrounding that have harmful effects on plants, animals and human beings. Pollutants exist in all the three states of matter. We have discussed only those pollutants, which are due to human activities, and can be controlled. Atmospheric pollution is generally studied as **tropospheric** and **stratospheric pollution**. Troposphere is the lowest region of the atmosphere (~10 km) in which man along with other organisms including plants exist. Whereas stratosphere extends above troposphere up to 50 km above sea level. Ozone layer is one of the important constituents of stratosphere. Tropospheric pollution is basically due to various oxides of sulphur, nitrogen, carbon, halogens and also due to particulate pollutants. The gaseous pollutants come down to the earth in the form of **acid rain**. 75% of the solar energy reaching earth is absorbed by the earth surface and rest is radiated back to the atmosphere. These gases mentioned above trap the heat which result into **global warming**. It is important to realise that these very gases are also responsible for the life on the earth as they trap the requisite amount of solar

energy for the sustainance of life. The increase in the **greenhouse gases** is raising the temperature of the earth's atmosphere which, if not checked, may eventually result in melting of polar ice caps and consequently may submerge the costal land mass. Many human activities are producing chemicals, which are responsible for the **depletion of ozone layer** in the stratosphere, leading to the formation of **ozone hole**. Through the ozone hole, ultraviolet radiations can penetrate into the earth's atmosphere causing mutation of genes. Water is the elixir of life but the same water, if polluted by pathogens, organic wastes, toxic heavy metals, pesticides etc., will turn into poison. Therefore, one should take care to follow international standards to maintain purity levels of drinking water. Industrial wastes and excessive use of pesticides, result into pollution of land mass and water bodies. Judicious use of chemicals required for agricultural practices can lead to sustainable development. **Strategies for controlling environmental pollution** can be: (i) waste management *i.e.*, reduction of the waste and proper disposal, also recycling of materials and energy, (ii) adopting methods in day-to-day life, which results in the reduction of environmental pollution. The second method is a new branch of chemistry, which is in its infancy known as **green chemistry**. It utilizes the existing knowledge and practices so as to bring about reduction in the production of pollutants.

EXERCISES

14.1 Define environmental chemistry.

14.2 Explain tropospheric pollution in 100 words.

14.3 Carbon monoxide gas is more dangerous than carbon dioxide gas. Why?

14.4 List gases which are responsible for greenhouse effect.

14.5 Statues and monuments in India are affected by acid rain. How?

14.6 What is smog? How is classical smog different from photochemical smogs?

14.7 Write down the reactions involved during the formation of photochemical smog.

14.8 What are the harmful effects of photochemical smog and how can they be controlled?

14.9 What are the reactions involved for ozone layer depletion in the stratosphere?

14.10 What do you mean by ozone hole? What are its consequences?

14.11 What are the major causes of water pollution? Explain.

14.12 Have you ever observed any water pollution in your area? What measures would you suggest to control it?

14.13 What do you mean by Biochemical Oxygen Demand (BOD)?

14.14 Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution?

14.15 What are pesticides and herbicides? Explain giving examples.

14.16 What do you mean by green chemistry? How will it help decrease environmental pollution?

14.17 What would have happened if the greenhouse gases were totally missing in the earth's atmosphere? Discuss.

14.18 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

14.19 How can domestic waste be used as manure?

14.20 For your agricultural field or garden you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

Chemistry

Part I

Textbook for Class XII

CHEMISTRY Part I

Class XII

NCERT

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Unit

1

The Solid State

Objectives

After studying this Unit, you will be able to

- describe general characteristics of solid state;
- distinguish between amorphous and crystalline solids;
- classify crystalline solids on the basis of the nature of binding forces;
- define crystal lattice and unit cell;
- explain close packing of particles;
- describe different types of voids and close packed structures;
- calculate the packing efficiency of different types of cubic unit cells;
- correlate the density of a substance with its unit cell properties;
- describe the imperfections in solids and their effect on properties;
- correlate the electrical and magnetic properties of solids and their structure.

The vast majority of solid substances like high temperature superconductors, biocompatible plastics, silicon chips, etc. are destined to play an ever expanding role in future development of science.

We are mostly surrounded by solids and we use them more often than liquids and gases. For different applications we need solids with widely different properties. These properties depend upon the nature of constituent particles and the binding forces operating between them. Therefore, study of the structure of solids is important. The correlation between structure and properties helps in discovering new solid materials with desired properties like high temperature superconductors, magnetic materials, biodegradable polymers for packaging, biocompliant solids for surgical implants, etc.

From our earlier studies, we know that liquids and gases are called *fluids* because of their ability to flow. The fluidity in both of these states is due to the fact that the molecules are free to move about. On the contrary, the constituent particles in solids have fixed positions and can only oscillate about their mean positions. This explains the rigidity in solids. In crystalline solids, the constituent particles are arranged in regular patterns.

In this Unit, we shall discuss different possible arrangements of particles resulting in several types of structures. The correlation between the nature of interactions within the constituent particles and several properties of solids will also be explored. How these properties get modified due to the structural imperfections or by the presence of impurities in minute amounts would also be discussed.

11 General Characteristics of Solid State

In Class XI you have learnt that matter can exist in three states namely, solid, liquid and gas. Under a given set of conditions of temperature and pressure, which of these would be the most stable state of a given substance depends upon the net effect of two opposing factors. Intermolecular forces tend to keep the molecules (or atoms or ions) closer, whereas thermal energy tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state. The following are the characteristic properties of the solid state:

(i) They have definite mass, volume and shape.

(ii) Intermolecular distances are short.

(iii) Intermolecular forces are strong.

(iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.

(v) They are incompressible and rigid.

12 Amorphous and Crystalline Solids

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only *short range order*. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no *long range order*. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

Fig. 1.1: *Two dimensional structure of (a) quartz and (b) quartz glass*

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called *pseudo solids* or *super cooled liquids*. Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Fig. 1.2: *Anisotropy in crystals is due to different arrangement of particles along different directions.*

Crystalline solids are *anisotropic* in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction.

Amorphous solids on the other hand are *isotropic* in nature. It is because there is no *long range* order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarised in Table 1.1.

Table 1.1: Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Amorphous solids are useful materials. Glass, rubber and plastics find many applications in our daily lives. Amorphous silicon is one of the best photovoltaic material available for conversion of sunlight into electricity.

Intext Questions

1.1 Why are solids rigid?

1.2 Why do solids have a definite volume?

1.3 Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

1.4 Why is glass considered a super cooled liquid?

1.5 Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

1.3 Classification of Crystalline Solids

In Section 1.2, we have learnt about amorphous substances and that they have only short range order. However, most of the solid substances are crystalline in nature. For example, all the metallic elements like iron, copper and silver; non – metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene form crystalline solids.

Crystalline solids can be classified on the basis of nature of intermolecular forces operating in them into four categories viz., molecular, ionic, metallic and covalent solids. Let us now learn about these categories.

1.3.1 Molecular Solids

Molecules are the constituent particles of molecular solids. These are further sub divided into the following categories:

(i) *Non polar Molecular Solids*: They comprise of either atoms, for example, argon and helium or the molecules formed by non polar covalent bonds for example H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces about which you have learnt in Class XI. These solids are soft and non-conductors of electricity. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) *Polar Molecular Solids*: The molecules of substances like HCl, SO_2, *etc.* are formed by polar covalent bonds. The molecules in such solids are held together by relatively stronger dipole-dipole interactions. These solids are soft and non-conductors of electricity. Their melting points are higher than those of non polar molecular solids yet most of these are gases or liquids under room temperature and pressure. Solid SO_2 and solid NH_3 are some examples of such solids.

(iii) *Hydrogen Bonded Molecular Solids*: The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

1.3.2 Ionic Solids

Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces. These solids are hard and brittle in nature. They have high melting and boiling points. Since the ions are not free to move about, they are electrical insulators in the solid state. However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

1.3.3 Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons. These electrons are mobile and are evenly spread out throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free and mobile electrons are responsible for high electrical and thermal conductivity of metals. When an electric field is applied, these electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons. Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them. Metals are highly malleable and ductile.

1.3.4 Covalent or Network Solids

A wide variety of crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms throughout the crystal. They are also called **giant molecules**. Covalent bonds are strong and directional in nature, therefore atoms are held very strongly at their positions. Such solids are very hard and brittle. They have extremely high melting points and may even decompose before melting. They are insulators and do not conduct electricity. Diamond (Fig. 1.3) and silicon carbide are typical examples of such solids. Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure (Fig. 1.4). Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

Fig. 1.3: Network structure of diamond

Fig. 1.4: Structure of graphite

The different properties of the four types of solids are listed in Table 1.2.

Table 1.2: Different Types of Solids

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular solids						
(i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN, $C_{(graphite)}$	Hard	Insulators	Very high
				Soft	Conductor (exception)	

Intext Questions

1.6 Classify the following solids in different categories based on the nature of intermolecular forces operating in them:

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

1.7 Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

1.8 Ionic solids conduct electricity in molten state but not in solid state. Explain.

1.9 What type of solids are electrical conductors, malleable and ductile?

1.4 Crystal Lattices and Unit Cells

The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called *crystal lattice*. Thus, a regular three dimensional arrangement of points in space is called a **crystal lattice**. A portion of a crystal lattice is shown in Fig. 1.5.

Fig. 1.5: *A portion of a three dimensional cubic lattice and its unit cell.*

There are only 14 possible three dimensional lattices. These are called **Bravais Lattices** (after the French mathematician who first described them). The following are the characteristics of a crystal lattice:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by:

(i) its dimensions along the three edges, *a*, *b* and *c*. These edges may or may not be mutually perpendicular.

(ii) angles between the edges, α (between *b* and *c*) β (between *a* and *c*) and γ (between *a* and *b*). Thus, a unit cell is characterised by six parameters, *a*, *b*, *c*, α, β and γ.

These parameters of a typical unit cell are shown in Fig. 1.6.

Fig. 1.6: *Illustration of parameters of a unit cell*

1.4.1 Primitive and Centred Unit Cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

(a) Primitive Unit Cells

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell**.

(b) Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a **centred unit cell**. Centred unit cells are of three types:

(i) *Body-Centred Unit Cells:* Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

(ii) *Face-Centred Unit Cells:* Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) *End-Centred Unit Cells:* In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

In all, there are seven types of primitive unit cells (Fig. 1.7).

Fig. 1.7: *Seven primitive unit cells in crystals*

Their characteristics along with the centred unit cells they can form have been listed in Table 1.3.

Table 1.3: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	Graphite, ZnO,CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar)

Unit Cells of 14 Types of Bravais Lattices

Primitive (or simple) | Body-centred | Face-centred

The three cubic lattices: all sides of same length, angles between faces all 90°

Primitive | Body-centred

The two tetragonal: one side different in length to the other, two angles between faces all 90°

Primitive | End-centred | Body-centred | Face-centred

The four orthorhombic lattices: unequal sides, angles between faces all 90°

Primitive | End-centred

The two monoclinic lattices: unequal sides, two faces have angles different to 90°

1.5 Number of Atoms in a Unit Cell

1.5.1 Primitive Cubic Unit Cell

Fig. 1.8: In a simple cubic unit cell, each corner atom is shared between 8 unit cells.

or ion) actually belongs to a particular unit cell. In Fig. 1.9, a primitive cubic unit cell has been depicted in three different ways. Each small sphere in Fig. 1.9 (a) represents only the centre of the particle occupying that position and not its actual size. Such structures are called *open structures*. The arrangement of particles is easier to follow in open structures. Fig. 1.9 (b) depicts space-filling representation of the unit cell with actual particle size and Fig. 1.9 (c) shows the actual portions of different atoms present in a cubic unit cell.

In all, since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$ atom.

Fig. 1.9: A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

1.5.2 Body-Centred Cubic Unit Cell

A body-centred cubic (*bcc*) unit cell has an atom at each of its corners and also one atom at its body centre. Fig. 1.10 depicts (a) open structure (b) space filling model and (c) the unit cell with portions of atoms actually belonging to it. It can be seen that the atom at the

(a) (b) (c)

Fig. 1.10: *A body-centred cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.*

body centre wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

(i) 8 corners × $\frac{1}{8}$ per corner atom $= 8 \times \frac{1}{8}$ = 1 atom

(ii) 1 body centre atom = 1 × 1 = 1 atom

∴ Total number of atoms per unit cell = 2 atoms

1.5.3 Face-Centred Cubic Unit Cell

A face-centred cubic (*fcc*) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 1.11 that each atom located at the face-centre is shared between two adjacent unit cells and only $\frac{1}{2}$ of each atom belongs to a unit cell. Fig. 1.12 depicts (a) open structure (b) space-filling model and (c) the unit cell with portions of atoms actually belonging to it. Thus, in a face-centred cubic (*fcc*) unit cell:

(i) 8 corners atoms × $\frac{1}{8}$ atom per unit cell $= 8 \times \frac{1}{8}$ = 1 atom

(ii) 6 face-centred atoms × $\frac{1}{2}$ atom per unit cell = 6 × $\frac{1}{2}$ = 3 atoms

∴ Total number of atoms per unit cell = 4 atoms

Fig. 1.11: *An atom at face centre of unit cell is shared between 2 unit cells*

(a) (b) (c)

Fig 1.12: *A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.*

Intext Questions

1.10 Give the significance of a 'lattice point'.

1.11 Name the parameters that characterise a unit cell.

1.12 Distinguish between

(i) Hexagonal and monoclinic unit cells

(ii) Face-centred and end-centred unit cells.

1.13 Explain how much portion of an atom located at (i) corner and (ii) body-centre of a cubic unit cell is part of its neighbouring unit cell.

1.6 Close Packed Structures

In solids, the constituent particles are close-packed, leaving the minimum vacant space. Let us consider the constituent particles as identical hard spheres and build up the three dimensional structure in three steps.

(a) Close Packing in One Dimension

There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other (Fig. 1.13).

Fig. 1.13: *Close packing of spheres in one dimension*

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its **coordination number**. Thus, in one dimensional close packed arrangement, the coordination number is 2.

(b) Close Packing in Two Dimensions

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways.

(i) The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 1.14 (a).

Fig. 1.14: *(a) Square close packing (b) hexagonal close packing of spheres in two dimensions*

In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two dimensional coordination number is 4. Also, if the centres of these 4 immediate neighbouring spheres are joined, a square is formed. Hence this packing is called **square close packing in two dimensions**.

(ii) The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB type. In this arrangement there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon (Fig. 1.14b) hence this packing is called **two dimensional hexagonal close-packing.** It can be seen in Figure 1.14 (b) that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

(c) Close Packing in Three Dimensions

All real structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other. In the last Section, we discussed close packing in two dimensions which can be of two types; square close-packed and hexagonal close-packed. Let us see what types of three dimensional close packing can be obtained from these.

(i) *Three dimensional close packing from two dimensional square close-packed layers:* While placing the second square close-packed layer above the first we follow the same rule that was followed when one row was placed adjacent to the other. The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in Fig. 1.15. Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA.... type pattern. The lattice thus generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (See Fig. 1.9).

Fig. 1.15: *Simple cubic lattice formed by A A A .... arrangement*

(ii) *Three dimensional close packing from two dimensional hexagonal close packed layers:* Three dimensional close packed structure can be generated by placing layers one over the other.

(a) Placing second layer over the first layer

Let us take a two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed from Fig. 1.16 that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is

Fig. 1.16: *A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void*

formed. These voids are called **tetrahedral voids** because a *tetrahedron* is formed when the centres of these four spheres are joined. They have been marked as 'T' in Fig. 1.16. One such void has been shown separately in Fig. 1.17.

Fig 1.17
Tetrahedral and octahedral voids
(a) top view
(b) exploded side view and
(c) geometrical shape of the void.

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in Fig. 1.16. Such voids are surrounded by six spheres and are called **octahedral voids.** One such void has been shown separately in Fig. 1.17. The number of these two types of voids depend upon the number of close packed spheres.

Let the number of close packed spheres be N, then:

The number of octahedral voids generated = N

The number of tetrahedral voids generated = $2N$

(b) Placing third layer over the second layer

When third layer is placed over the second, there are two possibilities.

(i) *Covering Tetrahedral Voids*: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB ..... pattern. This structure is called hexagonal close packed (*hcp*) structure (Fig. 1.18). This sort of arrangement of atoms is found in many metals like magnesium and zinc.

Fig. 1.18 *(a) Hexagonal cubic close-packing exploded view showing stacking of layers of spheres (b) four layers stacked in each case and (c) geometry of packing.*

Fig. 1.19 *(a) ABCABC... arrangement of layers when octahedral void is covered (b) fragment of structure formed by this arrangement resulting in cubic closed packed (ccp) or face centred cubic (fcc) structure.*

(ii) *Covering Octahedral Voids*: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called "C' type. Only when fourth layer is placed, its spheres are aligned with

those of the first layer as shown in Figs. 1.18 and 1.19. This pattern of layers is often written as ABCABC ..... This structure is called cubic close packed (*ccp*) or face-centred cubic (*fcc*) structure. Metals such as copper and silver crystallise in this structure.

Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

1.6.1 Formula of a Compound and Number of Voids Filled

Earlier in the section, we have learnt that when particles are close-packed resulting in either *ccp* or *hcp* structure, two types of voids are generated. While the number of octahedral voids present in a lattice is equal to the number of close packed particles, the number of tetrahedral voids generated is twice this number. In ionic solids, the bigger ions (usually anions) form the close packed structure and the smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids. Not all octahedral or tetrahedral voids are occupied. In a given compound, the fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound, as can be seen from the following examples.

Example 1.1 A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make *ccp* and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution The *ccp* lattice is formed by the element Y. The number of octahedral voids generated would be equal to the number of atoms of Y present in it. Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the element Y. Thus, the atoms of elements X and Y are present in equal numbers or 1:1 ratio. Therefore, the formula of the compound is XY.

Example 1.2 Atoms of element B form *hcp* lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?

Solution The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only 2/3rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is 2 × (2/3):1 or 4:3 and the formula of the compound is A_4B_3.

Locating Tetrahedral and Octahedral Voids

We know that close packed structures have both tetrahedral and octahedral voids. Let us take *ccp* (or *fcc*) structure and locate these voids in it.

(a) Locating Tetrahedral Voids

Let us consider a unit cell of *ccp* or *fcc* lattice [Fig. 1(a)]. The unit cell is divided into eight small cubes.

Each small cube has atoms at alternate corners [Fig. 1(a)]. In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of *ccp* structure. We know that *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.

(a) (b)

Fig. 1: *(a) Eight tetrahedral voids per unit cell of ccp structure (b) one tetrahedral void showing the geometry.*

(b) Locating Octahedral Voids

Let us again consider a unit cell of *ccp* or *fcc* lattice [Fig. 2(a)]. The body centre of the cube, C is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges. [Fig. 2(b)]. It is surrounded by six atoms, three belonging to the same unit cell (2 on the corners and 1 on face centre) and three belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. Only $\frac{1}{4}^{th}$ of each void belongs to a particular unit cell.

(a) (b)

Fig. 2: *Location of octahedral voids per unit cell of ccp or fcc lattice (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown).*

Thus in *cubic close packed structure*:

Octahedral void at the body-centre of the cube = 1

12 octahedral voids located at each edge and shared between four unit cells

$$= 12 \times \frac{1}{4} = 3$$

∴ Total number of octahedral voids = 4

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

1.7 Packing Efficiency

In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. **Packing efficiency** is the percentage of total space filled by the particles. Let us calculate the packing efficiency in different types of structures.

1.7.1 Packing Efficiency in *hcp* and *ccp* Structures

Both types of close packing (*hcp* and *ccp*) are equally efficient. Let us calculate the efficiency of packing in ccp structure. In Fig. 1.20 let the unit cell edge length be 'a' and face diagonal AC = b.

Fig. 1.20: Cubic close packing other sides are not provided with spheres for sake of clarity.

In Δ ABC

$AC^2 = b^2 = BC^2 + AB^2$

$= a^2 + a^2 = 2a^2$ or

$b = \sqrt{2}a$

If *r* is the radius of the sphere, we find

$b = 4r = \sqrt{2}a$

or $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r$

(we can also write, $r = \frac{a}{2\sqrt{2}}$)

We know, that each unit cell in ccp structure, has effectively 4 spheres. Total volume of four spheres is equal to $4 \times (4/3)\pi r^3$ and volume of the cube is a^3 or $(2\sqrt{2}r)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{4 \times (4/3)\pi r^3 \times 100}{(2\sqrt{2}r)^3}\%$$

$$= \frac{(16/3)\pi r^3 \times 100}{16\sqrt{2}r^3}\% = 74\%$$

1.7.2 Efficiency of Packing in Body-Centred Cubic Structures

From Fig. 1.21, it is clear that the atom at the centre will be in touch with the other two atoms diagonally arranged.

In Δ EFD,

$$b^2 = a^2 + a^2 = 2a^2$$

$$b = \sqrt{2}a$$

Now in Δ AFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

Fig. 1.21: *Body-centred cubic unit cell (sphere along the body diagonal are shown with solid boundaries).*

The length of the body diagonal c is equal to 4r, where r is the radius of the sphere (atom), as all the three spheres along the diagonal touch each other.

Therefore, $\sqrt{3}a = 4r$

$$a = \frac{4r}{\sqrt{3}}$$

Also we can write, $r = \frac{\sqrt{3}}{4}a$

In this type of structure, total number of atoms is 2 and their volume is $2 \times \left(\frac{4}{3}\right)\pi r^3$.

Volume of the cube, a^3 will be equal to $\left(\frac{4}{\sqrt{3}}r\right)^3$ or $a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3$.

Therefore,

$$\text{Packing efficiency} = \frac{\text{Volume occupied by two spheres in the unit cell} \times 100}{\text{Total volume of the unit cell}}\%$$

$$= \frac{2 \times (4/3)\pi r^3 \times 100}{\left[\left(4/\sqrt{3}\right)r\right]^3}\%$$

$$= \frac{(8/3)\pi r^3 \times 100}{64/\left(3\sqrt{3}\right)r^3}\% = 68\%$$

1.7.3 Packing Efficiency in Simple Cubic Lattice

In a simple cubic lattice the atoms are located only on the corners of the cube. The particles touch each other along the edge (Fig. 1.22). Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as

$$a = 2r$$

The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

Since a simple cubic unit cell contains only 1 atom

The volume of the occupied space = $\frac{4}{3}\pi r^3$

Fig. 1.22
Simple cubic unit cell. The spheres are in contact with each other along the edge of the cube.

$\therefore$ Packing efficiency

$$= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.36\% = 52.4\ \%$$

Thus, we may conclude that *ccp* and *hcp* structures have maximum packing efficiency.

1.8 Calculations Involving Unit Cell Dimensions

From the unit cell dimensions, it is possible to calculate the volume of the unit cell. Knowing the density of the metal, we can calculate the mass of the atoms in the unit cell. The determination of the mass of a single atom gives an accurate method of determination of Avogadro constant. Suppose, edge length of a unit cell of a cubic crystal determined by X-ray diffraction is a, d the density of the solid substance and M the molar mass. In case of cubic crystal:

Volume of a unit cell = a^3

Mass of the unit cell

= number of atoms in unit cell × mass of each atom = $z \times m$

(Here z is the number of atoms present in one unit cell and m is the mass of a single atom)

Mass of an atom present in the unit cell:

$$m = \frac{M}{N_A} \text{ (} M \text{ is molar mass)}$$

Therefore, density of the unit cell

$$= \frac{mass\,of\ unit\ cell}{volume\,of\ unit\ cell}$$

$$= \frac{z.m}{a^3} = \frac{z.M}{a^3.N_A} \quad or\ d = \frac{zM}{a^3 N_A}$$

Remember, the density of the unit cell is the same as the density of the substance. The density of the solid can always be determined by other methods. Out of the five parameters (d, z M, a and N_A), if any four are known, we can determine the fifth.

Example 1.3 An element has a body-centred cubic *(bcc)* structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?

Solution Volume of the unit cell = (288 pm)^3

= (288×10^{-12} m) = (288×10^{-10} cm)^3

= 2.39×10^{-23} cm^3

Volume of 208 g of the element

$$= \frac{mass}{density} = \frac{208g}{7.2\,g\,cm^{-3}} = 28.88\,cm^3$$

Number of unit cells in this volume

$$= \frac{28.88cm^3}{2.39\times10^{-23}cm^3/unit\ cell} = 12.08\times10^{23} \text{ unit cells}$$

Since each *bcc* cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g = 2 (atoms/unit cell) × 12.08 × 10^{23} unit cells

$= 24.16\times10^{23}$ atoms

Example 1.4

X-ray diffraction studies show that copper crystallises in an *fcc* unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3, calculate the atomic mass of copper.

Solution

In case of *fcc* lattice, number of atoms per unit cell, z = 4 atoms

$$\text{Therefore, } M = \frac{dN_A a^3}{z}$$

$$= \frac{8.92\,g\ cm^3 \times 6.022\times10^{23}\ atoms\,mol^{-1} \times (3.608\times10^{-8}\,cm)^3}{4\,atoms}$$

= 63.1 g/mol

Atomic mass of copper = 63.1u

Example 1.5

Silver forms *ccp* lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u).

Solution

Since the lattice is *ccp*, the number of silver atoms per unit cell = z = 4

Molar mass of silver = 107.9 g mol^{-1} = 107.9×10^{-3} kg mol^{-1}

Edge length of unit cell = a = 408.6 pm = 408.6×10^{-12} m

$$\text{Density, } d = \frac{z.M}{a^3.N_A}$$

$$= \frac{4\times\left(107.9\times10^{-3}\,kg\,mol^{-1}\right)}{\left(408.6\times10^{-12}\,m\right)^3\left(6.022\times10^{23}\,mol^{-1}\right)} = 10.5\times10^3\ kg\ m^{-3}$$

$= 10.5\ g\,cm^{-3}$

Intext Questions

1.14 What is the two dimensional coordination number of a molecule in *square close*-packed layer?

1.15 A compound forms *hexagonal close-packed* structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

1.16 A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

1.17 Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice?

1.18 An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^{3} kg^{-3}, what is the nature of the cubic unit cell?

1.9 Imperfections in Solids

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, *point defects* and *line defects*. **Point defects** are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the *line defects* are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called *crystal defects*. We shall confine our discussion to point defects only.

1.9.1 Types of Point Defects

Point defects can be classified into three types : (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects.

(a) Stoichiometric Defects

These are the point defects that do not disturb the stoichiometry of the solid. They are also called *intrinsic* or **thermodynamic defects.** Basically these are of two types, vacancy defects and interstitial defects.

(i) *Vacancy Defect*: When some of the lattice sites are vacant, the crystal is said to have **vacancy defect** (Fig. 1.23). This results in decrease in density of the substance. This defect can also develop when a substance is heated.

Fig. 1.23: *Vacancy defects*

(ii) *Interstitial Defect*: When some constituent particles (atoms or molecules) occupy an **interstitial** site, the crystal is said to have **interstitial defect** (Fig. 1.24). This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects.**

(iii) *Frenkel Defect*: This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 1.25). It creates a *vacancy defect* at its original site and an **interstitial defect** at its new location.

Fig. 1.24: *Interstitial defects*

Frenkel defect is also called **dislocation defect**. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^{+} ions.

(iv) *Schottky Defect*: It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (Fig. 1.26).

Fig. 1.25: *Frenkel defects*

Fig. 1.26: *Schottky defects*

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

Fig. 1.27: *Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}*

(b) Impurity Defects

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} (Fig.1.27). Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.

(c) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) *Metal Excess Defect*

- *Metal excess defect due to anionic vacancies*: Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 1.28). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres* (from the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

Fig. 1.28: *An F-centre in a crystal*

- *Metal excess defect due to the presence of extra cations at interstitial sites*: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) *Metal Deficiency Defect*

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

1.10 Electrical Properties

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^7 ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(i) *Conductors*: The solids with conductivities ranging between 10^4 to 10^7 $ohm^{-1}m^{-1}$ are called conductors. Metals have conductivities in the order of 10^7 $ohm^{-1}m^{-1}$ are good conductors.

(ii) *Insulators* : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} $ohm^{-1}m^{-1}$.

(iii) *Semiconductors* : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^{4} $ohm^{-1}m^{-1}$.

1.10.1 Conduction of Electricity in Metals

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a **band.** If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity (Fig. 1.29 a).

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an insulator (Fig. 1.29 b).

1.10.2 Conduction of Electricity in Semi-conductors

In case of semiconductors, the gap between the valence band and conduction band is small (Fig. 1.29c). Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called *intrinsic semiconductors.*

The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called

Fig. 1.29 *Distinction among (a) metals (b) insulators and (c) semiconductors. In each case, an unshaded area represents a conduction band.*

doping. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce *electronic defects* in them.

(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours (Fig. 1.30 a). When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal (Fig. 1.30 b). Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the *negatively* charged electron, hence silicon doped with electron-rich impurity is called *n*-type semiconductor.

(b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called *electron hole* or *electron vacancy* (Fig. 1.30 c). An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called *p-type* semiconductors.

Fig. 1.30: *Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements.*

Applications of n-type and p-type semiconductors

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. *Diode* is a combination of *n*-type and *p*-type semiconductors and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germanium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13 – 15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12 – 16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

1.11 Magnetic Properties

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis (Fig. 1.31). Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called *Bohr magneton*, μ_B. It is equal to 9.27×10^{-24}A m^2.

Fig.1.31: *Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.*

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) *Paramagnetism*: Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

(ii) *Diamagnetism*: Diamagnetic substances are weakly repelled by a magnetic field. H_2O, NaCl and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) *Ferromagnetism*: A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field (Fig. 1.32 a) and a strong magnetic effect is produced. This ordering of domains persist even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) *Antiferromagnetism*: Substances like MnO showing anti-ferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment (Fig. 1.32 b).

(v) *Ferrimagnetism*: Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers (Fig. 1.32 c). They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.

Fig 1.32: *Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.*

Intext Questions

1.19 What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

1.20 What type of stoichiometric defect is shown by:

(i) ZnS (ii) AgBr

1.21 Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

1.22 Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

1.23 A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

1.24 What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Summary

Solids have definite mass, volume and shape. This is due to the fixed position of their constituent particles, short distances and strong interactions between them. In **amorphous** solids, the arrangement of constituent particles has only **short range order** and consequently they behave like **super cooled liquids**, do not have sharp melting points and are isotropic in nature. In crystalline solids there is long range order in the arrangement of their constituent particles. They have sharp melting points, are anisotropic in nature and their particles have characteristic shapes. Properties of **crystalline** solids depend upon the nature of interactions between their constituent particles. On this basis, they can be divided into four categories, namely: **molecular**, **ionic**, **metallic** and **covalent** solids. They differ widely in their properties.

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each **lattice point** gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called **Bravais lattices**. Each lattice can be generated by repeating its small characteristic portion called **unit cell**. A unit cell is characterised by its edge lengths and three angles between these edges. Unit cells can be either **primitive** which have particles only at their corner positions or **centred**. The centred unit cells have additional particles at their body centre (**body-centred**), at the centre of each face (**face-centred**) or at the centre of two opposite faces (**end-centred**). There are seven types of **primitive unit** cells. Taking centred unit cells also into account, there are fourteen types of unit cells in all, which result in fourteen **Bravais lattices**.

Close-packing of particles result in two highly efficient lattices, **hexagonal close-packed** (**hcp**) and **cubic close-packed** (**ccp**). The latter is also called face-centred cubic (**fcc**) lattice. In both of these packings 74% space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not close-packings and have less

efficient packing of particles. While in **body-centred cubic lattice** (**bcc**) 68% space is filled, in simple cubic lattice only 52.4 % space is filled.

Solids are not perfect in structure. There are different types of **imperfections** or **defects** in them. Point defects and line defects are common types of defects. Point defects are of three types - **stoichiometric defects**, **impurity defects** and **non-stoichiometric defects**. **Vacancy defects** and **interstitial defects** are the two basic types of stoichiometric point defects. In ionic solids, these defects are present as **Frenkel** and **Schottky defects**. Impurity defects are caused by the presence of an impurity in the crystal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Non-stoichiometric defects are of metal excess type and metal deficient type. Sometimes calculated amounts of impurities are introduced by **doping in semiconductors** that change their electrical properties. Such materials are widely used in electronics industry. Solids show many types of magnetic properties like **paramagnetism**, **diamagnetism**, **ferromagnetism**, **antiferromagnetism** and **ferrimagnetism**. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configurations or structures.

Exercises

1.1 Define the term 'amorphous'. Give a few examples of amorphous solids.

1.2 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

1.3 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

(i) Tetra phosphorus decoxide (P_4O_{10})
(ii) Ammonium phosphate $(NH_4)_3PO_4$
(iii) SiC
(iv) I_2
(v) P_4
(vi) Plastic
(vii) Graphite
(viii) Brass
(ix) Rb
(x) LiBr
(xi) Si

1.4 (i) What is meant by the term 'coordination number'?

(ii) What is the coordination number of atoms:

(a) in a cubic close-packed structure?

(b) in a body-centred cubic structure?

1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.

1.6 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

1.7 How will you distinguish between the following pairs of terms:

(i) Hexagonal close-packing and cubic close-packing?

(ii) Crystal lattice and unit cell?

(iii) Tetrahedral void and octahedral void?

1.8 How many lattice points are there in one unit cell of each of the following lattice?

(i) Face-centred cubic

(ii) Face-centred tetragonal

(iii) Body-centred

1.9 Explain

(i) The basis of similarities and differences between metallic and ionic crystals.

(ii) Ionic solids are hard and brittle.

1.10 Calculate the efficiency of packing in case of a metal crystal for

(i) simple cubic

(ii) body-centred cubic

(iii) face-centred cubic (with the assumptions that atoms are touching each other).

1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

1.12 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

1.13 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93 u.

1.14 If the radius of the octahedral void is r and radius of the atoms in close-packing is R, derive relation between r and R.

1.15 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

1.16 Analysis shows that nickel oxide has the formula $Ni0_{.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

1.17 What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.

1.18 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a p-type semiconductor?

1.19 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

1.20 Classify each of the following as being either a p-type or a n-type semiconductor:

(i) Ge doped with In (ii) B doped with Si.

1.21 Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

1.22 In terms of band theory, what is the difference

(i) between a conductor and an insulator

(ii) between a conductor and a semiconductor?

1.23 Explain the following terms with suitable examples:

(i) Schottky defect (ii) Frenkel defect (iii) Interstitials and (iv) F-centres.

1.24 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

(i) What is the length of the side of the unit cell?

(ii) How many unit cells are there in 1.00 cm^3 of aluminium?

1.25 If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies?

1.26 Explain the following with suitable examples:

(i) Ferromagnetism

(ii) Paramagnetism

(iii) Ferrimagnetism

(iv) Antiferromagnetism

(v) 12-16 and 13-15 group compounds.

Answers to Some Intext Questions

1.14 4

1.15 Total number of voids = 9.033×10^{23}

Number of tetrahedral voids = 6.022×10^{23}

1.16 M_2N_3

1.18 ccp

Unit 2

Solutions

Objectives

After studying this Unit, you will be able to

- describe the formation of different types of solutions;
- express concentration of solution in different units;
- state and explain Henry's law and Raoult's law;
- distinguish between ideal and non-ideal solutions;
- explain deviations of real solutions from Raoult's law;
- describe colligative properties of solutions and correlate these with molar masses of the solutes;
- explain abnormal colligative properties exhibited by some solutes in solutions.

Almost all processes in body occur in some kind of liquid solutions.

In normal life we rarely come across pure substances. Most of these are mixtures containing two or more pure substances. Their utility or importance in life depends on their composition. For example, the properties of brass (mixture of copper and zinc) are quite different from those of German silver (mixture of copper, zinc and nickel) or bronze (mixture of copper and tin); 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example, sodium fluoride is used in rat poison); intravenous injections are always dissolved in water containing salts at particular ionic concentrations that match with blood plasma concentrations and so on.

In this Unit, we will consider mostly liquid solutions and their formation. This will be followed by studying the properties of the solutions, like vapour pressure and colligative properties. We will begin with types of solutions and then various alternatives in which concentrations of a solute can be expressed in liquid solution.

2.1 Types of Solutions

Solutions are **homogeneous** mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as **solvent**. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called **solutes.** In this Unit we shall consider only **binary solutions** (i.e.,

consisting of two components). Here each component may be solid, liquid or in gaseous state and are summarised in Table 2.1.

Table 2.1: Types of Solutions

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

2.2 Expressing Concentration of Solutions

Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in real life these kinds of description can add to lot of confusion and thus the need for a quantitative description of the solution.

There are several ways by which we can describe the concentration of the solution quantitatively.

(i) *Mass percentage (w/w)*: The mass percentage of a component of a solution is defined as:

Mass % of a component

$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100 \qquad (2.1)$$

For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

(ii) *Volume percentage (v/v)*: The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100 \qquad (2.2)$$

For example, 10% ethanol solution in water means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions containing liquids are commonly expressed in this unit. For example, a 35% (v/v) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. At this concentration the antifreeze lowers the freezing point of water to 255.4K (–17.6°C).

(iii) *Mass by volume percentage (w/v)*: Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

(iv) *Parts per million*: When a solute is present in **trace** quantities, it is convenient to express concentration in **parts per million (ppm)** and is defined as:

Parts per million =

$$= \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6 \quad (2.3)$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Such a small concentration is also expressed as 5.8 g per 10^6 g (5.8 ppm) of sea water. The concentration of pollutants in water or atmosphere is often expressed in terms of μg mL^{-1} or ppm.

(v) *Mole fraction*: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as:

Mole fraction of a component =

$$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}} \quad (2.4)$$

For example, in a binary mixture, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B} \quad (2.5)$$

For a solution containing i number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i} \quad (2.6)$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \ldots\ldots\ldots\ldots\ldots\ldots + x_i = 1 \quad (2.7)$$

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures.

Example 2.1 Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

Solution Assume that we have 100 g of solution (one can start with any amount of solution because the results obtained will be the same). Solution will contain 20 g of ethylene glycol and 80 g of water.

Molar mass of $C_2H_6O_2$ = 12 × 2 + 1 × 6 + 16 × 2 = 62 g mol^{-1}.

$$\text{Moles of } C_2H_6O_2 = \frac{20\text{ g}}{62\text{ g mol}^{-1}} = 0.322\text{ mol}$$

$$\text{Moles of water} = \frac{80\text{ g}}{18\text{ g mol}^{-1}} = 4.444\text{ mol}$$

$$x_{glycol} = \frac{\text{moles of } C_2H_6O_2}{\text{moles of } C_2H_6O_2 + \text{moles of } H_2O}$$

$$= \frac{0.322\text{ mol}}{0.322\text{ mol} + 4.444\text{ mol}} = 0.068$$

$$\text{Similarly, } x_{water} = \frac{4.444\text{ mol}}{0.322\text{ mol} + 4.444\text{ mol}} = 0.932$$

Mole fraction of water can also be calculated as: 1 – 0.068 = 0.932

(vi) *Molarity*: Molarity (*M*) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}} \quad (2.8)$$

For example, 0.25 mol L^{-1} (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre).

Example 2.2 Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution.

Solution $$\text{Moles of NaOH} = \frac{5\text{ g}}{40\text{ g mol}^{-1}} = 0.125\text{ mol}$$

Volume of the solution in litres = 450 mL / 1000 mL L^{-1}

Using equation (2.8),

$$\text{Molarity} = \frac{0.125\text{ mol} \times 1000\text{ mL L}^{-1}}{450\text{ mL}} = 0.278\text{ M}$$

$$= 0.278\text{ mol L}^{-1}$$

$$= 0.278\text{ mol dm}^{-3}$$

(vii) *Molality*: Molality (*m*) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \quad (2.9)$$

For example, 1.00 mol kg^{-1} (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Each method of expressing concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.

Example 2.3

Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Solution

Molar mass of $C_2H_4O_2$: $12 \times 2 + 1 \times 4 + 16 \times 2 = 60$ g mol^{-1}

$$\text{Moles of } C_2H_4O_2 = \frac{2.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0417 \text{ mol}$$

Mass of benzene in kg = 75 g/1000 g kg^{-1} = 75×10^{-3} kg

$$\text{Molality of } C_2H_4O_2 = \frac{\text{Moles of } C_2H_4O_2}{\text{kg of benzene}} = \frac{0.0417 \text{ mol} \times 1000 \text{ g kg}^{-1}}{75 \text{ g}}$$

$$= 0.556 \text{ mol kg}^{-1}$$

Intext Questions

2.1 Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

2.2 Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

2.3 Calculate the molarity of each of the following solutions: (a) 30 g of $Co(NO_3)_2 \cdot 6H_2O$ in 4.3 L of solution (b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL.

2.4 Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

2.5 Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}.

2.3 Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of a solid or a gas in a liquid.

2.3.1 Solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say **like dissolves like**.

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation. A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution} \qquad (2.10)$$

At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution**. An *unsaturated solution* is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility.

Earlier we have observed that solubility of one substance into another depends on the nature of the substances. In addition to these variables, two other parameters, i.e., temperature and pressure also control this phenomenon.

Effect of temperature

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation 2.10. This, being dynamic equilibrium, must follow **Le Chateliers Principle.** In general, if in a *nearly saturated solution*, the dissolution process is endothermic (Δ_{sol} H > 0), the solubility should increase with rise in temperature and if it is exothermic (Δ_{sol} H > 0) the solubility should decrease. These trends are also observed experimentally.

Effect of pressure

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

2.3.2 Solubility of a Gas in a Liquid

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and

temperature. The solubility of gases increase with increase of pressure. For solution of gases in a solvent, consider a system as shown in Fig. 2.1 (a). The lower part is solution and the upper part is gaseous system at pressure *p* and temperature *T*. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by compressing the gas to a smaller volume [Fig. 2.1 (b)]. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.

Fig. 2.1: *Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.*

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as **Henry's law**. The law states that at a constant temperature, **the solubility of a gas in a liquid is directly proportional to the pressure of the gas.** Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the **mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.** The most commonly used form of Henry's law states that "**the partial pressure of the gas in vapour phase (*p*) is proportional to the mole fraction of the gas (*x*) in the solution**" and is expressed as:

$$p = K_H\, x \qquad (2.11)$$

Here K_H is the Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 2.2.

Fig. 2.2: *Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant, K_H.*

Different gases have different K_H values at the same temperature (Table 2.2). This suggests that K_H is a function of the nature of the gas.

It is obvious from equation (2.11) that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. It can be seen from Table 2.2 that K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases

Table 2.2: Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H /kbar	Gas	Temperature/K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.84	Methane	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82			

increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

Example 2.4 If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water. Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 *k*bar.

Solution The solubility of gas is related to the mole fraction in aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus:

$$x\,(\text{Nitrogen}) = \frac{p\ (\text{nitrogen})}{K_H} = \frac{0.987\text{bar}}{76{,}480\ \text{bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N_2 in solution,

$$x\,(\text{Nitrogen}) = \frac{n\ \text{mol}}{n\ \text{mol} + 55.5\ \text{mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

(n in denominator is neglected as it is $<<$ 55.5)

Thus $n = 1.29 \times 10^{-5} \times 55.5$ mol $= 7.16 \times 10^{-4}$ mol

$$= \frac{7.16\times10^{-4}\ \text{mol} \times 1000\ \text{mol}}{1\ \text{mol}} = 0.716\ \text{mmol}$$

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as *bends*, which are painful and dangerous to life.

To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as *anoxia*.

Effect of Temperature

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt in the last Section that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

Intext Questions

2.6 H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

2.7 Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

2.4 Vapour Pressure of Liquid Solutions

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. Solutions of gases in liquids have already been discussed in Section 2.3.2. In this Section, we shall discuss the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile. We shall discuss the properties of only binary solutions, that is, the solutions containing two components, namely, the solutions of (i) liquids in liquids and (ii) solids in liquids.

2.4.1 Vapour Pressure of Liquid-Liquid Solutions

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be p_{total} and p_1 and p_2 be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the **Raoult's law** which states that **for a solution of volatile liquids,**

the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

Thus, for component 1

$$p_1 \propto x_1$$

and $$p_1 = p_1^0 x_1 \quad (2.12)$$

where p_1^0 is the vapour pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^0 x_2 \quad (2.13)$$

where p_2^0 represents the vapour pressure of the pure component 2.

According to **Dalton's law of partial pressures**, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$p_{total} = p_1 + p_2 \quad (2.14)$$

Substituting the values of p_1 and p_2, we get

$$p_{total} = x_1 p_1^0 + x_2 p_2^0$$

$$= (1 - x_2) p_1^0 + x_2 p_2^0 \quad (2.15)$$

$$= p_1^0 + (p_2^0 - p_1^0) x_2 \quad (2.16)$$

Following conclusions can be drawn from equation (2.16).

(i) Total vapour pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

(iii) Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

Fig. 2.3: *The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2, respectively). The total vapour pressure is given by line marked III in the figure.*

A plot of p_1 or p_2 versus the mole fractions x_1 and x_2 for a solution gives a linear plot as shown in Fig. 2.3. These lines (I and II) pass through the points and respectively when x_1 and x_2 equal unity. Similarly the plot (line III) of p_{total} versus x_2 is also linear (Fig. 2.3). The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0, assuming that component 1 is less volatile than component 2, i.e., $p_1^0 < p_2^0$.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the

components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_1 = y_1\, p_{total} \quad (2.17)$$

$$p_2 = y_2\, p_{total} \quad (2.18)$$

In general

$$p_i = y_i\, p_{total} \quad (2.19)$$

Example 2.5

Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K and, (ii) mole fractions of each component in vapour phase.

Solution

(i) Molar mass of CH_2Cl_2 = $12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85$ g mol^{-1}

Molar mass of $CHCl_3$ = $12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5$ g mol^{-1}

Moles of CH_2Cl_2 = $\dfrac{40 \text{ g}}{85 \text{ g mol}^{-1}}$ = 0.47 mol

Moles of $CHCl_3$ = $\dfrac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}}$ = 0.213 mol

Total number of moles = 0.47 + 0.213 = 0.683 mol

$$x_{CH_2Cl_2} = \frac{0.47 \text{ mol}}{0.683 \text{ mol}} = 0.688$$

$$x_{CHCl_3} = 1.00 - 0.688 = 0.312$$

Using equation (2.16),

$$p_{total} = p_1^0 + (p_2^0 - p_1^0)\, x_2 = 200 + (415 - 200) \times 0.688$$

$$= 200 + 147.9 = 347.9 \text{ mm Hg}$$

(ii) Using the relation (2.17), $y_i = p_i/p_{total}$, we can calculate the mole fraction of the components in gas phase (y_i).

$$p_{CH_2Cl_2} = 0.688 \times 415 \text{ mm Hg} = 285.5 \text{ mm Hg}$$

$$p_{CHCl_3} = 0.312 \times 200 \text{ mm Hg} = 62.4 \text{ mm Hg}$$

$$y_{CH_2Cl_2} = 285.5 \text{ mm Hg}/347.9 \text{ mm Hg} = 0.82$$

$$y_{CHCl_3} = 62.4 \text{ mm Hg}/347.9 \text{ mm Hg} = 0.18$$

Note: Since, CH_2Cl_2 is a more volatile component than $CHCl_3$, [$p^0_{CH_2Cl_2}$ = 415 mm Hg and $p^0_{CHCl_3}$ = 200 mm Hg] and the vapour phase is also richer in CH_2Cl_2 [$y_{CH_2Cl_2}$ = 0.82 and y_{CHCl_3} = 0.18], it may thus be concluded that **at equilibrium, vapour phase will be always rich in the component which is more volatile.**

2.4.2 Raoult's Law as a special case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i\, p_i^0$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_H\, x.$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant K_H differs from p_1^0. Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_1^0.

2.4.3 Vapour Pressure of Solutions of Solids in Liquids

Another important class of solutions consists of solids dissolved in liquid, for example, sodium chloride, glucose, urea and cane sugar in water and iodine and sulphur dissolved in carbon disulphide. Some physical properties of these solutions are quite different from those of pure solvents. For example, vapour pressure. We have learnt in Unit 5, Class XI, that liquids at a given temperature vapourise and under equilibrium conditions the pressure exerted by the vapours of the liquid over the liquid phase is called vapour pressure [Fig. 2.4 (a)]. In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non-volatile solute is added to a solvent to give a solution [Fig. 2.4.(b)], the vapour pressure of the solution is solely from the solvent alone. This vapour pressure of the solution at a given temperature is found to be lower than the vapour pressure of the pure solvent at the same temperature. In the solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.

Fig. 2.4: Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.

The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature. For example, decrease in the vapour pressure of water by adding 1.0 mol of sucrose to one kg of water is nearly similar to that produced by adding 1.0 mol of urea to the same quantity of water at the same temperature.

Raoult's law in its general form can be stated as, **for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction**.

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure. Let p_1 be

Fig. 2.5
If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.

the vapour pressure of the solvent, x_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

and $$p_1 = x_1 \; p_1^0 \qquad (2.20)$$

The proportionality constant is equal to the vapour pressure of pure solvent, p_1^0. A plot between the vapour pressure and the mole fraction of the solvent is linear (Fig. 2.5).

2.5 Ideal and Non-ideal Solutions

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

2.5.1 Ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions*. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{mix}H = 0, \qquad \Delta_{mix}V = 0 \qquad (2.21)$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

2.5.2 Non-ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law (equation 2.16). If it is higher, the solution exhibits **positive deviation** and if it is lower, it exhibits **negative deviation** from Raoult's law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in Fig. 2.6.

The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour

Fig.2.6 *The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.*

pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 2.6 (a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.

This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. 2.6. (b)].

Some liquids on mixing, form **azeotropes** which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotrope and maximum boiling azeotrope**. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Intext Question

2.8 The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K . Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

2.6 Colligative Properties and Determination of Molar Mass

We have learnt in Section 2.4.3 that the vapour pressure of solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (1) relative lowering of vapour pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. **All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called *colligative properties*** (colligative: from Latin: co means together, ligare means to bind). In the following Sections we will discuss these properties one by one.

2.6.1 Relative Lowering of Vapour Pressure

We have learnt in Section 2.4.3 that the vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation (2.20) given in Section 2.4.3 establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1 \, p_1^0 \qquad (2.22)$$

The reduction in the vapour pressure of solvent (Δp_1) is given as:

$$\Delta p_1 = p_1^0 - p_1 = p_1^0 - p_1^0 \, x_1$$
$$= p_1^0 \, (1 - x_1) \qquad (2.23)$$

Knowing that $x_2 = 1 - x_1$, equation (2.23) reduces to

$$\Delta p_1 = x_2 \, p_1^0 \qquad (2.24)$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Equation (2.24) can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \qquad (2.25)$$

The expression on the left hand side of the equation as mentioned earlier is called **relative lowering of vapour pressure and is equal to the mole fraction of the solute**. The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad \left(\text{since } x_2 = \frac{n_2}{n_1 + n_2}\right) \tag{2.26}$$

Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_2 << n_1$, hence neglecting n_2 in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \tag{2.27}$$

or

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \tag{2.28}$$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively.

From this equation (2.28), knowing all other quantities, the molar mass of solute (M_2) can be calculated.

Example 2.6 The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol^{-1}). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

Solution The various quantities known to us are as follows:

$p_1^0 = 0.850$ bar; $p = 0.845$ bar; $M_1 = 78$ g mol^{-1}; $w_2 = 0.5$ g; $w_1 = 39$ g

Substituting these values in equation (2.28), we get

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

Therefore, $M_2 = 170$ g mol^{-1}

2.6.2 Elevation of Boiling Point

We have learnt in Unit 5, Class XI, that the vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapour pressure of water is 1.013 bar (1 atmosphere). We have also learnt in the last section that vapour pressure of the solvent decreases in the presence of non-volatile solute. Fig. 2.7 depicts the variation of vapour pressure of the pure solvent and solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling

Fig. 2.7: *The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.*

point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 2.7. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.

Let T_b^0 be the boiling point of pure solvent and T_b be the boiling point of solution. The increase in the boiling point $\Delta T_b = T_b - T_b^0$ is known as **elevation of boiling point**.

Experiments have shown that for **dilute solutions** the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m \tag{2.29}$$

$$\text{or} \quad \Delta T_b = K_b\, m \tag{2.30}$$

Here m (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called **Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant)**. The unit of K_b is K kg mol^{-1}. Values of K_b for some common solvents are given in Table 2.3. If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is given by the expression:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \tag{2.31}$$

Substituting the value of molality in equation (2.30) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \tag{2.32}$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \tag{2.33}$$

Thus, in order to determine M_2, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

Example 2.7

18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar? K_b for water is 0.52 K kg mol^{-1}.

Solution

Moles of glucose = 18 g/ 180 g mol^{-1} = 0.1 mol
Number of kilograms of solvent = 1 kg
Thus molality of glucose solution = 0.1 mol kg^{-1}
For water, change in boiling point

$\ddot{A}T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be 373.15 + 0.052 = 373.202 K.

Example 2.8 The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is 2.53 K kg mol^{-1}

Solution The elevation ($\ddot{A}T_b$) in the boiling point = 354.11 K – 353. 23 K = 0.88 K

Substituting these values in expression (2.33) we get

$$M_2 = \frac{2.53 \text{ K kg mol}^{-1} \times 1.8 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.88 \text{ K} \times 90 \text{ g}} = 58 \text{ g mol}^{-1}$$

Therefore, molar mass of the solute, $M_2 = 58 \text{ g mol}^{-1}$

2.6.3 Depression of Freezing Point

The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 2 8). We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent as is clear from Fig. 2.8. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

Fig. 2.8: *Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.*

Let T_f^0 be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point (ΔT_f) for **dilute solution** (ideal solution) is directly proportional to molality, m of the solution. Thus,

$$\Delta T_f \propto m$$

or $$\Delta T_f = K_f\, m \qquad (2.34)$$

The proportionality constant, K_f, which depends on the nature of the solvent is known as **Freezing Point Depression Constant or Molal**

Depression Constant or Cryoscopic Constant. The unit of K_f is K kg mol^{-1}. Values of K_f for some common solvents are listed in Table 2.3.

If w_2 gram of the solute having molar mass as M_2, present in w_1 gram of solvent, produces the depression in freezing point ΔT_f of the solvent then molality of the solute is given by the equation (2.31).

$$m = \frac{w_2 / M_2}{w_1/1000} \tag{2.31}$$

Substituting this value of molality in equation (2.34) we get:

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \tag{2.35}$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \tag{2.36}$$

Thus for determining the molar mass of the solute we should know the quantities w_1, w_2, ΔT_f, along with the molal freezing point depression constant.

The values of K_f and K_b, which depend upon the nature of the solvent, can be ascertained from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus}H} \tag{2.37}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap}H} \tag{2.38}$$

Here the symbols R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, $\Delta_{fus}H$ and $\Delta_{vap}H$ represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

Table 2.3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

Solvent	b. p./K	K_b/K kg mol^{-1}	f. p./K	K_f/K kg mol^{-1}
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

Example 2.9 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

Solution Depression in freezing point is related to the molality, therefore, the molality of the solution with respect to ethylene glycol = $\frac{\text{moles of ethylene glycol}}{\text{mass of water in kilogram}}$

Moles of ethylene glycol = $\frac{45\text{ g}}{62\text{ g mol}^{-1}}$ = 0.73 mol

Mass of water in kg = $\frac{600\text{g}}{1000\text{g kg}^{-1}}$ = 0.6 kg

Hence molality of ethylene glycol = $\frac{0.73\text{ mol}}{0.60\text{ kg}}$ = 1.2 mol kg^{-1}

Therefore freezing point depression,

$$\text{Ä}T_f = 1.86\text{ K kg mol}^{-1} \times 1.2\text{ mol kg}^{-1} = 2.2\text{ K}$$

Freezing point of the aqueous solution = 273.15 K – 2.2 K = 270.95 K

Example 2.10 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute.

Solution Substituting the values of various terms involved in equation (2.36) we get,

$$M_2 = \frac{5.12\text{ K kg mol}^{-1} \times 1.00\text{ g} \times 1000\text{ g kg}^{-1}}{0.40 \times 50\text{ g}} = 256\text{ g mol}^{-1}$$

Thus, molar mass of the solute = 256 g mol^{-1}

2.6.4 Osmosis and Osmotic Pressure

There are many phenomena which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water); wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water, etc. If we look into these processes we find one thing common in all, that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent

Fig. 2.9 *Level of solution rises in the thistle funnel due to osmosis of solvent.*

molecules, like water, can pass through these holes but the passage of bigger molecules like solute is hindered. Membranes having this kind of properties are known as *semipermeable membranes* (SPM).

Assume that only solvent molecules can pass through these semi-permeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 2.9, the solvent molecules will flow through the membrane from pure solvent to the solution. **This process of flow of the solvent is called *osmosis*.**

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. **This pressure that just stops the flow of solvent is called *osmotic pressure* of the solution.** The flow of solvent from dilute solution to the concentrated solution across a semipermeable membrane is due to osmosis. The important point to be kept in mind is that solvent molecules always flow from lower concentration to higher concentration of solution. The osmotic pressure has been found to depend on the concentration of the solution.

Fig. 2.10: *The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.*

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 2.10. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that **osmotic pressure is proportional to the molarity, *C* of the solution at a given temperature *T*.** Thus:

$$\delta = C R T \qquad (2.39)$$

Here δ is the osmotic pressure and R is the gas constant.

$$\delta = (n_2 / V) R T \qquad (2.40)$$

Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2 / M_2$ and we can write,

$$\delta V = \frac{w_2 R T}{M_2} \qquad (2.41)$$

$$\text{or} \quad M_2 = \frac{w_2 R T}{\pi V} \qquad (2.42)$$

Thus, knowing the quantities w_2, T, δ and V we can calculate the molar mass of the solute.

Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other

macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

Example 2.11 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Solution The various quantities known to us are as follows: $\pi = 2.57 \times 10^{-3}$ bar,

$V = 200\ cm^3 = 0.200$ litre

$T = 300$ K

$R = 0.083$ L bar mol^{-1} K^{-1}

Substituting these values in equation (2.42) we get

$$M_2 = \frac{1.26\ g \times 0.083\ L\ bar\ K^{-1}\ mol^{-1} \times 300\ K}{2.57 \times 10^{-3} bar \times 0.200\ L} = 61{,}022\ g\ mol^{-1}$$

The phenomena mentioned in the beginning of this section can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into them through osmosis. When placed in water containing less than 0.9% (mass/volume) salt, blood cells collapse due to loss of water by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting

puffiness or swelling is called **edema**. Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

2.6.5 Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called **reverse osmosis** and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig. 2.11. When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

Fig. 2.11: Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

Intext Questions

2.9 Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

2.10 Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.

2.11 Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. K_f = 3.9 K kg mol^{-1}.

2.12 Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

2.7 Abnormal Molar Masses

We know that ionic compounds when dissolved in water dissociate into cations and anions. For example, if we dissolve one mole of KCl (74.5 g) in water, we expect one mole each of K^+ and Cl^- ions to be released in the solution. If this happens, there would be two moles of particles in the solution. If we ignore interionic attractions, one mole of KCl in one kg of water would be expected to increase the boiling point by 2 × 0.52 K = 1.04 K. Now if we did not know about the degree of

dissociation, we could be led to conclude that the mass of 2 mol particles is 74.5 g and the mass of one mole of KCl would be 37.25 g. This brings into light the rule that, when there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.

$$2\ CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Association of molecules is depicted as follows:

It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then ΔT_b or ΔT_f for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT_b or ΔT_f will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as **abnormal molar mass.**

In 1880 van't Hoff introduced a factor *i*, known as the van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as:

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of *i* is less than unity while for dissociation it is greater than unity. For example, the value of *i* for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^o - p_1}{p_1^o} = i.\frac{n_2}{n_1}$$

Elevation of Boiling point, $\Delta T_b = i\ K_b\ m$

Depression of Freezing point, $\Delta T_f = i\ K_f\ m$

Osmotic pressure of solution, ð $= i\ n_2\ R\ T\ /\ V$

Table 2.4 depicts values of the factor, *i* for several strong electrolytes. For KCl, NaCl and $MgSO_4$, *i* approach 2 as the solution becomes very dilute. As expected, the value of *i* gets close to 3 for K_2SO_4.

Table 2.4: Values of Van't Hoff factor, *i*, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4.

Salt	*Values of *i*			van't Hoff Factor *i* for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

* *represent* i *values for incomplete dissociation.*

Example 2.12

2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution?

Solution

The given quantities are: w_2 = 2 g; K_f = 4.9 K kg mol^{-1}; w_1 = 25 g, ÄT_f = 1.62 K

Substituting these values in equation (2.36) we get:

$$M_2 = \frac{4.9 \text{ K kg mol}^{-1} \times 2 \text{ g} \times 1000 \text{ g kg}^{-1}}{25 \text{ g} \times 1.62 \text{ K}} = 241.98 \text{ g mol}^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene is

$= 241.98 \text{ g mol}^{-1}$

Now consider the following equilibrium for the acid:

$$2\, C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

If *x* represents the degree of association of the solute then we would have (1 – *x*) mol of benzoic acid left in unassociated form and correspondingly $\frac{x}{2}$ as associated moles of benzoic acid at equilibrium. Therefore, total number of moles of particles at equilibrium is:

$$1 - x + \frac{x}{2} = 1 - \frac{x}{2}$$

Thus, total number of moles of particles at equilibrium equals van't Hoff factor *i*.

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}}$$

or $\frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$

or $x = 2 \times 0.496 = 0.992$

Therefore, degree of association of benzoic acid in benzene is 99.2 %.

Example 2.13 0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1}, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the van't Hoff factor and the dissociation constant of acid.

Solution Number of moles of acetic acid $= \frac{0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}^{-1}}$

$= 0.0106 \text{ mol} = n$

$$\text{Molality} = \frac{0.0106 \text{ mol}}{1000 \text{ mL} \times 1 \text{ g mL}^{-1}} = 0.0106 \text{ mol kg}^{-1}$$

Using equation (2.35)

$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} = 0.0197 \text{ K}$

$$\text{van't Hoff Factor } (i) = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

Acetic acid is a weak electrolyte and will dissociate into two ions: acetate and hydrogen ions per molecule of acetic acid. If x is the degree of dissociation of acetic acid, then we would have $n(1 - x)$ moles of undissociated acetic acid, nx moles of CH_3COO^- and nx moles of H^+ ions,

$CH_3COOH \rightleftharpoons$	H^+ +	CH_3COO^-
n mol	0	0
$n(1-x)$	nx mol	nx mol

Thus total moles of particles are: $n(1 - x + x + x) = n(1 + x)$

$$i = \frac{n(1+x)}{n} = 1 + x = 1.041$$

Thus degree of dissociation of acetic acid = x = 1.041– 1.000 = 0.041

Then $[CH_3COOH] = n(1 - x)\ 0.0106\ (1 - 0.041)$,

$[CH_3COO^-] = nx = 0.0106 \times 0.041$, $[H^+] = nx = 0.0106 \times 0.041$.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106\ (1.00 - 0.041)}$$

$= 1.86 \times 10^{-5}$

Summary

A solution is a homogeneous mixture of two or more substances. Solutions are classified as solid, liquid and gaseous solutions. The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in percentages. The dissolution of a gas in a liquid is governed by **Henry's law**, according to which, at a given temperature, the **solubility of a gas in a liquid is directly proportional to the partial pressure of the gas**. The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law, according to which the **relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution**. However, in a binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law is stated as: $p_{\text{total}} = p_1^0 x_1 + p_2^0 x_2$. **Solutions which obey Raoult's law over the entire range of concentration are called ideal solutions**. Two types of deviations from Raoult's law, called positive and negative deviations are observed. Azeotropes arise due to very large deviations from Raoult's law.

The properties of solutions which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. The process of osmosis can be reversed if a pressure higher than the osmotic pressure is applied to the solution. Colligative properties have been used to determine the molar mass of solutes. Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.

Quantitatively, the extent to which a solute is dissociated or associated can be expressed by van't Hoff factor *i*. This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

Exercises

2.1 Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

2.2 Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What kind of solid solution is this likely to be?

2.3 Define the following terms:

(i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.

2.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1}?

2.5 A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL^{-1}, then what shall be the molarity of the solution?

2.6 How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of both?

2.7 A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

2.8 An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1}, then what shall be the molarity of the solution?

2.9 A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):

(i) express this in percent by mass

(ii) determine the molality of chloroform in the water sample.

2.10 What role does the molecular interaction play in a solution of alcohol and water?

2.11 Why do gases always tend to be less soluble in liquids as the temperature is raised?

2.12 State Henry's law and mention some important applications?

2.13 The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

2.14 What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law?

2.15 An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

2.16 Heptane and octane form an ideal solution. At 373 *K*, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

2.17 The vapour pressure of water is 12.3 kPa at 300 *K*. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

2.18 Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

2.19 A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 *K*. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 *K*. Calculate:

(i) molar mass of the solute (ii) vapour pressure of water at 298 *K*.

2.20 A 5% solution (by mass) of cane sugar in water has freezing point of 271*K*. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 *K*.

2.21 Two elements A and B form compounds having formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 *K* whereas 1.0 g of AB_4 lowers it by 1.3 *K*. The molar depression constant for benzene is 5.1 *K* kg mol^{-1}. Calculate atomic masses of A and B.

2.22 At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?

2.23 Suggest the most important type of intermolecular attractive interaction in the following pairs.

(i) n-hexane and n-octane

(ii) I_2 and CCl_4

(iii) $NaClO_4$ and water

(iv) methanol and acetone

(v) acetonitrile (CH_3CN) and acetone (C_3H_6O).

2.24 Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, CH_3OH, CH_3CN.

2.25 Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?

(i) phenol (ii) toluene (iii) formic acid

(iv) ethylene glycol (v) chloroform (vi) pentanol.

2.26 If the density of some lake water is 1.25g mL^{-1} and contains 92 g of Na^+ ions per kg of water, calculate the molality of Na^+ ions in the lake.

2.27 If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

2.28 Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN.

2.29 Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of $1.5 - 10^{-3}$ m aqueous solution required for the above dose.

2.30 Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

2.31 The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

2.32 Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol^{-1}.

2.33 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0^0 C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

2.34 Vapour pressure of water at 293 *K* is 17.535 mm Hg. Calculate the vapour pressure of water at 293 *K* when 25 g of glucose is dissolved in 450 g of water.

2.35 Henry's law constant for the molality of methane in benzene at 298 *K* is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 *K* under 760 mm Hg.

2.36 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

2.37 Vapour pressures of pure acetone and chloroform at 328 *K* are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total}, $p_{chloroform}$, and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is:

$100 \times x_{acetone}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{acetone}$ /mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{chloroform}$ /mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

2.38 Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 *K* are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene.

2.39 The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 *K*. The water is in equilibrium with air at a pressure of 10 atm. At 298 *K* if the Henry's law constants for oxygen and nitrogen at 298 *K* are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

2.40 Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C.

2.41 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25° C, assuming that it is completely dissociated.

Answers to Some Intext Questions

2.1 C_6H_6 = 15.28%, CCl_4 = 84.72%

2.2 0.459, 0.541

2.3 0.024 M, 0.03 M

2.4 37.5 g

2.5 1.5 mol kg^{-1} , 1.45 mol L^{-1} 0.0263

2.9 289.5 bar

2.10 1.86 g

2.11 x_A = 0.4, y_A = 0.3; x_B = 0.6, y_B = 0.7

2.12 23.4 mm Hg, 0.017

Unit

3

Electrochemistry

Objectives

After studying this Unit, you will be able to

- describe an electrochemical cell and differentiate between galvanic and electrolytic cells;
- apply Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell;
- derive relation between standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant;
- define resistivity (ρ), conductivity (κ) and molar conductivity (Λ_m) of ionic solutions;
- differentiate between ionic (electrolytic) and electronic conductivity;
- describe the method for measurement of conductivity of electrolytic solutions and calculation of their molar conductivity;
- justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define Λ_m° (molar conductivity at zero concentration or infinite dilution);
- enunciate Kohlrausch law and learn its applications;
- understand quantitative aspects of electrolysis;
- describe the construction of some primary and secondary batteries and fuel cells;
- explain corrosion as an electrochemical process.

Chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously.

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are ecofriendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

3.1 Electrochemical Cells

In Class XI, Unit 8, we had studied the construction and functioning of **Daniell cell** (Fig. 3.1). This cell converts the chemical energy liberated during the redox reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad (3.1)$$

Fig. 3.1: *Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.*

to electrical energy and has an electrical potential equal to 1.1 V when concentration of Zn^{2+} and Cu^{2+} ions is unity (1 mol dm^{-3})*. Such a device is called a **galvanic** or a **voltaic** cell.

If an external opposite potential is applied [Fig. 3.2(a)] and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 3.2(b)] when, the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction [Fig. 3.2(c)]. It now functions as an **electrolytic cell**, a device for using electrical energy to carry non-spontaneous chemical reactions. Both types of cells are quite important and we shall study some of their salient features in the following pages.

When E_{ext} < 1.1 V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

(a)

When E_{ext} =1.1V
(i) No flow of electrons or current.
(ii) No chemical reaction.

(b)

**Strictly speaking activity should be used instead of concentration. It is directly proportional to concentration. In dilute solutions, it is equal to concentration. You will study more about it in higher classes.*

When E_{ext}>1.1V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

(c)

Fig. 3.2: *Functioning of Daniell cell when external voltage E_{ext} opposing the cell potential is applied.*

3.2 Galvanic Cells

As mentioned earlier (Class XI, Unit 8) a galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

(i) $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction) (3.2)

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction) (3.3)

These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

We can construct innumerable number of galvanic cells on the pattern of Daniell cell by taking combinations of different half-cells. Each half-cell consists of a metallic electrode dipped into an electrolyte. The two half-cells are connected by a metallic wire through a voltmeter and a switch externally. The electrolytes of the two half-cells are connected internally through a salt bridge as shown in Fig. 3.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we don't require a salt bridge.

At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The *cell potential* is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the *cell electromotive force (emf)* of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.

$$E_{cell} = E_{right} - E_{left}$$

This is illustrated by the following example:

Cell reaction:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\ Ag(s) \qquad (3.4)$$

Half-cell reactions:

$$\text{Cathode (}\textit{reduction}\text{):} \quad 2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s) \qquad (3.5)$$

$$\text{Anode (}\textit{oxidation}\text{):} \quad Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-} \qquad (3.6)$$

It can be seen that the sum of (3.5) and (3.6) leads to overall reaction (3.4) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

and we have $E_{cell} = E_{right} - E_{left} = E_{Ag^{+}|Ag} - E_{Cu^{2+}|Cu}$ (3.7)

3.2.1 Measurement of Electrode Potential

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-

cell) then that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode (Fig.3.3) represented by Pt(s) | H_2(g) | H^+(aq), is assigned a zero potential at all temperatures corresponding to the reaction

$$H^+ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)$$

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity (Fig. 3.3). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

Fig. 3.3: *Standard Hydrogen Electrode (SHE).*

At 298 K the emf of the cell, standard hydrogen electrode || second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, $E^\ominus_R$ of the given half-cell.

$$E^\ominus = E^\ominus_R - E^\ominus_L$$

As $E^\ominus_L$ for standard hydrogen electrode is zero.

$$E^\ominus = E^\ominus_R - 0 = E^\ominus_R$$

The measured emf of the cell :

Pt(s) | H_2(g, 1 bar) | H^+ (aq, 1 M) || Cu^{2+} (aq, 1 M) | Cu

is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction :

$$Cu^{2+} (aq, 1M) + 2 e^- \rightarrow Cu(s)$$

Similarly, the measured emf of the cell :

Pt(s) | H_2(g, 1 bar) | H^+ (aq, 1 M) || Zn^{2+} (aq, 1M) | Zn

is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

$$Zn^{2+} (aq, 1 M) + 2e^- \rightarrow Zn(s)$$

The positive value of the standard electrode potential in the first case indicates that Cu^{2+} ions get reduced more easily than H^+ ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion. The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidise zinc (or zinc can reduce hydrogen ions).

In view of this convention, the half reaction for the Daniell cell in Fig. 3.1 can be written as:

Left electrode : $Zn(s) \rightarrow Zn^{2+}(aq, 1\ M) + 2\ e^-$

Right electrode: $Cu^{2+}(aq, 1\ M) + 2\ e^- \rightarrow Cu(s)$

The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Emf of the cell $= E^0_{cell} = E^0_R - E^0_L$

$= 0.34V - (-0.76)V = 1.10\ V$

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used in the following half-cells:

Hydrogen electrode: $Pt(s) | H_2(g) | H^+(aq)$

With half-cell reaction: $H^+(aq) + e^- \rightarrow ½\ H_2(g)$

Bromine electrode: $Pt(s) | Br_2(aq) | Br^-(aq)$

With half-cell reaction: $½\ Br_2(aq) + e^- \rightarrow Br^-(aq)$

The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table 3.1. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species. It can be seen that the standard electrode potential for fluorine is the highest in the Table indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution. It may be seen that as we go from top to bottom in Table 3.1 the standard electrode potential decreases and with this, decreases the oxidising power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Electrochemical cells are extensively used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

Intext Questions

3.1 How would you determine the standard electrode potential of the system $Mg^{2+} | Mg$?

3.2 Can you store copper sulphate solutions in a zinc pot?

3.3 Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Table 3.1 The standard electrode potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne^-	→ Reduced form)	$E^\ominus$/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	–2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Increasing strength of oxidising agent (↑)

Increasing strength of reducing agent (↓)

1. A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

3.3 Nernst Equation

We have assumed in the previous section that the concentration of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:

$M^{n+}(aq) + ne^- \rightarrow M(s)$

the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad (3.8)$$

$E^{\ominus}_{(M^{n+}/M)}$ has already been defined, R is gas constant (8.314 $JK^{-1}\ mol^{-1}$), F is Faraday constant (96487 C mol^{-1}), T is temperature in kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}.

In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions, we write

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}(aq)]} \quad (3.9)$$

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}(aq)]} \quad (3.10)$$

The cell potential, $E_{(cell)} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$= E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}(aq)]} - E^{\ominus}_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}(aq)]}$$

$$= E^{\ominus}_{(Cu^{2+}/Cu)} - E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}(aq)]} - \ln \frac{1}{[Zn^{2+}(aq)]}$$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad (3.11)$$

It can be seen that $E_{(cell)}$ depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions.

By converting the natural logarithm in Eq. (3.11) to the base 10 and substituting the values of R, F and T = 298 K, it reduces to

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad (3.12)$$

We should use the same number of electrons (n) for both the electrodes and thus for the following cell

$Ni(s) \mid Ni^{2+}(aq) \mid\mid Ag^{+}(aq) \mid Ag$

The cell reaction is $Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

The Nernst equation can be written as

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Ni^{2+}]}{[Ag^{+}]^2}$$

and for a general electrochemical reaction of the type:

$$a\,A + bB \xrightarrow{ne} cC + dD$$

Nernst equation can be written as:

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{nF} \ln Q$$

$$= E^{\ominus}_{(cell)} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (3.13)$$

Example 3.1

Represent the cell in which the following reaction takes place

$Mg(s) + 2Ag^{+}(0.0001M) \rightarrow Mg^{2+}(0.130M) + 2Ag(s)$

Calculate its $E_{(cell)}$ if $E^{\ominus}_{(cell)} = 3.17$ V.

Solution

The cell can be written as $Mg \mid Mg^{2+}(0.130M) \mid\mid Ag^{+}(0.0001M) \mid Ag$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^{+}]^2}$$

$$= 3.17\ V - \frac{0.059V}{2} \log \frac{0.130}{(0.0001)^2} = 3.17\ V - 0.21V = 2.96\ V.$$

3.3.1 Equilibrium Constant from Nernst Equation

If the circuit in Daniell cell (Fig. 3.1) is closed then we note that the reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (3.1)$$

takes place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E_{(cell)} = 0 = E^{\ominus}_{(cell)} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{or } E^{\ominus}_{(cell)} = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c \text{ for the reaction 3.1}$$

and at T = 298K the above equation can be written as

$$E^{\ominus}_{(cell)} = \frac{0.059\ V}{2} \log K_C = 1.1\ V \qquad (E^{\ominus}_{(cell)} = 1.1V)$$

$$\log K_C = \frac{(1.1V \times 2)}{0.059\ V} = 37.288$$

$K_C = 2 \times 10^{37}$ at 298K.

In general,

$$E^{\ominus}_{(cell)} = \frac{2.303RT}{nF} \log K_C \qquad (3.14)$$

Thus, Eq. (3.14) gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding $E^{\ominus}$ value of the cell.

Example 3.2 Calculate the equilibrium constant of the reaction:

$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

$E^{\ominus}_{(cell)} = 0.46\ V$

Solution $E^{\ominus}_{(cell)} = \frac{0.059\ V}{2} \log K_C = 0.46\ V$ or

$$\log K_C = \frac{0.46\ V \times 2}{0.059\ V} = 15.6$$

$K_C = 3.92 \times 10^{15}$

3.3.2 Electro-chemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic cell then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_r G = -\ nFE_{(cell)} \qquad (3.15)$$

It may be remembered that $E_{(cell)}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n. Thus, if we write the reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad (3.1)$$

$$\Delta_r G = -2FE_{(cell)}$$

but when we write the reaction

$$2\ Zn(s) + 2\,Cu^{2+}(aq) \longrightarrow 2\ Zn^{2+}(aq) + 2\,Cu(s)$$

$\Delta_r G = -4FE_{(cell)}$

If the concentration of all the reacting species is unity, then $E_{(cell)} = E^{\ominus}_{(cell)}$ and we have

$$\Delta_r G^{\ominus} = -nFE^{\ominus}_{(cell)} \quad (3.16)$$

Thus, from the measurement of $E^{\ominus}_{(cell)}$ we can obtain an important thermodynamic quantity, $\Delta_r G^{\ominus}$, standard Gibbs energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$\Delta_r G^{\ominus} = -RT \ln K$.

Example 3.3 The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Solution $\Delta_r G^{\ominus} = -nFE^{\ominus}_{(cell)}$

n in the above equation is 2, F = 96487 C mol^{-1} and $E^{\ominus}_{(cell)} = 1.1$ V

Therefore, $\Delta_r G^{\ominus} = -2 \times 1.1V \times 96487 \text{ C mol}^{-1}$

$= -21227 \text{ J mol}^{-1}$

$= -21.227 \text{ kJ mol}^{-1}$

Intext Questions

3.4 Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

3.5 Calculate the emf of the cell in which the following reaction takes place

$Ni(s) + 2Ag^{+}(0.002 \text{ M}) \rightarrow Ni^{2+}(0.160 \text{ M}) + 2Ag(s)$

Given that $E^{\ominus}_{(cell)} = 1.05$ V

3.6 The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^{0}_{cell} = 0.236$ V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

3.4 Conductance of Electrolytic Solutions

It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol '*R*' and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m^2)/(s^3 A^2). It can be measured with the help of a Wheatstone bridge with which you are familiar

from your study of physics. The electrical resistance of any object is directly proportional to its length, l, and inversely proportional to its area of cross section, A. That is,

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A} \tag{3.17}$$

The constant of proportionality, ρ (Greek, rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often its submultiple, ohm centimetre (Ω cm) is also used. IUPAC recommends the use of the term resistivity over specific resistance and hence in the rest of the book we shall use the term resistivity. Physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that:

1 Ω m = 100 Ω cm or 1 Ω cm = 0.01 Ω m

The inverse of resistance, R, is called **conductance**, G, and we have the relation:

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l} \tag{3.18}$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). IUPAC has recommended the use of term conductivity over specific conductance and hence we shall use the term conductivity in the rest of the book. The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1}. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that 1 S cm^{-1} = 100 S m^{-1}.

Table 3.2 The values of Conductivity of some Selected Materials at 298.15 K

Material	Conductivity/ S m^{-1}	Material	Conductivity/ S m^{-1}
Conductors		***Aqueous Solutions***	
Sodium	2.1×10^{3}	Pure water	3.5×10^{-5}
Copper	5.9×10^{3}	0.1 M HCl	3.91
Silver	6.2×10^{3}	0.01M KCl	0.14
Gold	4.5×10^{3}	0.01M NaCl	0.12
Iron	1.0×10^{3}	0.1 M HAc	0.047
Graphite	1.2×10	0.01M HAc	0.016
Insulators		***Semiconductors***	
Glass	1.0×10^{-16}	CuO	1×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

It can be seen from Table 3.2 that the magnitude of conductivity varies a great deal and depends on the nature of the material. It also depends on the temperature and pressure at which the measurements

are made. Materials are classified into conductors, insulators and semiconductors depending on the magnitude of their conductivity. Metals and their alloys have very large conductivity and are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers* are also electronically conducting. Substances like glass, ceramics, etc., having very low conductivity are known as insulators. Substances like silicon, doped silicon and gallium arsenide having conductivity between conductors and insulators are called semiconductors and are important electronic materials. Certain materials called superconductors by definition have zero resistivity or infinite conductivity. Earlier, only metals and their alloys at very low temperatures (0 to 15 K) were known to behave as superconductors, but nowadays a number of ceramic materials and mixed oxides are also known to show superconductivity at temperatures as high as 150 K.

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on

(i) the nature and structure of the metal

(ii) the number of valence electrons per atom

(iii) temperature (it decreases with increase of temperature).

As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex.

We already know (Class XI, Unit 7) that even very pure water has small amounts of hydrogen and hydroxyl ions (~10^{-7}M) which lend it very low conductivity (3.5×10^{-5} S m^{-1}). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity also increases. The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on:

(i) the nature of the electrolyte added

(ii) size of the ions produced and their solvation

(iii) the nature of the solvent and its viscosity

(iv) concentration of the electrolyte

(v) temperature (it increases with the increase of temperature).

Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions (Section 3.4.1).

* *Electronically conducting polymers – In 1977 MacDiarmid, Heeger and Shirakawa discovered that acetylene gas can be polymerised to produce a polymer, polyacetylene when exposed to vapours of iodine acquires metallic lustre and conductivity. Since then several organic conducting polymers have been made such as polyaniline, polypyrrole and polythiophene. These organic metals, being composed wholly of elements like carbon, hydrogen and occasionally nitrogen, oxygen or sulphur, are much lighter than normal metals and can be used for making light-weight batteries. Besides, they have the mechanical properties of polymers such as flexibility so that one can make electronic devices such as transistors that can bend like a sheet of plastic. For the discovery of conducting polymers, MacDiarmid, Heeger and Shirakawa were awarded the Nobel Prize in Chemistry for the year 2000.*

3.4.1 Measurement of the Conductivity of Ionic Solutions

We know that accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. However, for measuring the resistance of an ionic solution we face two problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor. The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell.** It is available in several designs and two simple ones are shown in Fig. 3.4.

Fig. 3.4: *Two different types of conductivity cells.*

Basically it consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically). These have area of cross section equal to '*A*' and are separated by distance '*l*'. Therefore, solution confined between these electrodes is a column of length *l* and area of cross section *A*. The resistance of such a column of solution is then given by the equation:

$$R = \rho \frac{l}{A} = \frac{l}{\kappa A} \tag{3.17}$$

The quantity l/A is called cell constant denoted by the symbol, G^*. It depends on the distance between the electrodes and their area of cross-section and has the dimension of length^{-1} and can be calculated if we know *l* and *A*. Measurement of *l* and *A* is not only inconvenient but also unreliable. The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations (Table 3.3) and at different temperatures. The cell constant, G^*, is then given by the equation:

$$G^* = \frac{l}{A} = R\,\kappa \tag{3.18}$$

Molarity	Concentration	Conductivity		Molar Conductivity	
mol L^{-1}	mol m^{-3}	S cm^{-1}	S m^{-1}	S $cm^2 mol^{-1}$	S m^2 mol^{-1}
1.000	1000	0.1113	11.13	111.3	111.3×10^{-4}
0.100	100.0	0.0129	1.29	129.0	129.0×10^{-4}
0.010	10.00	0.00141	0.141	141.0	141.0×10^{-4}

Table 3.3 Conductivity and Molar conductivity of KCl solutions at 298.15K

Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. The set up for the measurement of the resistance is shown in Fig. 3.5.

Fig. 3.5: *Arrangement for measurement of resistance of a solution of an electrolyte.*

It consists of two resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The Wheatstone bridge is fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

$$\text{Unknown resistance } R_2 = \frac{R_1 R_4}{R_3} \qquad (3.19)$$

These days, inexpensive conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell. Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{cell constant}}{R} = \frac{G^*}{R} \qquad (3.20)$$

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient. It, therefore, becomes necessary to define a physically more meaningful quantity called **molar conductivity** denoted by the symbol Λ_m (Greek, lambda). It is related to the conductivity of the solution by the equation:

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c} \qquad (3.21)$$

In the above equation, if κ is expressed in S m^{-1} and the concentration,

c in mol m^{-3} then the units of Λ_m are in S m^2 mol^{-1}. It may be noted that:

1 mol m^{-3} = 1000(L/m^3) × molarity (mol/L), and hence

$$\Lambda_m(\text{S m}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S m}^{-1})}{1000\ \text{L m}^{-3} \times \text{molarity (mol L}^{-1})}$$

If we use S cm^{-1} as the units for κ and mol cm^{-3}, the units of concentration, then the units for $\ddot{E}_m$ are S cm^2 mol^{-1}. It can be calculated by using the equation:

$$L_m(\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1}) \times 1000\,(\text{cm}^3/\text{L})}{\text{molarity (mol/L)}}$$

Both type of units are used in literature and are related to each other by the equations:

1 S m^2mol^{-1} = 10^4 S cm^2mol^{-1} or

1 S cm^2mol^{-1} =10^{-4} S m^2mol^{-1}.

Example 3.4 Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m.

Solution The cell constant is given by the equation:

Cell constant = G^* = conductivity × resistance

= 1.29 S/m × 100 Ω = 129 m^{-1} = 1.29 cm^{-1}

Conductivity of 0.02 mol L^{-1} KCl solution = cell constant / resistance

$$= \frac{G^*}{R} = \frac{129\ \text{m}^{-1}}{520\ \Omega} = 0.248\ \text{S m}^{-1}$$

Concentration = 0.02 mol L^{-1}

= 1000 × 0.02 mol m^{-3}

= 20 mol m^{-3}

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{248 \times 10^{-3}\ \text{S m}^{-1}}{20\ \text{mol m}^{-3}}$$

$$= 124 \times 10^{-4}\ \text{S m}^2\text{mol}^{-1}$$

$$\text{Alternatively, } \kappa = \frac{1.29\ \text{cm}^{-1}}{520\ \Omega}$$

$$= 0.248 \times 10^{-2}\ \text{S cm}^{-1}$$

and $\Lambda_m = \kappa \times 1000\ \text{cm}^3\ \text{L}^{-1}\ \text{molarity}^{-1}$

$$= \frac{0.248\times10^{-2}\ \text{S cm}^{-1}\times1000\ \text{cm}^3\ \text{L}^{-1}}{0.02\ \text{mol L}^{-1}}$$

$$= 124\ \text{S cm}^2\ \text{mol}^{-1}$$

Example 3.5

The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution

$A = \pi r^2 = 3.14 \times 0.5^2\ \text{cm}^2 = 0.785\ \text{cm}^2 = 0.785 \times 10^{-4}\ \text{m}^2$

$l = 50\ \text{cm} = 0.5\ \text{m}$

$$R = \frac{\rho\, l}{A} \quad \text{or} \quad \rho = \frac{RA}{l} = \frac{5.55\times10^3\,\Omega\times0.785\,\text{cm}^2}{50\,\text{cm}} = 87.135\ \Omega\ \text{cm}$$

$$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left(\frac{1}{87.135}\right)\ \text{S cm}^{-1}$$

$$= 0.01148\ \text{S cm}^{-1}$$

$$\text{Molar conductivity},\ \Lambda_m = \frac{\kappa \times 1000}{c}\ \text{cm}^3\ \text{L}^{-1}$$

$$= \frac{0.01148\ \text{S cm}^{-1} \times1000\ \text{cm}^3\ \text{L}^{-1}}{0.05\ \text{mol L}^{-1}}$$

$$= 229.6\ \text{S cm}^2\ \text{mol}^{-1}$$

If we want to calculate the values of different quantities in terms of 'm' instead of 'cm',

$$\rho = \frac{RA}{l}$$

$$= \frac{5.55 \times 10^3\ \Omega \times 0.785\times10^{-4}\ \text{m}^2}{0.5\ \text{m}}$$

$$= 87.135 \times10^{-2}\ \Omega\ \text{m}$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135}\Omega\ \text{m} = 1.148\ \text{S m}^{-1}$$

$$\text{and} \quad \Lambda_m = \frac{\kappa}{c} = \frac{1.148\ \text{S m}^{-1}}{50\ \text{mol m}^{-3}}$$

$$= 229.6 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}.$$

3.4.2 Variation of Conductivity and Molar Conductivity with Concentration

Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two

platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$G = \frac{\kappa A}{l} = \kappa$ (both A and l are unity in their appropriate units in m or cm)

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore,

$$\Lambda_m = \frac{\kappa A}{l} = \kappa$$

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V \quad (3.22)$$

Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration, Λ_m can be defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol Λ_m°. The variation in Λ_m with concentration is different (Fig. 3.6) for strong and weak electrolytes.

Strong Electrolytes

For strong electrolytes, Λ increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda_m^\circ - A\, c^{1/2} \quad (3.23)$$

It can be seen that if we plot (Fig. 3.12) Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal to Λ_m° and slope equal to '$-A$'. The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in

Fig. 3.6: *Molar conductivity versus c½ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.*

the solution. Thus, NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for '*A*'.

Example 3.6

The molar conductivity of KCl solutions at different concentrations at 298 K are given below:

c/mol L^{-1}	**Λ_m/S cm^2 mol^{-1}**
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between $\ddot{E}_m$ and $c^{1/2}$ is a straight line. Determine the values of $\ddot{E}_m^\circ$ and A for KCl.

Solution

Taking the square root of concentration we obtain:

$c^{1/2}$/ (mol L^{-1})$^{1/2}$	**Λ_m/S cm^{2}mol^{-1}**
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

A plot of Λ_m(y-axis) and $c^{1/2}$ (*x*-axis) is shown in (Fig. 3.7).

It can be seen that it is nearly a straight line. From the intercept ($c^{1/2}$ = 0), we find that $\ddot{E}_m^\circ$= 150.0 S cm^2 mol^{-1} and

A = – slope = 87.46 S cm^2 mol^{-1}/(mol/L^{-1})$^{1/2}$.

Fig. 3.7: *Variation of $\ddot{E}_m$ against c½.*

Kohlrausch examined Λ_m° values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ_m° of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:

$$\Lambda^\circ_{m\,(KCl)} - \Lambda^\circ_{m\,(NaCl)} = \Lambda^\circ_{m\,(KBr)} - \Lambda^\circ_{m\,(NaBr)}$$
$$= \Lambda^\circ_{m\,(KI)} - \Lambda^\circ_{m\,(NaI)} \simeq 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

and similarly it was found that

$$\Lambda^\circ_{m\,(NaBr)} - \Lambda^\circ_{m\,(NaCl)} = \Lambda^\circ_{m\,(KBr)} - \Lambda^\circ_{m\,(KCl)} \simeq 1.8 \text{ S cm}^2 \text{ mol}^{-1}$$

On the basis of the above observations he enunciated **Kohlrausch law of independent migration of ions**. The law states that *limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if* $\lambda^\circ_{Na^+}$ *and* $\lambda^\circ_{Cl^-}$ *are limiting molar conductivity* of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda^\circ_{m\,(NaCl)} = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \qquad (3.24)$$

In general, if an electrolyte on dissociation gives υ_+ cations and υ_- anions then its limiting molar conductivity is given by:

$$\Lambda^\circ_m = \nu_+ \lambda^0_+ + \nu_- \lambda^0_- \qquad (3.25)$$

Here, λ^0_+ and λ^0_- are the limiting molar conductivities of the cation and anion respectively. The values of λ^0 for some cations and anions at 298 K are given in Table 3.4.

Table 3.4 Limiting molar conductivity for some ions in water at 298 K

Ion	λ^0/(S cm²mol⁻¹)	Ion	λ^0/(S cm² mol⁻¹)
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Ca^{2+}	119.0	CH_3COO^-	40.9
Mg^{2+}	106.0	SO_4^{2-}	160.0

Weak electrolytes

Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. In such cases Λ_m increases steeply (Fig. 3.12) on dilution, especially near lower concentrations. Therefore, Λ_m° cannot be obtained by extrapolation of Λ_m to zero concentration. At infinite dilution (i.e., concentration c $\rightarrow$ zero) electrolyte dissociates completely (α =1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore, Λ_m° for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions (Example 3.8). At any concentration c, if α is the degree of dissociation then it can be approximated to the ratio of molar conductivity Λ_m at the concentration c to limiting molar conductivity, Λ_m°. Thus we have:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} \tag{3.26}$$

But we know that for a weak electrolyte like acetic acid (Class XI, Unit 7),

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ 2}\left(1-\frac{\Lambda_m}{\Lambda_m^\circ}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^\circ\left(\Lambda_m^\circ - \Lambda_m\right)} \tag{3.27}$$

Applications of Kohlrausch law

Using Kohlrausch law of independent migration of ions, it is possible to calculate Λ_m° for any electrolyte from the λ° of individual ions. Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the Λ_m° and Λ_m at a given concentration c.

Example 3.7

Calculate Λ_m° for $CaCl_2$ and $MgSO_4$ from the data given in Table 3.4.

Solution

We know from Kohlrausch law that

$$\Lambda^\circ_{m(CaCl_2)} = \lambda^\circ_{Ca^{2+}} + 2\lambda^\circ_{Cl^-} = 119.0 \text{ S cm}^2 \text{ mol}^{-1} + 2(76.3) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= (119.0 + 152.6) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ_{m(MgSO_4)} = \lambda^\circ_{Mg^{2+}} + \lambda^\circ_{SO_4^{2-}} = 106.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 266 \text{ S cm}^2 \text{ mol}^{-1}.$$

Example 3.8

Λ_m° for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ° for HAc.

Solution

$$\Lambda^\circ_{m(HAc)} = \lambda^\circ_{H^+} + \lambda^\circ_{Ac^-} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{Ac^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+}$$

$$= \Lambda^\circ_{m(HCl)} + \Lambda^\circ_{m(NaAc)} - \Lambda^\circ_{m(NaCl)}$$

$$= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}.$$

Example 3.9

The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}.

Solution

$$\Lambda_m = \frac{\kappa}{c} = \frac{4.95\times10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} = 48.15 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{48.15 \text{ S cm}^2\text{mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1233$$

$$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \text{ mol L}^{-1} \times (0.1233)^2}{1-0.1233} = 1.78\times10^{-5} \text{ mol L}^{-1}$$

Intext Questions

3.7 Why does the conductivity of a solution decrease with dilution?

3.8 Suggest a way to determine the Λ_m° value of water.

3.9 The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(H^+)$ = 349.6 S cm^2 mol^{-1} and $\lambda^0(HCOO^-)$ = 54.6 S cm^2 mol^{-1}

3.5 Electrolytic Cells and Electrolysis

In an **electrolytic cell** external source of voltage is used to bring about a chemical reaction. The electrochemical processes are of great importance in the laboratory and the chemical industry. One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction takes place:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \qquad (3.28)$$

Copper metal is deposited on the cathode. At the anode, copper is converted into Cu^{2+} ions by the reaction:

$$Cu(s) \rightarrow Cu^{2+}(s) + 2e^- \qquad (3.29)$$

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at the cathode. Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

Sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced (Class XII, Unit 6) by electrolysis of aluminium oxide in presence of cryolite.

Quantitative Aspects of Electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Now Faraday's laws also flow from what has been discussed earlier.

Faraday's Laws of Electrolysis

After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of the following well known Faraday's two laws of electrolysis:

1. First Law

The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

2. Second Law

The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

There were no constant current sources available during Faraday's times. The general practice was to put a coulometer (a standard electrolytic cell) for determining the quantity of electricity passed from the amount of metal (generally silver or copper) deposited or consumed. However, coulometers are now obsolete and we now have constant current (I) sources available and the quantity of electricity Q, passed is given by

$$Q = It$$

Q is in coloumbs when I is in ampere and t is in second.

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s) \quad (3.30)$$

One mole of the electron is required for the reduction of one mole of silver ions. We know that charge on one electron is equal to 1.6021×10^{-19}C. Therefore, the charge on one mole of electrons is equal to:

$$N_A \times 1.6021 \times 10^{-19} \quad C = 6.02 \times 10^{23} mol^{-1} \times 1.6021 \times 10^{-19}$$
$$C = 96487 \ C \ mol^{-1}$$

This quantity of electricity is called **Faraday** and is represented by the symbol **F**.

For approximate calculations we use $1F \simeq 96500 \ C \ mol^{-1}$.

For the electrode reactions:

$$Mg^{2+}(l) + 2e^{-} \longrightarrow Mg(s) \quad (3.31)$$

$$Al^{3+}(l) + 3e^{-} \longrightarrow Al(s) \quad (3.32)$$

It is obvious that one mole of Mg^{2+} and Al^{3+} require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively. The charge passed through the electrolytic cell during electrolysis is equal to the product of current in amperes and time in seconds. In commercial production of metals, current as high as 50,000 amperes are used that amounts to about 0.518 F per second.

Example 3.10

A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Solution

t = 600 s charge = current × time = 1.5 A × 600 s = 900 C

According to the reaction:

$Cu^{2+}(aq) + 2e^{-} = Cu(s)$

We require 2F or 2 × 96487 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited = $(63 \ g \ mol^{-1} \times 900 \ C)/(2 \times 96487 \ C \ mol^{-1})$ = 0.2938 g.

3.5.1 Products of Electrolysis

Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert

electrodes.The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these don't seem to take place and extra potential (called *overpotential*) has to be applied, which makes such process more difficult to occur.

For example, if we use molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas. Here we have only one cation (Na^+) which is reduced at the cathode ($Na^+ + e^- \rightarrow Na$) and one anion ($Cl^-$) which is oxidised at the anode ($Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl_2 and H_2. In this case besides Na^+ and Cl^- ions we also have H^+ and OH^- ions along with the solvent molecules, H_2O.

At the cathode there is competition between the following reduction reactions:

$$Na^+ (aq) + e^- \rightarrow Na (s) \qquad E^{\ominus}_{(cell)} = -2.71 \text{ V}$$

$$H^+ (aq) + e^- \rightarrow \tfrac{1}{2} H_2 (g) \qquad E^{\ominus}_{(cell)} = 0.00 \text{ V}$$

The reaction with higher value of $E^{\ominus}$ is preferred and, therefore, the reaction at the cathode during electrolysis is:

$$H^+ (aq) + e^- \rightarrow \tfrac{1}{2} H_2 (g) \qquad (3.33)$$

but H^+ (aq) is produced by the dissociation of H_2O, i.e.,

$$H_2O (l) \rightarrow H^+ (aq) + OH^- (aq) \qquad (3.34)$$

Therefore, the net reaction at the cathode may be written as the sum of (3.33) and (3.34) and we have

$$H_2O (l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^- \qquad (3.35)$$

At the anode the following oxidation reactions are possible:

$$Cl^- (aq) \rightarrow \tfrac{1}{2} Cl_2 (g) + e^- \qquad E^{\ominus}_{(cell)} = 1.36 \text{ V} \qquad (3.36)$$

$$2H_2O (l) \rightarrow O_2 (g) + 4H^+(aq) + 4e^- \qquad E^{\ominus}_{(cell)} = 1.23 \text{ V} \qquad (3.37)$$

The reaction at anode with lower value of $E^{\ominus}$ is preferred and therefore, water should get oxidised in preference to Cl^- (aq). However, on account of overpotential of oxygen, reaction (3.36) is preferred. Thus, the net reactions may be summarised as:

$$NaCl (aq) \xrightarrow{H_2O} Na^+ (aq) + Cl^- (aq)$$

Cathode: $H_2O(l) + e^- \rightarrow \tfrac{1}{2} H_2(g) + OH^- (aq)$

Anode: $Cl^- (aq) \rightarrow \tfrac{1}{2} Cl_2(g) + e^-$

Net reaction:

$$NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g)$$

The standard electrode potentials are replaced by electrode potentials given by Nernst equation (Eq. 3.8) to take into account the concentration effects. During the electrolysis of sulphuric acid, the following processes are possible at the anode:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^{\ominus}_{(cell)} = +1.23 \text{ V}, \qquad (3.38)$$

$$2SO_4^{2-}\ (aq) \rightarrow S_2O_8^{2-}\ (aq) + 2e^- \qquad E^{\ominus}_{(cell)} = 1.96\ V \qquad (3.39)$$

For dilute sulphuric acid, reaction (3.38) is preferred but at higher concentrations of H_2SO_4 process, reaction (3.39) is preferred.

Intext Questions

3.10 If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

3.11 Suggest a list of metals that are extracted electrolytically.

3.12 Consider the reaction:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

3.6 Batteries

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

3.6.1 Primary Batteries

In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again. The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon (Fig.3.8). The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The electrode reactions are complex, but they can be written approximately as follows :

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

Mercury cell, (Fig. 3.9) suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

Fig. 3.8: A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.

Fig. 3.9: *Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.*

The overall reaction is represented by

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

3.6.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery (Fig. 3.10) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$$Pb(s)+PbO_2(s)+2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

Fig. 3.10: *The Lead storage battery.*

Another important secondary cell is the nickel-cadmium cell (Fig. 3.11) which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

Fig. 3.11: A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

$$Cd\ (s) + 2Ni(OH)_3\ (s) \rightarrow CdO\ (s) + 2Ni(OH)_2\ (s) + H_2O(l)$$

3.7 Fuel Cells

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.

Fig. 3.12: Fuel cell using H_2 and O_2 produces electricity.

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (Fig. 3.12). The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode: $2H_2\ (g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Overall reaction being:

$2H_2(g) + O_2(g) \longrightarrow 2\ H_2O(l)$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

3.8 Corrosion

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion.

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot (Fig. 3.13) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction

Anode: $2\ Fe\ (s) \longrightarrow 2\ Fe^{2+} + 4\ e^-$ $\quad E^{\ominus}_{(Fe^{2+}/Fe)} = -\ 0.44\ V$

Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$
Reduction: $O_2\ (g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
Atomospheric
oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + ½O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

Fig. 3.13: *Corrosion of iron in atmosphere.*

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

Cathode: $O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O\ (l)$ $\quad E^{\ominus}_{H^+|O_2\ |H_2O} = 1.23\ V$

The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2\ +}(aq) + 2\ H_2O\ (l)$ $\quad E^{\ominus}_{(cell)} = 1.67\ V$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . x H_2O$) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Intext Questions

3.13 Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

3.14 Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

3.15 Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

The Hydrogen Economy

At present the main source of energy that is driving our economy is fossil fuels such as coal, oil and gas. As more people on the planet aspire to improve their standard of living, their energy requirement will increase. In fact, the per capita consumption of energy used is a measure of development. Of course, it is assumed that energy is used for productive purpose and not merely wasted. We are already aware that carbon dioxide produced by the combustion of fossil fuels is resulting in the 'Greenhouse Effect'. This is leading to a rise in the temperature of the Earth's surface, causing polar ice to melt and ocean levels to rise. This will flood low-lying areas along the coast and some island nations such as Maldives face total submergence. In order to avoid such a catastrope, we need to limit our use of carbonaceous fuels. Hydrogen provides an ideal alternative as its combustion results in water only. Hydrogen production must come from splitting water using solar energy. Therefore, hydrogen can be used as a renewable and non polluting source of energy. This is the vision of the Hydrogen Economy. Both the production of hydrogen by electrolysis of water and hydrogen combustion in a fuel cell will be important in the future. And both these technologies are based on electrochemical principles.

Summary

An **electrochemical cell** consists of two metallic electrodes dipping in electrolytic solution(s). Thus an important component of the electrochemical cell is the ionic conductor or electrolyte. Electrochemical cells are of two types. In **galvanic cell**, the **chemical**

energy of a **spontaneous redox reaction** is converted into electrical work, whereas in an electrolytic cell, electrical energy is used to carry out a **non-spontaneous redox reaction**. The **standard electrode potential** for any electrode dipping in an appropriate solution is defined with respect to standard electrode potential of **hydrogen electrode** taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode ($E^{\ominus}_{(cell)} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$). The standard potential of the cells are related to standard Gibbs energy ($\Delta_r G^{\ominus} = -nFE^{\ominus}_{(cell)}$) and **equilibrium constant** ($\Delta_r G^{\ominus} = -RT \ln K$) of the reaction taking place in the cell. Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.

The **conductivity**, κ, of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature. **Molar conductivity**, Λ_m, is defined by $= \kappa / c$ where c is the concentration. Conductivity decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrausch found that molar conductivity at infinite dilution, for an electrolyte is sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as **law of independent migration of ions** and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions take place at the electrodes in an electrochemical cell. **Batteries** and **fuel cells** are very useful forms of galvanic cell. **Corrosion** of metals is essentially an **electrochemical phenomenon**. Electrochemical principles are relevant to the **Hydrogen Economy**.

Exercises

3.1 Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

3.2 Given the standard electrode potentials,

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,

$Hg^{2+}/Hg = 0.79V$

$Mg^{2+}/Mg = -2.37\ V$, $Cr^{3+}/Cr = -0.74V$

Arrange these metals in their increasing order of reducing power.

3.3 Depict the galvanic cell in which the reaction $Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$ takes place. Further show:

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

3.4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place:

(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$

(ii) $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the $\Delta_r G^{\ominus}$ and equilibrium constant of the reactions.

3.5 Write the Nernst equation and emf of the following cells at 298 K:

(i) $Mg(s) | Mg^{2+}(0.001M) || Cu^{2+}(0.0001\ M) | Cu(s)$

(ii) $Fe(s) | Fe^{2+}(0.001M) || H^+(1M) | H_2(g)(1bar) | Pt(s)$

(iii) $Sn(s) | Sn^{2+}(0.050\ M) || H^+(0.020\ M) | H_2(g)\ (1\ bar) | Pt(s)$

(iv) $Pt(s) | Br_2(l) | Br^-(0.010\ M) || H^+(0.030\ M) | H_2(g)\ (1\ bar) | Pt(s)$.

3.6 In the button cells widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^\ominus$ and $E^\ominus$ for the reaction.

3.7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

3.9 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}.

3.10 The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa$/S m^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{½}$. Find the value of Λ_m^0.

3.11 Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ_m^0 for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

3.12 How much charge is required for the following reductions:

(i) 1 mol of Al^{3+} to Al.

(ii) 1 mol of Cu^{2+} to Cu.

(iii) 1 mol of MnO_4^- to Mn^{2+}.

3.13 How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten $CaCl_2$.

(ii) 40.0 g of Al from molten Al_2O_3.

3.14 How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2.

(ii) 1 mol of FeO to Fe_2O_3.

3.15 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

3.16 Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

3.17 Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

(i) $Fe^{3+}(aq)$ and $I^-(aq)$

(ii) Ag^+ (aq) and Cu(s)

(iii) Fe^{3+} (aq) and Br^- (aq)

(iv) Ag(s) and Fe^{3+} (aq)

(v) Br_2 (aq) and Fe^{2+} (aq).

3.18 Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes.

(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.

(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

Answers to Some Intext Questions

3.5 $E_{(cell)} = 0.91$ V

3.6 $\Delta_r G^\ominus = -45.54\ kJ\ mol^{-1}$, $K_c = 9.62 \times 10^7$

3.9 0.114, 3.67×10^{-4} mol L^{-1}

Unit

4

Chemical Kinetics

Objectives

After studying this Unit, you will be able to

- define the average and instantaneous rate of a reaction;
- express the rate of a reaction in terms of change in concentration of either of the reactants or products with time;
- distinguish between elementary and complex reactions;
- differentiate between the molecularity and order of a reaction;
- define rate constant;
- discuss the dependence of rate of reactions on concentration, temperature and catalyst;
- derive integrated rate equations for the zero and first order reactions;
- determine the rate constants for zeroth and first order reactions;
- describe collision theory.

Chemical Kinetics helps us to understand how chemical reactions occur.

Chemistry, by its very nature, is concerned with change. Substances with well defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out

(a) the feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);

(b) extent to which a reaction will proceed can be determined from chemical equilibrium;

(c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **chemical kinetics**. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all. Therefore, most people think

that diamond is forever. Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions, are discussed.

In this Unit, we shall be dealing with average and instantaneous rate of reaction and the factors affecting these. Some elementary ideas about the collision theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate.

4.1 Rate of a Chemical Reaction

Some reactions such as ionic reactions occur very fast, for example, precipitation of silver chloride occurs instantaneously by mixing of aqueous solutions of silver nitrate and sodium chloride. On the other hand, some reactions are very slow, for example, rusting of iron in the presence of air and moisture. Also there are reactions like inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed. Can you think of more examples from each category?

You must be knowing that speed of an automobile is expressed in terms of change in the position or distance covered by it in a certain period of time. Similarly, the speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

(i) the rate of decrease in concentration of any one of the reactants, or

(ii) the rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta[P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \qquad (4.1)$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \qquad (4.2)$$

Since, Δ[R] is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.

Equations (4.1) and (4.2) given above represent the average rate of a reaction, r_{av}.

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur (Fig. 4.1).

Fig. 4.1: *Instantaneous and average rate of a reaction*

Units of rate of a reaction

From equations (4.1) and (4.2), it is clear that units of rate are concentration time^{-1}. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol L^{-1}s^{-1}. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

Example 4.1

From the concentrations of C_4H_9Cl (butyl chloride) at different times given below, calculate the average rate of the reaction:

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

during different intervals of time.

t/s	0	50	100	150	200	300	400	700	800
$[C_4H_9Cl]$/mol L^{-1}	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

Solution

We can determine the difference in concentration over different intervals of time and thus determine the average rate by dividing Δ[R] by Δt (Table 4.1).

Table 4.1: Average rates of hydrolysis of butyl chloride

$[C_4H_9Cl]_{t_1}$ / mol L^{-1}	$[C_4H_9Cl]_{t_2}$ / mol L^{-1}	t_1/s	t_2/s	$r_{av} \times 10^4$/mol $L^{-1}s^{-1}$ $= -\{[C_4H_9Cl]_{t_2} - [C_4H_9Cl]_{t_1} / (t_2 - t_1)\} \times 10^4$
0.100	0.0905	0	50	1.90
0.0905	0.0820	50	100	1.70
0.0820	0.0741	100	150	1.58
0.0741	0.0671	150	200	1.40
0.0671	0.0549	200	300	1.22
0.0549	0.0439	300	400	1.10
0.0439	0.0335	400	500	1.04
0.0210	0.017	700	800	0.4

It can be seen (Table 4.1) that the average rate falls from 1.90×0^{-4} mol $L^{-1}s^{-1}$ to 0.4×10^{-4} = mol $L^{-1}s^{-1}$. However, average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the **instantaneous rate**. It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero). Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \qquad (4.3)$$

As $\Delta t \rightarrow 0$ or $r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$

Fig 4.2
Instantaneous rate of hydrolysis of butyl chloride(C_4H_9Cl)

It can be determined graphically by drawing a tangent at time t on either of the curves for concentration of R and P vs time t and calculating its slope (Fig. 4.1). So in problem 4.1, r_{inst} at 600s for example, can be calculated by plotting concentration of butyl chloride as a function of time. A tangent is drawn that touches the curve at $t = 600$ s (Fig. 4.2).

The slope of this tangent gives the instantaneous rate.

$$\text{So, } r_{inst} \text{ at } 600 \text{ s} = \left(\frac{0.0165 - 0.037}{(800 - 400)\text{ s}}\right) \text{ mol L}^{-1} = 5.12 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

At $t = 250$ s $\quad r_{inst} = 1.22 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 350$ s $\quad r_{inst} = 1.0 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 450$ s $\quad r_{inst} = 6.4 \times 10^{-5}$ mol $L^{-1}s^{-1}$

Now consider a reaction

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Where stoichiometric coefficients of the reactants and products are same, then rate of the reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

i.e., rate of disappearance of any of the reactants is same as the rate of appearance of the products. But in the following reaction, two moles of HI decompose to produce one mole each of H_2 and I_2,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometric coefficients. Since rate of consumption of HI is twice the rate of formation of H_2 or I_2, to make them equal, the term $\Delta[HI]$ is divided by 2. The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Similarly, for the reaction

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change in partial pressure of the reactant or the product.

Example 4.2 The decomposition of N_2O_5 in CCl_4 at 318K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1}. The reaction takes place according to the equation

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period?

Solution

$$\text{Average Rate} = \frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\} = -\frac{1}{2}\left[\frac{(2.08-2.33)\,\text{mol L}^{-1}}{184\,\text{min}}\right]$$

$= 6.79 \times 10^{-4}$ mol L^{-1}/min = (6.79×10^{-4} mol L^{-1} min^{-1}) × (60 min/1h)

$= 4.07 \times 10^{-2}$ mol L^{-1}/h

$= 6.79 \times 10^{-4}$ mol L^{-1} × 1min/60s

$= 1.13 \times 10^{-5}$ mol $L^{-1}s^{-1}$

It may be remembered that

$$\text{Rate} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$$\frac{\Delta[NO_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4 \text{ mol L}^{-1}\text{ min}^{-1} = 2.72 \times 10^{-3} \text{ mol L}^{-1}\text{min}^{-1}$$

Intext Questions

4.1 For the reaction R → P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

4.2 In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

4.2 Factors Influencing Rate of a Reaction

Rate of reaction depends upon the experimental conditions such as concentration of reactants (pressure in case of gases), temperature and catalyst.

4.2.1 Dependence of Rate on Concentration

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

4.2.2 Rate Expression and Rate Constant

The results in Table 4.1 clearly show that rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, rate of a reaction depends upon the concentration of reactants.

Consider a general reaction

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

where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

$$\text{Rate} \propto [A]^x \ [B]^y \tag{4.4}$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

$$\text{Rate} = k\,[A]^x \ [B]^y \tag{4.4a}$$

$$-\frac{d[R]}{dt} = k[A]^x[B]^y \tag{4.4b}$$

This form of equation (4.4 b) is known as differential rate equation, where k is a proportionality constant called **rate constant**. The equation like (4.4), which relates the rate of a reaction to concentration of reactants is called rate law or rate expression. Thus, **rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation**. For example:

$$2NO(g) + O_2(g) \rightarrow 2NO_2\ (g)$$

We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants. The following results are obtained (Table 4.2).

Table 4.2: Initial rate of formation of NO_2

Experiment	Initial [NO]/ mol L^{-1}	Initial $[O_2]$/ mol L^{-1}	Initial rate of formation of NO_2/ mol $L^{-1}s^{-1}$
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.192
4.	0.60	0.60	0.768

It is obvious, after looking at the results, that when the concentration of NO is doubled and that of O_2 is kept constant then the initial rate increases by a factor of four from 0.096 to 0.384 mol $L^{-1}s^{-1}$. This indicates that the rate depends upon the square of the concentration of NO. When concentration of NO is kept constant and concentration of O_2 is doubled the rate also gets doubled indicating that rate depends on concentration of O_2 to the first power. Hence, the rate equation for this reaction will be

$$\text{Rate} = k[NO]^2[O_2]$$

The differential form of this rate expression is given as

$$-\frac{d[R]}{dt} = k[NO]^2[O_2]$$

Now, we observe that for this reaction in the rate equation derived from the experimental data, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.

Some other examples are given below:

Reaction	Experimental rate expression
1. $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	Rate = $k[CHCl_3][Cl_2]^{1/2}$
2. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$	Rate = $k[CH_3COOC_2H_5]^1[H_2O]^0$

In these reactions, the exponents of the concentration terms are not the same as their stoichiometric coefficients. Thus, we can say that:

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

4.2.3 Order of a Reaction

In the rate equation (4.4)

Rate = $k[A]^x[B]^y$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (4.4) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction**.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

Example 4.3

Calculate the overall order of a reaction which has the rate expression

(a) Rate = $k[A]^{1/2}[B]^{3/2}$

(b) Rate = $k[A]^{3/2}[B]^{-1}$

Solution

(a) Rate = $k[A]^x[B]^y$

order = x + y

So order = 1/2 + 3/2 = 2, i.e., second order

(b) order = 3/2 + (–1) = 1/2, i.e., half order.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.

These may be consecutive reactions (e.g., oxidation of ethane to CO_2 and H_2O passes through a series of intermediate steps in which alcohol, aldehyde and acid are formed), reverse reactions and side reactions (e.g., nitration of phenol yields *o*-nitrophenol and *p*-nitrophenol).

Units of rate constant

For a general reaction

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

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

Where x + y = n = order of the reaction

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

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concerntration})^n}$$

Taking SI units of concentration, mol L^{-1} and time, s, the units of *k* for different reaction order are listed in Table 4.3

Table 4.3: Units of rate constant

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1}$

Example 4.4

Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

(ii) $k = 3 \times 10^{-4}$ s^{-1}

Solution

(i) The unit of second order rate constant is L mol^{-1} s^{-1}, therefore $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} represents a second order reaction.

(ii) The unit of a first order rate constant is s^{-1} therefore $k = 3 \times 10^{-4}$ s^{-1} represents a first order reaction.

4.2.4 Molecularity of a Reaction

Another property of a reaction called molecularity helps in understanding its mechanism. **The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction**. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \rightarrow H_2 + I_2$$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$$2NO + O_2 \rightarrow 2NO_2$$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

This reaction which apparently seems to be of tenth order is actually a second order reaction. This shows that this reaction takes place in several steps. Which step controls the rate of the overall reaction? The question can be answered if we go through the mechanism of reaction, for example, chances to win the relay race competition by a team depend upon the slowest person in the team. Similarly, the overall rate of the reaction is controlled by the slowest step in a reaction called the **rate determining step**. Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be

$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

This reaction is first order with respect to both H_2O_2 and I^-. Evidences suggest that this reaction takes place in two steps

(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$

(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

Both the steps are bimolecular elementary reactions. Species IO^- is called as an intermediate since it is formed during the course of the reaction but not in the overall balanced equation. The first step, being slow, is the rate determining step. Thus, the rate of formation of intermediate will determine the rate of this reaction.

Thus, from the discussion, till now, we conclude the following:

(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

(iii) For complex reaction, order is given by the slowest step and generally, molecularity of the slowest step is same as the order of the overall reaction.

Intext Questions

4.3 For a reaction, A + B $\rightarrow$ Product; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

4.4 The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ?

4.3 Integrated Rate Equations

We have already noted that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point '*t*' in concentration vs time plot (Fig. 4.1). This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant.

The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

4.3.1 Zero Order Reactions

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

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

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[R]}{dt} = k \times 1$$

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -k\,t + I \qquad (4.5)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant R = $[R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (4.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (4.5)

$$[R] = -kt + [R]_0 \qquad (4.6)$$

Fig. 4.3: *Variation in the concentration vs time plot for a zero order reaction*

Comparing (4.6) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line (Fig. 4.3) with slope = $-k$ and intercept equal to $[R]_0$.

Further simplifying equation (4.6), we get the rate constant, k as

$$k = \frac{[R]_0 - [R]}{t} \tag{4.7}$$

Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2(g) + 3H_2(g)$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero order reaction.

4.3.2 First Order Reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant R. For example,

$$R \rightarrow P$$

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

$$\text{or} \quad \frac{d[R]}{[R]} = -k\,dt$$

Integrating this equation, we get

$$\ln [R] = -kt + I \tag{4.8}$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

Substituting the value of I in equation (4.8)

$$\ln[R] = -kt + \ln[R]_0 \tag{4.9}$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$

$$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad (4.10)$$

At time t_1 from equation (4.8)

$$*\ln[R]_1 = -kt_1 + *\ln[R]_0 \quad (4.11)$$

At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \quad (4.12)$$

where, $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting (4.12) from (4.11)

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \quad (4.13)$$

Equation (4.9) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0 \, e^{-kt} \quad (4.14)$$

Comparing equation (4.9) with y = mx + c, if we plot ln [R] against t (Fig. 4.4) we get a straight line with slope = $-k$ and intercept equal to ln $[R]_0$

The first order rate equation (4.10) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad (4.15)$$

$$*\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between log $[R]_0/[R]$ vs t, (Fig. 4.5), the slope = $k/2.303$

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Rate = $k\,[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

* *Refer to Appendix-IV for ln and log (logarithms).*

Fig. 4.4: *A plot between ln[R] and t for a first order reaction*

Fig. 4.5: *Plot of log $[R]_0/[R]$ vs time for a first order reaction*

$$^{226}_{88}Ra \rightarrow {}^{4}_{2}He + {}^{222}_{86}Rn$$

Rate = k [Ra]

Decomposition of N_2O_5 and N_2O are some more examples of first order reactions.

Example 4.5 The initial concentration of N_2O_5 in the following first order reaction $N_2O_5(g) \rightarrow 2\ NO_2(g) + 1/2O_2\ (g)$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

Solution For a first order reaction

$$\log \frac{[R]_1}{[R]_2} = \frac{k(t_2 - t_1)}{2.303}$$

$$k = \frac{2.303}{(t_2 - t_1)} \log \frac{[R]_1}{[R]_2}$$

$$= \frac{2.303}{(60\,\text{min} - 0\,\text{min})} \log \frac{1.24 \times 10^{-2}\ \text{mol L}^{-1}}{0.20 \times 10^{-2}\ \text{mol L}^{-1}}$$

$$= \frac{2.303}{60} \log 6.2\ \text{min}^{-1}$$

$$k = 0.0304\ \text{min}^{-1}$$

Let us consider a typical first order gas phase reaction

$A(g) \rightarrow B(g) + C(g)$

Let p_i be the initial pressure of A and p_t the total pressure at time 't'. Integrated rate equation for such a reaction can be derived as

Total pressure $p_t = p_A + p_B + p_C$ (pressure units)

p_A, p_B and p_C are the partial pressures of A, B and C, respectively.

If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

	A(g)	→	B(g)	+	C(g)
At $t = 0$	p_i atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

where, p_i is the initial pressure at time $t = 0$.

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i)$

$$= 2p_i - p_t$$

$$k = \left(\frac{2.303}{t}\right)\left(\log\frac{p_i}{p_A}\right) \qquad (4.16)$$

$$= \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

Example 4.6

The following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

Solution

Let the pressure of N_2O_5(g) decrease by 2x atm. As two moles of N_2O_5 decompose to give two moles of N_2O_4(g) and one mole of O_2 (g), the pressure of N_2O_4 (g) increases by 2x atm and that of O_2 (g) increases by x atm.

	$2N_2O_5(g)$	→	$2N_2O_4(g)$	+	$O_2(g)$
Start $t = 0$	0.5 atm		0 atm		0 atm
At time t	(0.5 – 2x) atm		2x atm		x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2\,(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Using equation (4.16)

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A} = \frac{2.303}{100\,s}\log\frac{0.5\,atm}{0.476\,atm}$$

$$= \frac{2.303}{100\,s} \times 0.0216 = 4.98 \times 10^{-4}\,s^{-1}$$

4.3.3 Half-Life of a Reaction

The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is given by equation 4.7.

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \tag{4.15}$$

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2} \tag{4.16}$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]/2}$$

$$\text{or} \quad t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \tag{4.17}$$

It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.

Example 4.7

A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half-life of the reaction.

Solution

Half-life for a first order reaction is

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} s^{-1}} = 1.26 \times 10^{14} s$$

Example 4.8

Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

Solution

When reaction is completed 99.9%, $[R]_n = [R]_0 - 0.999[R]_0$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

For half-life of the reaction

$$t_{1/2} = 0.693/k$$

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table 4.4 summarises the mathematical features of integrated laws of zero and first order reactions.

Table 4.4: Integrated Rate Laws for the Reactions of Zero and First Order

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	R→P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	[R] vs t	$[R]_0/2k$	conc time^{-1} or mol $L^{-1}s^{-1}$
1	R→P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	$\ln 2/k$	time^{-1} or s^{-1}

4.4 Pseudo First Order Reaction

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning (t = 0) and completion (t) of the reaction are given as under.

	$CH_3COOC_2H_5$	+ H_2O	$\xrightarrow{H^+}$	CH_3COOH	+ C_2H_5OH
t = 0	0.01 mol	10 mol		0 mol	0 mol
t	0 mol	9.9 mol		0.01 mol	0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k' [CH_3COOC_2H_5] [H_2O]$$

the term $[H_2O]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k [CH_3COOC_2H_5]$$

where $k = k' [H_2O]$

and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane sugar — Glucose — Fructose

$$\text{Rate} = k\ [C_{12}H_{22}O_{11}]$$

Example 4.9 Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below.

t/min	0	30	60	90
C/mol L^{-1}	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant (55 mol L^{-1}), during the course of the reaction. What is the value of k' in this equation?

$$\text{Rate} = k' [CH_3COOCH_3][H_2O]$$

Solution For pseudo first order reaction, the reaction should be first order with respect to ester when $[H_2O]$ is constant. The rate constant k for pseudo first order reaction is

$$k = \frac{2.303}{t} \log \frac{C_0}{C} \qquad \text{where} \quad k = k'[H_2O]$$

From the above data we note

t/min	C/ mol L^{-1}	k/mol L^{-1}
0	0.8500	–
30	0.8004	2.004×10^{-3}
60	0.7538	2.002×10^{-3}
90	0.7096	2.005×10^{-3}

It can be seen that $k\,[H_2O]$ is constant and equal to 2.004×10^{-3} min^{-1} and hence, it is pseudo first order reaction. We can now determine k from

$$k\,[H_2O] = 2.004 \times 10^{-3}\ min^{-1}$$

$$k\,[55\ mol\ L^{-1}] = 2.004 \times 10^{-3}\ min^{-1}$$

$$k = 3.64 \times 10^{-5}\ mol^{-1}\ L\ min^{-1}$$

Intext Questions

4.5 A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

4.6 Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

4.5 Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of N_2O_5, the time taken for half of the original amount of material to decompose is 12 min at 50°C, 5 h at 25°C and 10 days at 0°C. You also know that in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

It has been found that **for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.**

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation (4.18). It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$k = A\ e^{-Ea/RT} \qquad (4.18)$$

where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and E_a is activation energy measured in joules/mole (J mol^{-1}).

It can be understood clearly using the following simple reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

Fig. 4.6: Formation of HI through the intermediate

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 4.6). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

Fig. 4.7: Diagram showing plot of potential energy vs reaction coordinate.

The energy required to form this intermediate, called **activated complex** (C), is known as **activation energy (E_a)**. Fig. 4.7 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products.

Some energy is released when the complex decomposes to form products. So, the final heat of the reaction depends upon the nature of reactants and products.

Fig. 4.8: Distribution curve showing energies among gaseous molecules

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules. According to them, the distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E) vs kinetic energy (Fig. 4.8). Here, N_E is the number of molecules with energy E and N_T is total number of molecules.

Fig. 4.9: Distribution curve showing temperature dependence of rate of a reaction

The peak of the curve corresponds to the **most probable kinetic energy,** i.e., kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 4.9) and the curve broadens out, i.e., spreads to the right such that there is a greater

proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of E_a on Maxwell Boltzmann distribution curve (Fig. 4.9).

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a. It is clear from the diagram that in the curve at (t + 10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (4.18) the factor $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a. Taking natural logarithm of both sides of equation (4.18)

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (4.19)$$

The plot of ln k vs 1/T gives a straight line according to the equation (4.19) as shown in Fig. 4.10.

Thus, it has been found from Arrhenius equation (4.18) that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

In Fig. 4.10, slope = $-\frac{E_a}{R}$ and intercept = ln A. So we can calculate E_a and A using these values.

At temperature T_1, equation (4.19) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad (4.20)$$

At temperature T_2, equation (4.19) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \qquad (4.21)$$

(since A is constant for a given reaction)

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively.

Subtracting equation (4.20) from (4.21), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (4.22)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Fig. 4.10: *A plot between ln k and 1/T*

Example 4.10 The rate constants of a reaction at 500K and 700K are $0.02 s^{-1}$ and $0.07 s^{-1}$ respectively. Calculate the values of E_a and A.

Solution

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314\, JK^{-1}mol^{-1}}\right)\left[\frac{700-500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_a = 0.544 \times 19.15/5.714 \times 10^{-4} = 18230.8 \text{ J}$$

Since $k = Ae^{-Ea/RT}$

$$0.02 = Ae^{-18230.8/8.314 \times 500}$$

$$A = 0.02/0.012 = 1.61$$

Example 4.11 The first order rate constant for the decomposition of ethyl iodide by the reaction

$$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$$

at 600K is $1.60 \times 10^{-5} s^{-1}$. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

Solution We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \log(1.60 \times 10^{-5}) + \frac{209000\, J\, mol\, L^{-1}}{2.303 \times 8.314\, J\, mol\, L^{-1} K^{-1}}\left[\frac{1}{600K} - \frac{1}{700K}\right]$$

$$\log k_2 = -4.796 + 2.599 = -2.197$$

$$k_2 = 6.36 \times 10^{-3}\ s^{-1}$$

4.5.1 Effect of Catalyst

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$$

The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

Fig. 4.11: *Effect of catalyst on activation energy*

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. 4.11.

It is clear from Arrhenius equation (4.18) that lower the value of activation energy faster will be the rate of a reaction.

A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

4.6 Collision Theory of Chemical Reactions

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z)**. Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

$$A + B \rightarrow \text{Products}$$

rate of reaction can be expressed as

$$\text{Rate} = Z_{AB} e^{-E_a/RT} \qquad (4.23)$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than E_a. Comparing (4.23) with Arrhenius equation, we can say that A is related to collision frequency.

Equation (4.23) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions.**

* *Threshold energy = Activation Energy + energy possessed by reacting species.*

Fig. 4.12: *Diagram showing molecules having proper and improper orientation*

For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 4.12. *The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.*

To account for effective collisions, another factor *P*, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Collision theory also has certain drawbacks as it considers atoms/ molecules to be hard spheres and ignores their structural aspect. You will study details about this theory and more on other theories in your higher classes.

Intext Questions

4.7 What will be the effect of temperature on rate constant ?

4.8 The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate E_a.

4.9 The activation energy for the reaction

$$2\,HI(g) \rightarrow H_2 + I_2\,(g)$$

is 209.5 kJ mol^{-1} at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Summary

Chemical kinetics is the study of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms and formation of intermediates. The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst, affect the rate of a reaction. Mathematical representation of rate of a reaction is given by **rate law**. It has to be determined experimentally and cannot be predicted. **Order of a reaction** with respect to a

reactant is the power of its concentration which appears in the rate law equation. The order of a reaction is the sum of all such powers of concentration of terms for different reactants. **Rate constant** is the proportionality factor in the rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation. **Molecularity** is defined only for an elementary reaction. Its values are limited from 1 to 3 whereas order can be 0, 1, 2, 3 or even a fraction. Molecularity and order of an elementary reaction are same.

Temperature dependence of rate constants is described by Arrhenius equation ($k = Ae^{-E_a/RT}$). E_a corresponds to the **activation energy** and is given by the energy difference between activated complex and the reactant molecules, and A (Arrhenius factor or pre-exponential factor) corresponds to the collision frequency. The equation clearly shows that increase of temperature or lowering of E_a will lead to an increase in the rate of reaction and presence of a catalyst lowers the activation energy by providing an alternate path for the reaction. According to collision theory, another factor P called steric factor which refers to the orientation of molecules which collide, is important and contributes to effective collisions, thus, modifying the Arrhenius equation to $k = PZ_{AB}e^{-E_a/RT}$.

Exercises

4.1 From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) $3NO(g) \rightarrow N_2O\ (g)$ Rate $= k[NO]^2$

(ii) $H_2O_2\ (aq) + 3I^-\ (aq) + 2H^+ \rightarrow 2H_2O\ (l) + I_3^-$ Rate $= k[H_2O_2][I^-]$

(iii) $CH_3CHO\ (g) \rightarrow CH_4\ (g) + CO(g)$ Rate $= k[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl\ (g) \rightarrow C_2H_4\ (g) + HCl\ (g)$ Rate $= k[C_2H_5Cl]$

4.2 For the reaction:

$$2A + B \rightarrow A_2B$$

the rate $= k[A][B]^2$ with $k = 2.0 \times 10^{-6}\ mol^{-2}\ L^2\ s^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1\ mol\ L^{-1}$, $[B] = 0.2\ mol\ L^{-1}$. Calculate the rate of reaction after [A] is reduced to $0.06\ mol\ L^{-1}$.

4.3 The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}\ mol^{-1}\ L\ s^{-1}$?

4.4 The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

$$\text{Rate} = k\ [CH_3OCH_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

$$\text{Rate} = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

4.5 Mention the factors that affect the rate of a chemical reaction.

4.6 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled (ii) reduced to half ?

4.7 What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

4.8 In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
[Ester]/mol L^{-1}	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

4.9 A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

4.10 In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

A/ mol L^{-1}	0.20	0.20	0.40
B/ mol L^{-1}	0.30	0.10	0.05
r_0/mol $L^{-1}s^{-1}$	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

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

4.11 The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \rightarrow C + D$$

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

4.12 The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	–	0.2	4.0×10^{-2}
III	0.4	0.4	–
IV	–	0.2	2.0×10^{-2}

4.13 Calculate the half-life of a first order reaction from their rate constants given below:

(i) 200 s^{-1} (ii) 2 min^{-1} (iii) 4 $years^{-1}$

4.14 The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

4.15 The experimental data for decomposition of N_2O_5

$$[2N_2O_5 \rightarrow 4NO_2 + O_2]$$

in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]$/ mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[N_2O_5]$ against t.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between $\log[N_2O_5]$ and t.
(iv) What is the rate law ?
(v) Calculate the rate constant.
(vi) Calculate the half-life period from k and compare it with (ii).

4.16 The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $1/16^{th}$ value?

4.17 During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

4.18 For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

4.19 A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

4.20 For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

4.21 The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

4.22 The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

T/°C	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between ln k and $1/T$ and calculate the values of A and E_a. Predict the rate constant at 30° and 50°C.

4.23 The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

4.24 Consider a certain reaction A → Products with $k = 2.0 \times 10^{-2} s^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

4.25 Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

4.26 The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} s^{-1})\ e^{-28000K/T}$$

Calculate E_a.

4.27 The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 K/T$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

4.28 The decomposition of A into product has value of k as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be $1.5 \times 10^4 s^{-1}$?

4.29 The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of A is $4 \times 10^{10} s^{-1}$. Calculate k at 318K and E_a.

4.30 The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Answers to Some Intext Questions

4.1 $r_{av} = 6.66 \times 10^{-6}\ Ms^{-1}$

4.2 Rate of reaction = rate of diappearance of A
= 0.005 mol $litre^{-1} min^{-1}$

4.3 Order of the reaction is 2.5

4.4 X → Y
Rate = $k[X]^2$
The rate will increase 9 times

4.5 t = 444 s

4.6 $1.925 \times 10^{-4}\ s^{-1}$

4.8 Ea = 26.43 kJ mol^{-1}

4.9 1.462×10^{-19}

Unit

5

Surface Chemistry

Some of the most important chemicals are produced industrially by means of reactions that occur on the surfaces of solid catalysts.

Objectives

After studying this Unit, you will be able to

- describe interfacial phenomenon and its significance;
- define adsorption and classify it into physical and chemical adsorption;
- explain mechanism of adsorption;
- explain the factors controlling adsorption from gases and solutions on solids;
- explain adsorption results on the basis of Freundlich adsorption isotherms;
- appreciate the role of catalysts in industry;
- enumerate the nature of colloidal state;
- describe preparation, properties and purification of colloids;
- classify emulsions and describe their preparation and properties;
- describe the phenomenon of gel formation;
- list the uses of colloids.

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

To accomplish surface studies meticulously, it becomes imperative to have a really clean surface. Under very high vacuum of the order of 10^{-8} to 10^{-9} pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

In this Unit, you will be studying some important features of surface chemistry such as adsorption, catalysis and colloids including emulsions and gels.

5.1 Adsorption

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. **The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption**. The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

Adsorption in action

(i) If a gas like O_2, H_2, CO, Cl_2, NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.

(ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

(iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.

(iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.

5.1.1 Distinction between Adsorption and Absorption

In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid. For example, when a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes.

5.1.2 Mechanism of Adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually

balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

5.1.3 Types of Adsorption

There are mainly two types of adsorption of gases on solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as **physical adsorption or physisorption**. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption or chemisorption**. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

Some of the important characteristics of both types of adsorption are described below:

Characteristics of physisorption

(i) *Lack of specificity:* A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals' forces are universal.

(ii) *Nature of adsorbate:* The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals' forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).

(iii) *Reversible nature:* Physical adsorption of a gas by a solid is generally reversible. Thus,

$$\text{Solid} + \text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$$

More of gas is adsorbed when pressure is increased as the volume of the gas decreases (Le–Chateliers's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le-Chatelier's principle).

(iv) *Surface area of adsorbent:* The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

(v) *Enthalpy of adsorption:* No doubt, physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20–40 kJ mol^{-1}). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

Characteristics of chemisorption

(i) *High specificity:* Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.

(ii) *Irreversibility:* As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.

(iii) *Surface area:* Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.

(iv) *Enthalpy of adsorption:* Enthalpy of chemisorption is high (80-240 kJ mol^{-1}) as it involves chemical bond formation.

Table 5.1: Comparison of Physisorption and Chemisorption

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	**1.** It is caused by chemical bond formation.
2. It is not specific in nature.	**2.** It is highly specific in nature.
3. It is reversible in nature.	**3.** It is irreversible.
4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	**4.** It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol^{-1})in this case.	**5.** Enthalpy of adsorption is high (80-240 kJ mol^{-1}) in this case.

6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the increase of temperature.
7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	8. It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	9. It results into unimolecular layer.

5.1.4 Adsorption Isotherms

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as **adsorption isotherm**.

Freundlich adsorption isotherm: Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{x}{m} = k.P^{1/n} \ (n > 1) \qquad \ldots (5.1)$$

Fig. 5.1: Adsorption isotherm

where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.1). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of eq. (5.1)

$$\log\frac{x}{m} = \log k + \frac{1}{n} \log P \qquad \ldots (5.2)$$

Fig. 5.2: Freundlich isotherm

The validity of Freundlich isotherm can be verified by plotting log $\frac{x}{m}$ on y-axis (ordinate) and log P on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.2). The slope of the straight line gives the value of $\frac{1}{n}$. The intercept on the y-axis gives the value of log k.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (5.2) holds good over a limited range of pressure.

When $\frac{1}{n} = 0, \frac{x}{m}$ = constant, the adsorption is independent of pressure.

When $\frac{1}{n} = 1, \frac{x}{m} = k\,P$, i.e. $\frac{x}{m} \propto P$, the adsorption varies directly with pressure.

Both the conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

5.1.5 Adsorption from Solution Phase

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of magneson reagent. The colour is due to adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with an increase in temperature.

(ii) The extent of adsorption increases with an increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\frac{x}{m} = k\,C^{1/n} \qquad ...(5.3)$$

(C is the equilibrium concentration, i.e., when adsorption is complete). On taking logarithm of the above equation, we have

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C \qquad ...(5.4)$$

Plotting log $\frac{x}{m}$ against log C a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations give the value of x. Using the above equation, validity of Freundlich isotherm can be established.

5.1.6 Applications of Adsorption

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

(i) *Production of high vacuum*: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) *Gas masks*: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) *Control of humidity*: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) *Removal of colouring matter from solutions*: Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(v) *Heterogeneous catalysis*: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

(vi) *Separation of inert gases*: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii) *In curing diseases*: A number of drugs are used to kill germs by getting adsorbed on them.

(viii) *Froth floatation process*: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent (see Unit 6).

(ix) *Adsorption indicators*: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.

(x) *Chromatographic analysis*: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

Intext Questions

5.1 Why are substances like platinum and palladium often used for carrying out electrolysis of aqueous solutions?

5.2 Why does physisorption decrease with the increase of temperature?

5.3 Why are powdered substances more effective adsorbents than their crystalline forms?

5.2 Catalysis

Potassium chlorate, when heated strongly decomposes slowly giving dioxygen. The decomposition occurs in the temperature range of 653-873K.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance.

The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by Berzelius, in 1835. He suggested the term **catalyst** for such substances.

Substances, which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis. You have already studied about catalysts and its functioning in Section 4.5.

Promoters and poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow[Mo(s)]{Fe(s)} 2NH_3(g)$$

5.2.1 Homogeneous and Heterogeneous Catalysis

Catalysis can be broadly divided into two groups:

(a) Homogeneous catalysis

When the reactants and the catalyst are in the same phase (i.e., liquid or gas), the process is said to be homogeneous catalysis. The following are some of the examples of homogeneous catalysis:

(i) Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

(ii) Hydrolysis of methyl acetate is catalysed by H^+ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$$

Both the reactants and the catalyst are in the same phase.

(iii) Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{Solution}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H_2SO(l)} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}}_{\text{Solution}}$$

Both the reactants and the catalyst are in the same phase.

(b) Heterogeneous catalysis

The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. Some of the examples of heterogeneous catalysis are given below:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.

$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactant is in gaseous state while the catalyst is in the solid state.

(ii) Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in Haber's process.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{Vegetable oils(l)} + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable ghee(s)}$$

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

5.2.2 Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. The old theory, known as adsorption theory of catalysis, was that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilised in enhancing the rate of the reaction.

The catalytic action can be explained in terms of the intermediate compound formation, the theory of which you have already studied in Section 4.5.1

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

(i) Diffusion of reactants to the surface of the catalyst.

(ii) Adsorption of reactant molecules on the surface of the catalyst.

(iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate (Fig. 5.3).

(iv) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.

(v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for the fresh reactant molecules.

This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective

Fig. 5.3 *Adsorption of reacting molecules, formation of intermediate and desorption of products*

even in small quantities. It however, does not explain the action of catalytic promoters and catalytic poisons.

Important features of solid catalysts

(a) Activity

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilised and other reactants are left with no space on the catalyst's surface for adsorption. It has been found that for hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table (Class XI, Unit 3).

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$

(b) Selectivity

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example, starting with H_2 and CO, and using different catalysts, we get different products.

$$\text{(i)}\ CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

$$\text{(ii)}\ CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO\text{-}Cr_2O_3} CH_3OH(g)$$

$$\text{(iii)}\ CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

Thus, it can be inferred that the action of a catalyst is highly selective in nature, i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means that a substance which acts as a catalyst in one reaction may fail to catalyse another reaction.

5.2.3 Shape-Selective Catalysis by Zeolites

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called **shape-selective catalysis.** Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous

aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. They are found in nature as well as synthesised for catalytic selectivity.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

5.2.4 Enzyme Catalysis

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts; catalyse numerous reactions, especially those connected with natural processes. Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are, thus, termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**.

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme-catalysed reactions:

(i) *Inversion of cane sugar*: The invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

(ii) *Conversion of glucose into ethyl alcohol*: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

(iii) *Conversion of starch into maltose*: The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n(aq)} + nH_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(aq)}$$

(iv) *Conversion of maltose into glucose*: The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(aq)}$$

(v) *Decomposition of urea into ammonia and carbon dioxide*: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2(aq) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3(g) + CO_2(g)$$

(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

(vii) *Conversion of milk into curd*: It is an enzymatic reaction brought about by lacto bacilli enzyme present in curd.

Table 5.2 gives the summary of some important enzymatic reactions.

Table 5.2: Some Enzymatic Reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Amino acids

Characteristics of enzyme catalysis

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

(i) *Most highly efficient*: One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) *Highly specific nature*: Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.

(iii) *Highly active under optimum temperature*: The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. Human body temperature being 310 K is suited for enzyme-catalysed reactions.

(iv) *Highly active under optimum pH*: The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.

(v) *Increasing activity in presence of activators and co-enzymes*: The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably.

Activators are generally metal ions such as Na^+, Mn^{2+}, Co^{2+}, Cu^{2+}, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e., Na^+ ions are catalytically very active.

(vi) *Influence of inhibitors and poisons*: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

Mechanism of enzyme catalysis

There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-NH_2$, -COOH, -SH, -OH, etc. These are actually the active

Fig. 5.4: Mechanism of enzyme catalysed reaction

centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

Step 1: Binding of enzyme to substrate to form an activated complex.

$$E + S \rightarrow ES^{\neq}$$

Step 2: Decomposition of the activated complex to form product.

$$ES^{\neq} \rightarrow E + P$$

5.2.5 Catalysts in Industry

Some of the important technical catalytic processes are listed in Table 5.3 to give an idea about the utility of catalysts in industries.

Table 5.3: Some Industrial Catalytic Processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773K temperature.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinised asbestos; temperature 573K.
3. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(l)$ oleum $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673-723K.

Intext Questions

5.4 Why is it necessary to remove CO when ammonia is obtained by Haber's process?

5.5 Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?

5.6 What is the role of desorption in the process of catalysis.

5.3 Colloids

We have learnt in Unit 2 that solutions are homogeneous systems. We also know that sand in water when stirred gives a suspension, which slowly settles down with time. Between the two extremes of suspensions and solutions we come across a large group of systems called colloidal dispersions or simply colloids.

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

The essential difference between a solution and a colloid is that of particle size. While in a solution, the constituent particles are ions or small molecules, in a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm^2. If it were divided equally into 10^{12} cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60,000 cm^2 or 6 m^2. This enormous surface area leads to some special properties of colloids to be discussed later in this Unit.

5.4 Classification of Colloids

Colloids are classified on the basis of the following criteria:

(i) Physical state of dispersed phase and dispersion medium

(ii) Nature of interaction between dispersed phase and dispersion medium

(iii) Type of particles of the dispersed phase.

5.4.1 Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 5.4.

Table 5.4: Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a liquid. Firefighting foams, used at emergency airplane landings are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Out of the various types of colloids given in Table 5.4, the most common are **sols** (solids in liquids), **gels** (liquids in solids) and **emulsions** (liquids in liquids). However, in the present Unit, we shall take up discussion of the 'sols' and 'emulsions' only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

5.4.2 Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, **lyophilic** (solvent attracting) and **lyophobic** (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

(i) *Lyophilic colloids*: The word 'lyophilic' means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called **reversible sols**. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.

(ii) *Lyophobic colloids*: The word 'lyophobic' means liquid-hating. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called lyophobic sols. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called **irreversible sols**. Lyophobic sols need stabilising agents for their preservation.

5.4.3 Classification Based on Type of Particles of the Dispersed Phase, Multimolecular, Macromolecular and Associated Colloids

Depending upon the type of the particles of the dispersed phase, colloids are classified as: multimolecular, macromolecular and associated colloids.

(i) *Multimolecular colloids*: On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (diameter<1nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

(ii) *Macromolecular colloids*: Macromolecules (Unit 15) in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.

(iii) *Associated colloids (Micelles)*: There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called **micelles**. These are also known as **associated colloids**. The formation of micelles takes place only above a particular temperature called **Kraft temperature** (T_k) and above a particular concentration called **critical micelle concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of micelle formation

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^-$ and Na^+ ions. The $RCOO^-$ ions, however, consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group COO^- (also called polar-ionic 'head'), which is hydrophilic (water loving).

Fig. 5.5: *Hydrophobic and hydrophilic parts of stearate ion*

Fig. 5.6: (a) Arrangement of stearate ions on the surface of water at low concentrations of soap (b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

The $RCOO^-$ ions are, therefore, present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as '**ionic micelle**'. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents, e.g., sodium laurylsulphate, $CH_3(CH_2)_{11}SO_4^-Na^+$, the polar group is $-SO_4^-$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

Cleansing action of soaps

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like central core. The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles (Fig. 5.7). Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

Fig. 5.7: (a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)

5.4.4 Preparation of Colloids

A few important methods for the preparation of colloids are as follows:

(a) Chemical methods

Colloidal solutions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompostion}} As_2S_3(sol) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2\,AuCl_3 + 3\,HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\,(sol) + 3HCl$$

(b) Electrical disintegration or Bredig's Arc method

This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared

Fig. 5.8: Bredig's Arc method

by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 5.8). The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

(c) Peptization

Peptization may be defined as the **process of converting a precipitate into colloidal sol** by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of the size of a colloid.

5.4.5 Purification of Colloidal Solutions

Colloidal solutions when prepared, generally contain excessive amount of electrolytes and some other soluble impurities. While the presence of traces of electrolyte is essential for the stability of the colloidal solution, larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. **The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution**. The purification of colloidal solution is carried out by the following mehods:

Fig. 5.9: Dialysis

(i) *Dialysis*: **It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane**. Since particles (ions or smaller molecules) in a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles, the membrane can be used for dialysis. The apparatus used for this purpose is called **dialyser**. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing (Fig. 5.9). The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

Fig. 5.10: Electro-dialysis

(ii) *Electro-dialysis*: Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig. 5.10. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

(iii) *Ultrafiltration*: Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with **colloidion** solution to stop the flow of colloidal particles. The usual colloidion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a colloidion solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

5.4.6 Properties of Colloidal Solutions

Various properties exhibited by the colloidal solutions are described below:

(i) *Colligative properties*: Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.

Fig. 5.11: *Tyndall effect*

(ii) *Tyndall effect*: If a homogeneous solution placed in dark is observed in the direction of light, it appears clear and, if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. Colloidal solutions viewed in the same way may also appear reasonably clear or translucent by the transmitted light but they show a mild to strong opalescence, when viewed at right angles to the passage of light, i.e., the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as **Tyndall effect**. The bright cone of the light is called **Tyndall cone** (Fig. 5.11). The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion.

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied.

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Tyndall effect is used to distinguish between a colloidal and true solution. Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render the actual colloidal particles visible but only observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

(iii) *Colour*: The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the manner in which the observer receives the light. For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue and finally golden.

(iv) *Brownian movement*: When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This motion was first observed by the British botanist, Robert Brown, and is known as Brownian movement (Fig. 5.12). This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion.

Fig. 5.12: *Brownian movement*

The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

(v) *Charge on colloidal particles*: Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative. A list of some common sols with the nature of charge on their particles is given below:

Positively charged sols	Negatively charged sols
Hydrated metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.	Metals, e.g., copper, silver, gold sols.
Basic dye stuffs, e.g., methylene blue sol.	Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS sols.
Haemoglobin (blood)	Acid dye stuffs, e.g., eosin, congo red sols.
Oxides, e.g., TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

The charge on the sol particles is due to one or more reasons, viz., due to electron capture by sol particles during electrodispersion of metals, due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer.

Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of +ve or –ve ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

(a) When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to $AgNO_3$ solution, positively charged sol results due to adsorption of Ag^+ ions from dispersion medium.

AgI/I^-	AgI/Ag^+
Negatively charged	Positively charged

(b) If $FeCl_3$ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH^- ions.

$Fe_2O_3.xH_2O/Fe^{3+}$	$Fe_2O_3.xH_2O/OH^-$
Positively charged	Negatively charged

Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.

$AgI/I^-\ K^+$ $\qquad$ AgI/Ag^+I^-

The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer. According to modern views, the first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between these layers. This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**.

The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

(vi) *Electrophoresis*: The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. The movement of colloidal particles under an applied electric potential is called electrophoresis. Positively charged particles move towards the cathode while negatively charged

Fig. 5.13: *Electrophoresis*

particles move towards the anode. This can be demonstrated by the following experimental set-up (Fig. 5.13).

When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed **electroosmosis**.

(vii) *Coagulation or precipitation*: The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity.

The process of settling of colloidal particles is called coagulation or precipitation of the sol.

The coagulation of the lyophobic sols can be carried out in the following ways:

(i) *By electrophoresis*: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.

(ii) *By mixing two oppositely charged sols*: Oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) bring them in the precipitated forms. This type of coagulation is called mutual coagulation.

(iii) *By boiling*: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.

(iv) *By persistent dialysis*: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.

(v) *By addition of electrolytes*: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.

It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule. In the coagulation of a negative sol, the flocculating power is in the order: $Al^{3+} > Ba^{2+} > Na^{+}$

Similarly, in the coagulation of a positive sol, the flocculating power is in the order: $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.

Coagulation of lyophilic sols

There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding an electrolyte and (ii) by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

Protection of colloids

Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

5.5 Emulsions

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion. Generally, one of the two liquids is water. There are two types of emulsions.

(i) Oil dispersed in water (O/W type) and

(ii) Water dispersed in oil (W/O type).

Fig. 5.14: *Types of emulsions*

In the first system, water acts as dispersion medium. Examples of this type of emulsion are milk and vanishing cream. In milk, liquid fat is dispersed in water. In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream.

Emulsions of oil in water are unstable and sometimes they separate into two layers on standing. For stabilisation of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc., and for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed, forms a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

5.6 Colloids Around Us

Most of the substances, we come across in our daily life, are colloids. The meals we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

Following are the interesting and noteworthy examples of colloids:

(i) *Blue colour of the sky*: Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

(ii) *Fog, mist and rain*: When a large mass of air containing dust particles, is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet.

It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

(iii) *Food articles*: Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.

(iv) *Blood*: It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

(v) *Soils*: Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.

(vi) *Formation of delta*: River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

Applications of colloids

Colloids are widely used in the industry. Following are some examples:

(i) *Electrical precipitation of smoke*: Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called Cottrell precipitator (Fig.5.15).

Fig. 5.15: *Cottrell smoke precipitator*

(ii) *Purification of drinking water*: The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) *Medicines*: Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.

(iv) *Tanning*: Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.

(v) *Cleansing action of soaps and detergents*: This has already been described in Section 5.4.3.

(vi) *Photographic plates and films*: Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

(vii) *Rubber industry*: Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

(viii) *Industrial products*: Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions.

Intext Questions

5.7 What modification can you suggest in the Hardy Schulze law?

5.8 Why is it essential to wash the precipitate with water before estimating it quantitatively?

Summary

Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a solid resulting into a higher concentration on the surface than in the bulk. The substance adsorbed is known as **adsorbate** and the substance on which adsorption takes place is called **adsorbent.** In physisorption, adsorbate is held to the adsorbent by weak van der Waals forces, and in chemisorption, adsorbate is held to the adsorbent by strong chemical bond. Almost all solids adsorb gases. The extent of adsorption of a gas on a solid depends upon nature of gas, nature of solid, surface area of the solid, pressure of gas and temperature of gas. The relationship between the extent of adsorption (x/m) and pressure of the gas at constant temperature is known as **adsorption isotherm**.

A **catalyst** is a substance which enhances the rate of a chemical reaction without itself getting used up in the reaction. The phenomenon using catalyst is known as **catalysis**. In homogeneous catalysis, the catalyst is in the same phase as are the reactants, and in heterogeneous catalysis the catalyst is in a different phase from that of the reactants.

Colloidal solutions are intermediate between true solutions and suspensions. The size of the colloidal particles range from 1 to 1000 nm. A colloidal system consists of two phases - the dispersed phase and the dispersion medium. Colloidal systems are classified in three ways depending upon (i) physical states of the dispersed phase and dispersion medium (ii) nature of interaction between the dispersed phase and dispersion medium and (iii) nature of particles of dispersed phase. The colloidal systems show interesting optical, mechanical and electrical properties. The process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes is known as **coagulation. Emulsions** are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of: (i) **oil in water type** and (ii) **water in oil type.** The process of making emulsion is known as **emulsification.** To stabilise an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers. Colloids find several applications in industry as well as in daily life.

Exercises

5.1 Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.

5.2 What is the difference between physisorption and chemisorption?

5.3 Give reason why a finely divided substance is more effective as an adsorbent.

5.4 What are the factors which influence the adsorption of a gas on a solid?

5.5 What is an adsorption isotherm? Describe Freundlich adsorption isotherm.

5.6 What do you understand by activation of adsorbent? How is it achieved?

5.7 What role does adsorption play in heterogeneous catalysis?

5.8 Why is adsorption always exothermic ?

5.9 How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?

5.10 Discuss the effect of pressure and temperature on the adsorption of gases on solids.

5.11 What are lyophilic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coagulated ?

5.12 What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?

5.13 What are enzymes ? Write in brief the mechanism of enzyme catalysis.

5.14 How are colloids classified on the basis of
(i) physical states of components
(ii) nature of dispersion medium and
(iii) interaction between dispersed phase and dispersion medium?

5.15 Explain what is observed
(i) when a beam of light is passed through a colloidal sol.
(ii) an electrolyte, NaCl is added to hydrated ferric oxide sol.
(iii) electric current is passed through a colloidal sol?

5.16 What are emulsions? What are their different types? Give example of each type.

5.17 What is demulsification? Name two demulsifiers.

5.18 Action of soap is due to emulsification and micelle formation. Comment.

5.19 Give four examples of heterogeneous catalysis.

5.20 What do you mean by activity and selectivity of catalysts?

5.21 Describe some features of catalysis by zeolites.

5.22 What is shape selective catalysis?

5.23 Explain the following terms:
(i) Electrophoresis (ii) Coagulation (iii) Dialysis (iv) Tyndall effect.

5.24 Give four uses of emulsions.

5.25 What are micelles? Give an example of a micellers system.

5.26 Explain the terms with suitable examples:
(i) Alcosol (ii) Aerosol (iii) Hydrosol.

5.27 Comment on the statement that "colloid is not a substance but a state of substance".

Unit

6

General Principles and Processes of Isolation of Elements

Objectives

After studying this Unit, you will be able to

- explain the terms minerals, ores, concentration, benefaction, calcination, roasting, refining, etc.;
- understand the principles of oxidation and reduction as applied to the extraction procedures;
- apply the thermodynamic concepts like that of Gibbs energy and entropy to the principles of extraction of Al, Cu, Zn and Fe;
- explain why reduction of certain oxides like Cu_2O is much easier than that of Fe_2O_3;
- explain why CO is a favourable reducing agent at certain temperatures while coke is better in some other cases;
- explain why specific reducing agents are used for the reduction purposes.

Thermodynamics illustrates why only a certain reducing element and a minimum specific temperature are suitable for reduction of a metal oxide to the metal in an extraction.

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry. A particular element may occur in a variety of compounds. The process of metallurgy and isolation should be such that it is chemically feasible and commercially viable. Still, some general principles are common to all the extraction processes of metals. For obtaining a particular metal, first we look for **minerals** which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as **ores**.

Rarely, an ore contains only a desired substance. It is usually contaminated with earthly or undesired materials known as **gangue**. The extraction and isolation of metals from ores involve the following major steps:

- Concentration of the ore,
- Isolation of the metal from its concentrated ore, and
- Purification of the metal.

The entire scientific and technological process used for isolation of the metal from its ores is known as **metallurgy**.

In the present Unit, first we shall describe various steps for effective concentration of ores. After that we shall discuss the principles of some of the common metallurgical processes. Those principles shall include the thermodynamic and electrochemical aspects involved in the effective reduction of the concentrated ore to the metal.

6.1 Occurrence of Metals

Elements vary in abundance. Among metals, aluminium is the most abundant. It is the third most abundant element in earth's crust (8.3% approx. by weight). It is a major component of many igneous minerals including mica and clays. Many gemstones are impure forms of Al_2O_3 and the impurities range from Cr (in 'ruby') to Co (in 'sapphire'). Iron is the second most abundant metal in the earth's crust. It forms a variety of compounds and their various uses make it a very important element. It is one of the essential elements in biological systems as well.

The principal ores of aluminium, iron, copper and zinc have been given in Table 6.1.

Table 6.1: Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

For the purpose of extraction, bauxite is chosen for aluminium. For iron, usually the oxide ores which are abundant and do not produce polluting gases (like SO_2 that is produced in case iron pyrites) are taken. For copper and zinc, any of the listed ores (Table 6.1) may be used depending upon availability and other relevant factors. Before proceeding for concentration, ores are graded and crushed to reasonable size.

6.2 Concentration of Ores

Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as *concentration*, *dressing* or *benefaction*. It involves several steps and selection of these steps depends upon the differences in physical properties of the compound of the metal present and that of the *gangue*. The type of the metal, the available facilities and the environmental factors are also taken into consideration. Some of the important procedures are described below.

6.2.1 Hydraulic Washing

This is based on the differences in gravities of the ore and the *gangue* particles. It is therefore a type of *gravity separation*. In one such process,

an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.

6.2.2 Magnetic Separation

This is based on differences in magnetic properties of the ore components. If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g., in case of iron ores). The ground ore is carried on a conveyer belt which passes over a magnetic roller (Fig.6.1).

Fig. 6.1: *Magnetic separation (schematic)*

6.2.3 Froth Floatation Method

This method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, *collectors* and *froth stabilisers* are added. Collectors (e. g., pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e. g., cresols, aniline) stabilise the froth.

Fig. 6.2: *Froth floatation process (schematic)*

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.

Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using '*depressants*'. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

The Innovative Washerwoman

One can do wonders if he or she has a scientific temperament and is attentive to observations. A washerwoman had an innovative mind too. While washing a miner's overalls, she noticed that sand and similar dirt fell to the bottom of the washtub. What was peculiar, the copper bearing compounds that had come to the clothes from the mines, were caught in the soapsuds and so they came to the top. One of her clients was a chemist, Mrs. Carrie Everson. The washerwoman told her experience to Mrs. Everson. The latter thought that the idea could be used for separating copper compounds from rocky and earth materials on large scale. This way an invention was born. At that time only those ores were used for extraction of copper, which contained large amounts of the metal. Invention of the *Froth Floatation Method* made copper mining profitable even from the low-grade ores. World production of copper soared and the metal became cheaper.

6.2.4 Leaching

Leaching is often used if the ore is soluble in some suitable solvent. The following examples illustrate the procedure:

(a) Leaching of alumina from bauxite

The principal ore of aluminium, bauxite, usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. This way, Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind:

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) \quad (6.1)$$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation:

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3\ (aq) \quad (6.2)$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3:

$$Al_2O_3.xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g) \quad (6.3)$$

(b) Other examples

In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement:

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)\ (M = Ag\ or\ Au) \quad (6.4)$$

$$2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s) \quad (6.5)$$

Intext Questions

6.1 Which of the ores mentioned in Table 6.1 can be concentrated by magnetic separation method?

6.2 What is the significance of leaching in the extraction of aluminium?

6.3 Extraction of Crude Metal from Concentrated Ore

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce (for the reason see box). Thus isolation of metals from concentrated ore involves two major steps *viz.*,

(a) conversion to oxide, and

(b) reduction of the oxide to metal.

(a) Conversion to oxide

(i) *Calcination*: Calcinaton involves heating when the volatile matter escapes leaving behind the metal oxide:

$$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3\ (s) + xH_2O(g) \quad (6.6)$$

$$ZnCO_3\ (s) \xrightarrow{\Delta} ZnO(s) + CO_2(g) \quad (6.7)$$

$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s) + 2CO_2(g) \quad (6.8)$$

Fig. 6.3: *A section of a modern reverberatory furnace*

(ii) *Roasting*: In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. Some of the reactions involving sulphide ores are:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \quad (6.9)$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \quad (6.10)$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \quad (6.11)$$

The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, it is mixed with silica before heating. Iron oxide 'slags of'* as iron silicate and copper is produced in the form of *copper matte* which contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow \underset{\text{(slag)}}{FeSiO_3} \quad (6.12)$$

The SO_2 produced is utilised for manufacturing H_2SO_4 .

(b) Reduction of oxide to the metal

Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal). The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + y\ CO \quad (6.13)$$

Some metal oxides get reduced easily while others are very difficult to be reduced (reduction means electron gain or electronation). In any case, heating is required. To understand the variation in the temperature requirement for thermal reductions *(pyrometallurgy)* and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are made.

6.4 Thermodynamic Principles of Metallurgy

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term here.The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S \quad (6.14)$$

where, ΔH is the enthalpy change and ΔS is the entropy change for the process. For any reaction, this change could also be explained through the equation:

$$\Delta G^{\ominus} = -RT\ln K \quad (6.15)$$

where, K is the equilibrium constant of the 'reactant – product' system at the temperature,T. A negative ΔG implies a +ve K in equation 6.15. And this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:

* *During metallurgy, 'flux' is added which combines with 'gangue' to form 'slag'. Slag separates more easily from the ore than the gangue. This way, removal of gangue becomes easier.*

1. When the value of ΔG is negative in equation 6.14, only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become –ve.
2. If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their ΔG and looking for its magnitude and *sign*. Such coupling is easily understood through Gibbs energy ($\Delta G^{\ominus}$) vs T plots for formation of the oxides (Fig. 6.4).

Ellingham Diagram

The graphical representation of Gibbs energy was first used by H.J.T.Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham Diagram. Such diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.

(a) Ellingham diagram normally consists of plots of $\Delta_f G^{\ominus}$ *vs* T for formation of oxides of elements i.e., for the reaction,

$$2xM(s) + O_2(g) \rightarrow 2M_xO(s)$$

In this reaction, the gaseous amount (hence molecular randomness) is decreasing from left to right due to the consumption of gases leading to a –ve value of ΔS which changes the sign of the second term in equation (6.14). Subsequently ΔG shifts towards higher side despite rising T (normally, ΔG decreases i.e., goes to lower side with increasing temperature). The result is +ve slope in the curve for most of the reactions shown above for formation of $M_xO(s)$.

(b) Each plot is a straight line except when some change in phase (s→liq or liq→g) takes place. The temperature at which such change occurs, is indicated by an increase in the slope on +ve side (e.g., in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve).

(c) There is a point in a curve below which ΔG is negative (So M_xO is stable). Above this point, M_xO will decompose on its own.

(d) In an Ellingham diagram, the plots of $\Delta G^{\ominus}$ for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of $\Delta_f G^{\ominus}$, etc.(for formation of oxides) at different temperatures are depicted which make the interpretation easy.

(e) Similar diagrams are also constructed for sulfides and halides and it becomes clear why reductions of M_xS is difficult. There, the $\Delta_f G^{\ominus}$ of M_xS is not compensated.

Limitations of Ellingham Diagram

1. The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be ?).
2. The interpretation of $\Delta G^{\ominus}$ is based on K ($\Delta G^{\ominus} = -RT \ln K$). Thus it is presumed that the reactants and products are in equilibrium:

$$M_xO + A_{red} \rightleftharpoons xM + AO_{ox}$$

This is not always true because the reactant/product may be solid. [However it explains how the reactions are sluggish when every species is in solid state and smooth when

the ore melts down.It is interestng to note here that ΔH (enthalpy change) and the ΔS (entropy change) values for any chemical reaction remain nearly constant even on varying temperature. So the only dominant variable in equation(6.14) becomes T. However, ΔS depends much on the physical state of the compound. Since entropy depends on disorder or randomness in the system, it will increase if a compound melts ($s \rightarrow l$) or vapourises ($l \rightarrow g$) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas].

The reducing agent forms its oxide when the metal oxide is reduced. The role of reducing agent is to provide $\Delta G^{\ominus}$ negative and large enough to make the sum of $\Delta G^{\ominus}$ of the two reactions (oxidation of the reducing agent and reduction of the metal oxide) negative.

As we know, during reduction, the oxide of a metal decomposes:

$$M_xO(s) \rightarrow xM \text{ (solid or liq)} + \frac{1}{2}O_2(g) \quad (6.16)$$

The reducing agent takes away the oxygen. Equation 6.16 can be visualised as reverse of the oxidation of the metal. And then, the $\Delta_f G^{\ominus}$ value is written in the usual way:

$$xM(s \text{ or } l) + \frac{1}{2}O_2(g) \rightarrow M_xO(s) \qquad [\Delta G^{\ominus}_{(M, MxO)}] \quad (6.17)$$

If reduction is being carried out through equation 6.16, the oxidation of the reducing agent (e.g., C or CO) will be there:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad [\Delta G_{(C, CO)}] \quad (6.18)$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad [\Delta G_{(CO, CO_2)}] \quad (6.19)$$

If carbon is taken, there may also be complete oxidation of the element to CO_2:

$$\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g) \qquad [\frac{1}{2}\ \Delta G_{(C, CO_2)}] \quad (6.20)$$

On subtracting equation 6.17 [it means adding its negative or the reverse form as in equation 6.16] from one of the three equations, we get:

$$M_xO(s) + C(s) \rightarrow xM(s \text{ or } l) + CO(g) \quad (6.21)$$

$$M_xO(s) + CO(g) \rightarrow xM(s \text{ or } l) + CO_2(g) \quad (6.22)$$

$$M_xO(s) + \frac{1}{2}C(s) \rightarrow xM(s \text{ or } l) + \frac{1}{2}CO_2(g) \quad (6.23)$$

These reactions describe the actual reduction of the metal oxide, M_xO that we want to accomplish. The $\Delta_r G^{\ominus}$ values for these reactions in general, can be obtained by similar subtraction of the corresponding $\Delta_f G^{\ominus}$ values.

As we have seen, heating (i.e., increasing T) favours a negative value of $\Delta_r G^{\ominus}$. Therefore, the temperature is chosen such that the sum of $\Delta_r G^{\ominus}$ in the two combined redox process is negative. In $\Delta_r G^{\ominus}$ vs T plots, this is indicated by the point of intersection of the two curves (curve for M_xO and that for the oxidation of the reducing substance). After that point, the $\Delta_r G^{\ominus}$ value becomes more negative for the combined process including the reduction of M_xO. The difference in the two $\Delta_r G^{\ominus}$ values after that point determines whether reductions of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier.

Example 6.1 Suggest a condition under which magnesium could reduce alumina.

Solution The two equations are:

(a) $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$ (b) $2Mg + O_2 \rightarrow 2MgO$

At the point of intersection of the Al_2O_3 and MgO curves (marked "A" in diagram 6.4), the $\Delta G^{\ominus}$ becomes ZERO for the reaction:

$$\frac{2}{3}Al_2O_3 + 2Mg \rightarrow 2MgO + \frac{4}{3}Al$$

Above that point magnesium can reduce alumina.

Example 6.2 Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why ?

Solution Temperatures above the point of intersection of Al_2O_3 and MgO curves, magnesium can reduce alumina. But the temperature required would be so high that the process will be uneconomic and technologically difficult.

Example 6.3 Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

Solution The entropy is higher if the metal is in liquid state than when it is in solid state. The value of entropy change (ΔS) of the reduction process is more on +ve side when the metal formed is in liquid state and the metal oxide being reduced is in solid state. Thus the value of $\Delta G^{\ominus}$ becomes more on negative side and the reduction becomes easier.

6.4.1 Applications

(a) Extraction of iron from its oxides

Oxide ores of iron, after concentration through calcination/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a *Blast furnace* from its top. Here, the oxide is reduced to the metal. Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is:

$$FeO(s) + C(s) \rightarrow Fe(s/l) + CO(g) \quad (6.24)$$

It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO:

$$FeO(s) \rightarrow Fe(s) + \frac{1}{2}O_2(g) \quad [\Delta G_{(FeO,\ Fe)}] \quad (6.25)$$

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad [\Delta G_{(C,\ CO)}] \quad (6.26)$$

When both the reactions take place to yield the equation (6.23), the net Gibbs energy change becomes:

$$\Delta G_{(C,\ CO)} + \Delta G_{(FeO,\ Fe)} = \Delta_r G \quad (6.27)$$

Naturally, the resultant reaction will take place when the right hand side in equation 6.27 is negative. In $\Delta G^{\ominus}$ vs T plot representing reaction 6.25, the plot goes upward and that representing the change C→CO

(C,CO) goes downward. At temperatures above 1073K (approx.), the C,CO line comes below the Fe,FeO line [$\Delta G_{(C, CO)} < \Delta G_{(Fe, FeO)}$]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve in Fig. 6.4.

Fig. 6.4: *Gibbs energy ($\Delta G^{\ominus}$) vs T plots (schematic) for formation of some oxides (Ellingham diagram)*

In the Blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself. The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace. In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO. Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the $\Delta_r G^{\ominus}$ vs T plots. These reactions can be summarised as follows:

At 500 – 800 K (lower temperature range in the blast furnace)–

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2 \quad (6.28)$$

$$Fe_3O_4 + 4\ CO \rightarrow 3Fe + 4\ CO_2 \quad (6.29)$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \quad (6.30)$$

Fig. 6.5: *Blast furnace*

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \rightarrow 2\ CO \qquad (6.31)$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad (6.32)$$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

The iron obtained from Blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as *pig iron* and cast into variety of shapes. *Cast iron* is different from *pig iron* and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Further Reductions

Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:

$$Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO \qquad (6.33)$$

Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

(b) Extraction of copper from cuprous oxide [copper(I) oxide]

In the graph of $\Delta_r G^\ominus$ vs T for formation of oxides (Fig. 6.4), the Cu_2O line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500 – 600K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \qquad (6.34)$$

The oxide can then be easily reduced to metallic copper using coke:

$$Cu_2O + C \rightarrow 2\ Cu + CO \qquad (6.35)$$

In actual process, the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of *copper matte*. This contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow \underset{\text{(Slag)}}{FeSiO_3} \qquad (6.36)$$

Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining

FeS_2, FeO and Cu_2S/Cu_2O to the metallic copper. Following reactions take place:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 \quad (6.37)$$

$$FeO + SiO_2 \rightarrow FeSiO_3 \quad (6.38)$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \quad (6.39)$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \quad (6.40)$$

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called *blister copper.*

(c) Extraction of zinc from zinc oxide

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C \xrightarrow{\text{coke, 673 K}} Zn + CO \quad (6.41)$$

The metal is distilled off and collected by rapid chilling.

Intext Questions

6.3 The reaction,

$$Cr_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Cr \qquad (\Delta G^{\ominus} = -421\ kJ)$$

is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?

6.4 Is it true that under certain conditions, Mg can reduce SiO_2 and Si can reduce MgO? What are those conditions?

6.5 Electrochemical Principles of Metallurgy

We have seen how principles of thermodyamics are applied to pyrometallurgy. Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element.

In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^{\ominus} = -nE^{\ominus}F \quad (6.42)$$

here n is the number of electrons and $E^{\ominus}$ is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two $E^{\ominus}$ values corresponds to a positive $E^{\ominus}$ and consequently negative $\Delta G^{\ominus}$ in equation 6.42, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,

$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq) \quad (6.43)$$

In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

Aluminium

In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \quad (6.44)$$

This process of electrolysis is widely known as *Hall-Heroult* process.

Fig. 6.6: *Electrolytic cell for the extraction of aluminium*

The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are:

$$\text{Cathode: } Al^{3+}(melt) + 3e^- \rightarrow Al(l) \quad (6.45)$$

$$\text{Anode: } C(s) + O^{2-}(melt) \rightarrow CO(g) + 2e^- \quad (6.46)$$

$$C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e^- \quad (6.47)$$

Copper from Low Grade Ores and Scraps

Copper is extracted by *hydrometallurgy* from low grade ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 (equations 6.42; 6.48).

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq) \quad (6.48)$$

Example 6.4

At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

Solution

Zinc being above iron in the electrochemical series (more reactive metal is zinc), the reduction will be faster in case zinc scraps are used. But zinc is costlier metal than iron so using iron scraps will be advisable and advantageous.

6.6 Oxidation Reduction

Besides reductions, some extractions are based on oxidation particularly for non-metals. A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt) .

$$2Cl^-(aq) + 2H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g) \quad (6.49)$$

The $\Delta G^\ominus$ for this reaction is + 422 kJ. When it is converted to $E^\ominus$ (using $\Delta G^\ominus = -nE^\ominus F$), we get $E^\ominus = -2.2$ V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

As studied earlier, extraction of gold and silver involves leaching the metal with CN^-. This is also an oxidation reaction ($Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$). The metal is later recovered by displacement method.

$$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq) \quad (6.50)$$

$$2[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq) \quad (6.51)$$

In this reaction zinc acts as a reducing agent.

6.7 Refining

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

(a) Distillation **(b)** Liquation

(c) Electrolysis **(d)** Zone refining

(e) Vapour phase refining **(f)** Chromatographic methods

These are described in detail here.

(a) Distillation

This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation

In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) Electrolytic refining

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy which you have seen in previous sections. The reactions are:

Anode: $M \rightarrow M^{n+} + ne^-$

Cathode: $M^{n+} + ne^- \rightarrow M$ (6.52)

Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

Anode: $Cu \rightarrow Cu^{2+} + 2\,e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (6.53)

Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.

Zinc may also be refined this way.

(d) *Zone refining*

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal (Fig. 6.7). The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

Fig. 6.7: *Zone refining process*

(e) *Vapour phase refining*

In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. So, the two requirements are:

(i) the metal should form a volatile compound with an available reagent,

(ii) the volatile compound should be easily decomposable, so that the recovery is easy.

Following examples will illustrate this technique.

Mond Process for Refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

$$Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4 \quad (6.54)$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:

$$Ni(CO)_4 \xrightarrow{450-470\ K} Ni + 4CO \quad (6.55)$$

van Arkel Method for Refining Zirconium or Titanium: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4 \quad (6.56)$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2 \quad (6.57)$$

(f) *Chromatographic methods*

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.

Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvents (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method* is given the name. In one such method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of *column chromatography*. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc. Procedures followed in column chromatography have been depicted in Fig. 6.8.

Fig. 6.8: *Schematic diagrams showing column chromatography*

* *Looking it the other way, chromatography in general, involves a mobile phase and a stationary phase. The sample or sample extract is dissolved in a mobile phase. The mobile phase may be a gas, a liquid or a supercritical fluid. The stationary phase is immobile and immiscible (like the Al_2O_3 column in the example of column chromatography above). The mobile phase is then forced through the stationary phase. The mobile phase and the stationary phase are chosen such that components of the sample have different solubilities in the two phases. A component which is quite soluble in the stationary phase takes longer time to travel through it than a component which is not very soluble in the stationary phase but very soluble in the mobile phase. Thus sample components are separated from each other as they travel through the stationary phase. Depending upon the two phases and the way sample is inserted/injected, the chromatographic technique is named. These methods have been described in detail in Unit 12 of Class XI text book (12.8.5).*

6.8 Uses of Aluminium, Copper, Zinc and Iron

Aluminium foils are used as wrappers for chocolates. The fine dust of the metal is used in paints and lacquers. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides. Wires of aluminium are used as electricity conductors. Alloys containing aluminium, being light, are very useful.

Copper is used for making wires used in electrical industry and for water and steam pipes. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Zinc is used for galvanising iron. It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40–50%). Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes , toys, etc. It is used in the manufacture of wrought iron and steel. Wrought iron is used in making anchors, wires, bolts, chains and agricultural implements. Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.

Summary

Metals are required for a variety of purposes. For this, we need their extraction from the minerals in which they are present and from which their extraction is commercially feasible.These minerals are known as **ores**. Ores of the metal are associated with many impurities. Removal of these impurities to certain extent is achieved in **concentration** steps. The concentrated ore is then treated chemically for obtaining the metal. Usually the metal compounds (e.g., oxides, sulphides) are reduced to the metal. The reducing agents used are carbon, CO or even some metals. In these reduction processes, the **thermodynamic** and **electrochemical** concepts are given due consideration. The metal oxide reacts with a reducing agent; the oxide is reduced to the metal and the reducing agent is oxidised. In the two reactions, the net Gibbs energy change is negative, which becomes more negative on raising the temperature. Conversion of the physical states from solid to liquid or to gas, and formation of gaseous states favours decrease in the Gibbs energy for the entire system. This concept is graphically displayed in plots of $\Delta G^{\ominus}$ vs T (Ellingham diagram) for such oxidation/reduction reactions at different temperatures. The concept of electrode potential is useful in the isolation of metals (e.g., Al, Ag, Au) where the sum of the two redox couples is +ve so that the Gibbs energy change is negative. The metals obtained by usual methods still contain minor impurities. Getting pure metals require **refining**. Refining process depends upon the differences in properties of the metal and the impurities. Extraction of aluminium is usually carried out from its bauxite ore by leaching it with NaOH. Sodium aluminate, thus formed, is separated and then neutralised to give back the hydrated oxide, which is then electrolysed using cryolite as a flux. Extraction of iron is done by reduction of its oxide ore in blast furnace. Copper is extracted by smelting and heating in a reverberatory furnace. Extraction of zinc from zinc oxides is done using coke. Several methods are employed

in refining the metal. Metals, in general, are very widely used and have contributed significantly in the development of a variety of industries.

Aluminium	1. Bauxite, $Al_2O_3 . x H_2O$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.

Exercises

6.1 Copper can be extracted by hydrometallurgy but not zinc. Explain.

6.2 What is the role of depressant in froth floatation process?

6.3 Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

6.4 Explain: (i) Zone refining (ii) Column chromatography.

6.5 Out of C and CO, which is a better reducing agent at 673 K ?

6.6 Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present ?

6.7 Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

6.8 Write chemical reactions taking place in the extraction of zinc from zinc blende.

6.9 State the role of silica in the metallurgy of copper.

6.10 What is meant by the term "chromatography"?

6.11 What criterion is followed for the selection of the stationary phase in chromatography?

6.12 Describe a method for refining nickel.

6.13 How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

6.14 Giving examples, differentiate between 'roasting' and 'calcination'.

6.15 How is 'cast iron' different from 'pig iron"?

6.16 Differentiate between "minerals" and "ores".

6.17 Why copper *matte* is put in silica lined converter?

6.18 What is the role of cryolite in the metallurgy of aluminium?

6.19 How is leaching carried out in case of low grade copper ores?

6.20 Why is zinc not extracted from zinc oxide through reduction using CO?

6.21 The value of $\Delta_f G^\ominus$ for formation of Cr_2O_3 is – 540 $kJmol^{-1}$ and that of Al_2O_3 is – 827 $kJmol^{-1}$. Is the reduction of Cr_2O_3 possible with Al ?

6.22 Out of C and CO, which is a better reducing agent for ZnO ?

6.23 The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.

6.24 Name the processes from which chlorine is obtained as a by-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?

6.25 What is the role of graphite rod in the electrometallurgy of aluminium?

6.27 Outline the principles of refining of metals by the following methods:

(i) Zone refining

(ii) Electrolytic refining

(iii) Vapour phase refining

6.28 Predict conditions under which Al might be expected to reduce MgO. (Hint: See Intext question 6.4)

Answers to Some Intext Questions

6.1 Ores in which one of the components (either the impurity or the actual ore) is magnetic can be concentrated, e.g., ores containing iron (haematite, magnetite, siderite and iron pyrites).

6.2 Leaching is significant as it helps in removing the impurities like SiO_2, Fe_2O_3, etc. from the bauxite ore.

6.3 Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.

6.4 Yes, below 1350°C Mg can reduce Al_2O_3 and above 1350°C, Al can reduce MgO. This can be inferred from $\Delta G^\ominus$ Vs T plots (Fig. 6.4).

Unit

7

The *p*-Block Elements

Objectives

After studying this Unit, you will be able to

- appreciate general trends in the chemistry of elements of groups 15,16,17 and 18;
- learn the preparation, properties and uses of dinitrogen and phosphorus and some of their important compounds;
- describe the preparation, properties and uses of dioxygen and ozone and chemistry of some simple oxides;
- know allotropic forms of sulphur, chemistry of its important compounds and the structures of its oxoacids;
- describe the preparation, properties and uses of chlorine and hydrochloric acid;
- know the chemistry of interhalogens and structures of oxoacids of halogens;
- enumerate the uses of noble gases;
- appreciate the importance of these elements and their compounds in our day to day life.

Diversity in chemistry is the hallmark of p–block elements manifested in their ability to react with the elements of s–, d– and f–blocks as well as with their own.

In Class XI, you have learnt that the *p*-block elements are placed in groups 13 to 18 of the periodic table. Their valence shell electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration). The properties of *p*-block elements like that of others are greatly influenced by atomic sizes, ionisation enthalpy, electron gain enthalpy and electronegativity. The absence of *d*-orbitals in second period and presence of *d* and/or *f* orbitals in heavier elements (starting from third period onwards) have significant effects on the properties of elements. In addition, the presence of all the three types of elements; metals, metalloids and non-metals bring diversification in chemistry of these elements.

Having learnt the chemistry of elements of Groups 13 and 14 of the *p*-block of periodic table in Class XI, you will learn the chemistry of the elements of subsequent groups in this Unit.

7.1 Group 15 Elements

Group 15 includes nitrogen, phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal.

7.1.1 Occurrence

Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins in plants and animals. Phosphorus occurs in minerals

of the apatite family, $Ca_9(PO_4)_6.\ CaX_2$ (X = F, Cl or OH) (e.g., fluorapatite $Ca_9\ (PO_4)_6.\ CaF_2$) which are the main components of phosphate rocks. Phosphorus is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. Arsenic, antimony and bismuth are found mainly as sulphide minerals.

The important atomic and physical properties of this group elements along with their electronic configurations are given in Table 7.1.

Table 7.1: Atomic and Physical Properties of Group 15 Elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass/g mol^{-1}		14.01	30.97	74.92	121.75	208.98
Electronic configuration		$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Ionisation enthalpy	I	1402	1012	947	834	703
($\Delta_i H$/(kJ mol^{-1})	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
Covalent radius/pm[a]		70	110	121	141	148
Ionic radius/pm		171[b]	212[b]	222[b]	76[c]	103[c]
Melting point/K		63*	317[d]	1089[e]	904	544
Boiling point/K		77.2*	554[d]	888[f]	1860	1837
Density/[g cm^{-3}(298 K)]		0.879[g]	1.823	5.778[h]	6.697	9.808

*[a] E^{III} single bond (E = element); [b] E^{3-}; [c] E^{3+}; [d] White phosphorus; [e] Grey α-form at 38.6 atm; [f] Sublimation temperature; [g] At 63 K; [h] Grey α-form; * Molecular N_2.*

Trends of some of the atomic, physical and chemical properties of the group are discussed below.

7.1.2 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^3. The *s* orbital in these elements is completely filled and *p* orbitals are half-filled, making their electronic configuration extra stable.

7.1.3 Atomic and Ionic Radii

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled *d* and/or *f* orbitals in heavier members.

7.1.4 Ionisation Enthalpy

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled *p* orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$ (Table 7.1).

7.1.5 Electronegativity

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

7.1.6 Physical Properties

All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

7.1.7 Chemical Properties

Oxidation states and trends in chemical reactivity

The common oxidation states of these elements are –3, +3 and +5. The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. In fact last member of the group, bismuth hardly forms any compound in –3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_5. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one *s* and three *p*) orbitals are available for bonding. The heavier elements have vacant *d* orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF_6^-.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its smaller size, high electronegativity, high ionisation enthalpy and non-availability of *d* orbitals. Nitrogen has unique ability to form ***pπ-pπ* multiple** bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form *pπ-pπ* bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one *s* and two *p*) between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol^{-1}) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state. However, the single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in

nitrogen. Another factor which affects the chemistry of nitrogen is the absence of *d* orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form ***dπ–pπ* bond** as the heavier elements can e.g., $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphorus and arsenic can form ***dπ–dπ* bond** also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) *Reactivity towards hydrogen*: All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table 7.2. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

Table 7.2: Properties of Hydrides of Group 15 Elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) Distance/pm	101.7	141.9	151.9	170.7	–
HEH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H^\ominus$/kJ mol^{-1}	–46.1	13.4	66.4	145.1	278
$\Delta_{diss}H^\ominus$(E–H)/kJ mol^{-1}	389	322	297	255	–

(ii) *Reactivity towards oxygen*: All these elements form two types of oxides: E_2O_3 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

(iii) *Reactivity towards halogens*: These elements react to form two series of halides: EX_3 and EX_5. Nitrogen does not form pentahalide due to non-availability of the *d* orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) *Reactivity towards metals*: All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason. *Example 7.1*

Nitrogen with n = 2, has *s* and *p* orbitals only. It does not have *d* orbitals to expand its covalence beyond four. That is why it does not form pentahalide. *Solution*

PH_3 has lower boiling point than NH_3. Why? *Example 7.2*

Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3. *Solution*

Intext Questions

7.1 Why are pentahalides more covalent than trihalides ?

7.2 Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements ?

7.2 Dinitrogen

Preparation

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq)$$

Small amounts of NO and HNO_3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

Properties

Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. It has two stable isotopes: ^{14}N and ^{15}N. It has a very low solubility in water (23.2 cm^3 per litre of water at 273 K and 1 bar pressure) and low freezing and boiling points (Table 7.1).

Dinitrogen is rather inert at room temperature because of the high bond enthalpy of N≡N bond. Reactivity, however, increases rapidly with rise in temperature. At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

$$6Li + N_2 \xrightarrow{Heat} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

$$N_2(g) + 3H_2(g) \xrightleftharpoons{773\ k} 2NH_3(g); \qquad \Delta_f H^{\ominus} = -46.1\ kJmol^{-1}$$

Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$$N_2 + O_2(g) \xrightleftharpoons{Heat} 2NO(g)$$

Uses: The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide). It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals). Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Example 7.3 Write the reaction of thermal decomposition of sodium azide.

Solution Thermal decomposition of sodium azide gives dinitrogen gas.

$$2NaN_3 \rightarrow 2Na + 3N_2$$

Intext Question

7.3 Why is N_2 less reactive at room temperature?

7.3 Ammonia

Preparation

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or lime.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2\ SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

On a large scale, ammonia is manufactured by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta_f H^{\ominus} = -\ 46.1\ kJ\ mol^{-1}$$

In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium. The flow chart for the production of ammonia is shown in Fig. 7.1.

Fig. 7.1
Flow chart for the manufacture of ammonia

Properties

Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 198.4 and 239.7 K respectively. In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass. The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons as shown in the structure.

Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example,

$$2FeCl_3(aq) + 3NH_4OH(aq) \rightarrow \underset{\text{(brown ppt)}}{Fe_2O_3.xH_2O(s)} + 3NH_4Cl(aq)$$

$$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow \underset{\text{(white ppt)}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu^{2+}, Ag^+:

$$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4\,NH_3(aq) \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$

$$\underset{\text{(colourless)}}{Ag^+(aq)} + Cl^-(aq) \rightarrow \underset{\text{(white ppt)}}{AgCl(s)}$$

$$\underset{\text{(white ppt)}}{AgCl(s)} + 2NH_3(aq) \rightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses: Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

Example 7.4 Why does NH_3 act as a Lewis base ?

Solution Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

Intext Questions

7.4 Mention the conditions required to maximise the yield of ammonia.

7.5 How does ammonia react with a solution of Cu^{2+}?

7.4 Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table 7.3.

Table 7.3: Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673\,K} 4NO_2 + 2PbO$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

Lewis dot main resonance structures and bond parameters of oxides are given in Table 7.4.

Table 7.4: Structures of Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O	$\ddot{N}=N=\ddot{O} \longleftrightarrow :N\equiv N-\ddot{O}:$	N — N — O 113 pm 119 pm Linear
NO	$:N=\ddot{O}: \longleftrightarrow :\dot{N}=\ddot{O}:$	N — O 115 pm
N_2O_3		 Planar
NO_2		 Angular
N_2O_4		 Planar
N_2O_5		 Planar

Example 7.5

Why does NO_2 dimerise ?

Solution

NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

Intext Question

7.6 What is the covalence of nitrogen in N_2O_5 ?

7.5 Nitric Acid

Nitrogen forms oxoacids such as $H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid). Amongst them HNO_3 is the most important.

Preparation

In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH_3(g) + \underset{\text{(from air)}}{5O_2(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt / Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$$

Nitric oxide thus formed combines with oxygen giving NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Nitrogen dioxide so formed, dissolves in water to give HNO_3.

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Properties

It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown.

In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

$$3Cu + 8\ HNO_3(\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Zinc reacts with dilute nitric acid to give N_2O and with concentrated acid to give NO_2.

$$4Zn + 10HNO_3(\text{dilute}) \rightarrow 4\ Zn\ (NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(\text{conc.}) \rightarrow Zn\ (NO_3)_2 + 2H_2O + 2NO_2$$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non–metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4, and phosphorus to phosphoric acid.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10\ NO_2 + 4H_2O$$
$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$
$$S_8 + 48HNO_3(conc.) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$
$$P_4 + 20HNO_3(conc.) \rightarrow 4H_3PO_4 + 20\ NO_2 + 4H_2O$$

Brown Ring Test: The familiar brown ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

Uses: The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the *pickling of stainless steel*, etching of metals and as an oxidiser in rocket fuels.

7.6 Phosphorus — Allotropic Forms

Phosphorus is found in many allotropic forms, the important ones being white, red and black.

White phosphorus is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60°. It readily catches fire in air to give dense white fumes of P_4O_{10}.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

It consists of discrete tetrahedral P_4 molecule as shown in Fig. 7.2.

Fig. 7.2
White phosphorus

Red phosphorus is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus are formed. Red phosphorus possesses iron grey lustre. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.

Fig.7.3: *Red phosphorus*

It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig. 7.3.

Black phosphorus has two forms α-black phosphorus and β-black phosphorus. α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air. β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

7.7 Phosphine

Preparation

Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

(sodium hypophosphite)

When pure, it is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

Properties

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2. When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$$

Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,

$$PH_3 + HBr \rightarrow PH_4Br$$

Uses: The spontaneous combustion of phosphine is technically used in *Holme's signals*. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal. It is also used in *smoke screens*.

In what way can it be proved that PH_3 is basic in nature? *Example 7.6*

PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature. *Solution*

$$PH_3 + HI \rightarrow PH_4I$$

Due to lone pair on phosphorus atom, PH_3 is acting as a Lewis base in the above reaction.

Intext Questions

7.7 Bond angle in PH_4^+ is higher than that in PH_3. Why?

7.8 What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2 ?

7.8 Phosphorus Halides

Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

7.8.1 Phosphorus Trichloride

Preparation

It is obtained by passing dry chlorine over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

It is also obtained by the action of thionyl chloride with white phosphorus.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties

It is a colourless oily liquid and hydrolyses in the presence of moisture.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

It has a pyramidal shape as shown, in which phosphorus is sp^3 hybridised.

7.8.2 Phosphorus Pentachloride

Preparation

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

Properties

PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

When heated, it sublimes but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

It reacts with organic compounds containing –OH group converting them to chloro derivatives.

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

Finely divided metals on heating with PCl_5 give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

It is used in the synthesis of some organic compounds, e.g., C_2H_5Cl, CH_3COCl.

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown below. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$octahedral.

Example 7.7 Why does PCl_3 fume in moisture ?

Solution PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Example 7.8 Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Solution PCl_5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

Intext Questions

7.9 What happens when PCl_5 is heated?

7.10 Write a balanced equation for the hydrolytic reaction of PCl_5 in heavy water.

7.9 Oxoacids of Phosphorus

Phosphorus forms a number of oxoacids. The important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures are given in Table 7.5.

Table 7.5: Oxoacids of Phosphorus

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	$P_4O_{10}+H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2, heat in a sealed tube

* *Exists in polymeric forms only. Characteristic bonds of $(HPO_3)_3$ have been given in the Table.*

The compositions of the oxoacids are interrelated in terms of loss or gain of H_2O molecule or O-atom.

The structures of some important oxoacids are given below:

Fig. 7.4 *Structures of some important oxoacids of phosphorus*

In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain one P=O and at least one P–OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P=O and P–OH bonds, either P–P (e.g., in $H_4P_2O_6$) or P–H (e.g., in H_3PO_2) bonds but not both. These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, orthophophorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces, for example, $AgNO_3$ to metallic silver.

$$4\ AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

These P–H bonds are not ionisable to give H^+ and do not play any role in basicity. Only those H atoms which are attached with oxygen in P–OH form are ionisable and cause the basicity. Thus, H_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P–OH bonds and H_3PO_4 three.

Example 7.9 How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure ?

Solution In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

Intext Questions

7.11 What is the basicity of H_3PO_4?

7.12 What happens when H_3PO_3 is heated?

7.10 Group 16 Elements

Oxygen, sulphur, selenium, tellurium and polonium constitute Group 16 of the periodic table. This is sometimes known as group of *chalcogens*. The name is derived from the Greek word for brass and points to the association of sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur and frequently the other members of the group.

7.10.1 Occurrence

Oxygen is the most abundant of all the elements on earth. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.

However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as *gypsum* $CaSO_4.2H_2O$, *epsom salt* $MgSO_4.7H_2O$, *baryte* $BaSO_4$ and sulphides such as *galena* PbS, *zinc blende* ZnS, *copper pyrites* $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

The important atomic and physical properties of Group16 along with electronic configuration are given in Table 7.6. Some of the atomic, physical and chemical properties and their trends are discussed below.

7.10.2 Electronic Configuration

The elements of Group16 have six electrons in the outermost shell and have ns^2np^4 general electronic configuration.

7.10.3 Atomic and Ionic Radii

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.

7.10.4 Ionisation Enthalpy

Ionisation enthalpy decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group15 in the corresponding periods. This is due to the fact that Group 15 elements have extra stable half-filled *p* orbitals electronic configurations.

7.10.5 Electron Gain Enthalpy

Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium.

7.10.6 Electronegativity

Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decreases with an increase in atomic number. This implies that the metallic character increases from oxygen to polonium.

Example 7.10

Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

Solution

Due to extra stable half-filled *p* orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

7.10.7 Physical Properties

Some of the physical properties of Group 16 elements are given in Table 7.6. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8).

7.10.8 Chemical Properties

Oxidation states and trends in chemical reactivity

The elements of Group 16 exhibit a number of oxidation states (Table 7.6). The stability of -2 oxidation state decreases down the group. Polonium hardly shows –2 oxidation state. Since electronegativity of oxygen is very high, it shows only negative oxidation state as –2 except

Table 7.6: Some Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/g mol^{-1}	16.00	32.06	78.96	127.60	210.00
Electronic configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]3d^{10} 4s^2 4p^4$	$[Kr]4d^{10} 5s^2 5p^4$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius/(pm)[a]	66	104	117	137	146
Ionic radius, E^{2-}/pm	140	184	198	221	230[b]
Electron gain enthalpy, $/\Delta_{eg}H$ kJ mol^{-1}	–141	–200	–195	–190	–174
Ionisation enthalpy ($\Delta_i H_1$) /kJ mol^{-1}	1314	1000	941	869	813
Electronegativity	3.50	2.44	2.48	2.01	1.76
Density /g cm^{-3} (298 K)	1.32[c]	2.06[d]	4.19[e]	6.25	–
Melting point/K	55	393[f]	490	725	520
Boiling point/K	90	718	958	1260	1235
Oxidation states*	–2,–1,1,2	–2,2,4,6	–2,2,4,6	–2,2,4,6	2,4

[a]*Single bond;* [b]*Approximate value;* [c]*At the melting point;* [d] *Rhombic sulphur;* [e]*Hexagonal grey;* [f]*Monoclinic form, 673 K.*
* *Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF_2 and O_2F_2 respectively.*

in the case of OF_2 where its oxidation state is + 2. Other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and + 6 with fluorine. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increase (inert pair effect). Bonding in +4 and +6 oxidation states are primarily covalent.

Anomalous behaviour of oxygen

The anomalous behaviour of oxygen, like other members of *p*-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S.

The absence of *d* orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shells can be expanded and covalence exceeds four.

(i) *Reactivity with hydrogen*: All the elements of Group 16 form hydrides of the type H_2E (E = S, Se, Te, Po). Some properties of hydrides are given in Table 7.7. Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of decrease in bond (H–E) dissociation enthalpy down the group. Owing to the decrease in bond (H–E) dissociation enthalpy down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Table 7.7: Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p/K	273	188	208	222
b.p/K	373	213	232	269
H–E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	–286	–20	73	100
$\Delta_{diss} H$ (H–E)/kJ mol^{-1}	463	347	276	238
Dissociation constant[a]	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

[a] *Aqueous solution, 298 K*

(ii) *Reactivity with oxygen*: All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(iii) *Reactivity towards the halogens*: Elements of Group 16 form a large number of halides of the type, EX_6, EX_4 and EX_2 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as *see-saw* geometry.

All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp^3 hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below:

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

Example 7.11

H_2S is less acidic than H_2Te. Why?

Solution

Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

Intext Questions

7.13 List the important sources of sulphur.

7.14 Write the order of thermal stability of the hydrides of Group 16 elements.

7.15 Why is H_2O a liquid and H_2S a gas ?

7.11 Dioxygen

Preparation

Dioxygen can be obtained in the laboratory by the following ways:

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g); \qquad 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$

$$2HgO(s) \rightarrow 2Hg(l) + O_2(g); \qquad 2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(1) + O_2(g)$$

(iv) On large scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

Industrially, dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties

Dioxygen is a colourless and odourless gas. Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is just sufficient for the vital support of marine and aquatic life. It liquefies at 90 K and freezes at 55 K. It has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. Molecular oxygen, O_2 is unique in being paramagnetic inspite of having even number of electrons (see Class XI Chemistry Book, Unit 4).

Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxgyen-oxygen double bond is high (493.4 kJ mol^{-1}).

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:

$$2Ca + O_2 \rightarrow 2CaO$$

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

$$C + O_2 \rightarrow CO_2$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

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

Some compounds are catalytically oxidised. For e.g.,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

Uses: In addition to its importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel. Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering. The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

Intext Questions

7.16 Which of the following does not react with oxygen directly?
Zn, Ti, Pt, Fe

7.17 Complete the following reactions:
(i) $C_2H_4 + O_2 \rightarrow$
(ii) $4Al + 3\ O_2 \rightarrow$

7.12 Simple Oxides

A binary compound of oxygen with another element is called oxide. As already stated, oxygen reacts with most of the elements of the periodic table to form oxides. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties.

Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). Simple oxides can be classified on the basis of their acidic, basic or amphoteric character. An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5). For example, SO_2 combines with water to give H_2SO_3, an acid.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7, CrO_3, V_2O_5). The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). For example, CaO combines with water to give $Ca(OH)_2$, a base.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

In general, metallic oxides are basic.

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N_2O. For example, Al_2O_3 reacts with acids as well as alkalies.

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \rightarrow 2Na_3[Al(OH)_6](aq)$$

7.13 Ozone

Ozone is an allotropic form of oxygen. It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

Preparation

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

$$3O_2 \rightarrow 2O_3 \quad \Delta H^{\ominus}(298\ K) = +142\ kJ\ mol^{-1}$$

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition.

If concentrations of ozone greater than 10 per cent are required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

Properties

Pure ozone is a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell and in small concentrations it is harmless. However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen. It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive.

Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For e.g., it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$

$$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

The two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. It is a resonance hybrid of two main forms:

Uses: It is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc. It acts as an oxidising agent in the manufacture of potassium permanganate.

Intext Questions

7.18 Why does O_3 act as a powerful oxidising agent?

7.19 How is O_3 estimated quantitatively?

7.14 Sulphur — Allotropic Forms

Sulphur forms numerous allotropes of which the **yellow rhombic** (α-sulphur) and **monoclinic** (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

Rhombic sulphur (α-sulphur)

This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2.

Monoclinic sulphur (β-sulphur)

Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β-sulphur are formed. It is stable above 369 K and transforms into α-sulphur below it. Conversely, α-sulphur is stable below 369 K and transforms into β-sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in Fig. 7.5(a).

Fig. 7.5: *The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form*

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo-S_6, the ring adopts the chair form and the molecular dimensions are as shown in Fig. 7.5 (b). At elevated temperatures (~1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Example 7.12

Which form of sulphur shows paramagnetic behaviour ?

Solution

In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

7.15 Sulphur Dioxide

Preparation

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$$S(s) + O_2(g) \rightarrow SO_2\ (g)$$

In the laboratory it is readily generated by treating a sulphite with dilute sulphuric acid.

$$SO_3^{2-}(aq) + 2H^+\ (aq) \rightarrow H_2O(l) + SO_2\ (g)$$

Industrially, it is produced as a by-product of the roasting of sulphide ores.

$$4FeS_2\,(s) + 11O_2\,(g) \rightarrow 2Fe_2O_3\,(s) + 8SO_2\,(g)$$

The gas after drying is liquefied under pressure and stored in steel cylinders.

Properties

Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water. It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.

Sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

$$SO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2SO_3\,(aq)$$

It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

In its reaction with water and alkalies, the behaviour of sulphur dioxide is very similar to that of carbon dioxide.

Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride, SO_2Cl_2. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

$$SO_2(g) + Cl_2\ (g) \rightarrow SO_2Cl_2(l)$$

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3\,(g)$$

When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution; the latter reaction is a convenient test for the gas.

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:

Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

Intext Questions

7.20 What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

7.21 Comment on the nature of two S–O bonds formed in SO_2 molecule. Are the two S–O bonds in this molecule equal ?

7.22 How is the presence of SO_2 detected ?

7.16 Oxoacids of Sulphur

Sulphur forms a number of oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in Fig. 7.6.

Sulphurous acid (H_2SO_3) | Sulphuric acid (H_2SO_4) | Peroxodisulphuric acid ($H_2S_2O_8$) | Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Fig. 7.6: *Structures of some important oxoacids of sulphur*

7.17 Sulphuric Acid

Manufacture

Sulphuric acid is one of the most important industrial chemicals worldwide.

Sulphuric acid is manufactured by the **Contact Process** which involves three steps:

(i) burning of sulphur or sulphide ores in air to generate SO_2.

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(iii) absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$).

A flow diagram for the manufacture of sulphuric acid is shown in (Fig. 7.7). The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta_r H^\ominus = -196.6\,\text{kJmol}^{-1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is

Fig. 7.7: *Flow diagram for the manufacture of sulphuric acid*

absorbed in concentrated H_2SO_4 to produce *oleum*. Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

The sulphuric acid obtained by Contact process is 96-98% pure.

Properties

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

The chemical reactions of sulphuric acid are as a result of the following characteristics: (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent. In aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq); K_{a_1} = \text{very large } (K_{a_1} > 10)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq) \; ; K_{a_2} = 1.2 \times 10^{-2}$$

The larger value of K_{a_1} ($K_{a_1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-. Greater the value of dissociation constant (K_a), the stronger is the acid.

The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate).

Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.

$$2\ MX + H_2SO_4 \rightarrow 2\ HX + M_2SO_4\ (X = F,\ Cl,\ NO_3)$$

(M = Metal)

Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + 2\ H_2SO_4(conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$3S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2\ SO_2 + 2\ H_2O$$

Uses: Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in: (a) petroleum refining (b) manufacture of pigments, paints and dyestuff intermediates (c) detergent industry (d) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising (e) storage batteries (f) in the manufacture of nitrocellulose products and (g) as a laboratory reagent.

Intext Questions

7.23 Mention three areas in which H_2SO_4 plays an important role.

7.24 Write the conditions to maximise the yield of H_2SO_4 by Contact process.

7.25 Why is $K_{a_2} \ll K_{a_1}$ for H_2SO_4 in water ?

7.18 Group 17 Elements

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the **halogens** (Greek *halo* means salt and *genes* means born i.e., salt producers). The halogens are highly reactive non-metallic elements. Like Groups 1 and 2, the elements of Group 17 show great similarity amongst themselves. That much similarity is not found in the elements of other groups of the periodic table. Also, there is a regular gradation in their physical and chemical properties. Astatine is a radioactive element.

7.18.1 Occurrence

Fluorine and chlorine are fairly abundant while bromine and iodine less so. Fluorine is present mainly as insoluble fluorides (fluorspar CaF_2, cryolite Na_3AlF_6 and fluoroapatite $3Ca_3(PO_4)_2.CaF_2$) and small quantities are present in soil, river water plants and bones and teeth of animals. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass). The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, $KCl.MgCl_2.6H_2O$. Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

The important atomic and physical properties of Group 17 elements along with their electronic configurations are given in Table 7.8.

Table 7.8: Atomic and Physical Properties of Halogens

Property	F	Cl	Br	I	At[a]
Atomic number	9	17	35	53	85
Atomic mass/g mol^{-1}	19.00	35.45	79.90	126.90	210
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
Covalent radius/pm	64	99	114	133	–
Ionic radius X^-/pm	133	184	196	220	–
Ionisation enthalpy/kJ mol^{-1}	1680	1256	1142	1008	–
Electron gain enthalpy/kJ mol^{-1}	–333	–349	–325	–296	–
Electronegativity[b]	4	3.2	3.0	2.7	2.2
$\Delta_{Hyd}H(X^-)$/kJ mol^{-1}	515	381	347	305	–
	F_2	Cl_2	Br_2	I_2	–
Melting point/K	54.4	172.0	265.8	386.6	–
Boiling point/K	84.9	239.0	332.5	458.2	–
Density/g cm^{-3}	1.5 (85)[c]	1.66 (203)[c]	3.19(273)[c]	4.94(293)[d]	–
Distance X – X/pm	143	199	228	266	–
Bond dissociation enthalpy /(kJ mol^{-1})	158.8	242.6	192.8	151.1	–
$E^{\ominus}/V$[e]	2.87	1.36	1.09	0.54	–

[a] *Radioactive;* [b] *Pauling scale;* [c] *For the liquid at temperatures (K) given in the parentheses;* [d] *solid;* [e] *The half-cell reaction is* $X_2(g) + 2e^- \rightarrow 2X^-(aq)$.

The trends of some of the atomic, physical and chemical properties are discussed below.

7.18.2 Electronic Configuration All these elements have seven electrons in their outermost shell (ns^2np^5) which is one electron short of the next noble gas.

7.18.3 Atomic and Ionic Radii The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. The atomic radius of fluorine like the other elements of second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

7.18.4 Ionisation Enthalpy They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.

7.18.5 Electron Gain Enthalpy Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small $2p$ orbitals of fluorine and thus, the incoming electron does not experience much attraction.

7.18.6 Electronegativity They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

Example 7.14

Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Solution

Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

7.18.7 Physical Properties Halogens display smooth variations in their physical properties. Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2, has yellow, Cl_2 , greenish yellow, Br_2, red and I_2, violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

One curious anomaly we notice from Table 7.8 is the smaller enthalpy of dissociation of F_2 compared to that of Cl_2 whereas X-X bond dissociation enthalpies from chlorine onwards show the expected

trend: Cl – Cl > Br – Br > I – I. A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

Example 7.15 Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

Solution It is due to

(i) low enthalpy of dissociation of F-F bond (Table 7.8).

(ii) high hydration enthalpy of F^- (Table 7.8).

7.18.8 Chemical Properties

Oxidation states and trends in chemical reactivity

All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also as explained below:

	ns	np	nd	
Halogen atom in ground state (other than fluorine)	↑↓	↑↓ ↑↓ ↑		1 unpaired electron accounts for –1 or +1 oxidation states
First excited state	↑↓	↑↓ ↑ ↑	↑	3 unpaired electrons account for +3 oxidation states
Second excited state	↑↓	↑ ↑ ↑	↑ ↑	5 unpaired electrons account for +5 oxidation state
Third excited state	↑↓	↑ ↑ ↑	↑ ↑ ↑	7 unpaired electrons account for +7 oxidation state

The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids. The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine. The fluorine atom has no *d* orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \text{ (X = Cl, Br or I)}$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \text{ (X = Br or I)}$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials (Table 7.8) which are dependent on the parameters indicated below:

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\,\Delta_{diss}H^{\ominus}} X(g) \xrightarrow{\Delta_{eg}H^{\ominus}} X^-(g) \xrightarrow{\Delta_{hyd}H^{\ominus}} X^-(aq)$$

The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is non-spontaneous. In fact, I^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$$

(where X = Cl or Br)

$$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$$

Anomalous behaviour of fluorine

Like other elements of *p*-block present in second period of the periodic table, fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, enthalpy of bond dissociation and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p. and electron gain enthalpy are quite lower than expected. The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of *d* orbitals in valence shell.

Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) *Reactivity towards hydrogen*: They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. They dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are given in Table 7.9. The acidic strength of these acids varies in the order: HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H–X) dissociation enthalpy in the order: H–F > H–Cl > H–Br > H–I.

Table 7.9: Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point/K	190	159	185	222
Boiling point/K	293	189	206	238
Bond length (H – X)/pm	91.7	127.4	141.4	160.9
$\Delta_{diss}H^{\ominus}$/kJ mol^{-1}	574	432	363	295
pK_a	3.2	–7.0	–9.5	–10.0

(ii) *Reactivity towards oxygen*: Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298 K. These oxides

are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

The bromine oxides, Br_2O, BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.

The iodine oxides, I_2O_4 , I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) *Reactivity towards metals*: Halogens react with metals to form metal halides. For e.g., bromine reacts with magnesium to give magnesium bromide.

$$Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$$

The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is a monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For e.g., $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

(iv) *Reactivity of halogens towards other halogens*: Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX' , XX_3', XX_5' and XX_7' where X is a larger size halogen and X' is smaller size halogen.

Example 7.16 Fluorine exhibits only –1 oxidation state whereas other halogens exhibit + 1, + 3, + 5 and + 7 oxidation states also. Explain.

Solution Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d* orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

Intext Questions

7.26 Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2.

7.27 Give two examples to show the anomalous behaviour of fluorine.

7.28 Sea is the greatest source of some halogens. Comment.

7.19 Chlorine

Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO_2. In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, *chloros* = greenish yellow).

Preparation

It can be prepared by any one of the following methods:

(i) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

(ii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of chlorine

(i) *Deacon's process*: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

(ii) *Electrolytic process*: Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

Properties

It is a greenish yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It can be liquefied easily into greenish yellow liquid which boils at 239 K. It is soluble in water.

Chlorine reacts with a number of metals and non-metals to form chlorides.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3; \qquad P_4 + 6Cl_2 \rightarrow 4PCl_3$$

$$2Na + Cl_2 \rightarrow 2NaCl; \qquad S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3;$$

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$H_2S + Cl_2 \rightarrow 2HCl + S$$

$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2; \qquad NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

(excess) (excess)

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$

(cold and dilute)

$$6\ NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(hot and conc.)

With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$.

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{UV} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethene}}{C_2H_4} + Cl_2 \xrightarrow{\text{Room temp.}} \underset{\text{1,2-Dichloroethane}}{C_2H_4Cl_2}$$

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

(ii) It is a powerful bleaching agent; bleaching action is due to oxidation.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

$$\text{Coloured substance} + O \rightarrow \text{Colourless substance}$$

It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

Uses: It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Example 7.17 Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify.

Solution $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

Intext Questions

7.29 Give the reason for bleaching action of Cl_2.

7.30 Name two poisonous gases which can be prepared from chlorine gas.

7.20 Hydrogen Chloride

Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

Preparation

In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420\,K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\,K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing through concentrated sulphuric acid.

Properties

It is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K). It is extremely soluble in water and ionises as below:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \quad K_a = 10^7$$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl.

$$NH_3 + HCl \rightarrow NH_4Cl$$

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$

Uses: It is used (i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch), (ii) for extracting glue from bones and purifying bone black, (iii) in medicine and as a laboratory reagent.

Example 7.18

When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

Solution

Its reaction with iron produces H_2.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Liberation of hydrogen prevents the formation of ferric chloride.

7.21 Oxoacids of Halogens

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts. The oxoacids of halogens are given in Table 7.10 and their structures are given in Fig. 7.8.

Table 7.10: Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**HOCl** (Hypochlorous acid)	**HOBr** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	– –	HOCIO (chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	$HOClO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	– –	$HOClO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)

Fig. 7.8 *The structures of oxoacids of chlorine*

7.22 Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX', XX_3', XX_5' and XX_7' where X is halogen of larger size and X' of smaller size and X is more electropositive than X'. As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF_7 (having maximum number of atoms).

Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For e.g.,

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\,K} 2ClF;$$

$$\underset{\text{(excess)}}{I_2 + 3Cl_2} \rightarrow 2ICl_3$$

$$\underset{\text{(excess)}}{Cl_2 + 3F_2} \xrightarrow{573\,K} 2ClF_3;$$

$$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl;$$

$$\underset{\text{(excess)}}{Br_2 + 5F_2} \rightarrow 2BrF_5$$

Properties

Some properties of interhalogen compounds are given in Table 7.11.

Table 7.11: Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
XX'_1	ClF	colourless gas	–
	BrF	pale brown gas	–
	IF[a]	detected spectroscopically	–
	BrCl[b]	gas	
	ICl	ruby red solid (α-form)	–
		brown red solid (β-form)	–
	IBr	black solid	–
XX'_3	ClF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped (?)
	ICl_3[c]	orange solid	Bent T-shaped (?)
XX'_5	IF_5	colourless gas but solid below 77 K	Square pyramidal
	BrF_5	colourless liquid	Square pyramidal
	ClF_5	colourless liquid	Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

[a]Very unstable; [b]The pure solid is known at room temperature; [c]Dimerises as Cl–bridged dimer (I_2Cl_6)

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids except ClF which is a gas at 298 K. Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–X′ bond in interhalogens is weaker than X–X bond in halogens except F–F bond. All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX′), halite (when XX'_3), halate (when XX'_5) and perhalate (when XX'_7) anion derived from the larger halogen.

$$XX' + H_2O \rightarrow HX' + HOX$$

Their molecular structures are very interesting which can be explained on the basis of VSEPR theory (Example 7.19). The XX_3 compounds have the bent 'T' shape, XX_5 compounds square pyramidal and IF_7 has pentagonal bipyramidal structures (Table 7.11).

Example 7.19 Deduce the molecular shape of BrF_3 on the basis of VSEPR theory.

Solution The central atom Br has seven electrons in the valence shell. Three of these will form electron-pair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.

Uses: These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$$

Intext Question

7.31 Why is ICl more reactive than I_2?

7.23 Group 18 Elements

Group 18 consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

7.23.1 Occurrence

All the noble gases except radon occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of ^{226}Ra.

$$^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

Example 7.20 Why are the elements of Group 18 known as noble gases ?

Solution The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

The important atomic and physical properties of the Group 18 elements along with their electronic configurations are given in Table 7.12. The trends in some of the atomic, physical and chemical properties of the group are discussed here.

Table 7.12: Atomic and Physical Properties of Group 18 Elements

Propery	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]\ 3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Atomic radius/pm	120	160	190	200	220	–
Ionisation enthalpy /kJmol^{-1}	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /kJmol^{-1}	48	116	96	96	77	68
Density (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

* *radioactive*

7.23.2 Electronic Configuration

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$ (Table 7.12). Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

7.23.3 Ionisation Enthalpy

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increase in atomic size.

7.23.4 Atomic Radii

Atomic radii increase down the group with increase in atomic number.

7.23.5 Electron Gain Enthalpy

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

Physical Properties

All the noble gases are monoatomic. They are colourless, odourless and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces. Helium has the lowest boiling point (4.2 K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Example 7.21

Noble gases have very low boiling points. Why?

Solution

Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

Chemical Properties

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally, ever since their discovery, but all attempts to force them to react to form the compounds, were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 $kJmol^{-1}$) was almost identical with that of xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^+PtF_6^-$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

(a) Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe\,(g) + F_2\,(g)} \xrightarrow{673\,K,\,1\,bar} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe\,(g) + 2F_2\,(g)} \xrightarrow{873\,K,\,7\,bar} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe\,(g) + 3F_2\,(g)} \xrightarrow{573\,K,\,60\text{-}70\,bar} XeF_6(s)$$

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

$$2XeF_2\,(s) + 2H_2O(l) \rightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$$

The structures of the three xenon fluorides can be deduced from VSEPR and these are shown in Fig. 7.9. XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase.

Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \rightarrow [XeF]^+\,[PF_6]^-; \quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+\,[SbF_6]^-$$

$$XeF_6 + MF \rightarrow M^+\,[XeF_7]^- \text{ (M = Na, K, Rb or Cs)}$$

(b) Xenon-oxygen compounds

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12\ H_2O \rightarrow 4Xe + 2XeO_3 + 24\ HF + 3\ O_2$$

$$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\ HF$$

$$XeF_6 + 2\ H_2O \rightarrow XeO_2F_2 + 4HF$$

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure (Fig. 7.9). $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure (Fig.7.9).

(a) Linear (b) Square planar (c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

Fig. 7.9 *The structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ and (e) XeO_3*

Example 7.22

Does the hydrolysis of XeF_6 lead to a redox reaction?

Solution

No, the products of hydrolysis are $XeOF_4$ and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

Uses: Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive. There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

Intext Questions

7.32 Why is helium used in diving apparatus?

7.33 Balance the following equation: $XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$

7.34 Why has it been difficult to study the chemistry of radon?

Summary

Groups 13 to 18 of the periodic table consist of ***p*-block elements** with their valence shell electronic configuration ns^2np^{1-6}. Groups 13 and 14 were dealt with in Class XI. In this Unit remaining groups of the *p*-block have been discussed.

Group 15 consists of five elements namely, N, P, As, Sb and Bi which have general electronic configuration ns^2np^3. Nitrogen differs from other elements of this group due to small size, formation of **$p\pi$–$p\pi$ multiple bonds** with itself and with highly electronegative atom like O or C and **non-availability of *d* orbitals** to expand its valence shell. Elements of group 15 show gradation in properties. They react with oxygen, hydrogen and halogens. They exhibit two important oxidation states, + 3 and + 5 but +3 oxidation is favoured by heavier elements due to 'inert pair effect'.

Dinitrogen can be prepared in laboratory as well as on industrial scale. It forms oxides in various oxidation states as N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5. These oxides have **resonating structures** and have multiple bonds. Ammonia can be prepared on large scale by **Haber's process**. HNO_3 is an important industrial chemical. It is a strong monobasic acid and is a powerful oxidising agent. Metals and non-metals react with HNO_3 under different conditions to give NO or NO_2.

Phosphorus exists as P_4 in elemental form. It exists in several **allotropic forms**. It forms hydride, PH_3 which is a highly poisonous gas. It forms two types of halides as PX_3 and PX_5. PCl_3 is prepared by the reaction of white phosphorus with dry chlorine while PCl_5 is prepared by the reaction of phosphorus with SO_2Cl_2. Phosphorus forms a number of oxoacids. Depending upon the number of P–OH groups, their basicity varies. The oxoacids which have P–H bonds are good reducing agents.

The Group 16 elements have general electronic configuration ns^2np^4. They show maximum oxidation state, +6. Gradation in physical and chemical properties is observed in the group 16 elements. In laboratory, dioxygen is prepared by heating $KClO_3$ in presence of MnO_2. It forms a number of oxides with metals. Allotropic form of oxygen is O_3 which is a highly oxidising agent. Sulphur forms a number of allotropes. Of these, α– and β– forms of sulphur are the most important. Sulphur combines with oxygen to give oxides such as SO_2 and SO_3. SO_2 is prepared by the direct union of sulphur with oxygen. SO_2 is used in the manufacture of H_2SO_4. Sulphur forms a number of oxoacids. Amongst them, most important is H_2SO_4. It is prepared by **contact process**. It is a dehydrating and oxidising agent. It is used in the manufacture of several compounds.

Group 17 of the periodic table consists of the following elements F, Cl, Br, I and At.These elements are extremely reactive and as such they are found in the combined state only. The common oxidation state of these elements is –1. However, highest oxidation state can be +7. They show regular gradation in physical and chemical properties. They form oxides, hydrogen halides, interhalogen compounds and oxoacids. Chlorine is conveniently obtained by the reaction of HCl with $KMnO_4$. HCl is prepared by heating NaCl with concentrated H_2SO_4. Halogens combine with one another to form **interhalogen compounds** of the type $X\ X^1_n$ (n = 1, 3, 5, 7) where X^1 is lighter than X. A number of oxoacids of halogens are known. In the structures of these oxoacids, halogen is the central atom which is bonded in each case with one OH bond as X–OH. In some cases X = 0 bonds are also found.

Group 18 of the periodic table consists of **noble gases**. They have $ns^2\,np^6$ valence shell electronic configuration except He which has $1s^2$. All the gases except Rn occur in atmosphere. Rn is obtained as the decay product of ^{226}Ra.

Due to complete octet of outermost shell, they have less tendency to form compounds. The best characterised compounds are those of xenon with fluorine and oxygen only under certain conditions. These gases have several uses. Argon is used to provide inert atmosphere, helium is used in filling balloons for meteorological observations, neon is used in discharge tubes and fluorescent bulbs.

Exercises

7.1 Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.

7.2 Why does the reactivity of nitrogen differ from phosphorus?

7.3 Discuss the trends in chemical reactivity of group 15 elements.

7.4 Why does NH_3 form hydrogen bond but PH_3 does not?

7.5 How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

7.6 How is ammonia manufactured industrially?

7.7 Illustrate how copper metal can give different products on reaction with HNO_3.

7.8 Give the resonating structures of NO_2 and N_2O_5.

7.9 The HNH angle value is higher than HPH, HAsH and HSbH angles. Why? [**Hint:** Can be explained on the basis of sp^3 hybridisation in NH_3 and only *s–p* bonding between hydrogen and other elements of the group].

7.10 Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

7.11 Explain why NH_3 is basic while BiH_3 is only feebly basic.

7.12 Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

7.13 Write main differences between the properties of white phosphorus and red phosphorus.

7.14 Why does nitrogen show catenation properties less than phosphorus?

7.15 Give the disproportionation reaction of H_3PO_3.

7.16 Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

7.17 Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

7.18 Why is dioxygen a gas but sulphur a solid?

7.19 Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-?
(**Hint:** Consider lattice energy factor in the formation of compounds).

7.20 Which aerosols deplete ozone?

7.21 Describe the manufacture of H_2SO_4 by contact process?

7.22 How is SO_2 an air pollutant?

7.23 Why are halogens strong oxidising agents?

7.24 Explain why fluorine forms only one oxoacid, HOF.

7.25 Explain why inspite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

7.26 Write two uses of ClO_2.

7.27 Why are halogens coloured?

7.28 Write the reactions of F_2 and Cl_2 with water.

7.29 How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only.

7.30 What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?

7.31 What are the oxidation states of phosphorus in the following:
(i) H_3PO_3 (ii) PCl_3 (iii) Ca_3P_2 (iv) Na_3PO_4 (v) POF_3?

7.32 Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO_2.

(ii) Chlorine gas is passed into a solution of NaI in water.

7.33 How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

7.34 With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

7.35 How are XeO_3 and $XeOF_4$ prepared?

7.36 Arrange the following in the order of property indicated for each set:

(i) F_2, Cl_2, Br_2, I_2 - increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI - increasing acid strength.

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 – increasing base strength.

7.37 Which one of the following does not exist?

(i) $XeOF_4$ (ii) NeF_2 (iii) XeF_2 (iv) XeF_6

7.38 Give the formula and describe the structure of a noble gas species which is isostructural with:

(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-

7.39 Why do noble gases have comparatively large atomic sizes?

7.40 List the uses of neon and argon gases.

Answers to Some Intext Questions

7.1 Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.

7.2 Because BiH_3 is the least stable among the hydrides of Group 15.

7.3 Because of strong $p\pi$–$p\pi$ overlap resulting into the triple bond, N≡N.

7.6 From the structure of N_2O_5 it is evident that covalence of nitrogen is four.

7.7 Both are sp^3 hybridised. In PH_4^+ all the four orbitals are bonded whereas in PH_3 there is a lone pair of electrons on P, which is responsible for lone pair-bond pair repulsion in PH_3 reducing the bond angle to less than 109° 28′.

7.10 $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$

7.11 Three P–OH groups are present in the molecule of H_3PO_4. Therefore, its basicity is three.

7.15 Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state.

7.21 Both the S–O bonds are covalent and have equal strength due to resonating structures.

7.25 H_2SO_4 is a very strong acid in water largely because of its first ionisation to H_3O^+ and HSO_4^-. The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. That is why $K_{a_2} << K_{a_1}$.

7.31 In general, interhalogen compounds are more reactive than halogens due to weaker $X–X^1$ bonding than X–X bond. Thus, ICl is more reactive than I_2.

7.34 Radon is radioactive with very short half-life which makes the study of chemistry of radon difficult.

Unit

8

The *d*- and *f*-Block Elements

Objectives

After studying this Unit, you will be able to

- learn the positions of the *d*– and *f*-block elements in the periodic table;
- know the electronic configurations of the transition (*d*-block) and the inner transition (*f*-block) elements;
- appreciate the relative stability of various oxidation states in terms of electrode potential values;
- describe the preparation, properties, structures and uses of some important compounds such as $K_2Cr_2O_7$ and $KMnO_4$;
- understand the general characteristics of the *d*– and *f*–block elements and the general horizontal and group trends in them;
- describe the properties of the *f*-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.

Iron, copper, silver and gold are among the transition elements that have played important roles in the development of human civilisation. The inner transition elements such as Th, Pa and U are proving excellent sources of nuclear energy in modern times.

The *d*-block of the periodic table contains the elements of the groups 3-12 in which the *d* orbitals are progressively filled in each of the four long periods. The elements constituting the *f* -block are those in which the 4 *f* and 5 *f* orbitals are progressively filled in the latter two long periods; these elements are formal members of group 3 from which they have been taken out to form a separate *f*-block of the periodic table. The names *transition metals* and *inner transition* metals are often used to refer to the elements of *d*-and *f*-blocks respectively.

There are mainly three series of the transition metals, 3*d* series (Sc to Zn), 4*d* series (Y to Cd) and 5*d* series (La to Hg, omitting Ce to Lu). The fourth 6*d* series which begins with Ac is still incomplete. The two series of the inner transition metals, (4*f* and 5*f*) are known as *lanthanoids* and *actinoids* respectively.

Strictly speaking, a transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states. Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the three transition series, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled *d* or *f* orbitals in their atoms sets the study of the transition elements and

their compounds apart from that of the main group elements. However, the usual theory of valence as applicable to the main group elements can also be applied successfully to the transition elements.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium form part of the transition metals.

In this Unit, besides introduction, we shall first deal with the electronic configuration, occurrence and general characteristics of the transition elements with special emphasis on the trends in the properties of the first row (3*d*) transition metals and the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

THE TRANSITION ELEMENTS (*d*-BLOCK)

8.1 Position in the Periodic Table

The *d*–block occupies the large middle section flanked by *s*– and *p*– blocks in the periodic table. The very name 'transition' given to the elements of *d*-block is only because of their position between *s*– and *p*– block elements. The *d*–orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals, i.e., 3*d*, 4*d* and 5*d*. The fourth row of 6*d* is still incomplete. These series of the transition elements are shown in Table 8.1.

8.2 Electronic Configurations of the d-Block Elements

In general the electronic configuration of these elements is $(n-1)d^{1-10}ns^{1-2}$. The (n–1) stands for the inner *d* orbitals which may have one to ten electrons and the outermost n*s* orbital may have one or two electrons. However, this generalisation has several exceptions because of very little energy difference between (n-1)*d* and n*s* orbitals. Furthermore, half and completely filled sets of orbitals are relatively more stable. A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3*d* series. Consider the case of Cr, for example, which has $3d^5 4s^1$ instead of $3d^4 4s^2$; the energy gap between the two sets (3*d* and 4*s*) of orbitals is small enough to prevent electron entering the 3*d* orbitals. Similarly in case of Cu, the configuration is $3d^{10} 4s^1$ and not $3d^9 4s^2$. The outer electronic configurations of the transition elements are given in Table 8.1.

Table 8.1: Outer Electronic Configurations of the Transition Elements (ground state)

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10

3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7*s*	2	2	2	2	2	2	2	2	1	2
6*d*	1	2	3	4	5	6	7	8	10	10

The electronic configurations of Zn, Cd and Hg are represented by the general formula $(n-1)d^{10}ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

The *d* orbitals of the transition elements project to the periphery of an atom more than the other orbitals (i.e., *s* and *p*), hence, they are more influenced by the surroundings as well as affecting the atoms or molecules surrounding them. In some respects, ions of a given d^n configuration (n = 1 – 9) have similar magnetic and electronic properties. With partly filled *d* orbitals these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands.

The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. All these characteristics have been discussed in detail later in this Unit.

There are greater horizontal similarities in the properties of the transition elements in contrast to the main group elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3*d* row) and then consider some group similarities.

Example 8.1

On what ground can you say that scandium (*Z* = 21) is a transition element but zinc (*Z* = 30) is not?

Solution

On the basis of incompletely filled 3*d* orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d* orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.

Intext Question

8.1 Silver atom has completely filled *d* orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

8.3 General Properties of the Transition Elements (d-Block)

8.3.1 Physical Properties

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

Lattice Structures of Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
hcp (ccp,bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure).

Fig. 8.1: *Trends in melting points of transition elements*

The transition metals (with the exception of Zn, Cd and Hg) are very much hard and have low volatility. Their melting and boiling points are high. Fig. 8.1 depicts the melting points of the 3*d*, 4*d* and 5*d* transition metals. The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)*d* in addition to the n*s* electrons in the interatomic metallic bonding. In any row the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. They have high enthalpies of atomisation which are shown in Fig. 8.2. The maxima at about the middle of each series indicate that one unpaired electron per *d* orbital is particularly

favourable for strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions (see later for electrode potentials).

Another generalisation that may be drawn from Fig. 8.2 is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series; this is an important factor in accounting for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition metals.

Fig. 8.2 *Trends in enthalpies of atomisation of transition elements*

8.3.2 Variation in Atomic and Ionic Sizes of Transition Metals

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a *d* orbital each time the nuclear charge increases by unity. It may be recalled that the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small. An interesting point emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The curves in Fig. 8.3 show an increase from the first (3*d*) to the second (4*d*) series of the elements but the radii of the third (5*d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4*f* orbitals which must be filled before the 5*d* series of elements begin. The filling of 4*f* before 5*d* orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected

increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third *d* series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

Fig. 8.3: *Trends in atomic radii of transition elements*

The factor responsible for the lanthanoid contraction is somewhat similar to that observed in an ordinary transition series and is attributed to similar cause, i.e., the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one 4*f* electron by another is less than that of one *d* electron by another, and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire $4f^n$ orbitals.

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (Z = 22) to copper (Z = 29) the significant increase in the density may be noted (Table 8.2).

Table 8.2: Electronic Configurations and some other Properties of the First Series of Transition Elements

Element		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_a H^\ominus$/kJ mol^{-1}		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy/$\Delta_i H^\ominus$/kJ mol^{-1}											
$\Delta_i H^\ominus$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\ominus$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\ominus$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829
Metallic/ionic radii/pm	M	164	147	135	129	137	126	125	125	128	137
	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard electrode potential $E^\ominus$/V	M^{2+}/M	–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	-0.76
	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–
Density/g cm^{-3}		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

Example 8.2

Why do the transition elements exhibit higher enthalpies of atomisation?

Solution

Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

Intext Question

8.2 In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest, i.e., 126 kJ mol^{-1}. Why?

8.3.3 Ionisation Enthalpies

Due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 8.2 gives the values for the first three ionisation enthalpies of the first row elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Although the first ionisation enthalpy, in general, increases, the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.

The irregular trend in the first ionisation enthalpy of the 3*d* metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals. So the unipositive ions have d^n configurations with no 4*s* electrons. There is thus, a reorganisation energy accompanying ionisation with some gains in exchange energy as the number of electrons increases and from the transference of *s* electrons into *d* orbitals. There is the generally expected increasing trend in the values as the effective nuclear charge increases. However, the value of Cr is lower because of the absence of any change in the *d* configuration and the value for Zn higher because it represents an ionisation from the 4*s* level. The lowest common oxidation state of these metals is +2. To form the M^{2+} ions from the gaseous atoms, the sum of the first and second ionisation energies is required in addition to the enthalpy of atomisation for each element. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where the d^5 and d^{10} configurations of the M^+ ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionisation consists of the removal of an electron which allows the production of the stable d^{10} configuration. The trend in the third ionisation enthalpies is not complicated by the 4*s* orbital factor and shows the greater difficulty of removing an electron from the d^5 (Mn^{2+}) and d^{10} (Zn^{2+}) ions superimposed upon the general increasing trend. In general, the third ionisation enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}. Also the high values for

copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these elements.

Although ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is very complex and not amendable to ready generalisation.

8.3.4 Oxidation States

One of the notable features of a transition element is the great variety of oxidation states it may show in its compounds. Table 8.3 lists the common oxidation states of the first row transition elements.

Table 8.3: Oxidation States of the first row Transition Metals (the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the *s* and *d* electrons upto manganese ($Ti^{IV}O_2$, $V^{V}O_2^{+}$, $Cr^{VI}O_4^{2-}$, $Mn^{VII}O_4^{-}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III}, V^{IV}, V^{V}. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.

An interesting feature in the variability of oxidation states of the *d*–block elements is noticed among the groups (groups 4 through 10). Although in the *p*–block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

Name a transition element which does not exhibit variable oxidation states. *Example 8.3*

Scandium (Z = 21) does not exhibit variable oxidation states. *Solution*

Intext Question

8.3.5 Trends in the M^{2+}/M Standard Electrode Potentials

Fig. 8.4: *Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow {}^{\circ}M$) of the elements Ti to Zn*

Table 8.4 contains the thermochemical parameters related to the transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials. The observed values of $E^{\ominus}$ and those calculated using the data of Table 8.4 are compared in Fig. 8.4.

The unique behaviour of Cu, having a positive $E^{\ominus}$, accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy. The general trend towards less negative $E^{\ominus}$ values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the value of $E^{\ominus}$ for Mn, Ni and Zn are more negative than expected from the trend.

Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration. *Example 8.4*

Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level (see Unit 9) . On the other hand, the change from Mn^{2+} to Mn^{3+} results in the half-filled (d^5) configuration which has extra stability. *Solution*

Intext Question

8.4 The $E^{\ominus}(M^{2+}/M)$ value for copper is positive (+0.34V). What is possibly the reason for this? (Hint: consider its high $\Delta_a H^{\ominus}$ and low $\Delta_{hyd} H^{\ominus}$)

Table 8.4: Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M.

Element (M)	$\Delta_a H^\ominus$ (M)	$\Delta_i H_1^\ominus$	$\Delta_i H_2^\ominus$	$\Delta_{hyd} H^\ominus (M^{2+})$	$E^\ominus$/V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

The stability of the half-filled *d* sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their $E^\ominus$ values, whereas $E^\ominus$ for Ni is related to the highest negative $\Delta_{hyd}H^\ominus$.

8.3.6 Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

An examination of the $E^\ominus(M^{3+}/M^{2+})$ values (Table 8.2) shows the varying trends. The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+}. The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5). The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level, Unit 9).

8.3.7 Trends in Stability of Higher Oxidation States

Table 8.5 shows the stable halides of the 3*d* series of transition metals. The highest oxidation numbers are achieved in TiX_4 (tetrahalides), VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6.

Although V^V is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxohalides, VOX_3. Another feature of fluorides is their instability in the low oxidation states e.g., VX_2 (X = Cl, Br or I)

Table 8.5: Formulas of Halides of 3*d* Metals

Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX_4^I	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX_3^I	CoF_3			
+ 2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+ 1								CuX^{III}	

Key: X = F → I; X^I = F → Br; X^{II} = F, Cl; X^{III} = Cl → I

and the same applies to CuX. On the other hand, all Cu^{II} halides are known except the iodide. In this case, Cu^{2+} oxidises I^- to I_2:

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$$

However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

The stability of Cu^{2+} (aq) rather than Cu^+(aq) is due to the much more negative $\Delta_{hyd}H^{\ominus}$ of Cu^{2+} (aq) than Cu^+, which more than compensates for the second ionisation enthalpy of Cu.

The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides (Table 8.6) coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond Group 7, no higher oxides of Fe above Fe_2O_3, are known, although ferrates (VI)$(FeO_4)^{2-}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2. Besides the oxides, oxocations stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}. The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7. The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The tetrahedral $[MO_4]^{n-}$ ions are known for V^V, Cr^{VI}, Mn^V, Mn^{VI} and Mn^{VII}.

Table 8.6: Oxides of 3d Metals

Oxidation Number	Groups 3	4	5	6	7	8	9	10	11	12
+ 7					Mn_2O_7					
+ 6				CrO_3						
+ 5			V_2O_5							
+ 4		TiO_2	V_2O_4	CrO_2	MnO_2					
+ 3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					Mn_3O_4*	Fe_3O_4*	Co_3O_4*			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1									Cu_2O	

* *mixed oxides*

Example 8.5

How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?

Solution

This is due to the increasing stability of the lower species to which they are reduced.

Intext Question

8.5 How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements?

8.3.8 Chemical Reactivity and $E^{\ominus}$ Values

Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by simple acids.

The metals of the first series with the exception of copper are relatively more reactive and are oxidised by 1M H^+, though the actual rate at which these metals react with oxidising agents like hydrogen ion (H^+) is sometimes slow. For example, titanium and vanadium, in practice, are passive to dilute non oxidising acids at room temperature. The $E^{\ominus}$ values for M^{2+}/M (Table 8.2) indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative $E^{\ominus}$ values is related to the increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the $E^{\ominus}$ values for Mn, Ni and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled *d* subshell (d^5) in Mn^{2+} and completely filled *d* subshell (d^{10}) in zinc are related to their E° values; for nickel, E° value is related to the highest negative enthalpy of hydration.

An examination of the $E^{\ominus}$ values for the redox couple M^{3+}/M^{2+} (Table 8.2) shows that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solutions. The ions Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.,

$$2\ Cr^{2+}(aq) + 2\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + H_2(g)$$

Example 8.6 For the first row transition metals the E° values are:

E°	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	−1.18	− 0.91	−1.18	− 0.44	− 0.28	− 0.25	+0.34

Explain the irregularity in the above values.

Solution The $E^{\ominus}$ (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

Example 8.7 Why is the $E^{\ominus}$ value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}? Explain.

Solution Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Intext Questions

8.6 Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

8.7 Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why ?

8.3.9 Magnetic Properties

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism* and *paramagnetism* (Unit 1). Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are

attracted very strongly are said to be *ferromagnetic*. In fact, ferromagnetism is an extreme form of paramagnetism. Many of the transition metal ions are paramagnetic.

Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

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

where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM). A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion. The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some ions of the first row transition elements are given in Table 8.7. The experimental data are mainly for hydrated ions in solution or in the solid state.

Table 8.7: Calculated and Observed Magnetic Moments (BM)

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

Example 8.8

Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Solution

With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment, μ is

$$\mu = \sqrt{5(5+2)} = 5.92\,\text{BM}$$

Intext Question

8.8 Calculate the 'spin only' magnetic moment of $M^{2+}_{(aq)}$ ion (Z = 27).

8.3.10 Formation of Coloured Ions

When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed (Unit 9). This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colours of the ions observed are listed in Table 8.8. A few coloured solutions of *d*–block elements are illustrated in Fig. 8.5.

Fig. 8.5: *Colours of some of the first row transition metal ions in aqueous solutions. From left to right:* V^{4+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} *and* Cu^{2+} .

Table 8.8: Colours of Some of the First Row (aquated) Transition Metal Ions

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6 3d^7$	$Co^{3+} Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

8.3.11 Formation of Complex Compounds

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is

dealt with in detail in Unit 9). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

8.3.12 Catalytic Properties

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2SO_4^{2-}$$

8.3.13 Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as *interstitial* compounds. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

8.3.14 Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

Example 8.9 What is meant by 'disproportionation' of an oxidation state? Give an example.

Solution When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.

$$3\ Mn^{VI}O_4^{\ 2-} + 4\ H^+ \rightarrow 2\ Mn^{VII}O^-_4 + Mn^{IV}O_2 + 2H_2O$$

Intext Question

8.9 Explain why Cu^+ ion is not stable in aqueous solutions?

8.4 Some Important Compounds of Transition Elements

8.4.1 Oxides and Oxoanions of Metals

These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Besides the oxides, the oxocations stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant.

Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives $VO_4^{\ 3-}$ as well as VO_2^+ salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Similarly, V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_4^+ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Potassium dichromate $K_2Cr_2O_7$

Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.\ 2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2\ CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + H_2O$$

Chromate ion

Dichromate ion

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.

Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O\ (E^{\ominus} = 1.33V)$$

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$$6\ I^- \rightarrow 3I_2 + 6\ e^-; \qquad 3\ Sn^{2+} \rightarrow 3Sn^{4+} + 6\ e^-$$

$$3\ H_2S \rightarrow 6H^+ + 3S + 6e^-; \qquad 6\ Fe^{2+} \rightarrow 6Fe^{3+} + 6\ e^-$$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

Potassium permanganate $KMnO_4$

Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (Vl).

$$MnO_2 \xrightarrow{\text{Fused with KOH, oxidised with air or } KNO_3} \underset{\text{manganate ion}}{MnO_4^{2-}}\ ;$$

$$\underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow{\text{Electrolytic oxidation in alkaline solution}} \underset{\text{permanganate ion}}{MnO_4^-}$$

In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

It has two physical properties of considerable interest: its intense colour and its weak temperature dependent paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.

The manganate and permanganate ions are tetrahedral; the green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

The π-bonding takes place by overlap of *p* orbitals of oxygen with *d* orbitals of manganese.

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:

$$5 \begin{vmatrix} COO^- \\ \\ COO^- \end{vmatrix} \longrightarrow 10CO_2 + 10e^-$$

$$5\ Fe^{2+} \rightarrow 5\ Fe^{3+} + 5e^-$$

$$5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + 10e^-$$

$$10I^- \rightarrow 5I_2 + 10e^-$$

The full reaction can be written by adding the half-reaction for $KMnO_4$ to the half-reaction of the reducing agent, balancing wherever necessary.

If we represent the reduction of permanganate to manganate, manganese dioxide and manganese(II) salt by half-reactions,

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \qquad (E^\ominus = +\ 0.56\ V)$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \qquad (E^\ominus = +\ 1.69\ V)$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad (E^\ominus = +\ 1.52\ V)$$

We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at $[H^+] = 1$ should oxidise water but in practice the reaction is extremely slow unless either manganese(ll) ions are present or the temperature is raised.

A few important oxidising reactions of $KMnO_4$ are given below:

1. In acid solutions:

(a) Iodine is liberated from potassium iodide :

$$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

(b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

(c) Oxalate ion or oxalic acid is oxidised at 333 K:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(d) Hydrogen sulphide is oxidised, sulphur being precipitated:

$$H_2S \longrightarrow 2H^+ + S^{2-}$$

$$5S^{2-} + 2MnO^-_4 + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

(f) Nitrite is oxidised to nitrate:

$$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

2. In neutral or faintly alkaline solutions:

(a) A notable reaction is the oxidation of iodide to iodate:

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(c) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses: Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

THE INNER TRANSITION ELEMENTS (*f*-BLOCK)

The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study; the two series will be considered separately here.

8.5 The Lanthanoids

The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the general symbol Ln is used) are given in Table 8.9.

8.5.1 Electronic Configurations

It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of $4f$ level (Table 8.9). However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

8.5.2 Atomic and Ionic Sizes

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the **lanthanoid contraction**) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M^{3+} ions (Fig. 8.6). This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one $4f$ electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.

Fig. 8.6: Trends in ionic radii of lanthanoids

The cumulative effect of the contraction of the lanthanoid series, known as *lanthanoid contraction*, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

8.5.3 Oxidation States

In the lanthanoids, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^{\ominus}$ value for Ce^{4+}/Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f^{14} configuration is a reductant. Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

Table 8.9: Electronic Configurations and Radii of Lanthanum and Lanthanoids

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm		
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	–	–	–

* *Only electrons outside [Xe] core are indicated*

8.5.4 General Characteristics

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *f* electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within *f* level. The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3*d* orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals *f* level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium. Values for $E^{\ominus}$ for the half-reaction:

$$Ln^{3+}(aq) + 3e^- \rightarrow Ln(s)$$

Fig 8.7: *Chemical reactions of the lanthanoids.*

are in the range of –2.2 to –2.4 V except for Eu for which the value is –2.0 V. This is, of course, a small variation. The metals combine with hydrogen when gently heated in the gas. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. Their general reactions are depicted in Fig. 8.7.

The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

8.6 The Actinoids

The actinoids include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table 8.10.

Table 8.10: Some Properties of Actinium and Actinoids

Atomic Number	Name	Symbol	Electronic conifigurations*		Radii/pm		
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^17s^2$	$5f^0$		111	
90	Thorium	Th	$6d^27s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^26d^17s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^67s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^77s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^76d^17s^2$	$5f^7$	$5f^7$	99	88
97	Berkelium	Bk	$5f^97s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10}7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11}7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12}7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13}7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14}7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14}6d^17s^2$	$5f^{14}$	$5f^{13}$	–	–

The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

8.6.1 Electronic Configurations

All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5*f*, though not in thorium (Z = 90) but from Pa onwards the 5*f* orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^7 7s^2$ and [Rn] $5f^7 6d^1 7s^2$. Although the 5*f* orbitals resemble the 4*f* orbitals in their angular part of the wave-function, they are not as buried as 4*f* orbitals and hence 5*f* electrons can participate in bonding to a far greater extent.

8.6.2 Ionic Sizes

The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the *actinoid contraction* (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5*f* electrons.

8.6.3 Oxidation States

There is a greater range of oxidation states, which is in part attributed to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies. The known oxidation states of actinoids are listed in Table 8.11.

The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 8.11). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the earlier and latter elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

Table 8.11: Oxidation States of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

8.6.4 General Characteristics and Comparison with Lanthanoids

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 *f* electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5*f* orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons, will therefore, be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

Example 8.10 Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Solution Cerium (Z = 58)

Intext Question

8.10 Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

8.7 Some Applications of d- and f-Block Elements

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au

are restricted to collection items and the contemporary UK 'copper' coins are copper-coated steel. The 'silver' UK coins are a Cu/Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid. $TiCl_4$ with $Al(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from N_2/H_2 mixtures. Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.

Summary

The ***d*-block** consisting of **Groups 3-12** occupies the large middle section of the **periodic table**. In these elements the inner *d* orbitals are progressively filled. The ***f*-block** is placed **outside** at the **bottom** of the **periodic table** and in the elements of this block, 4*f* and 5*f* orbitals are progressively filled.

Corresponding to the filling of 3*d*, 4*d* and 5*d* orbitals, three series of transition elements are well recognised. All the transition elements exhibit typical metallic properties such as –high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character. Their melting and boiling points are high which are attributed to the involvement of $(n-1)\,d$ electrons resulting into **strong interatomic bonding**. In many of these properties, the maxima occur at about the middle of each series which indicates that one unpaired electron per *d* orbital is particularly a favourable configuration for strong interatomic interaction.

Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n-1)\,d$ orbitals is not energetically unfavourable. The involvement of **$(n-1)\,d$ electrons** in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.

The **transition elements** vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'. Of the first series, with the exception of copper, all the metals are relatively reactive.

The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxometallic salts. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore (MnO_2) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate ions are strong oxidising agents.

The two series of **inner transition elements**, **lanthanoids** and **actinoids** constitute the ***f*-block** of the periodic table. With the successive filling of the inner orbitals, 4*f*, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (**lanthanoid contraction**). This has far reacting consequences in the chemistry of the elements succeeding them. Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some

occasionally. The chemistry of the **actinoids** is more complex in view of their ability to exist in different oxidation states. Furthermore, many of the actinoid elements are radioactive which make the study of these elements rather difficult.

There are many useful applications of the *d*- and *f*-block elements and their compounds, notable among them being in varieties of steels, catalysts, complexes, organic syntheses, etc.

Exercises

8.1 Write down the electronic configuration of:

(i) Cr^{3+} (iii) Cu^{+} (v) $Co^{2}+$ (vii) Mn^{2+}

(ii) Pm^{3+} (iv) Ce^{4+} (vi) Lu^{2+} (viii) Th^{4+}

8.2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

8.3 Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

8.4 To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

8.5 What may be the stable oxidation state of the transition element with the following *d* electron configurations in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

8.6 Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

8.7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

8.8 What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

8.9 In what way is the electronic configuration of the transition elements different from that of the non transition elements?

8.10 What are the different oxidation states exhibited by the lanthanoids?

8.11 Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The enthalpies of atomisation of the transition metals are high.

(iii) The transition metals generally form coloured compounds.

(iv) Transition metals and their many compounds act as good catalyst.

8.12 What are interstitial compounds? Why are such compounds well known for transition metals?

8.13 How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

8.14 Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

8.15 Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide (ii) iron(II) solution and (iii) H_2S

8.16 Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic equations for the reactions.

8.17 For M^{2+}/M and M^{3+}/M^{2+} systems the $E^{\ominus}$ values for some metals are as follows:

Cr^{2+}/Cr	-0.9V	Cr^{3}/Cr^{2+}	-0.4 V
Mn^{2+}/Mn	-1.2V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	-0.4V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon:

(i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

8.18 Predict which of the following will be coloured in aqueous solution? Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

8.19 Compare the stability of +2 oxidation state for the elements of the first transition series.

8.20 Compare the chemistry of actinoids with that of the lanthanoids with special reference to:

(i) electronic configuration (iii) oxidation state

(ii) atomic and ionic sizes and (iv) chemical reactivity.

8.21 How would you account for the following:

(i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.

(ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(iii) The d^1 configuration is very unstable in ions.

8.22 What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

8.23 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

8.24 Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution?

8.25 Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

8.26 Indicate the steps in the preparation of:

(i) $K_2Cr_2O_7$ from chromite ore. (ii) $KMnO_4$ from pyrolusite ore.

8.27 What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

8.28 What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.

8.29 The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

8.30 Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

8.31 Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

8.32 Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.

8.33 Compare the chemistry of the actinoids with that of lanthanoids with reference to:

(i) electronic configuration (ii) oxidation states and (iii) chemical reactivity.

8.34 Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

8.35 Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

(i) electronic configurations (ii) oxidation states (iii) ionisation enthalpies and (iv) atomic sizes.

8.36 Write down the number of 3d electrons in each of the following ions: Ti^{2+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}. Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).

8.37 Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

8.38 What can be inferred from the magnetic moment values of the following complex species ?

Example	Magnetic Moment (BM)
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3
$K_2[MnCl_4]$	5.9

Answers to Some Intext Questions

8.1 Silver (Z = 47) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.

8.2 In the formation of metallic bonds, no eletrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds.

8.3 Manganese (Z = 25), as its atom has the maximum number of unpaired electrons.

8.5 Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (e.g., d^0, d^5, d^{10} are exceptionally stable).

8.6 Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.

8.7 Cr^{2+} is stronger reducing agent than Fe^{2+}

Reason: $d^4 \rightarrow d^3$ occurs in case of Cr^{2+} to Cr^{3+}

But $d^6 \rightarrow d^5$ occurs in case of Fe^{2+} to Fe^{3+}

In a medium (like water) d^3 is more stable as compared to d^5 *(see CFSE)*

8.9 Cu^+ in aqueous solution underoes disproportionation, i.e.,

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

The E^0 value for this is favourable.

8.10 The 5*f* electrons are more effectively shielded from nuclear charge. In other words the 5*f* electrons themselves provide poor shielding from element to element in the series.

Unit 9

Coordination Compounds

Coordination Compounds are the backbone of modern inorganic and bio–inorganic chemistry and chemical industry.

Objectives

After studying this Unit, you will be able to

- appreciate the postulates of Werner's theory of coordination compounds;
- know the meaning of the terms: coordination entity, central atom/ion, ligand, coordination number, coordination sphere, coordination polyhedron, oxidation number, homoleptic and heteroleptic;
- learn the rules of nomenclature of coordination compounds;
- write the formulas and names of mononuclear coordination compounds;
- define different types of isomerism in coordination compounds;
- understand the nature of bonding in coordination compounds in terms of the Valence Bond and Crystal Field theories;
- learn the stability of coordination compounds;
- appreciate the importance and applications of coordination compounds in our day to day life.

In the previous Unit we learnt that the transition metals form a large number of **complex compounds** in which the metal atoms are bound to a number of anions or neutral molecules. In modern terminology such compounds are called **coordination compounds**. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of vital components of biological systems. Chlorophyll, haemoglobin and vitamin B_{12} are coordination compounds of magnesium, iron and cobalt respectively. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

9.1 Werner's Theory of Coordination Compounds

Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques. Werner proposed the concept of a **primary valence** and a **secondary valence** for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol	$CoCl_3.6NH_3$ (Yellow)	gave	3 mol AgCl
1 mol	$CoCl_3.5NH_3$ (Purple)	gave	2 mol AgCl
1 mol	$CoCl_3.4NH_3$ (Green)	gave	1 mol AgCl
1 mol	$CoCl_3.4NH_3$ (Violet)	gave	1 mol AgCl

These observations, together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown in Table 9.1, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions. Werner proposed the term **secondary valence** for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Table 9.1: Formulation of Cobalt(III) Chloride-Ammonia Complexes

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co(NH_3)_6]^{3+}3Cl^-$	1:3 electrolyte
Purple	$[CoCl(NH_3)_5]^{2+}2Cl^-$	1:2 electrolyte
Green	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte
Violet	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte

Note that the last two compounds in Table 9.1 have identical empirical formula, $CoCl_3.4NH_3$, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination *polyhedra*. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.

He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^+$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

On the basis of the following observations made with aqueous solutions, assign secondary valences to metals in the following compounds: *Example 9.1*

Formula	Moles of AgCl precipitated per mole of the compounds with excess $AgNO_3$
(i) $PdCl_2.4NH_3$	2
(ii) $NiCl_2.6H_2O$	2
(iii) $PtCl_4.2HCl$	0
(iv) $CoCl_3.4NH_3$	1
(v) $PtCl_2.2NH_3$	0

Solution

(i) Secondary 4 (ii) Secondary 6
(iii) Secondary 6 (iv) Secondary 6 (v) Secondary 4

Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4Fe(CN)_6$, do not dissociate into Fe^{2+} and CN^- ions.

(1866-1919)

Werner was born on December 12, 1866, in Mülhouse, a small community in the French province of Alsace. His study of chemistry began in Karlsruhe (Germany) and continued in Zurich (Switzerland), where in his doctoral thesis in 1890, he explained the difference in properties of certain nitrogen containing organic substances on the basis of isomerism. He extended vant Hoff's theory of tetrahedral carbon atom and modified it for nitrogen. Werner showed optical and electrical differences between complex compounds based on physical measurements. In fact, Werner was the first to discover optical activity in certain coordination compounds.

He, at the age of 29 years became a full professor at Technische Hochschule in Zurich in 1895. Alfred Werner was a chemist and educationist. His accomplishments included the development of the theory of coordination compounds. This theory, in which Werner proposed revolutionary ideas about how atoms and molecules are linked together, was formulated in a span of only three years, from 1890 to 1893. The remainder of his career was spent gathering the experimental support required to validate his new ideas. Werner became the first Swiss chemist to win the Nobel Prize in 1913 for his work on the linkage of atoms and the coordination theory.

9.2 Definitions of Some Important Terms Pertaining to Coordination Compounds

(a) Coordination entity

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.

(b) Central atom/ion

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms/ions are also referred to as **Lewis acids**.

(c) Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins.

When a ligand is bound to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be **unidentate.**

When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate** ligand. The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands (for reasons see Section 9.8). Ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

nitrito-N

nitrito-O

M ← SCN
thiocyanato

M ← NCS
isothiocyanato

(d) Coordination number

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.

It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

(e) Coordination sphere

The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the **coordination sphere**. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+.

(f) Coordination polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar. Fig. 9.1 shows the shapes of different coordination polyhedra.

Fig. 9.1: *Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.*

(g) Oxidation number of central atom

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

(h) Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one kind of donor groups, *e.g.*, $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

9.3 Nomenclature of Coordination Compounds

Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

9.3.1 Formulas of Mononuclear Coordination Entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Note: The 2004 IUPAC draft recommends that ligands will be sorted alphabetically, irrespective of charge.

9.3.2 Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. These are placed within enclosing marks ( ).

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichlorobis(triphenylphosphine)nickel(II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $\left[Co(SCN)_4\right]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, *e.g.*, ferrate for Fe.

Note: *The 2004 IUPAC draft recommends that anionic ligands will end with–ido so that chloro would become chlorido, etc.*

(vii) The neutral complex molecule is named similar to that of the complex cation.

The following examples illustrate the nomenclature for coordination compounds.

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as:
   triamminetriaquachromium(III) chloride

   Explanation: The complex ion is inside the square bracket, which is a cation. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as:
   tris(ethane-1,2–diammine)cobalt(III) sulphate

   Explanation: The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2–diamine is a neutral molecule, so the oxidation number of cobalt in the complex ion must be +3. *Remember that you never have to indicate the number of cations and anions in the name of an ionic compound.*

Notice how the name of the metal differs in cation and anion even though they contain the same metal ions.

3. $[Ag(NH_3)_2][Ag(CN)_2]$ is named as:
   diamminesilver(I) dicyanoargentate(I)

Example 9.2 Write the formulas for the following coordination compounds:

(i) Tetraamineaquachloridocobalt(III) chloride
(ii) Potassium tetrahydroxozincate(II)
(iii) Potassium trioxalatoaluminate(III)
(iv) Dichloridobis(ethane-1,2-diamine)cobalt(III)
(v) Tetracarbonylnickel(0)

Solution (i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (ii) $K_2[Zn(OH)_4]$ (iii) $K_3[Al(C_2O_4)_3]$
(iv) $[CoCl_2(en)_2]^+$ (v) $[Ni(CO)_4]$

Example 9.3 Write the IUPAC names of the following coordination compounds:

(i) $[Pt(NH_3)_2Cl(NO_2)]$ (ii) $K_3[Cr(C_2O_4)_3]$ (iii) $[CoCl_2(en)_2]Cl$
(iv) $[Co(NH_3)_5(CO_3)]Cl$ (v) $Hg[Co(SCN)_4]$

Solution (i) Diamminechloridonitrito-N-platinum(II)
(ii) Potassium trioxalatochromate(III)
(iii) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
(iv) Pentaamminecarbonatocobalt(III) chloride
(v) Mercury tetrathiocyanatocobaltate(III)

Intext Questions

9.1 Write the formulas for the following coordination compounds:

(i) Tetraamminediaquacobalt(III) chloride
(ii) Potassium tetracyanonickelate(II)
(iii) Tris(ethane–1,2–diamine) chromium(III) chloride
(iv) Amminebromidochloridonitrito-N-platinate(II)
(v) Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate
(vi) Iron(III) hexacyanoferrate(II)

9.2 Write the IUPAC names of the following coordination compounds:

(i) $[Co(NH_3)_6]Cl_3$ (ii) $[Co(NH_3)_5Cl]Cl_2$ (iii) $K_3[Fe(CN)_6]$
(iv) $K_3[Fe(C_2O_4)_3]$ (v) $K_2[PdCl_4]$ (vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

9.4 Isomerism in Coordination Compounds

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

(a) Stereoisomerism

(i) Geometrical isomerism (ii) Optical isomerism

(b) Structural isomerism

(i) Linkage isomerism (ii) Coordination isomerism
(iii) Ionisation isomerism (iv) Solvate isomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below.

9.4.1 Geometric Isomerism

Fig. 9.2: *Geometrical isomers (cis and trans) of $Pt(NH_3)_2Cl_2$)*

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a ***cis*** isomer, or opposite to each other in a ***trans*** isomer as depicted in Fig. 9.2.

Fig. 9.3: *Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$*

Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers-two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented ***cis*** or ***trans*** to each other (Fig. 9.3).

Fig. 9.4: *Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$*

This type of isomerism also arises when didentate ligands L–L [*e.g.*, $NH_2\ CH_2\ CH_2\ NH_2$ (en)] are present in complexes of formula $[MX_2(L–L)_2]$ (Fig. 9.4).

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer** (Fig. 9.5).

Fig. 9.5 *The facial (fac) and meridional (mer) isomers of $[Co(NH_3)_3(NO_2)_3]$*

Example 9.4

Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Solution

Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

9.4.2 Optical Isomerism

Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro (d)* and *laevo (l)* depending upon the direction they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands (Fig. 9.6).

Fig.9.6: Optical isomers (d and l) of $[Co(en)_3]^{3+}$

In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the *cis*-isomer shows optical activity (Fig. 9.7).

Fig.9.7 *Optical isomers (d and l) of cis-$[PtCl_2(en)_2]^{2+}$*

Example 9.5 Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Solution

cis *trans*

Example 9.6 Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

Solution The two entities are represented as

(a) *cis* – $[CrCl_2(ox)_2]^{3-}$ (b) *trans* – $[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) *cis* - $[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

9.4.3 Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-NO_2$).

9.4.4 Coordination Isomerism

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

9.4.5 Ionisation Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

9.4.6 Solvate Isomerism

This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

Intext Questions

9.3 Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(i) $K[Cr(H_2O)_2(C_2O_4)_2]$ (ii) $[Co(en)_3]Cl_3$

(iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$ (iv) $[Pt(NH_3)(H_2O)Cl_2]$

9.4 Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

9.5 Bonding in Coordination Compounds

Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

(i) Why only certain elements possess the remarkable property of forming coordination compounds?

(ii) Why the bonds in coordination compounds have directional properties?

(iii) Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been put forth to explain the nature of bonding in coordination compounds *viz.* Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT). We shall focus our attention on elementary treatment of the application of VBT and CFT to coordination compounds.

9.5.1 Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)*d*, n*s*, n*p* or n*s*, n*p*, n*d* orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 9.2). These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. This is illustrated by the following examples.

Table 9.2: Number of Orbitals and Types of Hybridisations

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.

Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner *d* orbital (3*d*) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an **inner orbital** or **low spin** or **spin paired complex**. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4*d*) in hybridisation (sp^3d^2). It is thus called **outer orbital** or **high spin** or **spin free complex**. Thus:

In tetrahedral complexes one *s* and three *p* orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$. Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram.

Each Cl^- ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.

In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram:

Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

9.5.2 Magnetic Properties of Coordination Compounds

The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the structures adopted by metal complexes.

A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the *d* orbitals, like Ti^{3+} (d^1); V^{3+} (d^2); Cr^{3+} (d^3); two vacant *d* orbitals are available for octahedral hybridisation with 4*s* and 4*p* orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3*d* electrons are present, the required pair of 3*d* orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) cases, a vacant pair of *d* orbitals results only by pairing of 3*d* electrons which leaves two, one and zero unpaired electrons, respectively.

The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions. However, with species containing d^4 and d^5 ions there are complications. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_{6-}]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Example 9.7 The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion ?

Solution Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbitals.

9.5.3 Limitations of Valence Bond Theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

(i) It involves a number of assumptions.
(ii) It does not give quantitative interpretation of magnetic data.
(iii) It does not explain the colour exhibited by coordination compounds.
(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
(vi) It does not distinguish between weak and strong ligands.

9.5.4 Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.*, they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted. It results in splitting of the *d* orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

(a) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal *d* orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal *d* orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the *d* orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the

Fig.9.8: *d orbital splitting in an octahedral crystal field*

degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by Δ_o (the subscript o is for octahedral) (Fig.9.8). Thus, the energy of the two e_g orbitals will increase by (3/5) Δ_o and that of the three t_{2g} will decrease by (2/5)Δ_o.

The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d* orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

Such a series is termed as **spectrochemical series**. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the *d* orbitals of metal ion in octahedral coordination entities. Obviously, the single *d* electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the *d* electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

(i) If Δ_o < P, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which Δ_o < P are known as *weak field ligands* and form high spin complexes.

(ii) If Δ_o > P, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

(b) Crystal field splitting in tetrahedral coordination entities

Fig.9.9: *d orbital splitting in a tetrahedral crystal field.*

In tetrahedral coordination entity formation, the *d* orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\ \Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

9.5.5 Colour in Coordination Compounds

In the previous Unit, we learnt that one of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red. Table 9.3 gives the relationship of the different wavelength absorbed and the colour observed.

Table 9.3: Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

Coordinaton entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Purple

The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal *d* orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the empty e_g level. If light corresponding to the energy of yellow-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Consequently, the complex appears violet in colour (Fig. 9.10). The crystal field theory attributes the colour of the coordination compounds to *d-d* transition of the electron.

Fig.9.10: *Transition of an electron in $[Ti(H_2O)_6]^{3+}$*

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour. The influence of the ligand on the colour of a complex may be illustrated by considering the $[Ni(H_2O)_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water. If the didentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur:

$$[Ni(H_2O)_6]^{2+}(aq) + en(aq) = [Ni(H_2O)_4(en)]^{2+}(aq) + 2H_2O$$
green — pale blue

$$[Ni(H_2O)_4(en)]^{2+}(aq) + en(aq) = [Ni(H_2O)_2(en)_2]^{2+}(aq) + 2H_2O$$
blue/purple

$$[Ni(H_2O)_2(en)_2]^{2+}(aq) + en(aq) = [Ni(en)_3]^{2+}(aq) + 2H_2O$$
violet

This sequence is shown in Fig. 9.11.

Fig.9.11
Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands.

Colour of Some Gem Stones

The colours produced by electronic transitions within the *d* orbitals of a transition metal ion occur frequently in everyday life. Ruby [Fig.9.12(a)] is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}. We may view these chromium(III) species as octahedral chromium(III) complexes incorporated into the alumina lattice; *d–d* transitions at these centres give rise to the colour.

In emerald [Fig.9.12(b)], Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

(a) (b)

Fig.9.12: *(a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.*

9.5.6 Limitations of Crystal Field Theory

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study.

Intext Questions

9.5 Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

9.6 $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

9.7 $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

9.8 Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

9.9 Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

9.10 The hexaquo manganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

9.6 Bonding in Metal Carbonyls

The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonalbipyramidal while hexacarbonyl chromium(0) is octahedral.

Decacarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn – Mn bond. Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups (Fig.9.13).

Fig. 9.13 *Structures of some representative homoleptic metal carbonyls.*

Fig. 9.14: *Example of synergic bonding interactions in a carbonyl complex.*

The metal-carbon bond in metal carbonyls possess both *s* and *p* character. The M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fig.9.14).

9.7 Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightleftarrows ML_4$$

then the larger the stability constant, the higher the proportion of ML_4 that exists in solution. Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

$$M + L \quad ML \qquad K_1 = [ML]/[M][L]$$
$$ML + L \rightleftarrows ML_2 \qquad K_2 = [ML_2]/[ML][L]$$
$$ML_2 + L \rightleftarrows ML_3 \qquad K_3 = [ML_3]/[ML_2][L]$$
$$ML_3 + L \rightleftarrows ML_4 \qquad K_4 = [ML_4]/[ML_3][L]$$

where K_1, K_2, etc., are referred to as **stepwise stability constants.** Alternatively, we can write the **overall stability constant** thus:

$$M + 4L \quad ML_4 \qquad \beta_4 = [ML_4]/[M][L]^4$$

The stepwise and overall stability constant are therefore related as follows:

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally,

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots K_n$$

If we take as an example, the steps involved in the formation of the cuprammonium ion, we have the following:

$Cu^{2+} + NH_3 \quad Cu(NH_3)^{2+} \qquad K_1 = [Cu(NH_3)^{2+}]/[Cu^{2+}][NH_3]$

$Cu(NH_3)^{2+} + NH_3 \rightleftarrows Cu(NH_3)_2^{2+} \quad K_2 = [Cu(NH_3)_2^{2+}]/[Cu(NH_3)^{2+}][NH_3]$ etc.

where K_1, K_2 are the stepwise stability constants and overall stability constant.

Also $\beta_4 = [Cu(NH_3)_4^{2+}]/[Cu^{2+}][NH_3)^4$

The addition of the four amine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

$\log K_1 = 4.0$, $\log K_2 = 3.2$, $\log K_3 = 2.7$, $\log K_4 = 2.0$ or $\log \beta_4 = 11.9$

The **instability constant or the dissociation constant** of coordination compounds is defined as the reciprocal of the formation constant.

Intext Question

9.11 Calculate the overall complex dissociation equilibrium constant for the $Cu(NH_3)_4^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

9.8 Importance and Applications of Coordination Compounds

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc (Unit 6).
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*–platin and related compounds.

Summary

The **chemistry of coordination compounds** is an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in **chemical industry** and vital insights into the functioning of critical components of **biological systems**.

The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by **A. Werner**. His theory postulated the use of two types of **linkages** (**primary** and **secondary**) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number of coordination entities.

The Valence Bond Theory (VBT) explains with reasonable success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds.

The Crystal Field Theory (CFT) to coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of *d* orbital energies of the central metal atom/ion. The splitting of the *d* orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability

parameters. However, the assumption that ligands consititute point charges creates many theoretical difficulties.

The metal–carbon bond in **metal carbonyls** possesses both σ and π character. The ligand to metal is σ bond and metal to ligand is π bond. This unique synergic bonding provides stability to metal carbonyls.

The stability of coordination compounds is measured in terms of **stepwise stability (or formation) constant (K) or overall stability constant** (β). The stabilisation of coordination compound due to chelation is called the **chelate effect**. The stability of coordination compounds is related to Gibbs energy, enthalpy and entropy terms.

Coordination compounds are of great importance. These compounds provide critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in **metallurgical processes**, **analytical and medicinal chemistry**.

Exercises

9.1 Explain the bonding in coordination compounds in terms of Werner's postulates.

9.2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

9.3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

9.4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

9.5 Specify the oxidation numbers of the metals in the following coordination entities:

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$ (ii) $[CoBr_2(en)_2]^+$ (iii) $[PtCl_4]^{2-}$ (iv) $K_3[Fe(CN)_6]$ (v) $[Cr(NH_3)_3Cl_3]$

9.6 Using IUPAC norms write the formulas for the following:

(i) Tetrahydroxozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate
(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III)

9.7 Using IUPAC norms write the systematic names of the following:

(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
(iii) $[Ti(H_2O)_6]^{3+}$
(iv) $[Co(NH_3)_4Cl(NO_2)]Cl$
(v) $[Mn(H_2O)_6]^{2+}$
(vi) $[NiCl_4]^{2-}$
(vii) $[Ni(NH_3)_6]Cl_2$
(viii) $[Co(en)_3]^{3+}$
(ix) $[Ni(CO)_4]$

9.8 List various types of isomerism possible for coordination compounds, giving an example of each.

9.9 How many geometrical isomers are possible in the following coordination entities?

(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$

9.10 Draw the structures of optical isomers of:

(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$ (iii) $[Cr(NH_3)_2Cl_2(en)]^+$

9.11 Draw all the isomers (geometrical and optical) of:
(i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^+$

9.12 Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

9.13 Aqueous copper sulphate solution (blue in colour) gives:
(i) a green precipitate with aqueous potassium fluoride and
(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

9.14 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

9.15 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

9.16 Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.

9.17 What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

9.18 What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of *d* orbitals in a coordination entity?

9.19 $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

9.20 A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

9.21 $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

9.22 Discuss the nature of bonding in metal carbonyls.

9.23 Give the oxidation state, *d* orbital occupation and coordination number of the central metal ion in the following complexes:
(i) $K_3[Co(C_2O_4)_3]$ (iii) $(NH_4)_2[CoF_4]$
(ii) cis-$[Cr(en)_2Cl_2]Cl$ (iv) $[Mn(H_2O)_6]SO_4$

9.24 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:
(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (iii) $CrCl_3(py)_3$ (v) $K_4[Mn(CN)_6]$
(ii) $[Co(NH_3)_5Cl]Cl_2$ (iv) $Cs[FeCl_4]$

9.25 What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

9.26 What is meant by the *chelate effect*? Give an example.

9.27 Discuss briefly giving an example in each case the role of coordination compounds in:
(i) biological systems (iii) analytical chemistry
(ii) medicinal chemistry and (iv) extraction/metallurgy of metals.

9.28 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?
(i) 6 (ii) 4 (iii) 3 (iv) 2

9.29 Amongst the following ions which one has the highest magnetic moment value?
(i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Zn(H_2O)_6]^{2+}$

9.30 The oxidation number of cobalt in $K[Co(CO)_4]$ is
(i) +1 (ii) +3 (iii) –1 (iv) –3

9.31 Amongst the following, the most stable complex is

(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$ (iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$

9.32 What will be the correct order for the wavelengths of absorption in the visible region for the following:

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

Answers to Some Intext Questions

9.1 (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$
(ii) $K_2[Ni(CN)_4]$
(iii) $[Cr(en)_3]Cl_3$
(iv) $[Pt(NH_3)BrCl(NO_2)]^-$
(v) $[PtCl_2(en)_2](NO_3)_2$
(vi) $Fe_4[Fe(CN)_6]_3$

9.2 (i) Hexaamminecobalt(III) chloride
(ii) Pentaamminechloridocobalt(III) chloride
(iii) Potassium hexacyanoferrate(III)
(iv) Potassium trioxalatoferrate(III)
(v) Potassium tetrachloridopalladate(II)
(vi) Diamminechlorido(methylamine)platinum(II) chloride

9.3 (i) Both geometrical (*cis*-, *trans*-) and optical isomers for *cis* can exist.
(ii) Two optical isomers can exist.
(iii) There are 10 possible isomers. (Hint: There are geometrical, ionisation and linkage isomers possible).
(iv) Geometrical (*cis*-, *trans*-) isomers can exist.

9.4 The ionisation isomers dissolve in water to yield different ions and thus react differently to various reagents:

$[Co(NH_3)_5Br]SO_4 + Ba^{2+} \rightarrow BaSO_4$ (s)
$[Co(NH_3)_5SO_4]Br + Ba^{2+} \rightarrow$ No reaction
$[Co(NH_3)_5Br]SO_4 + Ag^+ \rightarrow$ No reaction
$[Co(NH_3)_5SO_4]Br + Ag^+ \rightarrow AgBr$ (s)

9.6 In $Ni(CO)_4$, Ni is in zero oxidation state whereas in $NiCl_4^{2-}$, it is in +2 oxidation state. In the presence of CO ligand, the unpaired *d* electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

9.7 In presence of CN^-, (a strong ligand) the 3*d* electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming inner orbital complex. In the presence of H_2O, (a weak ligand), 3*d* electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex containing five unpaired electrons, it is strongly paramagnetic.

9.8 In the presence of NH_3, the 3*d* electrons pair up leaving two *d* orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex in case of $[Co(NH_3)_6]^{3+}$.

In $Ni(NH_3)_6^{2+}$, Ni is in +2 oxidation state and has d^8 configuration, the hybridisation involved is sp^3d^2 forming outer orbital complex.

9.9 For square planar shape, the hybridisation is dsp^2. Hence the unpaired electrons in 5*d* orbital pair up to make one *d* orbital empty for dsp^2 hybridisation. Thus there is no unpaired electron.

9.11 The overall dissociation constant is the reciprocal of overall stability constant i.e. $1/\beta_4 = 4.7 \times 10^{-14}$

Answers to Some Questions in Exercises

UNIT 1

1.11 107.8 u

1.13 14.29 nm

1.15 8.97 g cm^{-3}

1.16 Ni^{2+} = 96% and Ni^{3+} = 4%

1.24 (i) 354 pm (ii) 2.26×10^{22} unit cells

1.25 6.02×10^{18} cation vacancies mol^{-1}

UNIT 2

2.4 16.23 M

2.5 0.617 m, 0.01 and 0.99, 0.67

2.6 157.8 mL

2.7 32% and 68%

2.8 17.95 m and 8.70 M

2.9 ~15×10^{-4} g, 1.25×10^{-4} m

2.15 41.35 g mol^{-1}

2.16 73.08 *k*Pa

2.17 12.08 *k*Pa

2.18 8 g

2.19 34 g mol^{-1}, 3.4 kPa

2.20 269.07 *K*

2.21 A = 25.58 u and B = 42.64 u

2.22 0.061 M

2.24 KCl, CH_3OH, CH_3CN, Cyclohexane

2.25 Toluene, chloroform; Phenol, Pentanol; Formic acid, ethylelne glycol

2.26 4 m

2.27 2.45×10^{-8} M

2.28 1.424%

2.29 3.2 g of water

2.30 4.575 g

2.32 0.65^0

2.33 i = 1.0753, $K_a = 3.07\times10^{-3}$

2.34 17.44 mm Hg

2.35 178×10^{-5}

2.36 280.7 torr, 32 torr

2.38 0.675 and 0.325

2.39 $x\,(O_2)$ 4.6×10^{-5}, $x\,(N_2)$ 9.22×10^{-5}

2.40 0.03 mol

2.41 5.27×10^{-3} atm.

UNIT 3

3.4 (i) $E^{\ominus}$ = 0.34V, $\Delta_r G^{\ominus}$ = – 196.86 kJ mol^{-1}, $K = 3.16 \times 10^{34}$
(ii) $E^{\ominus}$ = 0.03V, $\Delta_r G^{\ominus}$ = – 2.895 kJ mol^{-1}, K = 3.2

3.5 (i) 2.68 V, (ii) 0.53 V, (iii) 0.08 V, (iv) –1.315 V

3.6 1.105 V

3.8 124.0 S cm^2 mol^{-1}

3.9 0.219 cm^{-1}

3.11 1.85×10^{-5}

3.12 3F, 2F, 5F

3.13 1F, 4.44F

3.14 2F, 1F

3.15 1.803g

3.16 14.40 min, Copper 0.427g, Zinc 0.437 g

UNIT 4

4.2 (i) 8.0×10^{-9} mol^{-2} L^2 s^{-1}; 3.89×10^{-9} mol^{-2} L^2 s^{-1}

4.4 $bar^{-1/2}s^{-1}$

4.6 (i) 4 times (ii) ¼ times

4.8 (i) 4.67×10^{-3} mol $L^{-1}s^{-1}$ (ii) 1.92×10^{-2} s^{-1}

4.9 (i) rate = $k[A][B]^2$ (ii) 9 times

4.10 Orders with respect to A is 1.5 and order with respect to B is zero.

4.11 rate law = $k[A][B]^2$; rate constant = 6.0 $M^{-2}min^{-1}$

4.13 (i) 3.47×10^{-3} seconds (ii) 0.35 minutes (iii) 0.173 years

4.14 1845 years

4.16 4.6×10^{-2} s

4.17 0.7842 μg and 0.227 μg.

4.19 77.7 minutes

4.20 2.20×10^{-3} s^{-1}

4.21 2.23×10^{-3} s^{-1}, 7.8×10^{-4} atm s^{-1}

4.23 3.9×10^{12} s^{-1}

4.24 0.135 M

4.25 0.157 M

4.26 232.79 kJ mol^{-1}

4.27 239.339 kJ mol^{-1}

4.28 14°C

4.29 E_a = 479.77 kJ mol^{-1}, $k = 5.70 \times 10^{-70}$ s^{-1}

4.30 52.8 kJ mol^{-1}

UNIT 6

6.1 Zinc is highly reactive metal, it may not be possible to replace it from a solution of $ZnSO_4$ so easily.

6.2 It prevents one of the components from forming the froth by complexation.

6.3 The Gibbs energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

6.5 CO

6.6 Selenium, tellurium, silver, gold are the metals present in anode mud. This is because these are less reactive than copper.

6.9 Silica removes Fe_2O_3 remaining in the matte by forming silicate, $FeSiO_3$.

6.15 Cast iron is made from pig iron by melting pig iron with scrap iron and coke. It has slightly lower carbon content (» 3%) than pig iron (» 4% C)

6.17 To remove basic impurities, like Fe_2O_3

6.18 To lower the melting point of the mixture.

6.20 The reduction may require very high temperature if CO is used as a reducing agent in this case.

6.21 Yes, $2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \quad \Delta_r G^\ominus = -827$ kJ mol^{-1}

$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \quad \Delta_r G^\ominus = -827$ kJ mol^{-1}

Hence $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \quad -827 - (-540) = -287$ kJ mol^{-1}

6.22 Carbon is better reducing agent.

6.25 Graphite rods act as anode and get burnt away as CO and CO_2 during the process of electrolysis.

6.28 Above 1600K Al can reduce MgO.

UNIT 7

7.10 Because of inability of nitrogen to expand its covalency beyond 4.

7.20 Freons

7.22 It dissolves in rain water and produces acid rain.

7.23 Due to strong tendency to accept electrons, halogens act as strong oxidising agent.

7.24 Due to high electronegativity and small size, it cannot act as central atom in higher oxoacids.

7.25 Oxygen has smaller size than chlorine. Smaller size favours hydrogen bonding.

7.30 Synthesis of O_2PtF_6 inspired Bartlett to prepare $XePtF_6$ as Xe and oxygen have nearly same ionisation enthalpies.

7.31 (i) +3 (ii) +3 (iii) -3 (iv) +5 (v) +5

7.34 ClF, Yes.

7.36 (i) $I_2 < F_2 < Br_2 < Cl_2$

(ii) HF < HCl < HBr < HI

(iii) $BiH_3 \leq SbH_3 < AsH_3 < PH_3 < NH_3$

7.37 (ii) NeF_2

7.38 (i) XeF_4

(ii) XeF_2

(iii) XeO_3

UNIT 8

8.2 It is because Mn^{2+} has $3d^5$ configuration which has extra stability.

8.5 Stable oxidation states.

$3d^3$ (Vanadium): (+2), +3, +4, and +5

$3d^5$ (Chromium): +3, +4, +6

$3d^5$ (Manganese): +2, +4, +6, +7

$3d^8$ (Cobalt): +2, +3 (in complexes)

$3d^4$ There is no d^4 configuration in the ground state.

8.6 Vanadate VO_3^-, chromate CrO_4^{2-}, permanganate MnO_4^-

8.10 +3 is the common oxidation state of the lanthanoids

In addition to +3, oxidation states +2 and +4 are also exhibited by some of the lanthanoids.

8.13 In transition elements the oxidation states vary from +1 to any highest oxidation state by one

For example, for manganese it may vary as +2, +3, +4, +5, +6, +7. In the nontransition elements the variation is selective, always differing by 2, e.g. +2, +4, or +3, +5 or +4, +6 etc.

8.18 Except Sc^{3+}, all others will be coloured in aqueous solution because of incompletely filled $3d$-orbitals, will give rise to d-d transitions.

8.21 (i) Cr^{2+} is reducing as it involves change from d^4 to d^3, the latter is more stable configuration (t_{2g}^3) Mn(III) to Mn(II) is from $3d^4$ to $3d^5$ again $3d^5$ is an extra stable configuration.

(ii) Due to CFSE, which more than compensates the 3rd IE.

(iii) The hydration or lattice energy more than compensates the ionisation enthalpy involved in removing electron from d^1.

8.23 Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.

8.24 Unpaired electrons Mn^{3+} = 4, Cr^{3+} = 3, V^{3+} = 2, Ti^{3+} = 1. Most stable Cr^{3+}

8.28 Second part 59, 95, 102.

8.30 Lawrencium, 103, +3

8.36 $Ti^{2+} = 2$, $V^{2+} = 3$, $Cr^{3+} = 3$, $Mn^{2+} = 5$, $Fe^{2+} = 6$, $Fe^{3+} = 5$, $CO^{2+} = 7$, $Ni^{2+} = 8$, $Cu^{2+} = 9$

8.38 $M\sqrt{n(n+2)} = 2.2$, $n \approx 1$, d^2 sp^3, CN^- strong ligand

$= 5.3$, $n \approx 4$, sp^3, d^2, H_2O weak ligand

$= 5.9$, $n \approx 5$, sp^3, Cl^- weak ligand.

UNIT 9

9.5 (i) + 3 (ii) +3 (iii) +2 (iv) +3 (v) +3

9.6 (i) $[Zn(OH)_4]^{2-}$ (ii) $K_2[PdCl_4]$ (iii) $[Pt(NH_3)_2Cl_2]$ (iv) $K_2[Ni(CN)_4]$
(v) $[Co(NH_3)_5(ONO)]^{2+}$ (vi) $[Co(NH_3)_6]_2(SO_4)_3$ (vii) $K_3[Cr(C_2O_4)_3]$ (viii) $[Pt(NH_3)_6]^{4+}$
(ix) $[CuBr_4]^{2-}$ (x) $[Co(NH_3)_5(NO_2)]^{2+}$

9.9 (i) $[Cr(C_2O_4)_3]^{3-}$ – Nil
(ii) $[Co(NH_3)_3Cl_3]$ – Two (*fac*- and *mer*-)

9.12 Three (two *cis* and one *trans*)

9.13 Aqueous $CuSO_4$ solution exists as $[Cu(H_2O)_4]SO_4$ which has blue colour due to $[Cu(H_2O)_4]^{2+}$ ions.
(i) When KF is added, the weak H_2O ligands are replaced by F^- ligands, forming $[CuF_4]^{2-}$ ions which is a green precipitate.
$[Cu(H_2O)_4]^{2+} + 4F^- \rightarrow [CuF_4]^{2-} + 4H_2O$
(ii) When KCl is added, Cl^- ligands replace the weak H_2O ligands forming $[CuCl_4]^{2-}$ ions which has bright green colour.
$[Cu(H_2O)_4]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 4H_2O$

9.14 $[Cu(H_2O)_4]^{2+} + 4\ CN^- \rightarrow [Cu(CN)_4]^{2-} + 4H_2O$
As CN^- is a strong ligand, it forms a highly stable complex with Cu^{2+} ion. On passing H_2S, free Cu^{2+} ions are not available to form the precipitate of CuS.

9.23 (i) OS = +3, CN = 6, d-orbital occupation is $t_{2g}^6\ e_g^0$,
(ii) OS = +3, CN = 6, d^3 (t_{2g}^3),
(iii) OS = +2, CN = 4, d^7 ($t_{2g}^5\ e_g^2$),
(iv) OS = +2, CN = 6, d^5 ($t_{2g}^3\ e_g^2$).

9.28 (iii)

9.29 (ii)

9.30 (iii)

9.31 (iii)

9.32 (i) The order of the ligand in the spectrochemical series :
$H_2O < NH_3 < NO_2^-$
Hence the wavelength of the light observed will be in the order :
$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$
Thus, wavelengths absorbed ($E = hc/\lambda$) will be in the opposite order.

APPENDIX I

Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half-life.

APPENDIX II

Some Useful Conversion Factors

Common Unit of Mass and Weight
1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram
1 kilogram = 1000 grams = 2.205 pounds
1 gram = 10 decigrams = 100 centigrams
= 1000 milligrams
1 gram = 6.022×10^{23} atomic mass units or u
1 atomic mass unit = 1.6606×10^{-24} gram
1 metric tonne = 1000 kilograms
= 2205 pounds

Common Unit of Volume
1 quart = 0.9463 litre
1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre
1 millilitre = 1 cubic centimetre = 0.001 litre
= 1.056×10^{-3} quart
1 cubic foot = 28.316 litres = 29.902 quarts
= 7.475 gallons

Common Units of Energy
1 joule = 1×10^7 ergs

1 thermochemical calorie**
= 4.184 joules
= 4.184×10^7 ergs
= 4.129×10^{-2} litre-atmospheres
= 2.612×10^{19} electron volts
1 ergs = 1×10^{-7} joule = 2.3901×10^{-8} calorie
1 electron volt = 1.6022×10^{-19} joule
= 1.6022×10^{-12} erg
= 96.487 kJ/mol†
1 litre-atmosphere = 24.217 calories
= 101.32 joules
= 1.0132×10^9 ergs
1 British thermal unit = 1055.06 joules
= 1.05506×10^{10} ergs
= 252.2 calories

Common Units of Length
1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres
1 yard = 36 inches = 0.9144 metre
1 metre = 100 centimetres = 39.37 inches
= 3.281 feet
= 1.094 yards
1 kilometre = 1000 metres = 1094 yards
= 0.6215 mile
1 Angstrom = 1.0×10^{-8} centimetre
= 0.10 nanometre
= 1.0×10^{-10} metre
= 3.937×10^{-9} inch

Common Units of Force* and Pressure

1 atmosphere = 760 millimetres of mercury
= 1.013×10^5 pascals
= 14.70 pounds per square inch
1 bar = 10^5 pascals
1 torr = 1 millimetre of mercury
1 pascal = 1 kg/ms^2 = 1 N/m^2

Temperature
SI Base Unit: Kelvin (K)

K = -273.15°C
K = °C + 273.15
°F = 1.8(°C) + 32

$$°C = \frac{°F - 32}{1.8}$$

* *Force: 1 newton (N) = 1 kg m/s^2, i.e.,the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second.*
** *The amount of heat required to raise the temperature of one gram of water from 14.5°C to 15.5°C.*
† *Note that the other units are per particle and must be multiplied by 6.022×10^{23} to be strictly comparable.*

Standard potentials at 298 K in electrochemical order

Reduction half-reaction	E^J /V	Reduction half-reaction	E^J /V
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0	$Cu^+ + e^- \longrightarrow Cu$	+0.52
$F_2 + 2e^- \longrightarrow 2F-$	+2.87	$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07	$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$Ag^+ + e^- \longrightarrow Ag^+$	+1.98	$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81	$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Au^+ + e^- \longrightarrow Au$	+1.69	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67	$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.27
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63	$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3 + H_2O$	+0.17
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51	$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40	$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36	$2H^+ + 2e- \longrightarrow H_2$	0.0 by definition
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33	$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.04
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24	$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	–0.08
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23	$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + 2H_2O$	+1.23	$In^+ + e^- \longrightarrow In$	–0.14
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23	$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20	$AgI + e^- \longrightarrow Ag + I^-$	–0.15
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09	$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.23
$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97	$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96	$Co^{2+} + 2e^- \longrightarrow Co$	–0.28
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92	$In^{3+} + 3e^- \longrightarrow In$	–0.34
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89	$Tl^+ + e^- \longrightarrow Tl$	–0.34
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86	$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	–0.36
$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80	$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37
$Ag^+ + e^- \longrightarrow Ag$	+0.80	$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79	$In^{2+} + e^- \longrightarrow In^+$	–0.40
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76	$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62	$In^{3+} + 2e^- \longrightarrow In^+$	–0.44
$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60	$S + 2e^- \longrightarrow S^{2-}$	–0.48
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56	$In^{3+} + e^- \longrightarrow In^{2+}$	–0.49
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54	$U^{4+} + e^- \longrightarrow U^{3+}$	–0.61
$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
		$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76

(continued)

APPENDIX III CONTINUED

Reduction half-reaction	E^J/V	Reduction half-reaction	E^J/V
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	–0.81	$La^{3+} + 3e^- \longrightarrow La$	–2.52
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	–0.83	$Na^+ + e^- \longrightarrow Na$	–2.71
$Cr^{2+} + 2e^- \longrightarrow Cr$	–0.91	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18	$Sr^{2+} + 2e^- \longrightarrow Sr$	–2.89
$V^{2+} + 2e^- \longrightarrow V$	–1.19	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.91
$Ti^{2+} + 2e^- \longrightarrow Ti$	–1.63	$Ra^{2+} + 2e^- \longrightarrow Ra$	–2.92
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66	$Cs^+ + e^- \longrightarrow Cs$	–2.92
$U^{3+} + 3e^- \longrightarrow U$	–1.79	$Rb^+ + e^- \longrightarrow Rb$	–2.93
$Sc^{3+} + 3e^- \longrightarrow Sc$	–2.09	$K^+ + e^- \longrightarrow K$	–2.93
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36	$Li^+ + e^- \longrightarrow Li$	–3.05
$Ce^{3+} + 3e^- \longrightarrow Ce$	–2.48		

APPENDIX IV

Logarithms

Sometimes, a numerical expression may involve multiplication, division or rational powers of large numbers. For such calculations, logarithms are very useful. They help us in making difficult calculations easy. In Chemistry, logarithm values are required in solving problems of chemical kinetics, thermodynamics, electrochemistry, etc. We shall first introduce this concept, and discuss the laws, which will have to be followed in working with logarithms, and then apply this technique to a number of problems to show how it makes difficult calculations simple.

We know that

$2^3 = 8$, $3^2 = 9$, $5^3 = 125$, $7^0 = 1$

In general, for a positive real number a, and a rational number m, let $a^m = b$,

where b is a real number. In other words

the mth power of base a is b.

Another way of stating the same fact is

logarithm of b to base a is m.

If for a positive real number a, $a \neq 1$

$a^m = b$,

we say that m is the logarithm of b to the base a.

We write this as $\log_a^b = m$,

"log" being the abbreviation of the word "logarithm".

Thus, we have

$\log_2 8 = 3$, Since $2^3 = 8$

$\log_3 9 = 2$, Since $3^2 = 9$

$\log \frac{125}{5} = 3$, Since $5^3 = 125$

$\log_7 1 = 0$, Since $7^0 = 1$

Laws of Logarithms

In the following discussion, we shall take logarithms to any base a, ($a > 0$ and $a \neq 1$)

First Law: $\log_a (mn) = \log_a m + \log_a n$

Proof: Suppose that $\log_a m = x$ and $\log_a n = y$

Then $a^x = m$, $a^y = n$

Hence $mn = a^x.a^y = a^{x+y}$

It now follows from the definition of logarithms that

$\log_a (mn) = x + y = \log_a m - \log_a n$

Second Law: $\log_a \left(\frac{m}{n}\right) = \log_a m - \log_a n$

Proof: Let $\log_a m = x$, $\log_a n = y$

Then $a^x = m$, $a^y = n$

Hence $\frac{m}{n} = \frac{a^x}{a^y} = a^{x-y}$

Therefore

$$\log_a \left(\frac{m}{n}\right) = x - y = \log_a m - \log_a n$$

Third Law : $\log_a(m^n) = n \log_a m$

Proof : As before, if $\log_a m = x$, then $a^x = m$

Then $m^n = \left(a^x\right)^n = a^{nx}$

giving $\log_a(m^n) = nx = n \log_a m$

Thus according to First Law: "the log of the product of two numbers is equal to the sum of their logs. Similarly, the Second Law says: the log of the ratio of two numbers is the difference of their logs. Thus, the use of these laws converts a problem of multiplication / division into a problem of addition/ subtraction, which are far easier to perform than multiplication/division. That is why logarithms are so useful in all numerical computations.

Logarithms to Base 10

Because number 10 is the base of writing numbers, it is very convenient to use logarithms to the base 10. Some examples are:

$\log_{10} 10 = 1$,	since $10^1 = 10$
$\log_{10} 100 = 2$,	since $10^2 = 100$
$\log_{10} 10000 = 4$,	since $10^4 = 10000$
$\log_{10} 0.01 = -2$,	since $10^{-2} = 0.01$
$\log_{10} 0.001 = -3$,	since $10^{-3} = 0.001$
and $\log_{10} 1 = 0$	since $10^0 = 1$

The above results indicate that if n is an integral power of 10, i.e., 1 followed by several zeros or 1 preceded by several zeros immediately to the right of the decimal point, then log n can be easily found.

If n is not an integral power of 10, then it is not easy to calculate log n. But mathematicians have made tables from which we can read off approximate value of the logarithm of any positive number between 1 and 10. And these are sufficient for us to calculate the logarithm of any number expressed in decimal form. For this purpose, we always express the given decimal as the product of an integral power of 10 and a number between 1 and 10.

Standard Form of Decimal

We can express any number in decimal form, as the product of (i) an integral power of 10, and (ii) a number between 1 and 10. Here are some examples:

(i) 25.2 lies between 10 and 100

$$25.2 = \frac{25.2}{10} \times 10 = 2.52 \times 10^1$$

(ii) 1038.4 lies between 1000 and 10000.

$$\therefore 1038.4 = \frac{1038.4}{1000} \times 10^3 = 1.0384 \times 10^3$$

(iii) 0.005 lies between 0.001 and 0.01

$\therefore$ $0.005 = (0.005 \times 1000) \times 10^{-3} = 5.0 \times 10^{-3}$

(iv) 0.00025 lies between 0.0001 and 0.001

$\therefore$ $0.00025 = (0.00025 \times 10000) \times 10^{-4} = 2.5 \times 10^{-4}$

In each case, we divide or multiply the decimal by a power of 10, to bring one non-zero digit to the left of the decimal point, and do the reverse operation by the same power of 10, indicated separately.

Thus, any positive decimal can be written in the form

$n = m \times 10^p$

where p is an integer (positive, zero or negative) and $1 \leq m < 10$. This is called the "standard form of n."

Working Rule

1. Move the decimal point to the left, or to the right, as may be necessary, to bring one non-zero digit to the left of decimal point.
2. (i) If you move p places to the left, multiply by 10^p.
   (ii) If you move p places to the right, multiply by 10^{-p}.
   (iii) If you do not move the decimal point at all, multiply by 10^0.
   (iv) Write the new decimal obtained by the power of 10 (of step 2) to obtain the standard form of the given decimal.

Characteristic and Mantissa

Consider the standard form of n

$n = m \times 10^p$, where $1 \leq m < 10$

Taking logarithms to the base 10 and using the laws of logarithms

$\log n = \log m + \log 10^p$

$= \log m + p \log 10$

$= p + \log m$

Here p is an integer and as $1 \leq m < 10$, so $0 \leq \log m < 1$, i.e., m lies between 0 and 1. When log n has been expressed as p + log m, where p is an integer and 0 log m < 1, we say that p is the "characteristic" of log n and that log m is the "mantissa of log n. Note that characteristic is always an integer – positive, negative or zero, and mantissa is never negative and is always less than 1. If we can find the characteristics and the mantissa of log n, we have to just add them to get log n.

Thus to find log n, all we have to do is as follows:

1. Put n in the standard form, say

   $n = m \times 10^p$, $1 \leq m < 10$
2. Read off the characteristic p of log n from this expression (exponent of 10).
3. Look up log m from tables, which is being explained below.
4. Write log n = p + log m

If the characteristic p of a number n is say, 2 and the mantissa is .4133, then we have log n = 2 + .4133 which we can write as 2.4133. If, however, the characteristic p of a number m is say –2 and the mantissa is .4123, then we have log m = –2 + .4123. We cannot write this as –2.4123. (Why?) In order to avoid this confusion we write $\bar{2}$ for –2 and thus we write log m = $\bar{2}.4123$.

Now let us explain how to use the table of logarithms to find mantissas. A table is appended at the end of this Appendix.

Observe that in the table, every row starts with a two digit number, 10, 11, 12,... 97, 98, 99. Every column is headed by a one-digit number, 0, 1, 2, ...9. On the right, we have the section called "Mean differences" which has 9 columns headed by 1, 2...9.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
61	7853	7860	7868	7875	7882	7889	7896	7803	7810	7817	1	1	2	3	4	4	5	6	6
62	7924	7931	7935	7945	7954	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6

Now suppose we wish to find log (6.234). Then look into the row starting with 62. In this row, look

at the number in the column headed by 3. The number is 7945. This means that

log (6.230) = 0.7945*

But we want log (6.234). So our answer will be a little more than 0.7945. How much more? We look this up in the section on Mean differences. Since our fourth digit is 4, look under the column headed by 4 in the Mean difference section (in the row 62). We see the number 3 there. So add 3 to 7945. We get 7948. So we finally have

log (6.234) = 0.7948.

Take another example. To find log (8.127), we look in the row 81 under column 2, and we find 9096. We continue in the same row and see that the mean difference under 7 is 4. Adding this to 9096, and we get 9100. So, log (8.127) = 0.9100.

Finding *N* when log *N* is given

We have so far discussed the procedure for finding log n when a positive number n given. We now turn to its converse i.e., to find n when log n is given and give a method for this purpose. If log n = t, we sometimes say n = antilog t. Therefore our task is given t, find its antilog. For this, we use the ready-made antilog tables.

Suppose log n = 2.5372.

To find n, first take just the mantissa of log n. In this case it is .5372. (Make sure it is positive.) Now take up antilog of this number in the antilog table which is to be used exactly like the log table. In the antilog table, the entry under column 7 in the row .53 is 3443 and the mean difference for the last digit 2 in that row is 2, so the table gives 3445. Hence,

antilog (.5372) = 3.445

Now since log n = 2.5372, the characteristic of log n is 2. So the standard form of n is given by

$n = 3.445 \times 10^2$

or n = 344.5

Illustration 1:

If log x = 1.0712, find x.

Solution: We find that the number corresponding to 0712 is 1179. Since characteristic of log *x* is 1, we have

$x = 1.179 \times 10^1$

$= 11.79$

Illustration 2:

If log x = $\bar{2}.1352$, find x.

Solution: From antilog tables, we find that the number corresponding to 1352 is 1366. Since the characteristic is $\bar{2}$ i.e., –2, so

$x = 1.366 \times 10^{-2} = 0.01366$

Use of Logarithms in Numerical Calculations

Illustration 1:

Find 6.3 × 1.29

Solution: Let x = 6.3 × 1.29

Then log x = log (6.3 × 1.29) = log 6.3 + log 1.29

Now,

log 6.3 = 0.7993

log 1.29 = 0.1106

∴ log x = 0.9099,

Taking antilog

* *It should, however, be noted that the values given in the table are not exact. They are only approximate values, although we use the sign of equality which may give the impression that they are exact values. The same convention will be followed in respect of antilogarithm of a number.*

$x = 8.127$

Illustration 2:

Find $\dfrac{(1.23)^{1.5}}{11.2 \times 23.5}$

Solution: Let $x = \dfrac{(1.23)^{\frac{3}{2}}}{11.2 \times 23.5}$

Then $\log x = \log \dfrac{(1.23)^{\frac{3}{2}}}{11.2 \times 23.5}$

$= \dfrac{3}{2} \log 1.23 - \log (11.2 \times 23.5)$

$= \dfrac{3}{2} \log 1.23 - \log 11.2 - 23.5$

Now,

$\log 1.23 = 0.0899$

$\dfrac{3}{2} \log 1.23 = 0.13485$

$\log 11.2 = 1.0492$

$\log 23.5 = 1.3711$

$\log x = 0.13485 - 1.0492 - 1.3711$

$= \overline{3}.71455$

$\therefore x = 0.005183$

Illustration 3:

Find $\sqrt{\dfrac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}}$

Solution: Let $x = \sqrt{\dfrac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}}$

Then $\log x = \dfrac{1}{2} \log \left[\dfrac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}\right]$

$= \dfrac{1}{2} [\log (71.24)^5 + \log \sqrt{56} - \log (2.3)^7 - \log \sqrt{21}]$

$= \dfrac{5}{2} \log 71.24 + \dfrac{1}{4} \log 56 - \dfrac{7}{2} \log 2.3 - \dfrac{1}{4} \log 21$

Now, using log tables

$\log 71.24 = 1.8527$

$\log 56 = 1.7482$

$\log 2.3 = 0.3617$

$\log 21 = 1.3222$

$\therefore \log x = \dfrac{5}{2} \log (1.8527) + \dfrac{1}{4} (1.7482) - \dfrac{7}{2} (0.3617) - \dfrac{1}{4} (1.3222)$

$= 3.4723$

$\therefore x = 2967$

LOGARITHMS

TABLE I

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	2O	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6471	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

TABLE 1 (*Continued*)

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7768	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9997	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

TABLE II

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	3	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	3	4	5	6	6

ANTILOGARITHMS

TABLE II (*Continued*)

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	42S6	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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Chemistry

Part II

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Unit

10

Haloalkanes and Haloarenes

Objectives

After studying this Unit, you will be able to

- name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- correlate the structures of haloalkanes and haloarenes with various types of reactions;
- use stereochemistry as a tool for understanding the reaction mechanism;
- appreciate the applications of organo-metallic compounds;
- highlight the environmental effects of polyhalogen compounds.

Halogenated compounds persist in the environment due to their resistance to breakdown by soil bacteria.

The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful. These classes of compounds find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, *chloramphenicol,* produced by soil microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, *thyroxine,* the deficiency of which causes a disease called *goiter*. Synthetic halogen compounds, *viz.* chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.

In this Unit, you will study the important methods of preparation, physical and chemical properties and uses of organohalogen compounds.

10.1 Classification

Haloalkanes and haloarenes may be classified as follows:

10.1.1 On the Basis of Number of Halogen Atoms

These may be classified as mono, di, or polyhalogen (tri-,tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,

Monohaloalkane Dihaloalkane Trihaloalkane

Monohaloarene Dihaloarene Trihaloarene

Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

10.1.2 Compounds Containing sp^3 C—X Bond (X= F, Cl, Br, I)

This class includes

(a) Alkyl halides or haloalkanes (R—X)

In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.

Primary (1°) Secondary (2°) Tertiary (3°)

(b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to carbon-carbon double bond (C=C) *i.e.* to an allylic carbon.

(c) Benzylic halides

These are the compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to an aromatic ring.

(1°) $R' = CH_3$, $R'' = H$ (2°)

$R' = R'' = CH_3$ (3°)

10.1.3 Compounds Containing sp^2 C—X Bond

This class includes:

(a) Vinylic halides

These are the compounds in which the halogen atom is bonded to an sp^2-hybridised carbon atom of a carbon-carbon double bond (C = C).

(b) Aryl halides

These are the compounds in which the halogen atom is bonded to the sp^2-hybridised carbon atom of an aromatic ring.

10.2 Nomenclature

Having learnt the classification of halogenated compounds, let us now learn how these are named. The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halosubstituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.

	$CH_3CH_2CH_2Br$	$H_3C–\underset{\underset{Cl}{\vert}}{CH}–CH_3$	$H_3C–\overset{\overset{CH_3}{\vert}}{CH}–CH_2Cl$
Common name:	n-Propyl bromide	Isopropyl chloride	Isobutyl chloride
IUPAC name:	1-Bromopropane	2-Chloropropane	1-Chloro-2-methylpropane

Common name:	Bromobenzene	*m*-Dibromobenzene	*sym*-Tribromobenzene
IUPAC name:	Bromobenzene	1,3-Dibromobenzene	1,3,5-Tribromobenzene

	$H_3C–\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}–CH_2–Cl$	$H_3C–\underset{\underset{Br}{\vert}}{CH}–CH_3$
IUPAC name:	1-Chloro-2,2-dimethylpropane	2-Bromopropane

The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo-compounds having same type of halogen atoms are further classified as geminal halides (halogen atoms are present on the same carbon atom) and vicinal halides (halogen atoms are present on the adjacent carbon atoms). In common name system, *gem*-dihalides are named as alkylidene halides and *vic*-dihalides

are named as alkylene dihalides. In IUPAC system, they are named as dihaloalkanes.

	$H_3C-CHCl_2$	$H_2C(Cl)-CH_2(Cl)$
Common name:	Ethylidene chloride (*gem*-dihalide)	Ethylene dichloride (*vic-dihalide*)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

Some common examples of halocompounds are mentioned in Table 10.1.

Table 10.1: Common and IUPAC names of some Halides

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
	o-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

Example 10.1 Draw the structures of all the eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Solution

$CH_3CH_2CH_2CH_2CH_2Br$	1-Bromopentane (1°)
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane(2°)
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane (2°)
$(CH_3)_2CHCH_2CH_2Br$	1-Bromo-3-methylbutane (1°)

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$(CH_3)_2CHCHBrCH_3$	2-Bromo-3-methylbutane(2°)
$(CH_3)_2CBrCH_2CH_3$	2-Bromo-2-methylbutane (3°)
$CH_3CH_2CH(CH_3)CH_2Br$	1-Bromo-2-methylbutane(1°)
$(CH_3)_3CCH_2Br$	1-Bromo-2,2-dimethylpropane (1°)

Example 10.2

Write IUPAC names of the following:

(i)

(ii)

(iii)

(iv)

(v)

(vi)

Solution

(i) 4-Bromopent-2-ene
(ii) 3-Bromo-2-methylbut-1-ene
(iii) 4-Bromo-3-methylpent-2-ene
(iv) 1-Bromo-2-methylbut-2-ene
(v) 1-Bromobut-2-ene
(vi) 3-Bromo-2-methylpropene

Intext Question

10.1 Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane
(ii) 1-Chloro-4-ethylcyclohexane
(iii) 4-tert. Butyl-3-iodoheptane
(iv) 1,4-Dibromobut-2-ene
(v) 1-Bromo-4-sec. butyl-2-methylbenzene.

10.3 Nature of C-X Bond

Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.

Since the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, the largest. Consequently the carbon-halogen bond length also increases from C—F to C—I. Some typical bond lengths, bond enthalpies and dipole moments are given in Table 10.2.

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Table 10.2: Carbon-Halogen (C—X) Bond Lengths, Bond Enthalpies and Dipole Moments

Bond	Bond length/pm	C-X Bond enthalpies/ $kJmol^{-1}$	Dipole moment/Debye
CH_3–F	139	452	1.847
CH_3– Cl	178	351	1.860
CH_3–Br	193	293	1.830
CH_3–I	214	234	1.636

10.4 Methods of Preparation

10.4.1 From Alcohols

Alkyl halides are best prepared from alcohols, which are easily accessible. The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because the other two products are escapable gases. Hence the reaction gives pure alkyl halides. Phosphorus tribromide and triiodide are usually generated *in situ* (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine respectively. The preparation of alkyl chloride is carried out either by passing dry hydrogen chloride gas through a solution of alcohol or by heating a solution of alcohol in concentrated aqueous acid.

$$R\text{–}OH + HX \xrightarrow{ZnCl_2} R\text{–}X + H_2O$$

$$R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$$

$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$$

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

$$R\text{–}OH \xrightarrow[X_2=Br_2,I_2]{\text{red } P/X_2} R\text{–}X$$

$$R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$$

The reactions of primary and secondary alcohols with HX require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature. Constant boiling with HBr (48%) is used for preparing alkyl bromide. Good yields of R—I may be obtained by heating alcohols with sodium or potassium iodide in 95% phosphoric acid. The order of reactivity of alcohols with a given haloacid is 3 >2 >1 . The above method is not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond (Unit 11, Class XI).

10.4.2 From Hydrocarbons

(a) By free radical halogenation

Free radical chlorination or bromination of alkanes gives a complex

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mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds. Consequently, the yield of any one compound is low (Unit 13, Class XI).

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

Example 10.3

Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(CH_3)_2CHCH_2CH_3$.

Solution

In the given molecule, there are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following

$(CH_3)_2CHCH_2CH_2Cl$ $\quad$ $(CH_3)_2CHCH(Cl)CH_3$

$(CH_3)_2C(Cl)CH_2CH_3$ $\quad$ $CH_3CH(CH_2Cl)CH_2CH_3$

(b) *By electrophilic substitution*

Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.

o-Halotoluene $\quad$ *p*-Halotoluene

The *ortho* and *para* isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(c) *Sandmeyer's reaction*

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed (Unit 13, Class XII). Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.

Benzene diazonium halide

Aryl halide

X = Cl, Br

Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

(d) From alkenes

(i) *Addition of hydrogen halides*: An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.

Propene yields two products, however only one predominates as per Markovnikov's rule. (Unit 13, Class XI)

$$CH_3CH = CH_2 + H{-}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(ii) *Addition of halogens:* In the laboratory, addition of bromine in CCl_4 to an alkene resulting in discharge of reddish brown colour of bromine constitutes an important method for the detection of double bond in a molecule. The addition results in the synthesis of *vic*-dibromides, which are colourless (Unit 13, Class XI).

Example 10.4 Write the products of the following reactions:

Solution

10.4.3 Halogen Exchange

Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as **Finkelstein** reaction.

$$R\text{–}X + NaI \longrightarrow R\text{–}I + NaX$$

X=Cl, Br

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is termed as **Swarts** reaction.

$$H_3C\text{–}Br + AgF \longrightarrow H_3C\text{–}F + AgBr$$

Intext Questions

10.2 Why is sulphuric acid not used during the reaction of alcohols with KI?

10.3 Write structures of different dihalogen derivatives of propane.

10.4 Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(i) A single monochloride.

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

10.5 Draw the structures of major monohalo products in each of the following reactions:

(i)

(ii)

(iii)

(iv)

(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi)

10.5 Physical Properties

Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell.

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Melting and boiling points

Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids. As we have already learnt, molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

The attractions get stronger as the molecules get bigger in size and have more electrons. The pattern of variation of boiling points of different halides is depicted in Fig. 10.1. For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI> RBr> RCl> RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

Fig. 10.1: *Comparison of boiling points of some alkyl halides*

The boiling points of isomeric haloalkanes decrease with increase in branching (Unit 12, Class XI). For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.

	$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2CH(Br)CH_3$	$H_3C-C(Br)(CH_3)-CH_3$
b.p./K	375	364	346

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the *para*-isomers are high melting as compared to their *ortho*- and *meta*-isomers. It is due to symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.

b.p /K	453	446	448
m.p/K	256	249	323

Density

Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms (Table 10.3).

Table 10.3: Density of some Haloalkanes

Compound	Density (g/mL)	Compound	Density (g/mL)
n–C_3H_7Cl	0.89	CH_2Cl_2	1.336
n–C_3H_7Br	1.335	$CHCl_3$	1.489
n-C_3H_7I	1.747	CCl_4	1.595

Solubility

The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

Intext Question

10.6 Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

10.6 Chemical Reactions

10.6.1 Reactions of Haloalkanes

The reactions of haloalkanes may be divided into the following categories:

(i) Nucleophilic substitution

(ii) Elimination reactions

(iii) Reaction with metals.

(i) *Nucleophilic substitution reactions*

In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded

to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

It is one of the most useful classes of organic reactions of alkyl halides in which halogen is bonded to sp^3 hybridised carbon. The products formed by the reaction of haloalkanes with some common nucleophiles are given in Table 10.4.

Table 10.4: Nucleophilic Substitution of Alkyl Halides (R–X)

$$R-X + Nu^- \rightarrow R-Nu + X^-$$

Reagent	Nucleophile (Nu^-)	Substitution product R–Nu	Class of main product
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″H	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N$:	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N—O	R—O—N=O	Alkyl nitrite
$AgNO_2$	Ag—Ö—N=O	$R—NO_2$	Nitroalkane
R′COOAg	$R'COO^-$	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
R'^-M^+	R'^-	RR′	Alkane

Groups like cyanides and nitrites possess two nucleophilic centres and are called *ambident nucleophiles*. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways [$^{\ominus}C\equiv N \leftrightarrow :C=N^{\ominus}$], *i.e.*, linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage [$^-O—\ddot{N}=O$]. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

Example 10.5

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Solution

KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

Mechanism: This reaction has been found to proceed by two different mechanims which are described below:

(a) Substitution nucleophilic bimolecular (S_N2)

The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.

As you have already learnt in Section 12.3.2 of Class XI, the solid wedge represents the bond coming out of the paper, dashed line going down the paper and a straight line representing bond in the plane of the paper.

This can be represented diagrammatically as shown in Fig. 10.2.

Fig. 10.2: *Red dot represents the incoming hydroxide ion and green dot represents the outgoing halide ion*

In the year 1937, Edward Davies Hughes and Sir Christopher Ingold proposed a mechanism for an S_N2 reaction.

It depicts a bimolecular nucleophilic displacement (S_N2) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. As the reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away. This process is called as **inversion of configuration**. In the transition state, the carbon atom is simultaneously bonded to incoming nucleophile and the outgoing leaving

group and such structures are unstable and cannot be isolated. This is because the carbon atom in the transition state is simultaneously bonded to five atoms and therefore is unstable.

Hughes worked under Ingold and earned a D.Sc. degree from the University of London.

Since this reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom have a dramatic inhibiting effect. Of the simple alkyl halides, methyl halides react most rapidly in S_N2 reactions because there are only three small hydrogen atoms. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide.

Fig.10.3: *Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis*

(b) Substitution nucleophilic unimolecular (S_N1)

S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between *tert*-butyl bromide and hydroxide ion yields *tert*-butyl alcohol and follows the first order kinetics, *i.e.*, the rate of reaction depends upon the concentration of only one reactant, which is *tert*- butyl bromide.

$$(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^-$$

2-Bromo-2-methylpropane 2-Methylpropan-2-ol

It occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.

Step I is the slowest and reversible. It involves the C–Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3^0 alkyl halides undergo S_N1 reaction very fast because of the high stability of 3^0 carbocations. We can sum up the order of reactivity of alkyl halides towards S_N1 and S_N2 reactions as follows:

For S_N2 reaction

Tertiary halide; Secondary halide; Primary halide; CH_3X

For S_N1 reaction

For the same reasons, allylic and benzylic halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance (Unit 12, Class XI) as shown below.

For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms R–I> R–Br>R–Cl>>R–F.

Example 10.6

In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?

Solution

It is primary halide and therefore undergoes S_N2 reaction faster.

As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Example 10.7

Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

(i) The four isomeric bromobutanes

(ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Solution (i) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_N1)

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_N2)

Of the two primary bromides, the carbocation intermediate derived from $(CH_3)_2CHCH_2Br$ is more stable than derived from $CH_3CH_2CH_2CH_2Br$ because of greater electron donating inductive effect of $(CH_3)_2CH$- group. Therefore, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 reactions. $CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Hence the above order is followed in S_N1. The reactivity in S_N2 reactions follows the reverse order as the steric hinderance around the electrophilic carbon increases in that order.

(ii) $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1)

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2)

Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than obtained from $C_6H_5CH(CH_3)Br$ because it is stabilised by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in S_N1 reactions. A phenyl group is bulkier than a methyl group. Therefore, $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 reactions.

(c) Stereochemical aspects of nucleophilic substitution reactions

A S_N2 reaction proceeds with complete stereochemical inversion while a S_N1 reaction proceeds with racemisation.

In order to understand this concept, we need to learn some basic stereochemical principles and notations (**optical activity, chirality, retention, inversion, racemisation,** etc.).

William Nicol (1768-1851) developed the first prism that produced plane polarised light.

(i) *Plane polarised light and optical activity*: Certain compounds rotate the plane polarised light (produced by passing ordinary light through Nicol prism) when it is passed through their solutions. Such compounds are called **optically active** compounds. The angle by which the plane polarised light is rotated is measured by an instrument called polarimeter. If the compound rotates the plane polarised light to the right, i.e., clockwise direction, it is called *dextrorotatory* (Greek for right rotating) or the d-form and is indicated by placing a positive (+) sign before the degree of rotation. If the light is rotated towards left (anticlockwise direction), the compound is said to be laevo-rotatory or the l-form and a negative (–) sign is placed before the degree of rotation. Such (+) and (–) isomers of a compound are called **optical isomers** and the phenomenon is termed as **optical isomerism**.

(ii) *Molecular asymmetry, chirality and enantiomers*: The observation of Louis Pasteur (1848) that crystals of certain compounds exist in the form of mirror images laid the foundation of modern stereochemistry. He demonstrated that aqueous solutions of both types of crystals showed optical rotation, equal in magnitude (for solution of equal concentration) but opposite in direction. He believed that this difference in

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Jacobus Hendricus Van't Hoff (1852-1911) received the first Nobel Prize in Chemistry in 1901 for his work on solutions.

optical activity was associated with the three dimensional arrangements of atoms (**configurations**) in two types of crystals. Dutch scientist, *J. Van't Hoff* and French scientist, *C. Le Bel* in the same year (1874), independently argued that the spatial arrangement of four groups (valencies) around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, such a carbon is called **asymmetric carbon** or **stereocentre**. The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule is responsible for the optical activity in such organic compounds.

The symmetry and asymmetry are also observed in many day to day objects: a sphere, a cube, a cone, are all identical to their mirror images and can be superimposed. However, many objects are non superimposable on their mirror images. For example, your left and right hand look similar but if you put your left hand on your right hand, they do not coincide. The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be **chiral** and this property is known as **chirality**. While the objects, which are, superimposable on their mirror images are called **achiral**.

Fig 10.4: *Some common examples of chiral and achiral objects*

The above test of molecular chirality can be applied to organic molecules by constructing models and its mirror images or by drawing three dimensional structures and attempting to superimpose them in our minds. There are other aids, however, that can assist us in recognising chiral molecules. One such aid is the presence of a single asymmetric carbon atom. Let us consider two simple molecules propan-2-ol and butan-2-ol and their mirror images.

C obtained by rotating B by 180°
C is superimposable on its mirror image A

As you can see very clearly, propan-2-ol does not contain an asymmetric carbon, as all the four groups attached to the tetrahedral carbon are not different. Thus it is an **achiral** molecule.

F obtained by rotating E by 180°
F is non superimposable on its mirror image D

Fig. 10.5: *A chiral molecule and its mirror image*

Butan-2-ol has four different groups attached to the tetrahedral carbon and as expected is **chiral**. Some common examples of chiral molecules such as 2-chlorobutane, 2, 3-dihyroxypropanal, (OHC–CHOH–CH_2OH), bromochloro-iodomethane (BrClCHI), 2-bromopropanoic acid (H_3C–CHBr–COOH), etc.

The stereoisomers related to each other as non-superimposable mirror images are called **enantiomers** (Fig. 10.5).

Enantiomers possess identical physical properties namely, melting point, boiling point, solubility, refractive index, etc. They only differ with respect to the rotation of plane polarised light. If one of the enantiomer is *dextro rotatory,* the other will be *laevo rotatory.*

> However, the sign of optical rotation is not necessarily related to the absolute configuration of the molecule.

A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as **racemic mixture** or **racemic modification**. A racemic mixture is represented by prefixing *dl* or (±) before the name, for example (±) butan-2-ol. The process of conversion of enantiomer into a racemic mixture is known as **racemisation.**

Example 10.8 Identify chiral and achiral molecules in each of the following pair of compounds. (Wedge and Dash representations according to Class XI, Fig 12.1).

(i)

(i) (ii)

(ii)

(i) (ii)

(iii) $CH_3CH(Br)CH_2CH_3$ (i) $CH_3CH_2CH_2CH_2Br$ (ii)

(i)

(ii)

(iii)

Solution

(iii) *Retention:* Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. It is also the configurational correlation when a chemical species XCabc is converted into the chemical species YCabc having the same *relative configuration*.

In general, if during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration of groups around the stereocentre as that of reactant. Such a reaction is said to proceed with retention of the configuration. Consider as an example, the reaction that takes place when (–)-2-methylbutan-1-ol is heated with concentrated hydrochloric acid.

(–)–2-Methylbutan-1-ol (+)-1-Chloro-2-methylbutane

(iv) *Inversion, retention and racemisation:* There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction;

If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50:50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

Now let us have a fresh look at S_N1 and S_N2 mechanisms by taking examples of optically active alkyl halides.

In case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration as compared to the reactant. This is because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied.

Thus, S_N2 reactions of optically active halides are accompanied by inversion of configuration.

In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. Can you think of the reason why it happens? Actually the carbocation formed in the slow step being sp^2 hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side resulting in a mixture of products, one having the same configuration (the –OH attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butan-2-ol.

(+)-Butan-2-ol (–)Butan-2-ol

2. Elimination reactions

When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom. As a result, an alkene is formed as a product. Since β-hydrogen atom is involved in elimination, it is often called **β-elimination**.

B=Base ; X=Leaving group

If there is possibility of formation of more than one alkene due to the availability of more than one α-hydrogen atoms, usually one alkene is formed as the major product. These form part of a pattern first observed by Russian chemist, Alexander Zaitsev (also pronounced as Saytzeff) who in 1875 formulated a rule which can be summarised as "*in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.*" Thus, 2-bromopentane gives pent-2-ene as the major product.

Elimination versus substitution

A chemical reaction is the result of competition; it is a race that is won by the fastest runner. A collection of molecules tend to do, by and large, what is easiest for them. An alkyl halide with α-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and *vice versa*. Similarly, a primary alkyl halide will prefer a S_N2 reaction, a secondary halide- S_N2 or elimination depending upon the strength of base/nucleophile and a tertiary halide- S_N1 or elimination depending upon the stability of carbocation or the more substituted alkene.

Elimination *vs* Substitution

3. *Reaction with metals*

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organo-metallic compounds**. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide, RMgX, referred as **Grignard Reagents**. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

Victor Grignard had a strange start in academic life for a chemist - he took a maths degree. When he eventually switched to chemistry, it was not to the mathematical province of physical chemistry but to organic chemistry. While attempting to find an efficient catalyst for the process of methylation, he noted that Zn in diethyl ether had been used for this purpose and wondered whether the Mg/ether combination might be successful. Grignard reagents were first reported in 1900 and Grignard used this work for his doctoral thesis in 1901. In 1910, Grignard obtained a professorship at the University of Nancy and in 1912, he was awarded the Nobel prize for Chemistry which he shared with Paul Sabatier who had made advances in nickel catalysed hydrogenation.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.

$$\overset{\delta-}{R}\text{-}\overset{\delta+}{Mg}\,\overset{\delta-}{X}$$

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

It is therefore necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

Wurtz reaction

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction. (Unit 13, Class XI).

$$2RX + Na \longrightarrow RR + NaX$$

10.6.2 Reactions of Haloarenes

1. Nucleophilic substitution

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) *Resonance effect :* In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.

C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

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(ii) *Difference in hybridisation of carbon atom in C—X bond:* In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.

The sp^2 hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3-hybridised carbon in haloalkane with less *s*-chararcter. Thus, C—Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) *Instability of phenyl cation:* In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, S_N1 mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

Replacement by hydroxyl group

Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.

The presence of an electron withdrawing group (-NO_2) at *ortho*- and *para*-positions increases the reactivity of haloarenes.

The effect is pronounced when (-NO_2) group is introduced at *ortho*- and *para*- positions. However, no effect on reactivity of haloarenes is observed by the presence of electron withdrawing group at *meta*-position. Mechanism of the reaction is as depicted:

Can you think why does NO_2 group show its effect only at *ortho*- and *para*- positions and not at *meta*- position?

As shown, the presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*- positions with respect to the halogen substituent is stabilised by –NO_2 group while in case of *meta*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the –NO_2 group. Therefore, the presence of nitro group at *meta*- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of –NO_2 group at *meta*-position.

2. *Electrophilic substitution reactions*

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is *o, p*-directing; therefore, further substitution occurs at *ortho*- and *para*-positions with respect to the halogen atom. The *o, p*-directing influence of halogen atom can be easily understood if we consider the resonating structures of halobenzene as shown:

I II III IV

Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its –I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

(i) Halogenation

1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

(ii) Nitration

1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

(iii) Sulphonation

2-Chlorobenzene sulfonic acid (Minor)

4-Chlorobenzene sulfonic acid (Major)

(iv) Friedel-Crafts reaction

1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)

2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

Example 10.9 Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Solution Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.

Inductive effect destabilises the intermediate carbocation

(attack at *ortho*-position)

(attack at para-position)

Resonance effect stabilises the intermediate carbocation

Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para*-positions and hence makes the deactivation less for *ortho*- and *para*-attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

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3. Reaction with metals

Wurtz-Fittig reaction

A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.

Fittig reaction

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.

Intext Questions

10.7 Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

(i) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$ (ii) $CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$ or $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

(iii) $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2Br$ or $CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2Br$

10.8 In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)

and

(ii)

and

10.9 Identify A, B, C, D, E, R and R^1 in the following:

10.7 Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

10.7.1 Dichloromethane (Methylene chloride)

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

10.7.2 Trichloromethane (Chloroform)

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

10.7.3 Triiodomethane (Iodoform)

It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

10.7.4 Tetrachloromethane (Carbon tetrachloride)

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause

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permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

10.7.5 Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. By 1974, total freon production in the world was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance (Unit 14, Class XI).

10.7.6 *p,p'*-Dichlorodiphenyltrichloroethane(DDT)

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

DDT

Summary

Alkyl/ Aryl halides may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge, and the halogen atom bears a partial negative charge.

Alkyl halides are prepared by the **free radical halogenation** of alkanes, addition of halogen acids to alkenes, replacement of –OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by **electrophilic substitution** to arenes. Fluorides and iodides are best prepared by halogen exchange method.

The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and van der Waals forces of attraction. These are slightly soluble in water but completely soluble in organic solvents.

The polarity of carbon-halogen bond of alkyl halides is responsible for their **nucleophilic substitution, elimination** and their reaction with metal atoms to form **organometallic compounds**. Nucleophilic substitution reactions are categorised into **S_N1** and **S_N2** on the basis of their kinetic properties. **Chirality** has a profound role in understanding the reaction mechanisms of S_N1 and S_N2 reactions. S_N2 reactions of chiral alkyl halides are characterised by the inversion of configuration while S_N1 reactions are characterised by racemisation.

A number of polyhalogen compounds e.g., **dichloromethane**, **chloroform**, **iodoform**, **carbon tetrachloride**, **freon** and **DDT** have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving **environmental hazards**.

Exercises

10.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$ (ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$ (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$ (vi) $CH_3C(C_2H_5)_2CH_2Br$

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$ (viii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$

(ix) $CH_3CH{=}CHC(Br)(CH_3)_2$ (x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$

(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$ (xii) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

10.2 Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$ (ii) $CHF_2CBrClF$ (iii) $ClCH_2C{\equiv}CCH_2Br$

(iv) $(CCl_3)_3CCl$ (v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ (vi) $(CH_3)_3CCH{=}ClC_6H_4I\text{-}p$

10.3 Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane (ii) *p*-Bromochlorobenzene

(iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-iodooctane

(v) Perfluorobenzene (vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene (viii) 1,4-Dibromobut-2-ene

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10.4 Which one of the following has the highest dipole moment?

(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4

10.5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

10.6 Write the isomers of the compound having formula C_4H_9Br.

10.7 Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.

10.8 What are ambident nucleophiles? Explain with an example.

10.9 Which compound in each of the following pairs will react faster in S_N2 reaction with ^-OH?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

10.10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

10.11 How will you bring about the following conversions?

(i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

10.12 Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

10.13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

10.14 Write the structure of the major organic product in each of the following reactions:

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$

(viii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

10.15 Write the mechanism of the following reaction:

$$nBuBr + KCN \xrightarrow{EtOH\text{-}H_2O} nBuCN$$

10.16 Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

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(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

10.17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

10.18 *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers. Discuss.

10.19 How the following conversions can be carried out?

(i) Propene to propan-1-ol
(ii) Ethanol to but-1-yne
(iii) 1-Bromopropane to 2-bromopropane
(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to chlorobenzene
(ix) 2-Chlorobutane to 3, 4-dimethylhexane
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(xi) Ethyl chloride to propanoic acid
(xii) But-1-ene to n-butyliodide
(xiii) 2-Chloropropane to 1-propanol
(xiv) Isopropyl alcohol to iodoform
(xv) Chlorobenzene to *p*-nitrophenol
(xvi) 2-Bromopropane to 1-bromopropane
(xvii) Chloroethane to butane
(xviii) Benzene to diphenyl
(xix) *tert*-Butyl bromide to isobutyl bromide
(xx) Aniline to phenylisocyanide

10.20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

10.21 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

10.22 What happens when

(i) n-butyl chloride is treated with alcoholic KOH,
(ii) bromobenzene is treated with Mg in the presence of dry ether,
(iii) chlorobenzene is subjected to hydrolysis,
(iv) ethyl chloride is treated with aqueous KOH,
(v) methyl bromide is treated with sodium in the presence of dry ether,
(vi) methyl chloride is treated with KCN?

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Answers to Some Intext Questions

10.1 (i) $CH_3CH_2CH(CH_3)CHClCH_3$

(ii)

(iii) $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{H_3C}{\overset{|}{C}}}-CH(I)CH_2CH_3$

(iv) $BrCH_2CH = CHCH_2Br$

(v)

10.2 (i) H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding HI and then oxidises it to I_2.

10.3 (i) $ClCH_2CH_2CH_2Cl$ (ii) $ClCH_2CHClCH_3$ (iii) $Cl_2CH_2CH_2CH_3$ (iv) $CH_3CCl_2CH_3$

10.4 (i) $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ All the hydrogen atoms are equivalent and replacement of any hydrogen will give the same product.

(ii) $C^aH_3C^bH_2C^cH_2C^bH_2C^aH_3$ The equivalent hydrogens are grouped as a, b and c. The replacement of equivalent hydrogens will give the same product.

(iii) $C^aH_3\underset{\underset{CH_3{}^a}{|}}{C^b}HC^cH_2C^dH_3$ Similarly the equivalent hydrogens are grouped as a, b, c and d. Thus, four isomeric products are possible.

10.5 (i)

(ii)

(iii)

(iv)

(v) CH_3CH_2I

(vi)

10.6 (i) Chloromethane, Bromomethane, Dibromomethane, Bromoform. Boiling point increases with increase in molecular mass.

(ii) Isopropylchloride, 1-Chloropropane, 1-Chlorobutane. Isopropylchloride being branched has lower b.p. than 1-Chloropropane.

10.7 (i) $CH_3CH_2CH_2CH_2Br$ Being primary halide, there won't be any steric hinderance.

(ii) $CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$ Secondary halide reacts faster than tertiary halide.

(iii) $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2Br$ The presence of methyl group closer to the halide group will increase the steric hinderance and decrease the rate.

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10.8 (i)

Tertiary halide reacts faster than secondary halide because of the greater stability of tert-carbocation.

(ii)

Because of greater stability of secondary carbocation than primary.

10.9 A =

B =

C = RMgBr R = CH_3CHCH_3

$R^1 = H_3C-C(CH_3)_2$ D = $H_3C-C(CH_3)_2-MgX$ E = $H_3C-C(CH_3)_2-H$

Unit

11

Alcohols, Phenols and Ethers

Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.

Objectives

After studying this Unit, you will be able to

- name alcohols, phenols and ethers according to the IUPAC system of nomenclature;
- discuss the reactions involved in the preparation of alcohols from (i) alkenes (ii) aldehydes, ketones and carboxylic acids;
- discuss the reactions involved in the preparation of phenols from (i) haloarenes (ii) benzene sulphonic acids (iii) diazonium salts and (iv) cumene;
- discuss the reactions for preparation of ethers from (i) alcohols and (ii) alkyl halides and sodium alkoxides/aryloxides;
- correlate physical properties of alcohols, phenols and ethers with their structures;
- discuss chemical reactions of the three classes of compounds on the basis of their functional groups.

You have learnt that substitution of one or more hydrogen atom(s) from a hydrocarbon by another atom or a group of atoms result in the formation of an entirely new compound having altogether different properties and applications. **Alcohols** and **phenols** are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH group. These classes of compounds find wide applications in industry as well as in day-to-day life. For instance, have you ever noticed that ordinary spirit used for polishing wooden furniture is chiefly a compound containing hydroxyl group, ethanol. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing –OH groups. Just think of life without paper; no note-books, books, news-papers, currency notes, cheques, certificates, etc. The magazines carrying beautiful photographs and interesting stories would disappear from our life. It would have been really a different world.

An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s), of an aliphatic system (CH_3OH) while a phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).

The subsitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R–O/Ar–O) yields another class of compounds known as 'ethers', for example, CH_3OCH_3 (dimethyl ether). You may also visualise ethers as compounds formed by

substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

In this unit, we shall discuss the chemistry of three classes of compounds, namely — alcohols, phenols and ethers.

11.1 Classification

The classification of compounds makes their study systematic and hence simpler. Therefore, let us first learn how are alcohols, phenols and ethers classified?

11.1.1 Mono, Di, Tri or Polyhydric Compounds

Alcohols and phenols may be classified as mono–, di–, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:

Monohydric Dihydric Trihydric

Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

(i) *Compounds containing* $C_{sp^3}-OH$ *bond:* In this class of alcohols, the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows:

Primary, secondary and tertiary alcohols: In these three types of alcohols, the –OH group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:

Primary (1°) Secondary (2°) Tertiary (3°)

Allylic alcohols: In these alcohols, the —OH group is attached to a sp^3 hybridised carbon next to the carbon-carbon double bond, that is to an allylic carbon. For example

Primary Secondary Tertiary

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Benzylic alcohols: In these alcohols, the —OH group is attached to a sp^3—hybridised carbon atom next to an aromatic ring. For example

Primary Secondary Tertiary

Allylic and benzylic alcohols may be primary, secondary or tertiary.

(ii) *Compounds containing* $C_{sp^2}-OH$ *bond:* These alcohols contain —OH group bonded to a carbon-carbon double bond i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

Vinylic alcohol: $CH_2 = CH - OH$

Phenols:

11.1.2 Ethers

Ethers are classified as **simple** or **symmetrical**, if the alkyl or aryl groups attached to the oxygen atom are the same, and **mixed** or **unsymmetrical**, if the two groups are different. Diethyl ether, $C_2H_5OC_2H_5$, is a symmetrical ether whereas $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$ are unsymmetrical ethers.

Intext Questions

11.1 Classify the following as primary, secondary and tertiary alcohols:

(i)

(ii) $H_2C = CH - CH_2OH$

(iii) $CH_3 - CH_2 - CH_2 - OH$

(iv)

(v)

(vi)

11.2 Identify allylic alcohols in the above examples.

11.2 Nomenclature

(a) Alcohols: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, CH_3OH is methyl alcohol.

According to IUPAC system (Unit 12, Class XI), the name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'. The position of substituents are indicated by numerals. For this, the longest carbon chain (parent chain) is numbered starting at the end nearest to the hydroxyl group. The positions of the –OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached. For naming polyhydric alcohols, the 'e' of alkane is retained and the ending 'ol' is added. The number of –OH groups is indicated by adding the multiplicative prefix, di, tri, etc., before 'ol'. The positions of –OH groups are indicated by appropriate locants e.g., $HO–CH_2–CH_2–OH$ is named as ethane–1, 2-diol. Table 11.1 gives common and IUPAC names of a few alcohols as examples.

Table 11.1: Common and IUPAC names of some Alcohols

Compound	Common name	IUPAC name
$CH_3 – OH$	Methyl alcohol	Methanol
$CH_3 – CH_2 – CH_2 – OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3 – CH(OH) – CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3 – CH_2 – CH_2 – CH_2 – OH$	*n*-Butyl alcohol	Butan-1-ol
$CH_3 – CH(OH) – CH_2 – CH_3$	*sec*-Butyl alcohol	Butan-2-ol
$CH_3 – CH(OH) – CH_2 – CH_3$	Isobutyl alcohol	2-Methylpropan-1-ol
$CH_3 – C(CH_3)_2 – OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
$CH_2(OH) – CH(OH) – CH_2(OH)$	Glycerol	Propane -1, 2, 3-triol

Cyclic alcohols are named using the prefix cyclo and considering the —OH group attached to C–1.

Cyclohexanol

2-Methylcyclopentanol

(b) Phenols: The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name. As structure of phenol involves a benzene ring, in its substituted compounds the terms *ortho* (1,2- disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.

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Common name	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- and 1, 4-benzenediol.

Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

(c) Ethers: Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. For example, $CH_3OC_2H_5$ is ethylmethyl ether.

Table 11.2: Common and IUPAC names of some Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptylphenyl ether	1-Phenoxyheptane
$CH_3O-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	Methyl isopropyl ether	2-Methoxypropane
$C_6H_5-O-CH_2-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	Phenylisopentyl ether	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy--1,1-dimethylcyclohexane

If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether.

According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an –OR or –OAr group, where R and Ar represent alkyl and aryl groups, respectively. The larger (R) group is chosen as the parent hydrocarbon. The names of a few ethers are given as examples in Table 11.2.

Example 11.1 Give IUPAC names of the following compounds:

(i) $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$ (ii) $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_2CH_3$

(iii)

(iv)

Solution (i) 4-Chloro-2,3-dimethylpentan-1-ol (ii) 2-Ethoxypropane

(iii) 2,6-Dimethylphenol (iv) 1-Ethoxy-2-nitrocyclohexane

Intext Question

11.3 Name the following compounds according to IUPAC system.

(i) $CH_3-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-\overset{\overset{CH_2OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (ii) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-\overset{\overset{CH_2OH}{|}}{CH}-CH_3$

(iii)

(iv) $H_2C=CH-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3$ (v) $CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2OH$

11.3 Structures of Functional Groups

In alcohols, the oxygen of the –OH group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. Fig. 11.1 depicts structural aspects of methanol, phenol and methoxymethane.

Methanol Phenol Methoxymethane

Fig. 11.1: *Structures of methanol, phenol and methoxymethane*

The bond angle in alcohols is slightly less than the tetrahedral angle (109 -28′). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the –OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon– oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring (Section 11.4.4) and (ii) sp^2 hybridised state of carbon to which oxygen is attached.

In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (–R) groups. The C–O bond length (141 pm) is almost the same as in alcohols.

11.4 Alcohols and Phenols

11.4.1 Preparation of Alcohols

Alcohols are prepared by the following methods:

1. From alkenes

(i) *By acid catalysed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule (Unit 13, Class XI).

Mechanism

The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$H_2O + H^+ \rightarrow H_3O^+$

Step 2: Nucleophilic attack of water on carbocation.

Step 3: Deprotonation to form an alcohol.

Hydroboration - oxidation was first reported by H.C. Brown in 1959. For his studies on boron containing organic compounds, Brown shared the 1979 Nobel prize in Chemistry with G. Wittig.

(ii) *By hydroboration–oxidation*: Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp^2 carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

2. From carbonyl compounds

(i) *By reduction of aldehydes and ketones*: Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is a finely divided metal such as platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' \xrightarrow{NaBH_4} R-\underset{\underset{OH}{|}}{CH}-R'$$

The numbers in front of the reagents along the arrow indicate that the second reagent is added only when the reaction with first is complete.

(ii) *By reduction of carboxylic acids and esters*: Carboxylic acids are reduced to primary alcohols in excellent yields by lithium aluminium hydride, a strong reducing agent.

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

However, $LiAlH_4$ is an expensive reagent, and therefore, used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters (Section 11.4.4), followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

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3. *From Grignard reagents*

Alcohols are produced by the reaction of Grignard reagents (Unit 10, Class XII) with aldehydes and ketones.

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.

... (i)

$$\xrightarrow{H_2O} \; >C(R)-OH + Mg(OH)X \qquad \text{...(ii)}$$

The reaction of Grignard reagents with methanal produces a primary alcohol, with other aldehydes, secondary alcohols and with ketones, tertiary alcohols.

The overall reactions using different aldehydes and ketones are as follows:

$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

$$RCHO + R'MgX \xrightarrow{H_2O} R-CH(R')-OMgX \xrightarrow{H_2O} R-CH(R')-OH + Mg(OH)X$$

$$RCOR + R'MgX \longrightarrow R-C(R')(R)-OMgX \xrightarrow{H_2O} R-C(R')(R)-OH + Mg(OH)X$$

You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

Example 11.2

Give the structures and IUPAC names of the products expected from the following reactions:

(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute sulphuric acid.

(c) Reaction of propanone with methylmagnesium bromide followed by hydrolysis.

Solution

(a) $CH_3-CH_2-CH_2-CH_2-OH$ Butan-1-ol

(b) $CH_3-CH(OH)-CH_3$ Propan-2-ol

(c) $CH_3-C(CH_3)_2-OH$ 2-Methylpropan-2-ol

11.4.2 Preparation of Phenols

Phenol, also known as carbolic acid, was first isolated in the early nineteenth century from coal tar. Nowadays, phenol is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives by any of the following methods:

1. *From haloarenes*

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced (Unit 10, Class XII).

2. *From benzenesulphonic acid*

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol.

3. *From diazonium salts*

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($NaNO_2$ + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids (Unit 13, Class XII).

Most of the worldwide production of phenol is from cumene.

4. *From cumene*

Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.

Intext Questions

11.4 Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?

(i) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(ii)

11.5 Write structures of the products of the following reactions:

(i) $CH_3 - CH = CH_2 \xrightarrow{H_2O/H^+}$

(ii)

(iii) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{NaBH_4}$

11.4.3 Physical Properties

Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

Boiling Points

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:

It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.

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Ethanol
Molecular mass/b.p.
46/ 351 K

Methoxymethane
Molecular mass/b.p.
46/248 K

Propane
Molecular mass/b.p.
44/231 K

The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.

Solubility

Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups. Several of the lower molecular mass alcohols are miscible with water in all proportions.

Example 11.3 Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Solution (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

11.4.4 Chemical Reactions

Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as nucleophiles.

Alcohols as nucleophiles

(i)

(ii) The bond between C–O is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles

$$R\text{–}CH_2\text{–}OH + \overset{+}{H} \rightarrow R\text{–}CH_2\text{–}\overset{+}{O}H_2$$

Based on the cleavage of O–H and C–O bonds, the reactions of alcohols and phenols may be divided into two groups:

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(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

(i) Reaction with metals: Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.

$$2R{-}O{-}H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R{-}O{-}Na} + H_2$$

$$6\,CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH + 2\,Al \longrightarrow 2\left(CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}O\right)_3 Al + 3H_2$$

tert- Butyl alcohol Aluminium *tert*- butoxide

Phenol Sodium phenoxide

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.

Sodium phenoxide

The above reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are Brönsted acids i.e., they can donate a proton to a stronger base (B:).

Base Acid Conjugate acid Conjugate base

(ii) Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:

Primary Secondary Tertiary

Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.

$$\underset{\text{Base}}{R-\ddot{\bar{O}}:} + \underset{\text{Acid}}{H-\ddot{O}-H} \longrightarrow \underset{\text{Conjugate acid}}{R-O-H} + \underset{\text{Conjugate base}}{:\ddot{\bar{O}}H}$$

This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

(iii) Acidity of phenols: The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.

The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how a compound in which hydroxyl group attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group.

The ionisation of an alcohol and a phenol takes place as follows:

$$R-\ddot{O}-H \rightleftharpoons R-\ddot{O}:^{-} + H^+$$

Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of O–H bond and results in an increase in ionisation of phenols than that of alcohols. Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes

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phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.

I II III IV V

In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para* positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

The greater the pK_a *value, the weaker the acid.*

Table 11.3: pK_a Values of some Phenols and Ethanol

Compound	Formula	pK_a
o-Nitrophenol	*o*–O_2N–C_6H_4–OH	7.2
m-Nitrophenol	*m*–O_2N–C_6H_4–OH	8.3
p-Nitrophenol	*p*-O_2N–C_6H_4–OH	7.1
Phenol	C_6H_5–OH	10.0
o-Cresol	*o*-CH_3–C_6H_4–OH	10.2
m-Cresol	*m*-$CH_3C_6H_4$–OH	10.1
p-Cresol	*p*-CH_3–C_6H_4–OH	10.2
Ethanol	C_2H_5OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

Example 11.4

Arrange the following compounds in increasing order of their acid strength:
Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Solution

Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

2. *Esterification*

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

$$Ar/RO-H + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

Aspirin possesses analgesic, anti-inflammatory and antipyretic properties.

The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl (CH_3CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin.

(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

The reactions involving cleavage of C–O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

1. ***Reaction with hydrogen halides:*** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 10, Class XII).

$$ROH + HX \rightarrow R-X + H_2O$$

The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (**Lucas test**). Alcohols are soluble in Lucas reagent (conc. HCl and $ZnCl_2$) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

2. ***Reaction with phosphorus trihalides:*** Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide (Refer Unit 10, Class XII).

3. ***Dehydration:*** Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4, or catalysts such as anhydrous zinc chloride or alumina (Unit 13, Class XI).

$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[\text{Heat}]{H^+} >C=C< + H_2O$$

Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

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Secondary and tertiary alcohols are dehydrated under milder conditions. For example

$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

Thus, the relative ease of dehydration of alcohols follows the following order:

Tertiary > Secondary > Primary

The mechanism of dehydration of ethanol involves the following steps:

Tertiary carbocations are more stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.

Mechanism

Step 1: Formation of protonated alcohol.

Ethanol — Protonated alcohol (Ethyl oxonium ion)

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

Step 3: Formation of ethene by elimination of a proton.

Ethene

The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

4. *Oxidation:* Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.

Bond breaking

Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.

$$RCH_2OH \xrightarrow{\text{Oxidation}} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

Secondary alcohols are oxidised to ketones by chromic anhyride (CrO_3).

$$\underset{\textit{Sec-}\text{ alcohol}}{R-\underset{\underset{OH}{|}}{CH}-R'} \xrightarrow{CrO_3} \underset{\text{Ketone}}{R-\underset{\underset{O}{\|}}{C}-R'}$$

Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ($KMnO_4$) and elevated temperatures, cleavage of various C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.

$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[573K]{Cu} R-\underset{\underset{O}{\|}}{C}-R'$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

Biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol, mixed with methanol also called denatured alcohol. In the body, methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde (HCHO) to acid is swamped allowing time for kidneys to excrete methanol.

(c) Reactions of phenols

Following reactions are shown by phenols only.

1. *Electrophilic aromatic substitution*

In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions (Unit 13, Class XI). The –OH group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect caused by –OH group. The resonance structures are shown under acidity of phenols.

Common electrophilic aromatic substitution reactions taking place in phenol are as follows:

(i) *Nitration:* With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para* nitrophenols.

o-Nitrophenol *p*-Nitrophenol

The *ortho* and *para* isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

o-Nitrophenol (Intramolecular H-bonding) *p*-Nitrophenol (Intermolecular H-bonding)

2, 4, 6 - Trinitrophenol is a strong acid due to the presence of three electron withdrawing –NO_2 groups which facilitate the release of hydrogen ion.

With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.

2,4,6-Trinitrophenol (Picric acid)

Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved?

(ii) *Halogenation:* On treating phenol with bromine, different reaction products are formed under different experimental conditions.

(a) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.

The usual halogenation of benzene takes place in the presence of a Lewis acid, such as $FeBr_3$ (Unit 10, Class XII), which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of –OH group attached to the benzene ring.

(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.

2,4,6-Tribromophenol

Example 11.5 Write the structures of the major products expected from the following reactions:

(a) Mononitration of 3-methylphenol

(b) Dinitration of 3-methylphenol

(c) Mononitration of phenyl methanoate.

Solution The combined influence of –OH and $-CH_3$ groups determine the position of the incoming group.

2. *Kolbe's reaction*

Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.

2-Hydroxybenzoic acid
(Salicylic acid)

3. *Reimer-Tiemann reaction*

On treating phenol with chloroform in the presence of sodium hydroxide, a –CHO group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*.

The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.

Intermediate

Salicylaldehyde

4. *Reaction of phenol with zinc dust*

Phenol is converted to benzene on heating with zinc dust.

5. *Oxidation*

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.

benzoquinone

Intext Questions

11.6 Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl –$ZnCl_2$ (b) HBr and (c) $SOCl_2$.

(i) Butan-1-ol (ii) 2-Methylbutan-2-ol

11.7 Predict the major product of acid catalysed dehydration of

(i) 1-methylcyclohexanol and (ii) butan-1-ol

11.8 *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

11.9 Write the equations involved in the following reactions:

(i) Reimer - Tiemann reaction (ii) Kolbe's reaction

11.5 Some Commercially Important Alcohols

Methanol and ethanol are among the two commercially important alcohols.

1. Methanol

Methanol, CH_3OH, also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of ZnO – Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\ \text{atm} \\ 573\text{-}673\ \text{K}}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

2. Ethanol

Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.

Ingestion of ethanol acts on the central nervous system. In moderate amounts, it affects judgment and lowers inhibitions. Higher concentrations cause nausea and loss of consciousness. Even at higher concentrations, it interferes with spontaneous respiration and can be fatal.

The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 percent. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.

Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as **denaturation** of alcohol.

Nowadays, large quantities of ethanol are obtained by hydration of ethene (Section 11.4).

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11.6 Ethers

11.6.1 Preparation of Ethers

Diethyl ether has been used widely as an inhalation anaesthetic. But due to its slow effect and an unpleasant recovery period, it has been replaced, as an anaesthetic, by other compounds.

1. *By dehydration of alcohols*

Alcohols undergo dehydration in the presence of protic acids (H_2SO_4, H_3PO_4). The formation of the reaction product, alkene or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in the presence of sulphuric acid at 443 K. At 413 K, ethoxyethane is the main product.

$$CH_3CH_2OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2$$

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$$

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

(i) $CH_3{-}CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + H^+ \longrightarrow CH_3{-}CH_2{-}\overset{+}{\ddot{\underset{\cdot\cdot}{O}}}(H){-}H$

(ii) $CH_3CH_2{-}\ddot{O}(H){:} + CH_3{-}CH_2{-}\overset{+}{O}(H)_2 \longrightarrow CH_3CH_2{-}\overset{+}{O}(H){-}CH_2CH_3 + H_2O$

(iii) $CH_3CH_2{-}\overset{+}{O}(H){-}CH_2CH_3 \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + H^+$

Acidic dehydration of alcohols, to give an alkene is also associated with substitution reaction to give an ether.

The method is suitable for the preparation of ethers having primary alkyl groups only. The alkyl group should be unhindered and the temperature be kept low. Otherwise the reaction favours the formation of alkene. The reaction follows S_N1 pathway when the alcohol is secondary or tertiary about which you will learn in higher classes. However, the dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and as a consequence, alkenes are easily formed.

Can you explain why is bimolecular dehydration not appropriate for the preparation of ethyl methyl ether?

2. *Williamson synthesis*

Alexander William Williamson (1824–1904) was born in London of Scottish parents. In 1849, he became Professor of Chemistry at University College, London.

It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

$$R{-}X + R'{-}\ddot{\underset{\cdot\cdot}{O}}\,Na \longrightarrow R{-}\ddot{\underset{\cdot\cdot}{O}}{-}R' + Na\,X$$

Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide.

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Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(CH_3)_3C–Br$ gives exclusively 2-methylpropene.

2-Methylpropene

It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

Example 11.6 The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

(i) What would be the major product of this reaction ?

(ii) Write a suitable reaction for the preparation of t-butylethyl ether.

Solution (i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution.

(ii)

Phenols are also converted to ethers by this method. In this, phenol is used as the phenoxide moiety.

11.6.2 Physical Properties

The C-O bonds in ethers are polar and thus, ethers have a net dipole moment. The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling points of alcohols as shown in the following cases:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

The miscibility of ethers with water resembles those of alcohols of the same molecular mass. Both ethoxyethane and butan-1-ol are miscible to almost the same extent i.e., 7.5 and 9 g per 100 mL water, respectively while pentane is essentially immiscible with water. Can you explain this observation ? This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:

11.6.3 Chemical Reactions

1. Cleavage of C–O bond in ethers

Ethers are the least reactive of the functional groups. The cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.

$$R\text{–}O\text{–}R + HX \longrightarrow RX + R\text{–}OH$$

$$R\text{–}OH + HX \longrightarrow R\text{–}X + H_2O$$

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.

Ethers with two different alkyl groups are also cleaved in the same manner.

$$R\text{–}O\text{–}R' + HX \longrightarrow R\text{–}X + R'\text{–}OH$$

The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl. The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

Mechanism

The reaction of an ether with concentrated HI starts with protonation of ether molecule.

Step 1:

The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

Step 2:

Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step 3:

However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.

It is because in step 2 of the reaction, the departure of leaving group ($HO–CH_3$) creates a more stable carbocation [$(CH_3)_3C^+$], and the reaction follows S_N1 mechanism.

In case of anisole, methylphenyl oxonium ion, $C_6H_5-\overset{+}{\underset{H}{O}}-CH_3$ is formed by protonation of ether. The bond between $O–CH_3$ is weaker than the bond between $O–C_6H_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character.

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Therefore the attack by I^- ion breaks O–CH_3 bond to form CH_3I. Phenols do not react further to give halides because the sp^2 hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

Example 11.7

Give the major products that are formed by heating each of the following ethers with HI.

(i) $CH_3-CH_2-CH(CH_3)-CH_2-O-CH_2-CH_3$ (ii) $CH_3-CH_2-CH_2-O-C(CH_3)_2-CH_2-CH_3$

(iii)

Solution

(i) $CH_3-CH_2-CH(CH_3)-CH_2OH + CH_3CH_2I$ (ii) $CH_3CH_2CH_2OH + CH_3CH_2-C(CH_3)_2-I$

(iii)

2. *Electrophilic substitution*

The alkoxy group (-OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.

(i) *Halogenation*: Phenylalkyl ethers undergo usual halogenation in the benzene ring, *e.g.*, anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. *Para* isomer is obtained in 90% yield.

(ii) *Friedel-Crafts reaction*: Anisole undergoes Friedel-Crafts reaction, *i.e.*, the alkyl and acyl groups are introduced at *ortho* and *para* positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.

2-Methoxy-toluene (Minor) 4-Methoxy-toluene (Major)

Ethanoyl chloride 2-Methoxy-acetophenone (Minor) 4-Methoxy-acetophenone (Major)

(iii) *Nitration*: Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of *ortho* and *para* nitroanisole.

2-Nitroanisole (Minor) 4-Nitroanisole (Major)

Intext Questions

11.10 Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

11.11 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(i)

+ CH_3ONa

(ii)

+ CH_3Br

11.12 Predict the products of the following reactions:

(i) $CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow$

(ii)

$+ \quad HBr \longrightarrow$

(iii)

$\xrightarrow[\text{Conc. } HNO_3]{\text{Conc. } H_2SO_4}$

(iv) $(CH_3)_3 C - OC_2H_5 \xrightarrow{HI}$

Summary

Alcohols and **phenols** are classified (i) on the basis of the number of hydroxyl groups and (ii) according to the hybridisation of the carbon atom, sp^3 or sp^2 to which the –OH group is attached. **Ethers** are classified on the basis of groups attached to the oxygen atom.

Alcohols may be prepared (1) by hydration of alkenes (i) in presence of an acid and (ii) by hydroboration-oxidation reaction (2) from carbonyl compounds by (i) catalytic reduction and (ii) the action of Grignard reagents. Phenols may be prepared by (1) substitution of (i) halogen atom in haloarenes and (ii) sulphonic acid group in aryl sulphonic acids, by –OH group (2) by hydrolysis of diazonium salts and (3) industrially from cumene.

Alcohols are higher boiling than other classes of compounds, namely hydrocarbons, ethers and haloalkanes of comparable molecular masses. The ability of alcohols, phenols and ethers to form intermolecular hydrogen bonding with water makes them soluble in it.

Alcohols and phenols are acidic in nature. **Electron withdrawing groups** in phenol increase its acidic strength and **electron releasing groups** decrease it.

Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation.

The presence of –OH group in phenols activates the aromatic ring towards **electrophilic substitution** and directs the incoming group to *ortho* and *para* positions due to resonance effect. **Reimer-Tiemann reaction** of phenol yields salicylaldehyde. In presence of sodium hydroxide, phenol generates phenoxide ion which is even more reactive than phenol. Thus, in alkaline medium, phenol undergoes **Kolbe's reaction**.

Ethers may be prepared by (i) dehydration of alcohols and (ii) **Williamson synthesis**. The boiling points of ethers resemble those of alkanes while their solubility is comparable to those of alcohols having same molecular mass. The C–O bond in ethers can be cleaved by hydrogen halides. In electrophilic substitution, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions.

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Exercises

11.1 Write IUPAC names of the following compounds:

(i)

(ii)

(iii)

(iv)

(v)

(vi)

(vii)

(viii)

(ix)

(x) $C_6H_5–O–C_2H_5$

(xi) $C_6H_5–O–C_7H_{15}$(n–)

(xii)

11.2 Write structures of the compounds whose IUPAC names are as follows:

(i) 2-Methylbutan-2-ol
(ii) 1-Phenylpropan-2-ol
(iii) 3,5-Dimethylhexane –1, 3, 5-triol
(iv) 2,3 – Diethylphenol
(v) 1 – Ethoxypropane
(vi) 2-Ethoxy-3-methylpentane
(vii) Cyclohexylmethanol
(viii) 3-Cyclohexylpentan-3-ol
(ix) Cyclopent-3-en-1-ol
(x) 3-Chloromethylpentan-1-ol.

11.3 (i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.

(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

11.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

11.5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

11.6 What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

11.7 Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.

11.8 While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

11.9 Give the equations of reactions for the preparation of phenol from cumene.

11.10 Write chemical reaction for the preparation of phenol from chlorobenzene.

11.11 Write the mechanism of hydration of ethene to yield ethanol.

11.12 You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

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11.13 Show how will you synthesise:

(i) 1-phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by an S_N2 reaction.

(iii) pentan-1-ol using a suitable alkyl halide?

11.14 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

11.15 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol ?

11.16 Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

11.17 Give equations of the following reactions:

(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(ii) Bromine in CS_2 with phenol.

(iii) Dilute HNO_3 with phenol.

(iv) Treating phenol wih chloroform in presence of aqueous NaOH.

11.18 Explain the following with an example.

(i) Kolbe's reaction.

(ii) Reimer-Tiemann reaction.

(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

11.19 Write the mechanism of acid dehydration of ethanol to yield ethene.

11.20 How are the following conversions carried out?

(i) Propene $\rightarrow$ Propan-2-ol.

(ii) Benzyl chloride $\rightarrow$ Benzyl alcohol.

(iii) Ethyl magnesium chloride $\rightarrow$ Propan-1-ol.

(iv) Methyl magnesium bromide $\rightarrow$ 2-Methylpropan-2-ol.

11.21 Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan-2-ol to propene.

(vi) Butan-2-one to butan-2-ol.

11.22 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

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11.23 Give IUPAC names of the following ethers:

(i) $C_2H_5OCH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (ii) $CH_3OCH_2CH_2Cl$ (iii) $O_2N-C_6H_4-OCH_3$(*p*)

(iv) $CH_3CH_2CH_2OCH_3$ (v) (vi)

11.24 Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

(i) 1-Propoxypropane (ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

11.25 Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

11.26 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

11.27 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

11.28 Write the equation of the reaction of hydrogen iodide with:
(i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether.

11.29 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

11.30 Write the mechanism of the reaction of HI with methoxymethane.

11.31 Write equations of the following reactions:

(i) Friedel-Crafts reaction – alkylation of anisole.

(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

(iv) Friedel-Craft's acetylation of anisole.

11.32 Show how would you synthesise the following alcohols from appropriate alkenes?

(i) (ii)

(iii) (iv)

11.33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

Give a mechanism for this reaction.
(Hint : The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.

Answers to Some Intext Questions

11.1 Primary alcohols (i), (ii), (iii)

Secondary alcohols (iv) and (v)

Tertiary alcohols (vi)

11.2 Allylic alcohols (ii) and (vi)

11.3 (i) 3-Chloromethyl-2-isopropylpentan-1-ol

(ii) 2, 5-Dimethylhexane-1,3-diol

(iii) 3-Bromocyclohexanol

(iv) Hex-1-en-3-ol

(v) 2-Bromo-3-methylbut-2-en-1-ol

11.4 (i)

(ii)

11.5 (i) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ (ii)

(iii) $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2OH$

11.7 (i) 1-Methylcyclohexene

(ii) But-1-ene

11.10

2-Ethoxy-3-methylpentane

11.11 (ii)

11.12 (i) $CH_3CH_2CH_2OH + CH_3Br$

(ii)

$+ \quad C_2H_5Br$

(iii)

+

(iv) $(CH_3)_3\,C - I + C_2H_5OH$

Unit

12

Aldehydes, Ketones and Carboxylic Acids

Objectives

After studying this Unit, you will be able to

- write the common and IUPAC names of aldehydes, ketones and carboxylic acids;
- write the structures of the compounds containing functional groups namely carbonyl and carboxyl groups;
- describe the important methods of preparation and reactions of these classes of compounds;
- correlate physical properties and chemical reactions of aldehydes, ketones and carboxylic acids, with their structures;
- explain the mechanism of a few selected reactions of aldehydes and ketones;
- understand various factors affecting the acidity of carboxylic acids and their reactions;
- describe the uses of aldehydes, ketones and carboxylic acids.

Carbonyl compounds are of utmost importance to organic chemistry. They are constituents of fabrics, flavourings, plastics and drugs.

In the previous Unit, you have studied organic compounds with functional groups containing carbon-oxygen single bond. In this Unit, we will study about the organic compounds containing carbon-oxygen double bond (>C=O) called carboxyl group, which is one of the most important functional groups in organic chemistry.

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively. The general formulas of these classes of compounds are given below:

Aldehyde

Ketone

Carboxylic acid

Acyl halide; X = (Halogen)

Acid anhydride

Ester

Amide

Aldehydes, ketones and carboxylic acids are widespread in plants and animal kingdom. They play an important role in biochemical processes of life. They add fragrance and flavour to nature, for example, vanillin (from vanilla beans), salicylaldehyde (from meadow sweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.

Vanillin

Salicylaldehyde

Cinnamaldehyde

They are used in many food products and pharmaceuticals to add flavours. Some of these families are manufactured for use as solvents (i.e., acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics, etc.

12.1 Nomenclature and Structure of Carbonyl Group

12.1.1 Nomenclature

I. Aldehydes and ketones

Aldehydes and ketones are the simplest and most important carbonyl compounds.

There are two systems of nomenclature of aldehydes and ketones.

(a) Common names

Aldehydes and ketones are often called by their common names instead of IUPAC names. The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids [Section 12.6.1] by replacing the ending –*ic* of acid with aldehyde. At the same time, the names reflect the Latin or Greek term for the original source of the acid or aldehyde. The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ, δ, etc. The α-carbon being the one directly linked to the aldehyde group, β-carbon the next, and so on. For example

CH_3CHO

Acetaldehyde

Benzaldehyde

β-Bromobutyraldehyde

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The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. The locations of substituents are indicated by Greek letters, α α′, β β′ and so on beginning with the carbon atoms next to the carbonyl group, indicated as αα′. Some ketones have historical common names, the simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone. For example

Acetone Acetophenone Propiophenone Benzophenone

(b) IUPAC names

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *–e* with *–al* and *–one* respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain. The same applies to cyclic ketones, where the carbonyl carbon is numbered one. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane. The numbering of the ring carbon atoms start from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzenecarbaldehyde. However, the common name benzaldehyde is also accepted by IUPAC. Other aromatic aldehydes are hence named as substituted benzaldehydes.

Ethanal

4-Bromo-3-methylheptanal

3-Methylcyclopentanone

Cyclohexanecarbaldehyde

Pent-2-enal

1-Phenylpropan-1-one

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3-Oxopentanal

2,4-Dimethylpentan-3-one

4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde

Propane–1,2,3-tricarbaldehyde

Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.

The common and IUPAC names of some aldehydes and ketones are given in Table 12.1.

Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$(CH_3)_2CHCHO$	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexane	3-Methylcyclohexanecarbaldehyde
$CH_3CH(OCH_3)CHO$	α-Methoxypropionaldehyde	2-Methoxypropanal
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_2{=}CHCHO$	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C{=}CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

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12.1.2 Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its *p*-orbital and forms a π-bond with oxygen by overlap with *p*-orbital of an oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane. The bond angles are approximately 120 as expected of a trigonal coplanar structure (Figure 12.1).

Fig.12.1 *Orbital diagram for the formation of carbonyl group*

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moments and are polar than ethers. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structures as shown.

Intext Questions

12.1 Write the structures of the following compounds.

(i) α-Methoxypropionaldehyde
(ii) 3-Hydroxybutanal
(iii) 2-Hydroxycyclopentane carbaldehyde
(iv) 4-Oxopentanal
(v) Di-sec. butyl ketone
(vi) 4-Fluoroacetophenone

12.2 Preparation of Aldehydes and Ketones

Some important methods for the preparation of aldehydes and ketones are as follows:

12.2.1 Preparation of Aldehydes and Ketones

1. By oxidation of alcohols

Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively (Unit 11, Class XII).

2. By dehydrogenation of alcohols

This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively (Unit 11, Class XII).

3. From hydrocarbons

(*i*) *By ozonolysis of alkenes:* As we know, ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes,

ketones or a mixture of both depending on the substitution pattern of the alkene (Unit 13, Class XI).

(*ii*) *By hydration of alkynes:* Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction (Unit 13, Class XI).

12.2.2 Preparation of Aldehydes

1. From acyl chloride (acid chloride)

Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**.

Benzoyl chloride Benzaldehyde

2. From nitriles and esters

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

This reaction is called **Stephen** reaction.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:

$$RCN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} R\text{-}CHO$$

$$CH_3 — CH{=}CH\text{-}CH_2CH_2\text{-}CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} CH_3 — CH{=}CH\text{-}CH_2CH_2\text{-}CHO$$

Similarly, esters are also reduced to aldehydes with DIBAL-H.

$$CH_3(CH_2)_9 — \overset{O}{\overset{||}{C}} — OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3(CH_2)_9 — \overset{O}{\overset{||}{C}} — H$$

3. From hydrocarbons

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

(*i*) *By oxidation of methylbenzene*

Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose.

(a) Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

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This reaction is called **Etard reaction**.

(b) Use of chromic oxide (CrO_3): Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.

(ii) By side chain chlorination followed by hydrolysis

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.

(iii) By Gatterman – Koch reaction

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.

This reaction is known as **Gatterman-Koch** reaction.

12.2.3 Preparation of Ketones

1. From acyl chlorides

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

$$2\ R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$2\ R'-\underset{\underset{O}{\|}}{C}-Cl + R_2Cd \longrightarrow 2\ R'-\underset{\underset{O}{\|}}{C}-R + CdCl_2$$

2. *From nitriles*

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.

Propiophenone
(1-Phenylpropanone)

3. *From benzene or substituted benzenes*

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.

Example 12.1 Give names of the reagents to bring about the following transformations:

(i) Hexan-1-ol to hexanal
(ii) Cyclohexanol to cyclohexanone
(iii) *p*-Fluorotoluene to *p*-fluorobenzaldehyde
(iv) Ethanenitrile to ethanal
(v) Allyl alcohol to propenal
(vi) But-2-ene to ethanal

Solution

(i) $C_5H_5NH^+CrO_3Cl^-$(PCC)
(ii) $K_2Cr_2O_7$ in acidic medium
(iii) CrO_3 in the presence of acetic anhydride/ 1. CrO_2Cl_2 2. HOH
(iv) (Diisobutyl)aluminium hydride (DIBAL-H)
(v) PCC
(vi) O_3/H_2O-Zn dust

Intext Question

12.2 Write the structures of products of the following reactions;

(i)

(ii) $(C_6H_5CH_2)_2Cd + 2\ CH_3COCl \rightarrow$

(iii) $H_3C{-}C{\equiv}C{-}H \xrightarrow{Hg^{2+},\ H_2SO_4}$

(iv)

12.3 Physical Properties

The physical properties of aldehydes and ketones are described as follows.

Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. The following compounds of molecular masses 58 and 60 are ranked in order of increasing boiling points.

	b.p.(K)	Molecular Mass
n-Butane	273	58
Methoxyethane	281	60
Propanal	322	58
Acetone	329	58
Propan-1-ol	370	60

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water.

However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

Example 12.2

Arrange the following compounds in the increasing order of their boiling points:

$CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, H_5C_2-O-C_2H_5, $CH_3CH_2CH_2CH_2CH_3$

Solution

The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. *n*-Pentane molecules have only weak **van der Waals forces**. Hence increasing order of boiling points of the given compounds is as follows:

$CH_3CH_2CH_2CH_2CH_3 < H_5C_2$-O-$C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$

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Intext Question

12.3 Arrange the following compounds in increasing order of their boiling points.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

12.4 Chemical Reactions

Since aldehydes and ketones both possess the carbonyl functional group, they undergo similar chemical reactions.

1. Nucleophilic addition reactions

Contrary to electrophilic addition reactions observed in alkenes (refer Unit 13, Class XI), the aldehydes and ketones undergo nucleophilic addition reactions.

(i) Mechanism of nucleophilic addition reactions

A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon (Fig. 12.2). The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond as shown in Fig. 12.2.

Fig.12.2: *Nucleophilic attack on carbonyl carbon*

(ii) Reactivity

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former.

Example 12.3 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Solution The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

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(iii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:

(a) *Addition of hydrogen cyanide (HCN)*: Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

Cyanohydrins are useful synthetic intermediates.

(b) *Addition of sodium hydrogensulphite:* Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products.

The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.

(c) *Addition of Grignard reagents:* (refer Unit 11, Class XII).

(d) *Addition of alcohols:* Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give *a gem*-dialkoxy compound known as acetal as shown in the reaction.

Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals.

Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating

the nucleophilic attack of ethylene glycol. Acetals and ketals are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

(e) *Addition of ammonia and its derivatives*: Nucleophiles, such as ammonia and its derivatives H_2N-Z add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form >C=N-Z.

Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	>C=NH	Imine
-R	Amine	>C=NR	Substituted imine (Schiff's base)
—OH	Hydroxylamine	>C=N–OH	Oxime
—NH_2	Hydrazine	>C=N–NH_2	Hydrazone
—HN—C_6H_5	Phenylhydrazine	>C=N-NH—C_6H_5	Phenylhydrazone
—HN—$C_6H_3(O_2N)_2$	2,4-Dinitrophenyl-hydrazine	>C=N-NH—$C_6H_3(O_2N)_2$	2,4 Dinitrophenyl-hydrazone
—NH—C(=O)—NH_2	Semicarbazide	>C=N-NH—C(=O)—NH_2	Semicarbazone

* *2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.*

2. Reduction

(i) *Reduction to alcohols:* Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) as well as by catalytic hydrogenation (Unit 11, Class XII).

(ii) *Reduction to hydrocarbons:* The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and concentrated hydrochloric acid [**Clemmensen**

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reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).

$$>C{=}O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >CH_2 + H_2O \qquad \text{(Clemmensen reduction)}$$

$$>C{=}O \xrightarrow[-H_2O]{NH_2NH_2} >C{=}NNH_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$$

(Wolff-Kishner rduction)

3. *Oxidation*

Bernhard Tollens (1841-1918) was a Professor of Chemistry at the University of Gottingen, Germany.

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.

$$\text{R-CHO} \xrightarrow{[O]} \text{R-COOH}$$

Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

$$\overset{1}{R{-}CH_2}{-}\overset{2}{\underset{\underset{O}{\|}}{C}}{-}\overset{3}{CH_2}\text{-}R' \xrightarrow{[O]} \text{R-COOH} + \text{R'-}CH_2\text{COOH}$$

(By cleavage of C_1-C_2 bond)

+

$$\text{R-}CH_2\text{COOH} + \text{R'-COOH}$$

(By cleavage of C_2-C_3 bond)

The mild oxidising agents given below are used to distinguish aldehydes from ketones:

(i) *Tollens' test:* On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

$$\text{RCHO} + 2[Ag(NH_3)_2]^+ + 3\,\bar{O}H \longrightarrow \text{RCO}\bar{O} + 2Ag + 2H_2O + 4NH_3$$

(ii) *Fehling's test:* Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

$$\text{R-CHO} + 2Cu^{2+} + 5\bar{O}H \longrightarrow \text{RCO}\bar{O} + \underset{\text{Red-brown ppt}}{Cu_2O} + 3H_2O$$

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(iii) Oxidation of methyl ketones by haloform reaction: Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule.

Iodoform reaction with sodium hypoiodite is also used for detection of CH_3CO group or $CH_3CH(OH)$ group which produces CH_3CO group on oxidation.

Example 12.4 An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

Solution (A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring.

Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows:

C_8H_8O 2, 4-Dinitrophenylhydrazine 2, 4-DNP derivative

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4. *Reactions due to a-hydrogen*

Acidity of α-hydrogens of aldehydes and ketones: The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-hydrogen.

The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

(i) *Aldol condensation:* Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively. This is known as **Aldol reaction.**

The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give α,β-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation.** Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

(*ii*) *Cross aldol condensation:* When aldol condensation is carried out between two different aldehydes and / or ketones, it is called **cross aldol condensation**. If both of them contain α-hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.

Ketones can also be used as one component in the cross aldol reactions.

1, 3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

5. *Other reactions*

(*i*) *Cannizzaro reaction:* Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

Formaldehyde Methanol Potassium formate

Benzaldehyde Benzyl alcohol Sodium benzoate

(*ii*) *Electrophilic substitution reaction*: Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.

Benzaldehyde *m*-Nitrobenzaldehyde

Intext Questions

12.4 Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(i) Ethanal, Propanal, Propanone, Butanone.

(ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

Hint: Consider steric effect and electronic effect.

12.5 Predict the products of the following reactions:

(i)

(ii)

(iii) $R\text{-}CH{=}CH\text{-}CHO + NH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}NH_2 \xrightarrow{H^+}$

(iv)

12.5 Uses of Aldehydes and Ketones

In chemical industry aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products. Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products. Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs. Benzaldehyde is used in perfumery and in dye industries. Acetone and ethyl methyl ketone are common industrial solvents. Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

Carboxylic Acids

Carbon compounds containing a carboxyl functional group, –COOH are called carboxylic acids. The carboxyl group, consists of a *carbonyl* group attached to a *hydroxyl* group, hence its name *carboxyl*. Carboxylic acids may be aliphatic (RCOOH) or aromatic (ArCOOH) depending on the group, alkyl or aryl, attached to carboxylic carbon. Large number of carboxylic acids are found in nature. Some higher members of aliphatic carboxylic acids (C_{12} – C_{18}) known as **fatty acids,** occur in natural fats as esters of glycerol. Carboxylic acids serve as starting material for several other important organic compounds such as anhydrides, esters, acid chlorides, amides, etc.

12.6 Nomenclature and Structure of Carboxyl Group

12.6.1 Nomenclature

Since carboxylic acids are amongst the earliest organic compounds to be isolated from nature, a large number of them are known by their common names. The common names end with the suffix –*ic* acid and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: *formica* means ant), acetic acid (CH_3COOH) from vinegar (Latin: *acetum*, means vinegar), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin: *butyrum,* means butter).

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –*e* in the name of the corresponding alkane with – *oic acid*. In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the ending –*e* of the alkane is retained. The number of carboxyl groups are indicated by adding the multiplicative prefix, *di*, *tri*, etc. to the term **oic**. The position of –COOH groups are indicated by the arabic numeral before the multiplicative prefix. Some of the carboxylic acids along with their common and IUPAC names are listed in Table 12.3.

Table 12.3 Names and Structures of Some Carboxylic Acids

Structure	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC -CH_2-COOH	Malonic acid	Propanedioic acid
HOOC -$(CH_2)_2$-COOH	Succinic acid	Butanedioic acid
HOOC -$(CH_2)_3$-COOH	Glutaric acid	Pentanedioic acid
HOOC -$(CH_2)_4$-COOH	Adipic acid	Hexanedioic acid
HOOC -CH_2-CH(COOH)-CH_2-COOH	–	Propane-1, 2, 3-tricarboxylic acid

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	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

12.6.2 Structure of Carboxyl Group

In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120 . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:

Intext Question

12.6 Give the IUPAC names of the following compounds:

(i) Ph CH_2CH_2COOH (ii) $(CH_3)_2C{=}CHCOOH$

(iii)

(iv)

12.7 Methods of Preparation of Carboxylic Acids

Some important methods of preparation of carboxylic acids are as follows.

1. *From primary alcohols and aldehydes*

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media.

$$RCH_2OH \xrightarrow[2.\ H_3\overset{+}{O}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{CrO_3\text{-}H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

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Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents (Section 12.4).

2. *From alkylbenzenes*

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to the carboxyl group irrespective of length of the side chain. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected. Suitably substituted alkenes are also oxidised to carboxylic acids with these oxidising reagents (refer Unit 13, Class XI).

Benzoic acid

Benzoic acid

3. *From nitriles and amides*

Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or $\bar{O}H$ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

Ethanamide Ethanoic acid

Benzamide Benzoic acid

4. *From Grignard reagents*

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.

As we know, the Grignard reagents and nitriles can be prepared from alkyl halides (refer Unit 10, Class XII). The above methods

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(3 and 4) are useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (ascending the series).

5. *From acyl halides and anhydrides*

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acid(s) with water.

$$RCOCl \xrightarrow{H_2O} RCOOH + \bar{C}l$$

$$RCOCl \xrightarrow{\bar{O}H/H_2O} RCOO^- + \bar{C}l \xrightarrow{H_3O^+} RCOOH$$

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2\ C_6H_5COOH}$$

$$\underset{\text{Benzoic ethanoic anhydride}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

6. *From esters*

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.

Ethyl benzoate Benzoic acid

$$\underset{\text{Ethyl butanoate}}{CH_3CH_2CH_2COOC_2H_5} \xrightleftharpoons{NaOH} CH_3CH_2CH_2COONa + C_2H_5OH$$

$$CH_3CH_2CH_2COONa \xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

Example 12.5

Write chemical reactions to affect the following transformations:

(i) Butan-1-ol to butanoic acid

(ii) Benzyl alcohol to phenylethanoic acid

(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid

(iv) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid

(v) Cyclohexene to hexane-1,6-dioic acid

(vi) Butanal to butanoic acid.

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Solution

(i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} CH_3CH_2CH_2COOH$

Butan-1-ol → Butanoic acid

(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN$

Benzyl alcohol → Benzyl bromide → Benzyl cyanide

$\xrightarrow[\Delta]{H_3O^+} C_6H_5CH_2COOH$

Phenylethanoic acid

(iii)

3-Nitrobromobenzene → 3-Nitrobenzoic acid

(iv)

4-Methylacetophenone → Dipotassium benzene-1, 4-dicarboxylate → Benzene-1, 4-dicarboxylic acid (Terephthalic acid)

(v)

Cyclohexene → Hexane-1, 6-dioic acid (Adipic acid)

(vi) $CH_3CH_2CH_2CHO \xrightarrow[\text{(Tollens' reagent)}]{\text{Ammoniacal } AgNO_3} CH_3CH_2CH_2COOH$

Butanal → Butanoic acid

Intext Question

12.7 Show how each of the following compounds can be converted to benzoic acid.

(i) Ethylbenzene (ii) Acetophenone

(iii) Bromobenzene (iv) Phenylethene (Styrene)

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12.8 Physical Properties

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility. Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

In vapour state or in aprotic solvent

Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Hydrogen bonding of RCOOH with H_2O

12.9 Chemical Reactions

The reaction of carboxylic acids are classified as follows:

12.9.1 Reactions Involving Cleavage of O–H Bond

Acidity

Reactions with metals and alkalies

The carboxylic acids like alcohols evolve hydrogen with electropositive metals and form salts with alkalies similar to phenols. However, unlike phenols they react with weaker bases such as carbonates and hydrogencarbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.

$$2R\text{-}COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R\text{-}CO\bar{O}Na^+} + H_2$$

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}CO\bar{O}Na^+ + H_2O$$

$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}CO\bar{O}Na^+ + H_2O + CO_2$$

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.

For the above reaction:

$$K_{eq} = \frac{[H_3\overset{+}{O}]\,[RCO\overset{-}{O}]}{[H_2O]\,[RCOOH]} \qquad K_a = K_{eq}\,[H_2O] = \frac{[H_3\overset{+}{O}]\,[RCO\overset{-}{O}]}{[RCOOH]}$$

where K_{eq}, is equilibrium constant and K_a is the acid dissociation constant.

For convenience, the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

$$pK_a = -\log K_a$$

The pK_a of hydrochloric acid is –7.0, where as pK_a of trifluoroacetic acid (the strongest organic acid), benzoic acid and acetic acid are 0.23, 4.19 and 4.76, respectively.

Smaller the pK_a, the stronger the acid (the better it is as a proton donor). Strong acids have pK_a values < 1, the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15, and extremely weak acids have pK_a values >15.

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols (pK_a is ~16 for ethanol and 10 for phenol). In fact, carboxylic acids are amongst the most acidic organic compounds you have studied so far. You already know why phenols are more acidic than alcohols. The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion (Unit 11, Class XII). Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.

Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid

Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is

$$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$$

Thus, the following acids are arranged in order of decreasing acidity (based on pK_a values):

$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NC\text{-}CH_2COOH >$

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH >$
(continue)

$C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$
(continue)

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:

This is because of greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

4-Methoxy benzoic acid (pK_a = 4.46) | Benzoic acid (pK_a = 4.19) | 4-Nitrobenzoic acid (pK_a = 3.41)

12.9.2 Reactions Involving Cleavage of C–OH Bond

1. Formation of anhydride

Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride.

Ethanoic acid | Ethanoic anhydride

2. Esterification

Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.

$$RCOOH + R'OH \xrightleftharpoons{H^+} RCOOR' + H_2O$$

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Mechanism of esterification of carboxylic acids: The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-^{+}OH_2$ group, which, being a better leaving group, is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.

3. *Reactions with PCl_5, PCl_3 and $SOCl_2$*

The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl_5, PCl_3 or $SOCl_2$. Thionyl chloride ($SOCl_2$) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

4. *Reaction with ammonia*

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3\overset{-}{C}OO\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

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12.9.3 Reactions Involving –COOH Group

1. Reduction

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

$$\text{R-COOH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ether or } B_2H_6} \text{R-CH}_2\text{OH}$$

2. Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

$$\text{R-COONa} \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} \text{R-H} + Na_2CO_3$$

Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis** (Unit 13, Class XI).

12.9.4 Substitution Reactions in the Hydrocarbon Part

1. Halogenation

Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction.**

$$\text{R-CH}_2\text{-COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} \text{R-CH(X)-COOH}$$

X = Cl, Br

α – Halocarboxylic acid

2. *Ring substitution*

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).

m-Nitrobenzoic acid

m-Bromobenzoic acid

Intext Question

12.8 Which acid of each pair shown here would you expect to be stronger?

(i) CH_3CO_2H or CH_2FCO_2H (ii) CH_2FCO_2H or CH_2ClCO_2H

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

(iv)

12.10 Uses of Carboxylic Acids

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries. Ethanoic acid is used as solvent and as vinegar in food industry. Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.

Summary

Aldehydes, **ketones** and **carboxylic acids** are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules. Therefore, they boil at higher temperatures than the hydrocarbons and weakly polar compounds such as ethers of comparable molecular masses. The lower members are more soluble in water because they form hydrogen bonds with water. The higher members, because of large size of hydrophobic chain of carbon atoms, are insoluble in water but soluble in common organic solvents. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled or selective reduction of acyl halides. Aromatic aldehydes may also be prepared by oxidation of (i) methylbenzene with chromyl chloride or CrO_3 in the presence of acetic anhydride, (ii) formylation of arenes with carbon monoxide and hydrochloric acid in the presence of anhydrous aluminium chloride, and (iii) cuprous chloride or by hydrolysis of benzal chloride. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Ketones are also prepared by reaction of acyl chloride with dialkylcadmium. A good method for the preparation of aromatic ketones is the **Friedel-Crafts acylation** of aromatic hydrocarbons with acyl chlorides or anhydrides. Both aldehydes and ketones can be prepared by ozonolysis of alkenes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group with a number of nucleophiles such as, HCN, $NaHSO_3$, alcohols (or diols),

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ammonia derivatives, and **Grignard reagents**. The α-hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one α-hydrogen, undergo A**ldol condensation** in the presence of a base to give α-hydroxyaldehydes (aldol) and α-hydroxyketones(ketol), respectively. Aldehydes having no α-hydrogen undergo **Cannizzaro reaction** in the presence of concentrated alkali. Aldehydes and ketones are reduced to alcohols with $NaBH_4$, $LiAlH_4$, or by catalytic hydrogenation. The carbonyl group of aldehydes and ketones can be reduced to a methylene group by **Clemmensen reduction** or **Wolff-Kishner reduction**. Aldehydes are easily oxidised to carboxylic acids by mild oxidising reagents such as **Tollens' reagent** and **Fehling's reagent**. These oxidation reactions are used to distinguish aldehydes from ketones. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and alkenes by hydrolysis of nitriles, and by treatment of Grignard reagents with carbon dioxide. Aromatic carboxylic acids are also prepared by side-chain oxidation of alkylbenzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols. Carboxylic acids are reduced to primary alcohols with $LiAlH_4$, or better with diborane in ether solution and also undergo α-halogenation with Cl_2 and Br_2 in the presence of red phosphorus (**Hell-Volhard Zelinsky reaction**). Methanal, ethanal, propanone, benzaldehyde, formic acid, acetic acid and benzoic acid are highly useful compounds in industry.

Exercises

12.1 What is meant by the following terms ? Give an example of the reaction in each case.

(i) Cyanohydrin (ii) Acetal (iii) Semicarbazone
(iv) Aldol (v) Hemiacetal (vi) Oxime
(vii) Ketal (vii) Imine (ix) 2,4-DNP-derivative
(x) Schiff's base

12.2 Name the following compounds according to IUPAC system of nomenclature:

(i) $CH_3CH(CH_3)CH_2CH_2CHO$ (ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
(iii) $CH_3CH{=}CHCHO$ (iv) $CH_3COCH_2COCH_3$
(v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$ (vi) $(CH_3)_3CCH_2COOH$
(vii) $OHCC_6H_4CHO$-*p*

12.3 Draw the structures of the following compounds.

(i) 3-Methylbutanal (ii) *p*-Nitropropiophenone
(iii) *p*-Methylbenzaldehyde (iv) 4-Methylpent-3-en-2-one
(v) 4-Chloropentan-2-one (vi) 3-Bromo-4-phenylpentanoic acid
(vii) *p,p'*-Dihydroxybenzophenone (viii) Hex-2-en-4-ynoic acid

12.4 Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

(i) $CH_3CO(CH_2)_4CH_3$ (ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$
(iii) $CH_3(CH_2)_5CHO$ (iv) Ph-CH=CH-CHO
(v)

(vi) PhCOPh

12.5 Draw structures of the following derivatives.

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde
(ii) Cyclopropanone oxime
(iii) Acetaldehydedimethylacetal
(iv) The semicarbazone of cyclobutanone
(v) The ethylene ketal of hexan-3-one
(vi) The methyl hemiacetal of formaldehyde

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12.6 Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

(i) PhMgBr and then H_3O^+ (ii) Tollens' reagent
(iii) Semicarbazide and weak acid (iv) Excess ethanol and acid
(v) Zinc amalgam and dilute hydrochloric acid

12.7 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal (ii) 2-Methylpentanal (iii) Benzaldehyde
(iv) Benzophenone (v) Cyclohexanone (vi) 1-Phenylpropanone
(vii) Phenylacetaldehyde (viii) Butan-1-ol (ix) 2,2-Dimethylbutanal

12.8 How will you convert ethanal into the following compounds?

(i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid

12.9 Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

12.10 An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

12.11 An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

12.12 Arrange the following compounds in increasing order of their property as indicated:

(i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

12.13 Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanal and Propanone (ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid (iv) Benzoic acid and Ethyl benzoate
(v) Pentan-2-one and Pentan-3-one (vi) Benzaldehyde and Acetophenone
(vii) Ethanal and Propanal

12.14 How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom

(i) Methyl benzoate (ii) *m*-Nitrobenzoic acid
(iii) *p*-Nitrobenzoic acid (iv) Phenylacetic acid
(v) *p*-Nitrobenzaldehyde.

12.15 How will you bring about the following conversions in not more than two steps?

(i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal (iv) Benzene to *m*-Nitroacetophenone
(v) Benzaldehyde to Benzophenone (vi) Bromobenzene to 1-Phenylethanol
(vii) Benzaldehyde to 3-Phenylpropan-1-ol
(viii) Benazaldehyde to α-Hydroxyphenylacetic acid
(ix) Benzoic acid to *m*- Nitrobenzyl alcohol

12.16 Describe the following:

(i) Acetylation (ii) Cannizzaro reaction
(iii) Cross aldol condensation (iv) Decarboxylation

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12.17 Complete each synthesis by giving missing starting material, reagent or products

(i)

(ii)

(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iv)

(v)

(vi)

(vii) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{dil.NaOH}}$

(viii) $CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$

(ix)

(x)

(xi)

12.18 Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

12.19 An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

12.20 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

Answers to Some Intext Questions

12.1

(i) $H_3C-\underset{}{\overset{CH_3O}{CH}}-\overset{O}{\overset{\|}{C}}-H$

(ii) $H_3C-\overset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H$

(iii)

(iv) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CHO$

(v) $CH_3CH_2\overset{CH_3O}{CH}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{CH}-CH_2CH_3$

(vi)

12.2 (i)

(ii)

(iii)

(iv)

12.3 $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

12.4 (i) Butanone < Propanone < Propanal < Ethanal

(ii) Acetophenone < *p*-Tolualdehyde , Benzaldehyde < *p*-Nitrobenzaldehyde.

12.5 (i)

(ii)

(iii) R–CH=CH–CH=N–NH–C(=O)–NH_2

(iv)

12.6 (i) 3-Phenylpropanoic acid (ii) 3-Methylbut-2-enoic acid

(iii) 2-Methylcyclopentanecarboxylic acid. (iv) 2,4,6-Trinitrobenzoic acid

12.7

(i)

(ii)

(iii)

(iv)

12.8 (i) CH_3COOH (ii) CH_2FCOOH (iii) CH_3CHFCH_2COOH (iv) F_3C COOH

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Unit 13

Amines

Objectives

After studying this Unit, you will be able to

- describe amines as derivatives of ammonia having a pyramidal structure;
- classify amines as primary, secondary and tertiary;
- name amines by common names and IUPAC system;
- describe some of the important methods of preparation of amines;
- explain the properties of amines;
- distinguish between primary, secondary and tertiary amines;
- describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.

"The chief commercial use of amines is as intermediates in the synthesis of medicines and fibres" .

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s). In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dyestuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes. In this Unit, you will learn about amines and diazonium salts.

I. AMINES

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

For example:

$$CH_3{-}NH_2,\ C_6H_5{-}NH_2,\ CH_3{-}NH{-}CH_3,\ CH_3{-}N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

13.1 Structure of Amines

Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore, sp^3 hybridised and the geometry of amines is pyramidal. Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C–N–E, (where E is

C or H) is less than 109.5 ; for instance, it is 108° in case of trimethylamine as shown in Fig. 13.1.

Fig. 13.1 *Pyramidal shape of trimethylamine*

13.2 Classification

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. If one hydrogen atom of ammonia is replaced by R or Ar , we get RNH_2 or $ArNH_2$, a primary amine (1°). If two hydrogen atoms of ammonia or one hydrogen atom of R-NH_2 are replaced by another alkyl/aryl(R') group, what would you get? You get R-NHR', secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine. Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.

13.3 Nomenclature

In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, amines are named as **alkanamines**, derived by replacement of 'e' of alkane by the word amine. For example, CH_3NH_2 is named as methanamine. In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing $-NH_2$ groups and suitable prefix such as di, tri, etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained. For example, $H_2N-CH_2-CH_2-NH_2$ is named as ethane-1, 2-diamine.

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In arylamines, $-NH_2$ group is directly attached to the benzene ring. $C_6H_5NH_2$ is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'. Thus in IUPAC system, $C_6H_5-NH_2$ is named as benzenamine. Common and IUPAC names of some alkylamines and arylamines are given in Table 13.1.

Table 13.1: Nomenclature of Some Alkylamines and Arylamines

Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
$CH_3-\underset{\underset{NH_2}{\vert}}{CH}-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-\underset{\underset{H}{\vert}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
$CH_3-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
$C_2H_5-\underset{\underset{C_2H_5}{\vert}}{N}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	o-Toluidine	2-Aminotoluene
	p-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

Intext Questions

13.1 Classify the following amines as primary, secondary or tertiary:

(i)

(ii)

(iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$

13.2 (i) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

(ii) Write IUPAC names of all the isomers.

(iii) What type of isomerism is exhibited by different pairs of amines?

13.4 Preparation of Amines

Amines are prepared by the following methods:

1. Reduction of nitro compounds

Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

(i)

(ii)

Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

2. Ammonolysis of alkyl halides

You have read (Unit 10, Class XII) that the carbon - halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group. This process of cleavage of the C–X bond by ammonia molecule is known as **ammonolysis**. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.

$$\underset{\text{Nucleophile}}{\ddot{N}H_3} + R-X \longrightarrow \underset{\text{Substituted ammonium salt}}{R-\overset{+}{N}H_3\,\overset{-}{X}}$$

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

$$R\text{–}\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R\text{–}NH_2 + H_2O + \overset{+}{N}a\overset{-}{X}$$

Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia.

The order of reactivity of halides with amines is RI > RBr >RCl.

Example 13.1

Write chemical equations for the following reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.

Solution

(i) $$\underset{\text{Chloroethane}}{C_2H_5\text{–}Cl} \xrightarrow{NH_3} \underset{\text{Ethanamine}}{C_2H_5\text{–}NH_2} \xrightarrow{C_2H_5\text{-}Cl} \underset{\text{N-Ethylethanamine}}{C_2H_5\text{–}\overset{H}{\overset{|}{N}}\text{–}C_2H_5} \xrightarrow{C_2H_5\text{-}Cl} \underset{\text{N,N-Diethylethanamine}}{C_2H_5\text{–}\underset{C_2H_5}{\underset{|}{N}}\text{–}C_2H_5}$$

(ii) $$\underset{\text{Benzylchloride}}{C_6H_5\text{–}CH_2\text{–}Cl} \xrightarrow{NH_3} \underset{\text{Benzylamine}}{C_6H_5\text{–}CH_2NH_2} \xrightarrow{2CH_3Cl} \underset{\text{N,N-Dimethylphenylmethanamine}}{C_6H_5\text{–}CH_2\text{–}\underset{CH_3}{\underset{|}{N}}\text{–}CH_3}$$

3. *Reduction of nitriles*

Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines. This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.

$$R\text{–}C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R\text{–}CH_2\text{–}NH_2$$

4. *Reduction of amides*

The amides on reduction with lithium aluminium hydride yield amines.

$$R\text{–}\overset{O}{\overset{||}{C}}\text{–}NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R\text{–}CH_2\text{–}NH_2$$

5. *Gabriel phthalimide synthesis*

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Phthalimide N-Alkylphthalimide

6. *Hoffmann bromamide degradation reaction*

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

$$R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Example 13.2 Write chemical equations for the following conversions:

(i) $CH_3–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$

(ii) $C_6H_5–CH_2–Cl$ into $C_6H_5–CH_2–CH_2–NH_2$

Solution

(i) $CH_3–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3–CH_2–C\equiv N \xrightarrow{\text{reduction}} CH_3–CH_2–CH_2–NH_2$

Chloroethane Propanenitrile Propan-1-amine

(ii) $C_6H_5–CH_2–Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5–CH_2–C\equiv N \xrightarrow{H_2/Ni} C_6H_5–CH_2–CH_2–NH_2$

Chlorophenylmethane (Benzyl chloride) Phenylethanenitrile (Benzyl cyanide) 2-Phenylethanamine

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Example 13.3

Write structures and IUPAC names of

(i) the amide which gives propanamine by Hoffmann bromamide reaction.

(ii) the amine produced by the Hoffmann degradation of benzamide.

Solution

(i) Propanamine contains three carbons. Hence, the amide molecule must contain four carbon atoms. Structure and IUPAC name of the starting amide with four carbon atoms are given below:

$$CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–NH_2$$ Butanamide

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.

Aniline or benzenamine

Intext Question

13.3 How will you convert

(i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline

(iii) $Cl–(CH_2)_4–Cl$ into hexan-1,6-diamine?

13.5 Physical Properties

The lower aliphatic amines are gases with fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid. Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Considering the electronegativity of nitrogen of amine and oxygen of alcohol as 3.0 and 3.5 respectively, you can predict the pattern of solubility of amines and alcohols in water. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why? Amines are soluble in organic solvents like alcohol, ether and benzene. You may remember that alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

Intermolecular hydrogen bonding in primary amines is shown in Fig. 13.2.

Fig. 13.2 *Intermolecular hydrogen bonding in primary amines*

Boiling points of amines, alcohols and alkanes of almost the same molar mass are shown in Table 13.2.

Table 13.2: Comparison of Boiling Points of Amines, Alcohols and Alkanes of Similar Molecular Masses

Sl. No.	Compound	Molar mass	b.p./K
1.	n-$C_4H_9NH_2$	73	350.8
2.	$(C_2H_5)_2NH$	73	329.3
3.	$C_2H_5N(CH_3)_2$	73	310.5
4.	$C_2H_5CH(CH_3)_2$	72	300.8
5.	n-C_4H_9OH	74	390.3

13.6 Chemical Reactions

Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also decides the course of reaction of amines; that is why primary ($-NH_2$), secondary $\left(>N-H\right)$ and tertiary amines $\left(>N-\right)$ differ in many reactions. Moreover, amines behave as nucleophiles due to the presence of unshared electron pair. Some of the reactions of amines are described below:

1. Basic character of amines

Amines, being basic in nature, react with acids to form salts.

Amine salts on treatment with a base like NaOH, regenerate the parent amine.

$$R\overset{+}{N}H_3\,\overset{-}{X} + \overset{-}{O}H \longrightarrow R\ddot{N}H_2 + H_2O + \overset{-}{X}$$

Amine salts are soluble in water but insoluble in organic solvents like ether. This reaction is the basis for the separation of amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as **Lewis base.** Basic character of amines can be better understood in terms of their K_b and pK_b values as explained below:

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + \overset{-}{O}H$$

$$K = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2][H_2O]}$$

$$\text{or } K[H_2O] = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$$

$$\text{or } K_b = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b, stronger is the base. The pK_b values of few amines are given in Table 13.3.

pK_b value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom. Their pK_b values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Table 13.3: pK_b Values of Amines in Aqueous Phase

Name of amine	pK_b
Methanamine	3.38
N-Methylmethanamine	3.27
N,N-Dimethylmethanamine	4.22
Ethanamine	3.29
N-Ethylethanamine	3.00
N,N-Diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
N-Methylaniline	9.30
N,N-Dimethylaniline	8.92

You may find some discrepancies while trying to interpret the K_b values of amines on the basis of +I or –I effect of the substituents present in amines. Besides inductive effect, there are other effects like solvation effect, steric hinderance, etc., which affect the basic strength of amines. Just ponder over. You may get the answer in the following paragraphs.

Structure-basicity relationship of amines

Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

(a) Alkanamines versus ammonia

Let us consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.

Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is followed in the gaseous phase. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3. The trend is not regular in the aqueous state as evident by their pK_b values given in Table 13.3. In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. The order of stability of ions are as follows:

Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order. Secondly, when the alkyl group is small, like $-CH_3$ group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH_3 group, there will be steric hinderance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from $-CH_3$ to $-C_2H_5$ results in change of the order of basic strength. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(b) Arylamines versus ammonia

pK_b value of aniline is quite high. Why is it so? It is because in aniline or other arylamines, the $-NH_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. If you write different resonating structures of aniline, you will find that aniline is a resonance hybrid of the following five structures.

I II III IV V

On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).

I II

We know that greater the number of resonating structures, greater is the stability. Thus you can infer that aniline (five resonating structures) is more stable than anilinium ion. Hence, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia. In case of substituted aniline, it is observed that electron releasing groups like $-OCH_3$, $-CH_3$ increase basic strength whereas electron withdrawing groups like $-NO_2$, $-SO_3$, –COOH, –X decrease it.

Example 13.4 Arrange the following in decreasing order of their basic strength:
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

Solution The decreasing order of basic strength of the above amines and ammonia follows the following order:
$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

2. Alkylation

Amines undergo alkylation on reaction with alkyl halides (refer Unit 10, Class XII).

3. Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. You can consider this reaction as the replacement of hydrogen atom of $-NH_2$ or $>N-H$ group by the acyl group. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

Ethanamine N-Ethylethanamide

N-Ethylethanamine N,N-Diethylethanamide

Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

Amines also react with benzoyl chloride (C_6H_5COCl). This reaction is known as benzoylation.

$$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$

Methanamine Benzoyl chloride N – Methylbenzamide

What do you think is the product of the reaction of amines with carboxylic acids ? They form salts with amines at room temperature.

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4. *Carbylamine reaction*

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

5. *Reaction with nitrous acid*

Three classes of amines react differently with nitrous acid which is prepared *in situ* from a mineral acid and sodium nitrite.

(a) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$R{-}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R{-}\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

(b) Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds discussed in Section 13.7.

$$\underset{\text{Aniline}}{C_6H_5{-}NH_2} \xrightarrow[273-278\ K]{NaNO_2 + 2HCl} \underset{\text{Benzenediazonium chloride}}{C_6H_5{-}\overset{+}{N}_2\overset{-}{Cl}} + NaCl + 2H_2O$$

Secondary and tertiary amines react with nitrous acid in a different manner.

6. *Reaction with arylsulphonyl chloride*

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.

N-Ethylbenzenesulphonamide (soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N,N-diethyl-benzenesulphonamide is formed.

N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.

7. Electrophilic substitution

You have read earlier that aniline is a resonance hybrid of five structures. Where do you find the maximum electron density in these structures? *Ortho*- and *para*-positions to the $-NH_2$ group become centres of high electron density. Thus $-NH_2$ group is *ortho* and *para* directing and a powerful activating group.

(a) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.

Aniline 2,4,6-Tribromoaniline

The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their very high reactivity. Substitution tends to occur at *ortho*- and *para*-positions. If we have to prepare monosubstituted aniline derivative, how can the activating effect of $-NH_2$ group be controlled ? This can be done by protecting the $-NH_2$ group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

Aniline *N*-Phenylethanamide (Acetanilide) (Major) 4-Bromoaniline

The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of $-NHCOCH_3$ group is less than that of amino group.

(b) *Nitration:* Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.

However, by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the *p*-nitro derivative can be obtained as the major product.

(c) *Sulphonation:* Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.

Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

Intext Questions

13.4 Arrange the following in increasing order of their basic strength:

(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

13.5 Complete the following acid-base reactions and name the products:

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$ (ii) $(C_2H_5)_3N + HCl \rightarrow$

13.6 Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

13.7 Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

13.8 Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

II. DIAZONIUM SALTS

The diazonium salts have the general formula $R\overset{+}{N}_2\overset{-}{X}$ where R stands for an aryl group and $\overset{-}{X}$ ion may be Cl^- Br^-, HSO_4^-, BF_4^-, etc. They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. The $\overset{+}{N}_2$ group is called diazonium group. For example, $C_6H_5\overset{+}{N}_2\overset{-}{Cl}$ is named as benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium hydrogensulphate.

Primary aliphatic amines form highly unstable alkyldiazonium salts (refer to Section 13.6). Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.

13.7 Method of Preparation of Diazonium Salts

Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into diazonium salts is known as **diazotisation**. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2Cl + NaCl + 2H_2O$$

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13.8 Physical Properties

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

13.9 Chemical Reactions

The reactions of diazonium salts can be broadly divided into two categories, namely (A) reactions involving displacement of nitrogen and (B) reactions involving retention of diazo group.

A. Reactions involving displacement of nitrogen

Diazonium group being a very good leaving group, is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. *Replacement by halide or cyanide ion*: The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called **Sandmeyer reaction**.

$$Ar\overset{+}{N}_2\overset{-}{X} \longrightarrow \begin{cases} \xrightarrow{CuCl/HCl} ArCl + N_2 \\ \xrightarrow{CuBr/HBr} ArBr + N_2 \\ \xrightarrow{CuCN/KCN} ArCN + N_2 \end{cases}$$

Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.

$$Ar\overset{+}{N}_2\overset{-}{X} \longrightarrow \begin{cases} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX \\ \xrightarrow{Cu/HBr} ArBr + N_2 + CuX \end{cases}$$

The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

2. *Replacement by iodide ion*: Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + KI \longrightarrow ArI + KCl + N_2$$

3. *Replacement by fluoride ion*: When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + HBF_4 \longrightarrow Ar-\overset{+}{N}_2\overset{-}{BF}_4 \xrightarrow{\Delta} Ar-F + BF_3 + N_2$$

4. *Replacement by H*: Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.

$$Ar\overset{+}{N_2}\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N_2}\overset{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

5. *Replacement by hydroxyl group*: If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to phenol.

$$Ar\overset{+}{N_2}\overset{-}{Cl} + H_2O \longrightarrow ArOH + N_2 + HCl$$

6. *Replacement by –NO_2 group*: When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by –NO_2 group.

B. Reactions involving retention of diazo group coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.

p-Hydroxyazobenzene (orange dye)

p-Aminoazobenzene
(yellow dye)

13.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

From the above reactions, it is clear that the diazonium salts are very good intermediates for the introduction of –F, –Cl, –Br, –I, –CN, –OH, –NO_2 groups into the aromatic ring.

Aryl fluorides and iodides cannot be prepared by direct halogenation. The cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorobenzene but cyanobenzene can be easily obtained from diazonium salt.

Thus, the replacement of diazo group by other groups is helpful in

preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

Example 13.5

How will you convert 4-nitrotoluene to 2-bromobenzoic acid ?

Solution

Intext Question

13.9 Convert

(i) 3-Methylaniline into 3-nitrotoluene.

(ii) Aniline into 1,3,5 - tribromobenzene.

Summary

Amines can be considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups. Replacement of one hydrogen atom of ammonia gives rise to structure of the type **R-NH$_2$**, known as **primary amine**. **Secondary amines** are characterised by the structure **R$_2$NH** or **R-NHR′** and **tertiary amines** by **R$_3$N, RNR′R″** or **R$_2$NR′**. Secondary and tertiary amines are known as simple amines if the alkyl or aryl groups are the same and mixed amines if the groups are different. Like ammonia, all the three types of amines have one unshared electron pair on nitrogen atom due to which they behave as **Lewis bases**.

Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influence their physical properties. In **alkylamines**, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. In **aromatic amines**, electron releasing and withdrawing groups, respectively increase and decrease their basic character. **Aniline** is a weaker base

than ammonia. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. *p*-Toluenesulphonyl chloride is used for the identification of primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Reactivity of aromatic amines can be controlled by **acylation** process, i.e., by treating with acetyl chloride or acetic anhydride. Tertiary amines like **trimethylamine** are used as insect attractants.

Aryldiazonium salts, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group. Coupling reaction of aryldiazonium salts with phenols or arylamines give rise to the formation of **azo dyes**.

Exercises

13.1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$

(iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) *m*–$BrC_6H_4NH_2$

13.2 Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Secondary and tertiary amines

(iii) Ethylamine and aniline (iv) Aniline and benzylamine

(v) Aniline and N-methylaniline.

13.3 Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is *o*– and *p*– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

13.4 Arrange the following:

(i) In decreasing order of the pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, *p*-nitroaniline and *p*-toluidine

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(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

(iv) In decreasing order of basic strength in gas phase:
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

13.5 How will you convert:

(i) Ethanoic acid into methanamine
(ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to ethanoic acid
(iv) Ethanamine into methanamine
(v) Ethanoic acid into propanoic acid
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine
(viii) Propanoic acid into ethanoic acid?

13.6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

13.7 Write short notes on the following:

(i) Carbylamine reaction
(ii) Diazotisation
(iii) Hofmann's bromamide reaction
(iv) Coupling reaction
(v) Ammonolysis
(vi) Acetylation
(vii) Gabriel phthalimide synthesis.

13.8 Accomplish the following conversions:

(i) Nitrobenzene to benzoic acid
(ii) Benzene to *m*-bromophenol
(iii) Benzoic acid to aniline
(iv) Aniline to 2,4,6-tribromofluorobenzene
(v) Benzyl chloride to 2-phenylethanamine
(vi) Chlorobenzene to *p*-chloroaniline
(vii) Aniline to *p*-bromoaniline
(viii) Benzamide to toluene
(ix) Aniline to benzyl alcohol.

13.9 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(iv) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H} C$

(v) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(vi) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

13.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

13.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\ (\text{conc.}) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2\ (aq) \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2\ O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[\text{(ii) } NaNO_2\ /\ Cu,\ \Delta]{\text{(i) } HBF_4}$

13.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

13.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

13.14 Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

Answers to Some Intext Questions

13.4 (i) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

Unit

14

Biomolecules

Objectives

After studying this Unit, you will be able to

- define the biomolecules like carbohydrates, proteins and nucleic acids;
- classify carbohydrates, proteins, nucleic acids and vitamins on the basis of their structures;
- explain the difference between DNA and RNA;
- appreciate the role of biomolecules in biosystem.

"It is the harmonious and synchronous progress of chemical reactions in body which leads to life".

A living system grows, sustains and reproduces itself. The most amazing thing about a living system is that it is composed of non-living atoms and molecules. The pursuit of knowledge of what goes on chemically within a living system falls in the domain of ***biochemistry***. Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. These biomolecules interact with each other and constitute the molecular logic of life processes. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms. Structures and functions of some of these biomolecules are discussed in this Unit.

14.1 Carbohydrates

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples are cane sugar, glucose, starch, etc. Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived. For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. But all the compounds which fit into this formula may not be classified as carbohydrates. Acetic acid (CH_3COOH) fits into this general formula, $C_2(H_2O)_2$ but is not a carbohydrate. Similarly, rhamnose, $C_6H_{12}O_5$ is a carbohydrate but does not fit in this definition. A large number of their reactions have shown that they contain specific functional groups. Chemically, *the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis*. Some of the carbohydrates,

which are sweet in taste, are also called sugars. The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose. Carbohydrates are also called saccharides (Greek: *sakcharon* means sugar).

14.1.1 Classification of Carbohydrates

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups.

(i) *Monosaccharides*: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. About 20 monosaccharides are known to occur in nature. Some common examples are glucose, fructose, ribose, etc.

(ii) *Oligosaccharides*: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. For example, sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.

(iii) *Polysaccharides*: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc. Polysaccharides are not sweet in taste, hence they are also called non-sugars.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are *reducing sugars.*

In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are non-reducing sugars e.g. sucrose. On the other hand, sugars in which these functional groups are free, are called reducing sugars, for example, maltose and lactose.

14.1.2 Monosaccharides

Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose. Number of carbon atoms constituting the monosaccharide is also introduced in the name as is evident from the examples given in Table 14.1

Table 14.1: Different Types of Monosaccharides

Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

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I Glucose

Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts. It is prepared as follows:

14.1.3 Preparation of Glucose

1. *From sucrose (Cane sugar)*: If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

2. *From starch*: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{393K; 2-3 atm}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

14.1.4 Structure of Glucose

Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth. It was assigned the structure given below on the basis of the following evidences:

1. Its molecular formula was found to be $C_6H_{12}O_6$.
2. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

3. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = 0) in glucose.

4. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.

5. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms.

6. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.

The exact spatial arrangement of different —OH groups was given by Fischer after studying many other properties. Its configuration is correctly represented as **I**. So gluconic acid is represented as **II** and saccharic acid as **III**.

I **II** **III**

Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It may be remembered that 'D' and 'L' have no relation with the optical activity of the compound. The meaning of D– and L– notations is given as follows.

The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer. This refers to their relation with a particular isomer of glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as shown below.

(+) – Glyceraldehyde (–) – Glyceraldehyde

All those compounds which can be chemically correlated to (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to (–) isomer of glyceraldehyde are said to have L—configuration. For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared. As in (+) glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+) glyceraldehyde, so it is assigned D-configuration. For this comparison, the structure is written in a way that most oxidised carbon is at the top.

D– (+) – Glyceraldehyde

D–(+) – Glucose

14.1.5 Cyclic Structure of Glucose

The structure **(I)** of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

1. Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.
2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.
3. Glucose is found to exist in two different crystalline forms which are named as α and β. The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

   This behaviour could not be explained by the open chain structure **(I)** for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure. It was found that glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation. This explains the absence of —CHO group and also existence of glucose in two forms as shown below. These two cyclic forms exist in equilibrium with open chain structure.

α – D – (+) – Glucose

β – D– (+) – Glucose

The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* (the aldehyde carbon before cyclisation). Such isomers, i.e., α-form and β-form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** (α– or β–), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.

Pyran

α – D – (+) – Glucopyranose

β – D – (+) – Glucopyranose

II. Fructose

Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose.

14.1.6 Structure of Fructose

Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. Its open chain structure is as shown.

D – (–) – Fructose

It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the (>C=O) group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan. Furan is a five membered cyclic compound with one oxygen and four carbon atoms.

Furan

α – D – (–) – Fructofuranose

β – D – (–) – Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given.

α – D – (–) – Fructofuranose

β – D – (–) – Fructofuranose

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14.1.7 Disaccharides

You have already read that disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage.*

(i) Sucrose: One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

These two monosaccharides are held together by a glycosidic linkage between C1 of α-glucose and C2 of β-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.

α – D – Glucose *β* – D – Fructose

Sucrose

Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4) is more than dextrorotation of glucose (+ 52.5), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as **invert sugar**.

(ii) Maltose: Another disaccharide, maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.

(I) *α* – D – Glucose (II) *α* – D – Glucose

Maltose

(iii) *Lactose*: It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of β-D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose. Hence it is also a reducing sugar.

β– D – Galactose β– D – Glucose

Lactose

14.1.8 Polysaccharides

Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials.

(i) *Starch*: Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components— **Amylose** and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units held by C1– C4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α-D-glucose

Amylose

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Amylopectin

units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.

(ii) *Cellulose*: Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain

Cellulose

polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

(iii) *Glycogen*: The carbohydrates are stored in animal body as glycogen. It is also known as *animal starch* because its structure is similar to amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

14.1.9 Importance of Carbohydrates

Carbohydrates are essential for life in both plants and animals. They form a major portion of our food. Honey has been used for a long time as an instant source of energy by '**Vaids**' in ayurvedic system of medicine. Carbohydrates are used as storage molecules as starch in plants and **glycogen** in animals. Cell wall of bacteria and plants is made up of cellulose. We build furniture, etc. from cellulose in the form of wood

and clothe ourselves with cellulose in the form of cotton fibre. They provide raw materials for many important industries like textiles, paper, lacquers and breweries.

Two aldopentoses viz. D-ribose and 2-deoxy-D-ribose (Section 14.5.1, Class XII) are present in nucleic acids. Carbohydrates are found in biosystem in combination with many proteins and lipids.

Intext Questions

14.1 Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.

14.2 What are the expected products of hydrolysis of lactose?

14.3 How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

14.2 Proteins

Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They occur in every part of the body and form the fundamental basis of structure and functions of life. They are also required for growth and maintenance of body. The word protein is derived from Greek word, "**proteios**" which means primary or of prime importance. All proteins are polymers of α-amino acids.

14.2.1 Amino Acids

Amino acids contain amino ($-NH_2$) and carboxyl (–COOH) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α, β, γ, δ and so on. Only α-amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.

α-amino acid
(R = side chain)

All α-amino acids have trivial names, which usually reflect the property of that compound or its source. Glycine is so named since it has sweet taste (in Greek *glykos* means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means cheese.) Amino acids are generally represented by a three letter symbol, sometimes one letter symbol is also used. Structures of some commonly occurring amino acids along with their 3-letter and 1-letter symbols are given in Table 14.2.

Table 14.2: Natural Amino Acids

Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-CH_3$	Ala	A
3. Valine*	$(H_3C)_2CH$-	Val	V
4. Leucine*	$(H_3C)_2CH-CH_2$-	Leu	L

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5. Isoleucine*	$H_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}$	Ile	I
6. Arginine*	$HN{=}C(NH_2)\text{-}NH\text{-}(CH_2)_3\text{-}$	Arg	R
7. Lysine*	$H_2N\text{-}(CH_2)_4\text{-}$	Lys	K
8. Glutamic acid	$HOOC\text{-}CH_2\text{-}CH_2\text{-}$	Glu	E
9. Aspartic acid	$HOOC\text{-}CH_2\text{-}$	Asp	D
10. Glutamine	$H_2N\text{-}C(=O)\text{-}CH_2\text{-}CH_2\text{-}$	Gln	Q
11. Asparagine	$H_2N\text{-}C(=O)\text{-}CH_2\text{-}$	Asn	N
12. Threonine*	$H_3C\text{-}CHOH\text{-}$	Thr	T
13. Serine	$HO\text{-}CH_2\text{-}$	Ser	S
14. Cysteine	$HS\text{-}CH_2\text{-}$	Cys	C
15. Methionine*	$H_3C\text{-}S\text{-}CH_2\text{-}CH_2\text{-}$	Met	M
16. Phenylalanine*	$C_6H_5\text{-}CH_2\text{-}$	Phe	F
17. Tyrosine	$(p)HO\text{-}C_6H_4\text{-}CH_2\text{-}$	Tyr	Y
18. Tryptophan*		Trp	W
19. Histidine*		His	H
20. Proline		Pro	P

** essential amino acid, a = entire structure*

14.2.2 Classification of Amino Acids

Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Equal number of amino and carboxyl groups makes it neutral; more number of amino than carboxyl groups makes it basic and more carboxyl groups as compared to amino groups makes it acidic. The amino acids, which can be synthesised in the body, are known as **non-essential amino acids.** On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as **essential amino acids** (marked with asterisk in Table 14.2).

Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges.

In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

Except glycine, all other naturally occurring α-amino acids are optically active, since the α-carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Aminoacids are represented by writing the $-NH_2$ group on left hand side.

14.2.3 Structure of Proteins

You have already read that proteins are the polymers of α-amino acids and they are connected to each other by **peptide bond** or **peptide linkage.** Chemically, peptide linkage is an amide formed between –COOH group and $-NH_2$ group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a **dipeptide**, glycylalanine.

Glycylalanine (Gly-Ala)

If a third amino acid combines to a dipeptide, the product is called a **tripeptide**. A tripeptide contains three amino acids linked by two peptide linkages. Similarly when four, five or six amino acids are linked, the respective products are known as **tetrapeptide, pentapeptide or hexapeptide**, respectively. When the number of such amino acids is more than ten, then the products are called **polypeptides**. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein. However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins if they ordinarily have a well defined conformation of a protein such as insulin which contains 51 amino acids.

Proteins can be classified into two types on the basis of their molecular shape.

(a) Fibrous proteins

When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

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(b) Globular proteins

This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

Fig. 14.1: α-Helix structure of proteins

(i) Primary structure of proteins: Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

(ii) Secondary structure of proteins: The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz. α-helix and β-pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between $-\overset{\overset{\displaystyle O}{\|}}{C}-$ and –NH– groups of the peptide bond.

α-Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the –NH group of each amino acid residue hydrogen bonded to the $>C=O$ of an adjacent turn of the helix as shown in Fig.14.1.

In β-structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β-pleated sheet.

Fig. 14.2: β-Pleated sheet structure of proteins

(iii) Tertiary structure of proteins: The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the 2 and 3 structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

(iv) Quaternary structure of proteins: Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

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A diagrammatic representation of all these four structures is given in Figure 14.3 where each coloured ball represents an amino acid.

Fig. 14.3: *Diagrammatic representation of protein structure (two sub-units of two types in quaternary structure)*

Fig. 14.4: *Primary, secondary, tertiary and quaternary structures of haemoglobin*

14.2.4 Denaturation of Proteins

Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of

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protein. During denaturation 2 and 3 structures are destroyed but 1º structure remains intact. The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

Intext Questions

14.4 The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

14.5 Where does the water present in the egg go after boiling the egg?

14.3 Enzymes

Life is possible due to the coordination of various chemical reactions in living organisms. An example is the digestion of food, absorption of appropriate molecules and ultimately production of energy. This process involves a sequence of reactions and all these reactions occur in the body under very mild conditions. This occurs with the help of certain biocatalysts called **enzymes.** Almost all the enzymes are globular proteins. Enzymes are very specific for a particular reaction and for a particular substrate. They are generally named after the compound or class of compounds upon which they work. For example, the enzyme that catalyses hydrolysis of maltose into glucose is named as *maltase*.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

Sometimes enzymes are also named after the reaction, where they are used. For example, the enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate are named as **oxidoreductase** enzymes. The ending of the name of an enzyme is **-ase**.

14.3.1 Mechanism of Enzyme Action

Enzymes are needed only in small quantities for the progress of a reaction. Similar to the action of chemical catalysts, enzymes are said to reduce the magnitude of activation energy. For example, activation energy for acid hydrolysis of sucrose is 6.22 kJ mol^{-1}, while the activation energy is only 2.15 kJ mol^{-1} when hydrolysed by the enzyme, sucrase. Mechanism for the enzyme action has been discussed in Unit 5.

14.4 Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called **vitamins.** Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them, so they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet. Different vitamins belong to various chemical classes and it is difficult to define them on the basis of structure. They are generally regarded as **organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth**

and health of the organism. Vitamins are designated by alphabets A, B, C, D, etc. Some of them are further named as sub-groups e.g. B_1, B_2, B_6, B_{12}, etc. Excess of vitamins is also harmful and vitamin pills should not be taken without the advice of doctor.

The term "**Vitamine**" was coined from the word vital + amine since the earlier identified compounds had amino groups. Later work showed that most of them did not contain amino groups, so the letter 'e' was dropped and the term **vitamin** is used these days.

14.4.1 Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) *Fat soluble vitamins*: Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) *Water soluble vitamins*: B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Some important vitamins, their sources and diseases caused by their deficiency are listed in Table 14.3.

Table 14.3: Some important Vitamins, their Sources and their Deficiency Diseases

Sl. No.	Name of Vitamins	Sources	Deficiency diseases
1.	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3.	Vitamin B_2 (Riboflavin)	Milk, eggwhite, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)

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8. Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9. Vitamin K	Green leafy vegetables	Increased blood clotting time

14.5: Nucleic Acids

Every generation of each and every species resembles its ancestors in many ways. How are these characteristics transmitted from one generation to the next? It has been observed that nucleus of a living cell is responsible for this transmission of inherent characters, also called **heredity**. The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids.** These are mainly of two types, the **deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).** Since nucleic acids are long chain polymers of **nucleotides,** so they are also called polynucleotides.

James Dewey Watson

Born in Chicago, Illinois, in 1928, Dr Watson received his Ph.D. (1950) from Indiana University in Zoology. He is best known for his discovery of the structure of DNA for which he shared with Francis Crick and Maurice Wilkins the 1962 Nobel prize in Physiology and Medicine. They proposed that DNA molecule takes the shape of a double helix, an elegantly simple structure that resembles a gently twisted ladder. The rails of the ladder are made of alternating units of phosphate and the sugar deoxyribose; the rungs are each composed of a pair of purine/ pyrimidine bases. This research laid the foundation for the emerging field of **molecular biology**. The complementary pairing of nucleotide bases explains how identical copies of parental DNA pass on to two daughter cells. This research launched a revolution in biology that led to modern recombinant DNA techniques.

14.5.1 Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecule, it is β-D-ribose.

β–D–ribose

β–D–2–deoxyribose

DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).

Adenine (A)

Guanine (G)

Cytosine (C)

Thymine (T)

Uracil (U)

14.5.2 Structure of Nucleic Acids

A unit formed by the attachment of a base to 1′ position of sugar is known as **nucleoside.** In nucleosides, the sugar carbons are numbered as 1′, 2′, 3′, etc. in order to distinguish these from the bases (Fig. 14.5a). When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide (Fig. 14.5).

(a)

(b)

Fig. 14.5: *Structure of (a) a nucleoside and (b) a nucleotide*

Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig. 14.6.

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Fig. 14.6: *Formation of a dinucleotide*

Fig. 14.7: *Double strand helix structure for DNA*

A simplified version of nucleic acid chain is as shown below.

Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig. 14.7). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA), ribosomal RNA (r-RNA) and transfer RNA (t-RNA).**

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Har Gobind Khorana

Har Gobind Khorana, was born in 1922. He obtained his M.Sc. degree from Punjab University in Lahore. He worked with Professor Vladimir Prelog, who moulded Khorana's thought and philosophy towards science, work and effort. After a brief stay in India in 1949, Khorana went back to England and worked with Professor G.W. Kenner and Professor A.R.Todd. It was at Cambridge, U.K. that he got interested in both proteins and nucleic acids. Dr Khorana shared the Nobel Prize for Medicine and Physiology in 1968 with Marshall Nirenberg and Robert Holley for cracking the genetic code.

DNA Fingerprinting

It is known that every individual has unique fingerprints. These occur at the tips of the fingers and have been used for identification for a long time but these can be altered by surgery. A sequence of bases on DNA is also unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment. DNA fingerprinting is now used

(i) in forensic laboratories for identification of criminals.

(ii) to determine paternity of an individual.

(iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children.

(iv) to identify racial groups to rewrite biological evolution.

14.5.3 Biological Functions of Nucleic Acids

DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. DNA is exclusively responsible for maintaining the identity of different species of organisms over millions of years. A DNA molecule is capable of self duplication during cell division and identical DNA strands are transferred to daughter cells. Another important function of nucleic acids is the protein synthesis in the cell. Actually, the proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is present in DNA.

Intext Questions

14.6 Why cannot vitamin C be stored in our body?

14.7 What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?

14.8 When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA?

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Summary

Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups — **monosaccharides**, **disaccharides** and **polysaccharides**. Glucose, the most important source of energy for mammals, is obtained by the digestion of starch. Monosaccharides are held together by glycosidic linkages to form disaccharides or polysaccharides.

Proteins are the **polymers** of about twenty different **α-amino acids** which are linked by peptide bonds. Ten amino acids are called essential amino acids because they cannot be synthesised by our body, hence must be provided through diet. Proteins perform various structural and dynamic functions in the organisms. Proteins which contain only α-amino acids are called simple proteins. The **secondary** or **tertiary structure of proteins** get disturbed on change of pH or temperature and they are not able to perform their functions. This is called **denaturation of proteins**. Enzymes are **biocatalysts** which speed up the reactions in biosystems. They are very specific and selective in their action and chemically all **enzymes** are proteins.

Vitamins are accessory food factors required in the diet. They are classified as fat soluble (A, D, E and K) and water soluble (B group and C). Deficiency of vitamins leads to many diseases.

Nucleic acids are the polymers of nucleotides which in turn consist of a base, a pentose sugar and phosphate moiety. Nucleic acids are responsible for the transfer of characters from parents to offsprings. There are two types of nucleic acids — **DNA** and **RNA**. DNA contains a five carbon sugar molecule called **2-deoxyribose** whereas RNA contains ribose. Both DNA and RNA contain adenine, guanine and cytosine. The fourth base is thymine in DNA and uracil in RNA. The structure of DNA is a double strand whereas RNA is a single strand molecule. DNA is the chemical basis of heredity and have the coded message for proteins to be synthesised in the cell. There are three types of RNA — mRNA, rRNA and tRNA which actually carry out the protein synthesis in the cell.

Exercises

14.1 What are monosaccharides?

14.2 What are reducing sugars?

14.3 Write two main functions of carbohydrates in plants.

14.4 Classify the following into monosaccharides and disaccharides.
Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.

14.5 What do you understand by the term glycosidic linkage?

14.6 What is glycogen? How is it different from starch?

14.7 What are the hydrolysis products of
(i) sucrose and (ii) lactose?

14.8 What is the basic structural difference between starch and cellulose?

14.9 What happens when D-glucose is treated with the following reagents?
(i) HI (ii) Bromine water (iii) HNO_3

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14.10 Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.

14.11 What are essential and non-essential amino acids? Give two examples of each type.

14.12 Define the following as related to proteins
(i) Peptide linkage (ii) Primary structure (iii) Denaturation.

14.13 What are the common types of secondary structure of proteins?

14.14 What type of bonding helps in stabilising the α-helix structure of proteins?

14.15 Differentiate between globular and fibrous proteins.

14.16 How do you explain the amphoteric behaviour of amino acids?

14.17 What are enzymes?

14.18 What is the effect of denaturation on the structure of proteins?

14.19 How are vitamins classified? Name the vitamin responsible for the coagulation of blood.

14.20 Why are vitamin A and vitamin C essential to us? Give their important sources.

14.21 What are nucleic acids? Mention their two important functions.

14.22 What is the difference between a nucleoside and a nucleotide?

14.23 The two strands in DNA are not identical but are complementary. Explain.

14.24 Write the important structural and functional differences between DNA and RNA.

14.25 What are the different types of RNA found in the cell?

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Unit 15

Polymers

Objectives

After studying this Unit, you will be able to

- explain the terms - monomer, polymer and polymerisation and appreciate their importance;
- distinguish between various classes of polymers and different types of polymerisation processes;
- appreciate the formation of polymers from mono- and bi-functional monomer molecules;
- describe the preparation of some important synthetic polymers and their properties;
- appreciate the importance of polymers in daily life.

"Copolymerisation has been used by nature in polypeptides which may contain as many as 20 different amino acids. Chemists are still far behind".

Do you think that daily life would have been easier and colourful without the discovery and varied applications of polymers? The use of polymers in the manufacture of plastic buckets, cups and saucers, children's toys, packaging bags, synthetic clothing materials, automobile tyres, gears and seals, electrical insulating materials and machine parts has completely revolutionised the daily life as well as the industrial scenario. Indeed, the polymers are the backbone of four major industries viz. plastics, elastomers, fibres and paints and varnishes.

The word 'polymer' is coined from two Greek words: *poly* means many and *mer* means unit or part. The term polymer is defined as very large molecules having high molecular mass (10^3-10^7u). These are also referred to as **macromolecules,** which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called **polymerisation**. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerisation reactions.

(i) $$\underset{\text{Ethene}}{nCH_2 = CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Repeating unit}}{n\left[CH_2-CH_2\right]} \longrightarrow \underset{\text{Polythene polymer}}{\left[CH_2-CH_2\right]_n}$$

(ii) $$\underset{\text{Hexamethylene diamine}}{nNH_2(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} \xrightarrow{\text{Polymerisation}} \underset{\text{Nylon 6,6}}{\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{||}{C}}-(CH_2)_4-\overset{O}{\overset{||}{C}}\right]_n}$$

15.1 Classification of Polymers

There are several ways of classification of polymers based on some special considerations. The following are some of the common classifications of polymers:

15.1.1 Classification Based on Source

Under this type of classification, there are three sub categories.

1. ***Natural polymers***

   These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber.

2. ***Semi-synthetic polymers***

   Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category.

3. ***Synthetic polymers***

   A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S) are examples of man-made polymers extensively used in daily life as well as in industry.

15.1.2 Classification Based on Structure of Polymers

There are three different types based on the structure of the polymers.

1. ***Linear polymers***

   These polymers consist of long and straight chains. The examples are high density polythene, polyvinyl chloride, etc. These are represented as:

2. ***Branched chain polymers***

   These polymers contain linear chains having some branches, *e.g.*, low density polythene. These are depicted as follows:

3. ***Cross linked or Network polymers***

   These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. bakelite, melamine, etc. These polymers are depicted as follows:

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15.1.3 Classification Based on Mode of Polymerisation

Polymers can also be classified on the basis of mode of polymerisation into two sub groups.

1. Addition polymers

The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, *e.g.*, the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as **homopolymers**, *e.g.*, polythene.

$$\underset{\text{Ethene}}{n\,CH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{\left(CH_2-CH_2\right)_n} \text{ Homopolymer}$$

The polymers made by addition polymerisation from two different monomers are termed as **copolymers**, *e.g.*, Buna-S, Buna-N, etc.

$$\underset{\text{1, 3-Butadiene}}{n\,CH_2=CH-CH=CH_2} + \underset{\text{Styrene}}{n\,C_6H_5CH=CH_2} \longrightarrow \underset{\text{Butadiene-styrene copolymer (Buna - S)}}{\left(CH_2-CH=CH-CH_2-CH_2-\overset{C_6H_5}{\overset{|}{C}}H\right)_n}$$

2. Condensation polymers

The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc. For example, nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.

$$n\,H_2N\,(CH_2)_6\,NH_2 + n\,HOOC\,(CH_2)_4\,COOH \longrightarrow \underset{\text{Nylon 6, 6}}{\left[NH\,(CH_2)_6\,NHCO(CH_2)_4CO\right]_n} + n\,H_2O$$

Example 15.1

Is $\left(CH_2-CH(C_6H_5)\right)_n$ a homopolymer or a copolymer?

Solution

It is a homopolymer and the monomer from which it is obtained is styrene $C_6H_5CH = CH_2$.

15.1.4 Classification Based on Molecular Forces

A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, *e.g.*, van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

1. Elastomers

These are rubber – like solids with elastic properties. In these

Neoprene

elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.

2. Fibres

Nylon 6,6

Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

3. Thermoplastic polymers

PVC

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

4 Thermosetting polymers

Bakelite

These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

15.1.5 Classification Based on Growth Polymerisation

The addition and condensation polymers are nowadays also referred as chain growth polymers and step growth polymers depending on the type of polymerisation mechanism they undergo during their formation.

Intext Questions

15.1 What are polymers ?

15.2 How are polymers classified on the basis of structure?

15.2 Types of Polymerisation Reactions

There are two broad types of polymerisation reactions, *i.e.*, the addition or chain growth polymerisation and condensation or step growth polymerisation.

15.2.1 Addition Polymerisation or Chain Growth Polymerisation

In this type of polymerisation, the molecules of the same monomer or diferent monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives. This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species. However, the free radical governed addition or chain growth polymerisation is the most common mode.

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1. *Free radical mechanism*

A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator. The process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical. This step is called **chain initiating step**. As this radical reacts with another molecule of ethene, another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as **chain propagating step**. Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymerised product. This step is called the **chain terminating step**. The sequence of steps may be depicted as follows:

Chain initiation steps

$$\underset{\text{Benzoyl peroxide}}{C_6H_5-\overset{O}{\overset{||}{C}}-O-O-\overset{O}{\overset{||}{C}}-C_6H_5} \longrightarrow 2C_6H_5-\overset{O}{\overset{||}{C}}-\dot{O} \longrightarrow \underset{\text{Phenyl radical}}{2\dot{C}_6H_5}$$

$$\dot{C}_6H_5 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

Chain propagating step

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2 = CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5\left(CH_2-CH_2\right)_nCH_2-\dot{C}H_2$$

Chain terminating step

For termination of the long chain, these free radicals can combine in different ways to form polythene. One mode of termination of chain is shown as under:

$$\begin{matrix} C_6H_5\left(CH_2-CH_2\right)_nCH_2-\dot{C}H_2 \\ C_6H_5\left(CH_2-\overset{+}{C}H_2\right)_nCH_2-\dot{C}H_2 \end{matrix} \longrightarrow \underset{\text{Polythene}}{C_6H_5\left(CH_2-CH_2\right)_nCH_2-CH_2-CH_2\left(CH_2-CH_2\right)_nC_6H_5}$$

2 *Preparation of some important addition polymers*

(a) *Polythene*

There are two types of polythene as given below:

(i) ***Low density polythene***: It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst). The low density

polythene (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure.

Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity. Hence, it is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

(ii) ***High density polythene:*** It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres. High density polythene (HDP) thus produced, consists of linear molecules and has a high density due to close packing. It is also chemically inert and more tougher and harder. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

G. Natta of Imperia and Karl Ziegler of Germany were awarded the Nobel Prize for Chemistry in 1963 for the development of Ziegler-Natta catalyst.

(b) Polytetrafluoroethene (Teflon)

Teflon is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures. It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals and gaskets and also used for non – stick surface coated utensils.

Teflon coatings undergo decomposition at temperatures above 300 C.

$$\underset{\text{Tetrafluoroethene}}{n\,CF_2 = CF_2} \xrightarrow[\text{High pressure}]{\text{Catalyst}} \underset{\text{Teflon}}{\left[CF_2 - CF_2\right]_n}$$

(c) Polyacrylonitrile

The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile.

Acrylic fibres have good resistance to stains, chemicals, insects and fungi.

$$\underset{\text{Acrylonitrile}}{n\,CH_2 = CHCN} \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \underset{\text{Polyacrylonitrile}}{\left[CH_2 - \overset{\overset{CN}{|}}{CH}\right]_n}$$

Polyacrylonitrile is used as a substitute for wool in making commercial fibres as orlon or acrilan.

15.2.2 Condensation Polymerisation or Step Growth polymerisation

This type of polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.

In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other, this process is also called as step growth polymerisation.

The formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerisation.

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Some important condensation polymerisation reactions characterised by their linking units are described below:

1. Polyamides

These polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons. The general method of preparation consists of the condensation polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.

(a) Preparation of nylons

(i) ***Nylon 6,6:*** It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

Nylon 6, 6 is used in making sheets, bristles for brushes and in textile industry.

(ii) ***Nylon 6:*** It is obtained by heating caprolactum with water at a high temperature.

Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

2. Polyesters

These are the polycondensation products of dicarboxylic acids and diols. Dacron or terylene is the best known example of polyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate-antimony trioxide catalyst as per the reaction given earlier. Dacron fibre (terylene) is crease resistant and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

3. *Phenol - formaldehyde polymer (Bakelite and related polymers)*

Phenol - formaldehyde polymers are the oldest synthetic polymers. These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The reaction starts with the initial formation of *o*-and/or *p*-hydroxymethylphenol derivatives, which further react with phenol to form compounds having rings joined to each other through $-CH_2$ groups. The initial product could be a linear product – **Novolac** used in paints.

Novolac

Novolac on heating with formaldehyde undergoes cross linking to form an infusible solid mass called **bakelite**. It is used for making combs, phonograph records, electrical switches and handles of various utensils.

Bakelite

4. *Melamine – formaldehyde polymer*

Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.

Melamine Formaldehyde Resin intermediate

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Melamine polymer

It is used in the manufacture of unbreakable crockery.

Intext Questions

15.3 Write the names of monomers of the following polymers:

(i) $\left[\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n$ (ii) $\left[\overset{O}{\overset{\|}{C}} - (CH_2)_5 - \overset{H}{\overset{|}{N}} \right]_n$ (iii) $\left[CF_2 - CF_2 \right]_n$

15.4 Classify the following as addition and condensation polymers: Terylene, Bakelite, Polyvinyl chloride, Polythene.

15.2.3 Copolymerisation

Copolymerisation is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also. It contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of 1, 3 – butadiene and styrene can form a copolymer.

1, 3-Butadiene Styrene Butadiene - styrene copolymer

Copolymers have properties quite different from homopolymers. For example, butadiene - styrene copolymer is quite tough and is a good substitute for natural rubber. It is used for the manufacture of autotyres, floortiles, footwear components, cable insulation, etc.

15.2.4 Rubber

1. Natural rubber

Rubber is a natural polymer and possesses elastic properties. It is also termed as elastomer and has a variety of uses. It is manufactured from rubber latex which is a colloidal dispersion of rubber in water. This latex is obtained from the bark of rubber tree and is found in India, Srilanka, Indonesia, Malaysia and South America.

Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as *cis* - 1, 4 - polyisoprene.

Natural rubber

$$H_2C=\overset{\overset{CH_3}{|}}{C}-CH=CH_2$$

Isoprene

The *cis*-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

Vulcanisation of rubber: Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperatures (<283 K) and shows high water absorption capacity. It is soluble in non-polar solvents and is non-resistant to attack by oxidising agents. To improve upon these physical properties, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K. On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.

In the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent. The probable structures of vulcanised rubber molecules are depicted below:

2. Synthetic rubbers

Synthetic rubber is any vulcanisable rubber like polymer, which is capable of getting stretched to twice its length. However, it returns to its original shape and size as soon as the external stretching force is released. Thus, synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

Preparation of Synthetic Rubbers

1. Neoprene

Neoprene or polychloroprene is formed by the free radical polymerisation of chloroprene.

$$n\ CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2 \right]_n$$

Chloroprene
2-Chloro-1, 3-butadiene

Neoprene

It has superior resistance to vegetable and mineral oils. It is used for manufacturing conveyor belts, gaskets and hoses.

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2. Buna – N

You have already studied about Buna-S, in Section 15.1.3. Buna –N is obtained by the copolymerisation of 1, 3 – butadiene and acrylonitrile in the presence of a peroxide catalyst.

$$n\,CH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\overset{\overset{\displaystyle CN}{|}}{CH} \xrightarrow{\text{Copolymerisation}} \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CN}{|}}{CH} \right]_n$$

1,3-Butadiene Acrylonitrile Buna-N

It is resistant to the action of petrol, lubricating oil and organic solvents. It is used in making oil seals, tank lining, etc.

Intext Questions

15.5 Explain the difference between Buna-N and Buna-S.

15.6 Arrange the following polymers in increasing order of their intermolecular forces.

(i) Nylon 6,6, Buna-S, Polythene.

(ii) Nylon 6, Neoprene, Polyvinyl chloride.

15.3 Molecular Mass of Polymers

Polymer properties are closely related to their molecular mass, size and structure. The growth of the polymer chain during their synthesis is dependent upon the availability of the monomers in the reaction mixture. Thus, the polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average. The molecular mass of polymers can be determined by chemical and physical methods.

15.4 Biodegradable Polymers

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable polymers. Some important examples are given below:

1. Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

$$CH_3{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_2{-}COOH + CH_3{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_2{-}COOH \longrightarrow \left(O{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{\displaystyle O}{||}}{C}{-}O{-}\underset{\underset{\displaystyle CH_2CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{\displaystyle O}{||}}{C} \right)_n$$

3-Hydroxybutanoic acid 3-Hydroxypentanoic acid PHBV

2. *Nylon 2–nylon 6*

It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid [$H_2N\ (CH_2)_5\ COOH$] and is biodegradable. Can you write the structure of this copolymer?

15.5 Polymers of Commercial Importance

Besides, the polymers already discussed, some other commercially important polymers along with their structures and uses are given below in Table 15.1.

Table 15.1: Some Other Commercially Important Polymers

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(CH_2\text{-}CH(CH_3)\right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left(CH_2\text{-}CH(C_6H_5)\right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left(CH_2\text{-}CH(Cl)\right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyle Resin	(a) Urea (b) Formaldehyde	$\left(NH–CO–NH–CH_2\right)_n$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid		Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde		For making combs, electrical switches, handles of utensils and computer discs.

Summary

Polymers are defined as high molecular mass **macromolecules**, which consist of repeating structural units derived from the corresponding **monomers**. These polymers may be of natural or synthetic origin and are classified in a number of ways.

In the presence of an organic peroxide initiator, the alkenes and their derivatives undergo **addition polymerisation** or **chain growth polymerisation** through a **free radical mechanism**. Polythene, teflon, orlon, etc. are formed by addition polymerisation of an appropriate alkene or its derivative. **Condensation polymerisation** reactions are

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shown by the interaction of bi – or poly functional monomers containing – NH_2, – OH and – COOH groups. This type of polymerisation proceeds through the elimination of certain simple molecules as H_2O, CH_3OH, etc. Formaldehyde reacts with phenol and melamine to form the corresponding condensation polymer products. The condensation polymerisation progresses through step by step and is also called as **step growth polymerisation**. Nylon, bakelite and dacron are some of the important examples of condensation polymers. However, a mixture of two unsaturated monomers exhibits **copolymerisation** and forms a **co-polymer** containing multiple units of each monomer. Natural rubber is a *cis* 1, 4-polyisoprene and can be made more tough by the process of **vulcanisation** with sulphur. Synthetic rubbers are usually obtained by copolymerisation of alkene and 1, 3 butadiene derivatives.

In view of the potential environmental hazards of synthetic polymeric wastes, certain **biodegradable polymers** such as PHBV and Nylon-2- Nylon-6 are developed as alternatives.

Exercises

15.1 Explain the terms polymer and monomer.

15.2 What are natural and synthetic polymers? Give two examples of each type.

15.3 Distinguish between the terms homopolymer and copolymer and give an example of each.

15.4 How do you explain the functionality of a monomer?

15.5 Define the term polymerisation.

15.6 Is $(NH\text{-}CHR\text{-}CO)_n$, a homopolymer or copolymer?

15.7 In which classes, the polymers are classified on the basis of molecular forces?

15.8 How can you differentiate between addition and condensation polymerisation?

15.9 Explain the term copolymerisation and give two examples.

15.10 Write the free radical mechanism for the polymerisation of ethene.

15.11 Define thermoplastics and thermosetting polymers with two examples of each.

15.12 Write the monomers used for getting the following polymers.

(i) Polyvinyl chloride (ii) Teflon (iii) Bakelite

15.13 Write the name and structure of one of the common initiators used in free radical addition polymerisation.

15.14 How does the presence of double bonds in rubber molecules influence their structure and reactivity?

15.15 Discuss the main purpose of vulcanisation of rubber.

15.16 What are the monomeric repeating units of Nylon-6 and Nylon-6,6?

15.17 Write the names and structures of the monomers of the following polymers:

(i) Buna-S (ii) Buna-N (iii) Dacron (iv) Neoprene

15.18 Identify the monomer in the following polymeric structures.

(i) $$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH \right]_n$$

(ii)

15.19 How is dacron obtained from ethylene glycol and terephthalic acid ?

15.20 What is a biodegradable polymer ? Give an example of a biodegradable aliphatic polyester.

Answers of Some Intext Questions

15.1 Polymers are high molecular mass substances consisting of large numbers of repeating structural units. They are also called as macromolecules. Some examples of polymers are polythene, bakelite, rubber, nylon 6, 6, etc.

15.2 On the basis of structure, the polymers are classified as below:
(i) Linear polymers such as polythene, polyvinyl chloride, etc.
(ii) Branched chain polymers such as low density polythene.
(iii) Cross linked polymers such as bakelite, melamine, etc.

15.3 (i) Hexamethylene diamine and adipic acid.
(ii) Caprolactam.
(iii) Tetrafluoroethene.

15.4 Addition polymers: Polyvinyl chloride, Polythene.
Condensation polymers: Terylene, Bakelite.

15.5 Buna-N is a copolymer of 1,3-butadiene and acrylonitrile and Buna-S is a copolymer of 1,3-butadiene and styrene.

15.6 In order of increasing intermolecular forces.
(i) Buna-S, Polythene, Nylon 6,6.
(ii) Neoprene, Polyvinyl chloride, Nylon 6.

Unit

16

Chemistry in Everyday Life

Objectives

After studying this Unit you will be able to

- visualise the importance of Chemistry in daily life;
- explain the term 'chemotherapy';
- describe the basis of classification of drugs;
- explain drug-target interaction of enzymes and receptors;
- explain how various types of drugs function in the body;
- know about artificial sweetening agents and food preservatives;
- discuss the chemistry of cleansing agents.

From living perception to abstract thought, and from this to practice.
V.I. Lenin.

By now, you have learnt the basic principles of chemistry and also realised that it influences every sphere of human life. The principles of chemistry have been used for the benefit of mankind. Think of cleanliness — the materials like soaps, detergents, household bleaches, tooth pastes, etc. will come to your mind. Look towards the beautiful clothes — immediately chemicals of the synthetic fibres used for making clothes and chemicals giving colours to them will come to your mind. Food materials — again a number of chemicals about which you have learnt in the previous Unit will appear in your mind. Of course, sickness and diseases remind us of medicines — again chemicals. Explosives, fuels, rocket propellents, building and electronic materials, etc., are all chemicals. Chemistry has influenced our life so much that we do not even realise that we come across chemicals at every moment; that we ourselves are beautiful chemical creations and all our activities are controlled by chemicals. In this Unit, we shall learn the application of Chemistry in three important and interesting areas, namely – medicines, food materials and cleansing agents.

16.1 Drugs and their Classification

Drugs are chemicals of low molecular masses (~100 – 500u). These interact with macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these chemicals are called **medicines** and are used in diagnosis, prevention and treatment of diseases. If taken in doses higher than those recommended, most of the drugs used as medicines are potential poisons. Use of chemicals for therapeutic effect is called **chemotherapy**,

16.1.1 Classification of Drugs

Drugs can be classified mainly on criteria outlined as follows:

(a) On the basis of pharmacological effect

This classification is based on pharmacological effect of the drugs. It is useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem. For example, analgesics have pain killing effect, antiseptics kill or arrest the growth of microorganisms.

(b) On the basis of drug action

It is based on the action of a drug on a particular biochemical process. For example, all antihistamines inhibit the action of the compound, histamine which causes inflammation in the body. There are various ways in which action of histamines can be blocked. You will learn about this in Section 16.3.2.

(c) On the basis of chemical structure

It is based on the chemical structure of the drug. Drugs classified in this way share common structural features and often have similar pharmacological activity. For example, sulphonamides have common structural feature, given below.

Structural features of sulphonamides

(d) On the basis of molecular targets

Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids. These are called target molecules or drug targets. Drugs possessing some common structural features may have the same mechanism of action on targets. The classification based on molecular targets is the most useful classification for medicinal chemists.

16.2 Drug-Target Interaction

Macromolecules of biological origin perform various functions in the body. For example, proteins which perform the role of biological catalysts in the body are called **enzymes**, those which are crucial to communication system in the body are called **receptors**. Carrier proteins carry polar molecules across the cell membrane. Nucleic acids have coded genetic information for the cell. Lipids and carbohydrates are structural parts of the cell membrane. We shall explain the drug-target interaction with the examples of enzymes and receptors.

16.2.1 Enzymes as Drug Targets

(a) Catalytic action of enzymes

For understanding the interaction between a drug and an enzyme, it is important to know how enzymes catalyse the reaction (Section 5.2.4). In their catalytic activity, enzymes perform two major functions:

(i) The first function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.

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Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole interaction (Fig. 16.1).

Fig. 16.1 *(a) Active site of an enzyme (b) Substrate (c) Substrate held in active site of the enzyme*

(ii) The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction.

(b) Drug-enzyme interaction

Drugs inhibit any of the above mentioned activities of enzymes. These can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called **enzyme inhibitors.**

Drugs inhibit the attachment of substrate on active site of enzymes in two different ways;

(i) Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called **competitive inhibitors** (Fig. 16.2).

Fig. 16.2 *Drug and substrate competing for active site*

Fig. 16.3: *Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site.*

(ii) Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called **allosteric site**. This binding of inhibitor at allosteric site (Fig.16.3) changes the shape of the active site in such a way that substrate cannot recognise it.

If the bond formed between an enzyme and an inhibitor is a strong covalent bond and

cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.

16.2.2 Receptors as Drug Targets

Receptors are proteins that are crucial to body's communication process. Majority of these are embedded in cell membranes (Fig. 16.4). Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane (Fig. 16.4).

Fig. 16.4 Receptor protein embedded in the cell membrane, the active site of the receptor opens on the outside region of the cell.

In the body, message between two neurons and that between neurons to muscles is communicated through certain chemicals. These chemicals, known as **chemical messengers** are received at the binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell. Thus, chemical messenger gives message to the cell without entering the cell (Fig. 16.5).

Fig. 16.5: (a) Receptor receiving chemical messenger
(b) Shape of the receptor changed after attachment of messenger
(c) Receptor regains structure after removal of chemical messenger.

There are a large number of different receptors in the body that interact with different chemical messengers. These receptors show selectivity for one chemical messenger over the other because their binding sites have different shape, structure and amino acid composition.

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Drugs that bind to the receptor site and inhibit its natural function are called **antagonists**. These are useful when blocking of message is required. There are other types of drugs that mimic the natural messenger by switching on the receptor, these are called **agonists**. These are useful when there is lack of natural chemical messenger.

16.3 Therapeutic Action of Different Classes of Drugs

In this Section, we shall discuss the therapeutic action of a few important classes of drugs.

16.3.1 Antacids

Over production of acid in the stomach causes irritation and pain. In severe cases, ulcers are developed in the stomach. Until 1970, only treatment for acidity was administration of antacids, such as sodium hydrogencarbonate or a mixture of aluminium and magnesium hydroxide. However, excessive hydrogencarbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides are better alternatives because of being insoluble, these do not increase the pH above neutrality. These treatments control only symptoms, and not the cause. Therefore, with these metal salts, the patients cannot be treated easily. In advanced stages, ulcers become life threatening and its only treatment is removal of the affected part of the stomach.

16.3.2 Antihistamines

A major breakthrough in the treatment of hyperacidity came through the discovery according to which a chemical, histamine, stimulates the secretion of pepsin and hydrochloric acid in the stomach. The drug cimetidine (Tegamet), was designed to prevent the interaction of histamine with the receptors present in the stomach wall. This resulted in release of lesser amount of acid. The importance of the drug was so much that it remained the largest selling drug in the world until another drug, ranitidine (Zantac), was discovered.

Histamine

Cimetidine

Ranitidine

Histamine is a potent vasodilator. It has various functions. It contracts the smooth muscles in the bronchi and gut and relaxes other muscles, such as those in the walls of fine blood vessels. Histamine is also responsible for the nasal congestion associated with common cold and allergic response to pollen.

Synthetic drugs, **brompheniramine (Dimetapp)** and **terfenadine (Seldane),** act as antihistamines. They interfere with the natural action

Brompheniramine
(Dimetapp, Dimetane)

Terfenadine (Seldane)

of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

Now the question that arises is, "Why do above mentioned antihistamines not affect the secretion of acid in stomach?" The reason is that antiallergic and antacid drugs work on different receptors.

16.3.3 Neurologically Active Drugs

(a) Tranquilizers

Tranquilizers and **analgesics** are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being. They form an essential component of sleeping pills. There are various types of tranquilizers. They function by different mechanisms. For example, noradrenaline is one of the neurotransmitters that plays a role in mood changes. If the level of noradrenaline is low for some reason, then the signal-sending activity becomes low, and the person suffers from depression. In such situations, **antidepressant drugs** are required. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer periods of time, thus counteracting the effect of depression. Iproniazid and phenelzine are two such drugs.

Iproniazid

Phenelzine (Nardil)

Some tranquilizers namely, chlordiazepoxide and meprobamate, are relatively mild tranquilizers suitable for relieving tension. Equanil is used in controlling depression and hypertension.

Chlordiazepoxide

Meprobamate

Equanil

Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal constitute an important class of tranquilizers. These derivatives are called **barbiturates**. Barbiturates are hypnotic, *i.e.*, sleep producing agents. Some other substances used as tranquilizers are valium and serotonin.

(b) *Analgesics*

Analgesics reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system. These are classified as follows:

(i) Non-narcotic (non-addictive) analgesics

(ii) Narcotic drugs

(i) ***Non-narcotic (non-addictive) analgesics:*** Aspirin and paracetamol belong to the class of **non-narcotic analgesics**. **Aspirin** is the most familiar example. Aspirin inhibits the synthesis of chemicals known as prostaglandins which stimulate inflammation in the tissue and cause pain. These drugs are effective in relieving skeletal pain such as that due to arthritis. These drugs have many other effects such as reducing fever **(antipyretic)** and preventing platelet coagulation. Because of its anti blood clotting action, aspirin finds use in prevention of heart attacks.

(ii) ***Narcotic analgesics:*** Morphine and many of its homologues, when administered in medicinal doses, relieve pain and produce sleep. In poisonous doses, these produce stupor, coma, convulsions and ultimately death. Morphine narcotics are sometimes referred to as opiates, since they are obtained from the opium poppy.

These analgesics are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.

16.3.4 Antimicrobials

Diseases in human beings and animals may be caused by a variety of microorganisms such as bacteria, virus, fungi and other pathogens. An antimicrobial tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively. Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

(a) Antibiotics

Antibiotics are used as drugs to treat infections because of their low toxicity for humans and animals. Initially antibiotics were classified as chemical substances produced by microorganisms (bacteria, fungi and molds) that inhibit the growth or even destroy microorganisms. The development of synthetic methods has helped in synthesising some of the compounds that were originally discovered as products of microorganisms. Also, some purely synthetic compounds have antibacterial activity, and therefore, definition of antibiotic has been modified. An antibiotic now refers to a substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes.

The search for chemicals that would adversely affect invading bacteria but not the host began in the nineteenth century. Paul Ehrlich, a German bacteriologist, conceived this idea. He investigated arsenic based structures in order to produce less toxic substances for the treatment of syphilis. He developed the medicine, **arsphenamine**, known as **salvarsan**. Paul Ehrlich got Nobel prize for Medicine in 1908 for this discovery. It was the first effective treatment discovered for syphilis. Although salvarsan is toxic to human beings, its effect on the bacteria, spirochete, which causes syphilis is much greater than on human beings. At the same time, Ehrlich was working on azodyes also. He noted that there is similarity in structures of salvarsan and

The structures of salvarsan, prontosil azodye and sulphapyridine showing structural similarity.

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azodyes. The –As = As– linkage present in arsphenamine resembles the –N = N – linkage present in azodyes in the sense that arsenic atom is present in place of nitrogen. He also noted tissues getting coloured by dyes selectively. Therefore, Ehrlich began to search for the compounds which resemble in structure to azodyes and selectively bind to bacteria. In 1932, he succeeded in preparing the first effective antibacterial agent, **prontosil**, which resembles in structure to the compound, salvarsan. Soon it was discovered that in the body prontosil is converted to a compound called **sulphanilamide**, which is the real active compound. Thus the sulpha drugs were discovered. A large range of sulphonamide analogues was synthesised. One of the most effective is sulphapyridine.

H.W. Florey and Alexander Fleming shared the Nobel prize for Medicine in 1945 for their independent contributions to the development of penicillin.

Despite the success of sulfonamides, the real revolution in antibacterial therapy began with the discovery of Alexander Fleming in 1929, of the antibacterial properties of a *Penicillium* fungus. Isolation and purification of active compound to accumulate sufficient material for clinical trials took thirteen years.

Antibiotics have either cidal (killing) effect or a static (inhibitory) effect on microbes. A few examples of the two types of antibiotics are as follows:

Bactericidal	**Bacteriostatic**
Penicillin	Erythromycin
Aminoglycosides	Tetracycline
Ofloxacin	Chloramphenicol

The range of bacteria or other microorganisms that are affected by a certain antibiotic is expressed as its spectrum of action. Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be **broad spectrum antibiotics**. Those effective mainly against Gram-positive or Gram-negative bacteria are **narrow spectrum antibiotics**. If effective against a single organism or disease, they are referred to as **limited spectrum** antibiotics. Penicillin G has a narrow spectrum. Ampicillin and Amoxycillin are synthetic modifications of penicillins. These have broad spectrum. It is absolutely essential to test the patients for sensitivity (allergy) to penicillin before it is administered. In India, penicillin is manufactured at the Hindustan Antibiotics in Pimpri and in private sector industry.

Chloramphenicol, isolated in 1947, is a broad spectrum antibiotic. It is rapidly absorbed from the gastrointestinal tract and hence can be given orally in case of typhoid, dysentery, acute fever, certain form of urinary infections, meningitis and pneumonia. *Vancomycin* and *ofloxacin* are the other important broad spectrum antibiotics. The antibiotic *dysidazirine* is supposed to be toxic towards certain strains of cancer cells.

General Sturcture of Pencillin

Chloramphenicol

(b) Antiseptics and disinfectants

Antiseptics and disinfectants are also the chemicals which either kill or prevent the growth of microorganisms.

Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. Examples are **furacine**, **soframicine,** etc. These are not ingested like antibiotics. Commonly used antiseptic, dettol is a mixture of **chloroxylenol** and **terpineol**. Bithionol (the compound is also called bithional) is added to soaps to impart antiseptic properties. Iodine is a powerful antiseptic. Its 2-3 per cent solution in alcohol-water mixture is known as **tincture of iodine**. It is applied on wounds. **Iodoform** is also used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes.

Chloroxylenol

Terpineol

Bithionol

Disinfectants are applied to inanimate objects such as floors, drainage system, instruments, etc. Same substances can act as an antiseptic as well as disinfectant by varying the concentration. For example, 0.2 per cent solution of phenol is an antiseptic while its one percent solution is disinfectant.

Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and sulphur dioxide in very low concentrations, are disinfectants.

16.3.5 Antifertility Drugs

Antibiotic revolution has provided long and healthy life to people. The life expectancy has almost doubled. The increased population has caused many social problems in terms of food resources, environmental issues, employment, etc. To control these problems, population is required to be controlled. This has lead to the concept of family planning. Antifertility drugs are of use in this direction. Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives. Both of these compounds are hormones. It is known that progesterone suppresses ovulation. Synthetic progesterone derivatives are more potent than progesterone. **Norethindrone** is an example of synthetic progesterone derivative most widely used as antifertility drug. The estrogen derivative which is used in combination with progesterone derivative is **ethynylestradiol (novestrol)**.

Norethindrone

Ethynylestradiol (novestrol)

Intext Questions

16.1 Sleeping pills are recommended by doctors to the patients suffering from sleeplessness but it is not advisable to take its doses without consultation with the doctor. Why ?

16.2 With reference to which classification has the statement, "ranitidine is an antacid" been given?

16.4 Chemicals in Food

Chemicals are added to food for (i) their preservation, (ii) enhancing their appeal, and (iii) adding nutritive value in them. Main categories of food additives are as follows:

(i) Food colours
(ii) Flavours and sweeteners
(iii) Fat emulsifiers and stabilising agents
(iv) Flour improvers - antistaling agents and bleaches
(v) Antioxidants
(vi) Preservatives
(vii) Nutritional supplements such as minerals, vitamins and amino acids.

Except for chemicals of category (vii), none of the above additives have nutritive value. These are added either to increase the shelf life of stored food or for cosmetic purposes. In this Section we will discuss only sweeteners and food preservatives.

16.4.1 Artificial Sweetening Agents

Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It has been used as a sweetening agent ever since it was discovered in 1879. It is about 550 times as sweet as cane sugar. It is excreted from the body in urine unchanged. It appears to be entirely inert and harmless when taken. Its use is of great value to diabetic persons and people who need to control intake of calories. Some other commonly marketed artificial sweeteners are given in Table 16.1.

Table 16.1: Artificial Sweeteners

Artificial sweetener	Structural formula	Sweetness value in comparison to cane sugar
Aspartame		100
Saccharin		550
Sucrolose		600

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Alitame		2000

Aspartame is the most successful and widely used artificial sweetener. It is roughly 100 times as sweet as cane sugar. It is methyl ester of dipeptide formed from aspartic acid and phenylalanine. Use of aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.

Alitame is high potency sweetener, although it is more stable than aspartame, the control of sweetness of food is difficult while using it.

Sucrolose is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature. It does not provide calories.

16.4.2 Food Preservatives

Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate, C_6H_5COONa. Sodium benzoate is used in limited quantities and is metabolised in the body. Salts of sorbic acid and propanoic acid are also used as preservatives.

Intext Question

16.3 Why do we require artificial sweetening agents ?

16.5 Cleansing Agents

In this Section, we will learn about **detergents**. Two types of detergents are used as cleansing agents. These are soaps and synthetic detergents. These improve cleansing properties of water. These help in removal of fats which bind other materials to the fabric or skin.

16.5.1 Soaps

Glyceryl ester of stearic acid (Fat) | Sodium hydroxide | Sodium stearate | Glycerol (or Glycerine)

Soaps are the detergents used since long. Soaps used for cleaning purpose are sodium or potassium salts of long chain fatty acids, e.g., stearic, oleic and palmitic acids. Soaps containing sodium salts are formed by heating fat (*i.e.*, glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as **saponification**.

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In this reaction, esters of fatty acids are hydrolysed and the soap obtained remains in colloidal form. It is precipitated from the solution by adding sodium chloride. The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation. Only sodium and potassium soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps. These can be prepared by using potassium hydroxide solution in place of sodium hydroxide.

Types of soaps

Basically all soaps are made by boiling fats or oils with suitable soluble hydroxide. Variations are made by using different raw materials.

Toilet soaps are prepared by using better grades of fats and oils and care is taken to remove excess alkali. Colour and perfumes are added to make these more attractive.

Soaps that float in water are made by beating tiny air bubbles before their hardening. *Transparent soaps* are made by dissolving the soap in ethanol and then evaporating the excess solvent.

In *medicated soaps,* substances of medicinal value are added. In some soaps, deodorants are added. *Shaving soaps* contain glycerol to prevent rapid drying. A gum called, rosin is added while making them. It forms sodium rosinate which lathers well. *Laundry soaps* contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.

Soap chips are made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces. *Soap granules* are dried miniature soap bubbles. *Soap powders* and *scouring soaps* contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate. Builders make the soaps act more rapidly. The cleansing action of soap has been discussed in Unit 5.

Why do soaps not work in hard water?

Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + CaCl_2 \longrightarrow 2NaCl + \underset{\text{Insoluble calcium stearate (Soap)}}{(C_{17}H_{35}COO)_2Ca}$$

These insoluble soaps separate as scum in water and are useless as cleansing agent. In fact these are hinderance to good washing, because the precipitate adheres onto the fibre of the cloth as gummy mass. Hair washed with hard water looks dull because of this sticky precipitate. Dye does not absorb evenly on cloth washed with soap using hard water, because of this gummy mass.

16.5.2 Synthetic Detergents

Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water. Some of the detergents give foam even in ice cold water.

Synthetic detergents are mainly classified into three categories: (i) Anionic detergents (ii) Cationic detergents and (iii) Non-ionic detergents

(i) Anionic Detergents: Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali.

$$\underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{Lauryl hydrogensulphate}}{CH_3(CH_2)_{10}CH_2OSO_3H} \xrightarrow{NaOH(aq)} \underset{\text{Sodium laurylsulphate (Anionic detergent)}}{CH_3(CH_2)_{10}CH_2O\overset{-}{S}O_3\overset{+}{N}a}$$

Dodecylbenzene Dodecylbenzenesulphonic acid Sodium dodecylbenzenesulphonate

In anionic detergents, the anionic part of the molecule is involved in the cleansing action. Sodium salts of alkylbenzenesulphonates are an important class of anionic detergents.

They are mostly used for household work. Anionic detergents are also used in toothpastes.

(ii) Cationic Detergents: Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents. Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.

Cetyltrimethyl ammonium bromide

Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use.

(iii) Non-ionic Detergents: Non-ionic detergents do not contain any ion in their constitution. One such detergent is formed when stearic acid reacts with polyethyleneglycol.

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethyleneglycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-H_2O} CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

Liquid dishwashing detergents are non-ionic type. Mechanism of cleansing action of this type of detergents is the same as that of soaps. These also remove grease and oil by micelle formation.

Main problem that appears in the use of detergents is that if their hydrocarbon chain is highly branched, then bacteria cannot degrade

this easily. Slow degradation of detergents leads to their accumulation. Effluents containing such detergents reach the rivers, ponds, etc. These persist in water even after sewage treatment and cause foaming in rivers, ponds and streams and their water gets polluted.

These days the branching of the hydrocarbon chain is controlled and kept to the minimum. Unbranched chains can be biodegraded more easily and hence pollution is prevented.

Intext Questions

16.4 Write the chemical equation for preparing sodium soap from glyceryl oleate and glyceryl palmitate. Structural formulae of these compounds are given below.

(i) $(C_{15}H_{31}COO)_3C_3H_5$ – Glyceryl palmitate

(ii) $(C_{17}H_{32}COO)_3C_3H_5$ – Glyceryl oleate

16.5 Following type of non-ionic detergents are present in liquid detergents, emulsifying agents and wetting agents. Label the hydrophilic and hydrophobic parts in the molecule. Identify the functional group(s) present in the molecule.

(x = 5 to 10)

Summary

Chemistry is essentially the study of materials and the development of new materials for the betterment of humanity. A **drug** is a chemical agent, which affects human metabolism and provides cure from ailment. If taken in doses higher than recommended, these may have poisonous effect. Use of chemicals for therapeutic effect is called **chemotherapy**. Drugs usually interact with biological macromolecules such as carbohydrates, proteins, lipids and nucleic acids. These are called **target molecules**. Drugs are designed to interact with specific targets so that these have the least chance of affecting other targets. This minimises the side effects and localises the action of the drug. Drug chemistry centres around arresting microbes/destroying microbes, preventing the body from various infectious diseases, releasing mental stress, etc. Thus, drugs like analgesics, antibiotics, antiseptics, disinfectants, antacids and tranquilizers are used for specific purpose. To check the population explosion, antifertility drugs have also become prominent in our life.

Food additives such as **preservatives**, **sweetening agents**, **flavours**, **antioxidants**, **edible colours** and **nutritional supplements** are added to the food to make it attractive, palatable and add nutritive value. Preservatives are added to the food to prevent spoilage due to microbial growth. Artificial sweeteners are used by those who need to check the calorie intake or are diabetic and want to avoid taking sucrose.

These days, **detergents** are much in vogue and get preference over soaps because they work even in hard water. Synthetic detergents are classified into

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three main categories, namely: **anionic, cationic** and **non-ionic,** and each category has its specific uses. Detergents with straight chain of hydrocarbons are preferred over branched chain as the latter are **non-biodegradable** and consequently cause **environmental pollution**.

Exercises

16.1 Why do we need to classify drugs in different ways ?

16.2 Explain the term, target molecules or drug targets as used in medicinal chemistry.

16.3 Name the macromolecules that are chosen as drug targets.

16.4 Why should not medicines be taken without consulting doctors ?

16.5 Define the term chemotherapy.

16.6 Which forces are involved in holding the drugs to the active site of enzymes ?

16.7 While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other ?

16.8 Low level of noradrenaline is the cause of depression. What type of drugs are needed to cure this problem ? Name two drugs.

16.9 What is meant by the term 'broad spectrum antibiotics' ? Explain.

16.10 How do antiseptics differ from disinfectants ? Give one example of each.

16.11 Why are cimetidine and ranitidine better antacids than sodium hydrogencarbonate or magnesium or aluminium hydroxide ?

16.12 Name a substance which can be used as an antiseptic as well as disinfectant.

16.13 What are the main constituents of dettol ?

16.14 What is tincture of iodine ? What is its use ?

16.15 What are food preservatives ?

16.16 Why is use of aspartame limited to cold foods and drinks ?

16.17 What are artificial sweetening agents ? Give two examples.

16.18 Name the sweetening agent used in the preparation of sweets for a diabetic patient.

16.19 What problem arises in using alitame as artificial sweetener ?

16.20 How are synthetic detergents better than soaps ?

16.21 Explain the following terms with suitable examples

(i) cationic detergents

(ii) anionic detergents and

(iii) non-ionic detergents.

16.22 What are biodegradable and non-biodegradable detergents ? Give one example of each.

16.23 Why do soaps not work in hard water ?

16.24 Can you use soaps and synthetic detergents to check the hardness of water ?

16.25 Explain the cleansing action of soaps.

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16.26 If water contains dissolved calcium hydrogencarbonate, out of soaps and synthetic detergents which one will you use for cleaning clothes ?

16.27 Label the hydrophilic and hydrophobic parts in the following compounds.

(i) $CH_3(CH_2)_{10}CH_2OSO_3^{-}\overset{+}{N}a$

(ii) $CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3\overset{-}{B}r$

(iii) $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$

Answers to Some Intext Questions

16.1 Most of the drugs taken in doses higher than recommended may cause harmful effect and act as poison. Therefore, a doctor should always be consulted before taking medicine.

16.2 This statement refers to the classification according to pharmacological effect of the drug because any drug which will be used to counteract the effect of excess acid in the stomach will be called antacid.

16.5

Answers to Some Questions in Exercises

UNIT 11

11.1 (i) 2,2,4-Trimethylpentan –3-ol (ii) 5-Ethylheptane –2, 4-diol

(iii) Butane –2,3-diol (iv) Propane –1,2,3,-triol

(v) 2- Methylphenol (vi) 4-Methylphenol

(vii) 2,5 – Dimethylphenol (viii) 2,6-Dimethylphenol

(ix) 1-Methoxy-2-methylpropane (x) Ethoxybenzene

(xi) 1-phenoxyheptane (xii) 2 –Ethoxybutane

11.2 (i) $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$

(ii)

(iii) $HOCH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$

(iv)

(v) $C_2H_5-O-CH_2-CH_2-CH_3$

(vi) $CH_3-\underset{\underset{OC_2H_5}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

(vii)

(viii) $CH_3-CH_2-\overset{\overset{OH}{|}}{C}-CH_2-CH_3$

(ix)

(x) $CH_3-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-CH_2-CH_2-OH$

11.3 (a) $CH_3CH_2CH_2CH_2CH_2OH$, Pentan-1-ol;

(b) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-OH$, 2-Methylbutan-1-ol;

(c) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$, 2,2-Dimethylpropan-1-ol

(d) $CH_3-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$, Pentan-2-ol

(e) $CH_3-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$, Pentan-2-ol

(f) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$, 3-Methylbutan-2-ol

(g) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$, 2-Methylbutan-2-ol

11.4 Hydrogen bonding in propanol.

11.5 Hydrogen bonding between alcohol and water molecules.

11.8 o-Nitrophenol is steam volatile because of intramolecular hydrogen bonding.

11.12 **Hint:** Carryout sulphonation followed by nucleophilic substitution.

11.13 (i)

(ii)

(iii) $CH_3(CH_2)_4Cl + NaOH \longrightarrow CH_3(CH_2)_4OH + NaCl$

11.14 Reaction with (i) sodium and (ii) sodium hydroxide

11.15 Due to electron withdrawing effect of nitro group and electron releasing effect of methoxy group.

11.20 (i) Hydration of Propene.

(ii) By nucleophilic substitution of –Cl in benzyl chloride using dilute NaOH.

(iii) $C_2H_5MgBr + HCHO \rightarrow C_2H_5CH_2OMgBr \xrightarrow{H_2O} C_2H_5CH_2OH$

(iv) $CH_3MgBr + CH_3COCH_3 \longrightarrow CH_3-C(CH_3)_2-OMgBr \xrightarrow{H_2O} CH_3-C(CH_3)_2-OH$

11.23 (i) 1-Ethoxy-2-methylpropane.

(ii) 2-Chloro-1-methoxyethane.

(iii) 4-Nitroanisole.

(iv) 1-Methoxypropane.

(v) 1-Ethoxy-4,4-dimethylcyclohexane.

(vi) Ethoxybenzene.

UNIT 12

12.2 (i) 4-Methylpentanal

(ii) 6-Chloro-4-ethylhexan-3-one

(iii) But-2-enal

(iv) Pentane-2,4-dione

(v) 3,3,5-Trimethylhexan-2-one

(vi) 3,3-Dimethylbutanoic acid

(vii) Benzene –1,4-dicarbaldehyde

12.3 (i) $H_3C-CH(CH_3)-CH_2-C(=O)-H$

(ii)

(iii)

(iv) $H_3C-C(=O)-CH=C(CH_3)-CH_3$

(v) $H_3C-C(=O)-CH_2-CH(Cl)-CH_3$

(vi) $H_3C-CH(C_6H_5)-CH(Br)-CH_2-C(=O)-OH$

(vii)

(viii) $H_3C–C\equiv C–CH=CH–\overset{O}{\overset{\|}{C}}–OH$

12.4 (i) Heptan-2-one (ii) 4-Bromo-2-methylhexanal (iii) Heptanal
(iv) 3-Phenylpropenal (v) γ-Cyclopentanecarbaldehyde (vi) Diphenylmethanone

12.5 (i)

(ii)

(iii) $CH_3–CH\begin{matrix}OCH_3\\OCH_3\end{matrix}$

(iv)

(v)

(vi)

12.6 (i)

(ii)

(iii)

(iv)

(v)

12.7 (ii), (v), (vi), (vii): Aldol condensation. (i), (iii), (ix) Cannizaro reaction. (iv), (viii) Neither.

12.10 2-Ethylbenzaldehyde (draw the structure yourself).

12.11 (A) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$, butyl butanoate.
(B) $CH_3CH_2CH_2$ COOH (C) $CH_3CH_2CH_2CH_2OH$. Write equation yourself.

12.12 (i) Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde
(ii) $(CH_3)_2CHCOOH$ < $CH_3CH_2CH_2COOH$ < $CH_3CH(Br)CH_2COOH$ < $CH_3CH_2CH(Br)COOH$
(iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid.

12.17 (i)

(ii)

(iii) $C_6H_5CH=NNH\overset{O}{\overset{\|}{C}}–NH_2$

(iv) $C_6H_5COCl–AlCl_3$

(v)

(vi)

(vii) $C_6H_5CH=\underset{\underset{CH_3}{|}}{C}–CHO$

(viii) $CH_3CH(OH)CH_2COOC_2H_5$

(ix)

(x) 1. BH_3; 2. $H_2O_2/\bar{O}H$; 3. PCC

(xi)

12.19 The compound is methyl ketone and its structure would be: $CH_3COCH_2CH_2CH_3$

UNIT 13

13.1 (i) 1-methylethanamine (ii) Propan-1-amine
(iii) N-methyl-2-methylethanamine (iv) 2-methylpropan-2-amine
(v) N-methylbenzamine or N-methylaniline (vi) N-Ethyl-N-methylethanamine
(vii) 3-Bromoaniline or 3-Bromobenzenamine

13.4 (i) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$
(ii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
(iii) (a) p-nitroaniline < aniline < p-toluidine
(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$ (v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$
(vi) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

UNIT 15

15.1 Polymer is a high molecular mass macromolecule consisting of repeating structural units derived from monomers.

Monomer is a simple molecule capable of undergoing polymerisation and leading to the formation of the corresponding polymer.

15.2 Natural polymers are high molecular mass macromolecules and are found in plants and animals. The examples are proteins and nucleic acids.

Synthetic polymers are man-made high molecular mass macromolecules. These include synthetic plastics, fibres and rubbers. The two specific examples are polythene and dacron.

15.4 Functionality is the number of bonding sites in a monomer.

15.5 Polymerisation is a process of formation of a high molecular mass polymer from one or more monomers by linking together of repeating structural units with covalent bonds.

15.6 Since the unit $-(NH-CHR-CO)-_n$ is obtained from a single monomer unit, it is a homopolymer.

15.7 On the basis of molecular forces present between the chains of various polymers, the classification of polymers is given as follows.

(a) Elastomers (b) Fibres (c) Thermoplastics and (d) Thermosetting plastics.

15.8 In addition polymerisation, the molecules of the same or different monomers add together to form a large polymer molecule. Condensation polymerisation is a process in which two or more bi-functional molecules undergo a series of condensation reactions with the elimination of some simple molecules and leading to the formation of polymers.

15.9 Copolymerisation is a process in which a mixture of more than one monomeric species is allowed to polymerise. The copolymer contains multiple units of each monomer in the chain. The examples are copolymers of 1,3-butadiene and styrene and 1, 3-butadiene and acrylonitrile.

15.10

15.11 A thermoplastic polymer can be repeatedly softened on heating and hardened on cooling, hence it can be used again and again. The examples are polythene, polypropylene, etc.
A thermosetting polymer is a permanent setting polymer as it gets hardened and sets during

moulding process and cannot be softened again. The examples are bakelite and melamine-formaldehyde polymers.

15.12 (i) The monomer of polyvinyl chloride is $CH_2=CHCl$ (vinyl chloride).

(ii) The monomer of teflon is $CF_2=CF_2$ (tetrafluoroethylene).

(iii) The monomers involved in the formation of bakelite are HCHO (formaldehyde) and C_6H_5OH (phenol).

15.14 From the structural point of view, the natural rubber is a linear cis-1,4- polyisoprene. In this polymer the double bonds are located between C_2 and C_3 of isoprene units. This cis-configuration about double bonds do not allow the chains to come closer for effective attraction due to weak intermolecular attractions. Hence, the natural rubber has a coiled structure and shows elasticity.

15.16 The monomeric repeat unit of Nylon-6 polymer is:

$[NH-(CH_2)_5-CO]$

The monomeric repeat unit of Nylon-6,6 polymer is derived from the two monomers, hexamethylene diamine and adipic acid.

$[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]$

15.17 The names and structures of monomers are:

	Polymers	**Monomer Names**	**Monomer Structures**
(i)	Buna-S	1,3-Butadiene Styrene	$CH_2=CH-CH=CH_2$ $C_6H_5CH=CH_2$
(ii)	Buna-N	1,3- Butadiene Acrylonitrile	$CH_2=CH-CH=CH_2$ $CH_2=CH\ CN$
(iii)	Neoprene	Chloroprene	$CH_2=C(Cl)-CH=CH_2$
(iv)	Dacron	Ethylene glycol Terephthalic acid	$OHCH_2-CH_2OH$

15.18 The monomers forming the polymer are:

(i) Decanoic acid $HOOC-(CH_2)_8-COOH$ and Hexamethylene diamine $H_2N(CH_2)_6\ NH_2$

(ii) and HCHO

15.19 The following are the equations for the formation of Dacron.