



## UNIT 1

11082CH01

# SOME BASIC CONCEPTS OF CHEMISTRY

## Objectives

After studying this unit, you will be able to

- appreciate the contribution of India in the development of chemistry understand 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;
- use scientific notations and determine significant figures;
- differentiate between precision and accuracy;
- define SI base units and 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 component elements constituting a compound;
- determine empirical formula and molecular formula for a compound from the given experimental data; and
- 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**

Science can be viewed as a continuing human effort to systematise knowledge for describing and understanding nature. You have learnt in your previous classes that we come across diverse substances present in nature and changes in them in daily life. Curd formation from milk, formation of vinegar from sugarcane juice on keeping for prolonged time and rusting of iron are some of the examples of changes which we come across many times. For the sake of convenience, science is sub-divided into various disciplines: chemistry, physics, biology, geology, etc. The branch of science that studies the preparation, properties, structure and reactions of material substances is called chemistry.

## DEVELOPMENT OF CHEMISTRY

Chemistry, as we understand it today, is not a very old discipline. Chemistry was not studied for its own sake, rather it came up as a result of search for two interesting things:

- i. *Philosopher's stone (Paras)* which would convert all baser metals e.g., iron and copper into gold.
- ii. *'Elixir of life'* which would grant immortality.

People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied that knowledge in various walks of life. Chemistry developed mainly in the form of Alchemy and Iatrochemistry during 1300-1600 CE. Modern chemistry took shape in the 18<sup>th</sup> century Europe, after a few centuries of alchemical traditions which were introduced in Europe by the Arabs.

Other cultures – especially the Chinese and the Indian – had their own alchemical traditions. These included much knowledge of chemical processes and techniques.

In ancient India, chemistry was called *Rasayan Shastra*, *Rastantra*, *Ras Kriya* or *Rasvidya*. It included metallurgy, medicine, manufacture of cosmetics, glass, dyes, etc. Systematic excavations at Mohenjodaro in Sindh and Harappa in Punjab prove that the story of development of chemistry in India is very old. Archaeological findings show that baked bricks were used in construction work. It shows the mass production of pottery, which can be regarded as the earliest chemical process, in which materials were mixed, moulded and subjected to heat by using fire to achieve desirable qualities. Remains of glazed pottery have been found in Mohenjodaro. Gypsum cement has been used in the construction work. It contains lime, sand and traces of  $\text{CaCO}_3$ . Harappans made faience, a sort of glass which was used in ornaments. They melted and forged a variety of objects from metals, such as lead, silver, gold and copper. They improved the hardness of copper for making artefacts by using tin and arsenic. A number of glass objects were found in Maski in South India (1000–900 BCE), and Hastinapur and Taxila in North India (1000–200 BCE). Glass and glazes were coloured by addition of colouring agents like metal oxides.

Copper metallurgy in India dates back to the beginning of chalcolithic cultures in the subcontinent. There are much archeological evidences to support the view that technologies for extraction of copper and iron were developed indigenously.

According to *Rigveda*, tanning of leather and dyeing of cotton were practised during 1000–400 BCE. The golden gloss of the black polished ware of northern India could not be replicated and is still a chemical mystery. These wares indicate the mastery with which kiln temperatures could be controlled. Kautilya's *Arthashastra* describes the production of salt from sea.

A vast number of statements and material described in the ancient Vedic literature can

be shown to agree with modern scientific findings. Copper utensils, iron, gold, silver ornaments and terracotta discs and painted grey pottery have been found in many archaeological sites in north India. *Sushruta Samhita* explains the importance of Alkalies. The *Charaka Samhita* mentions ancient Indians who knew how to prepare sulphuric acid, nitric acid and oxides of copper, tin and zinc; the sulphates of copper, zinc and iron and the carbonates of lead and iron.

*Rasopanishada* describes the preparation of gunpowder mixture. Tamil texts also describe the preparation of fireworks using sulphur, charcoal, saltpetre (i.e., potassium nitrate), mercury, camphor, etc.

Nagarjuna was a great Indian scientist. He was a reputed chemist, an alchemist and a metallurgist. His work *Rasratnakar* deals with the formulation of mercury compounds. He has also discussed methods for the extraction of metals, like gold, silver, tin and copper. A book, *Rsarnavam*, appeared around 800 CE. It discusses the uses of various furnaces, ovens and crucibles for different purposes. It describes methods by which metals could be identified by flame colour.

*Chakrapani* discovered mercury sulphide. The credit for inventing soap also goes to him. He used mustard oil and some alkalies as ingredients for making soap. Indians began making soaps in the 18<sup>th</sup> century CE. Oil of *Eranda* and seeds of *Mahua* plant and calcium carbonate were used for making soap.

The paintings found on the walls of Ajanta and Ellora, which look fresh even after ages, testify to a high level of science achieved in ancient India. Varähmihir's *Brihat Samhita* is a sort of encyclopaedia, which was composed in the sixth century CE. It informs about the preparation of glutinous material to be applied on walls and roofs of houses and temples. It was prepared entirely from extracts of various plants, fruits, seeds and barks, which were concentrated by boiling, and then, treated with various resins. It will be interesting to test such materials scientifically and assess them for use.

A number of classical texts, like *Atharvaveda* (1000 BCE) mention some dye stuff, the material used were turmeric, madder, sunflower, orpiment, cochineal and lac. Some other substances having tinting property were *kamplcica*, *pattanga* and *jatuka*.

Varähmihir's *Brihat Samhita* gives references to perfumes and cosmetics. Recipes for hair dying were made from plants, like indigo and minerals like iron power, black iron or steel and acidic extracts of sour rice gruel. *Gandhayukli* describes recipes for making scents, mouth perfumes, bath powders, incense and talcum powder.

Paper was known to India in the 17<sup>th</sup> century as account of Chinese traveller I-tsing describes. Excavations at Taxila indicate that ink was used in India from the fourth century. Colours of ink were made from chalk, red lead and minimum.

It seems that the process of fermentation was well-known to Indians. Vedas and Kautilya's *Arthashastra* mention about many types of liquors. *Charaka Samhita* also mentions ingredients, such as barks of plants, stem, flowers, leaves, woods, cereals, fruits and sugarcane for making *Asavas*.

The concept that matter is ultimately made of indivisible building blocks, appeared in India a few centuries BCE as a part of philosophical speculations. Acharya Kanda, born in 600 BCE, originally known by the name Kashyap, was the first proponent of the 'atomic theory'. He formulated the theory of very small indivisible particles, which he named '*Paramānu*' (comparable to atoms). He authored the text *Vaisesika Sutras*. According to him, all substances are aggregated form of smaller units called atoms (*Paramānu*), which are eternal, indestructible, spherical, suprasensible and in motion in the original state. He explained that this individual entity cannot be sensed through any human organ. Kanda added that there are varieties of atoms that are as different as the different classes of substances. He said these (*Paramānu*) could form pairs or triplets, among other combinations and unseen

forces cause interaction between them. He conceptualised this theory around 2500 years before John Dalton (1766-1844).

*Charaka Samhita* is the oldest Ayurvedic epic of India. It describes the treatment of diseases. The concept of reduction of particle size of metals is clearly discussed in *Charaka Samhita*. Extreme reduction of particle size is termed as nanotechnology. *Charaka Samhita* describes the use of *bhasma* of metals in the treatment of ailments. Now-a-days, it has been proved that *bhasmas* have nanoparticles of metals.

After the decline of alchemy, Iatrochemistry reached a steady state, but it too declined due to the introduction and practise of western medicinal system in the 20<sup>th</sup> century. During this period of stagnation, pharmaceutical industry based on Ayurveda continued to exist, but it too declined gradually. It took about 100-150 years for Indians to learn and adopt new techniques. During this time, foreign products poured in. As a result, indigenous traditional techniques gradually declined. Modern science appeared in Indian scene in the later part of the nineteenth century. By the mid-nineteenth century, European scientists started coming to India and modern chemistry started growing.

From the above discussion, you have learnt that chemistry deals with the composition, structure, properties and interaction of matter and is of much use to human beings in daily life. These aspects can be best described and understood in terms of basic constituents of matter that are **atoms** and **molecules**. That is why, chemistry is also called the science of atoms and molecules. Can we see, weigh and perceive these entities (atoms and molecules)? 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 the number of these particles? We will get the answer of some of these questions in this Unit. We will further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.

## 1.1 IMPORTANCE OF CHEMISTRY

Chemistry plays a central role in science and is often intertwined with other branches of science.

Principles of chemistry are applicable in diverse areas, such as weather patterns, functioning of brain and operation of a computer, production in chemical industries, manufacturing fertilisers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys, etc., including new material.

Chemistry contributes in a big way to the national economy. It also plays an important role in meeting human needs for food, healthcare products and other material aimed at improving the quality of life. This is exemplified by the large-scale production of a variety of fertilisers, improved variety of pesticides and insecticides. Chemistry provides methods for the isolation of life-saving drugs from natural sources and makes possible synthesis of such drugs. Some of these drugs are **cisplatin** and **taxol**, which are effective in cancer therapy. The drug AZT (Azidothymidine) is used for helping AIDS patients.

Chemistry contributes to a large extent in the development and growth of a nation. With a better understanding of chemical principles it has now become possible to design and synthesise new material having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres, etc. Chemistry has helped in establishing industries which manufacture utility goods, like acids, alkalies, dyes, polymers, metals, etc. These industries contribute in a big way to the economy of a nation and generate employment.

In recent years, chemistry has helped in dealing with some of the pressing aspects of environmental degradation with a fair degree of success. 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 biochemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic material 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. To be a good chemist and to accept such challenges, one needs to understand the basic concepts of chemistry, which begin with the concept of matter. Let us start with the nature of matter.

## 1.2 NATURE OF MATTER

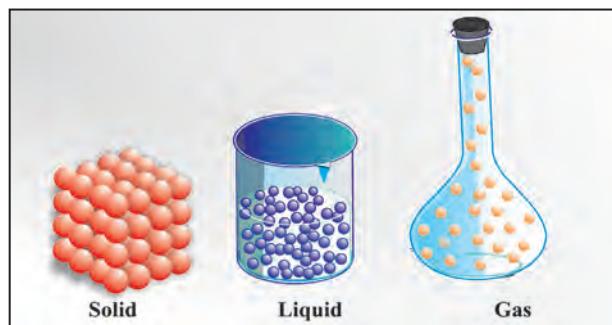
You are already familiar with the term **matter** from your earlier classes. Anything which has mass and occupies space is called **matter**. Everything around us, for example, book, pen, pencil, water, air, all living beings, etc., are composed of matter. You know that they have mass and they occupy space. Let us recall the characteristics of the states of matter, which you learnt in your previous classes.

### 1.2.1 States of Matter

You are 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.

Particles are held very close to each other in **solids** 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:

- Solids have *definite volume* and *definite shape*.
- Liquids have *definite volume* but *do not have definite shape*. They take the shape of the container in which they are placed.



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

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

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



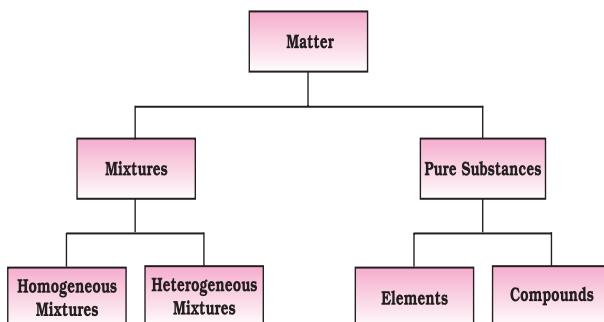
On heating, a solid usually changes to a liquid, and the liquid on further heating changes to gas (or vapour). In the reverse process, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid.

### 1.2.2. Classification of Matter

In Class IX (Chapter 2), you have learnt that at the macroscopic or bulk level, matter can be classified as **mixture** or **pure substance**. These can be further sub-divided as shown in Fig. 1.2.

When all constituent particles of a substance are same in chemical nature, it is said to be a pure substance. A mixture contains many types of particles.

A **mixture** contains particles of two or more pure substances which may be present in it in any ratio. Hence, their composition is variable. Pure substances forming mixture are called its components. Many of the substances present around you are **mixtures**. For example, sugar solution in water, air, tea, etc., are all mixtures. A mixture may be **homogeneous** or **heterogeneous**. In a **homogeneous mixture**, the components



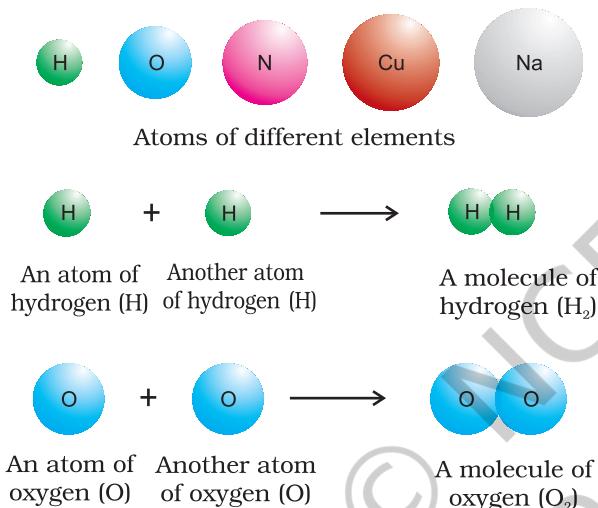
**Fig. 1.2** Classification of matter

completely mix with each other. This means particles of components of the mixture are uniformly distributed throughout the bulk of the mixture and its composition is uniform throughout. Sugar solution and air are the examples of homogeneous mixtures. In contrast to this, in a **heterogeneous mixture**, the composition is not uniform throughout and sometimes different components are visible. For example, 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 by using physical methods, such as simple hand-picking, filtration, crystallisation, distillation, etc.

**Pure substances** have characteristics different from mixtures. Constituent particles of pure substances have fixed composition. Copper, silver, gold, water and glucose are some examples of pure substances. Glucose contains carbon, hydrogen and oxygen in a fixed ratio and its particles are of same composition. Hence, like all other pure substances, glucose has a fixed composition. Also, its constituents—carbon, hydrogen and oxygen—cannot be separated by simple physical methods.

Pure substances can further be classified into **elements** and **compounds**. Particles of an **element** consist of only one type of atoms. These particles may exist as **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. Their all atoms are of one type. However, the atoms of different elements are different in nature. Some elements, such as sodium or copper, contain atoms as their constituent particles, whereas, in some others, the constituent particles are molecules which are formed by two or more atoms. For example, 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.



**Fig. 1.3** A representation of atoms and molecules

When two or more atoms of different elements combine together in a definite ratio, the molecule of a **compound** is obtained. Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods. Examples of some compounds are water, ammonia, carbon dioxide, sugar, etc. The molecules of water and carbon dioxide are represented in Fig. 1.4.

Note 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



Water molecule ( $H_2O$ )

Carbon dioxide molecule ( $CO_2$ )

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

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.

### 1.3 PROPERTIES OF MATTER AND THEIR MEASUREMENT

#### 1.3.1 Physical and chemical properties

Every substance has unique or characteristic properties. These properties can be classified into two categories — **physical properties**, such as colour, odour, melting point, boiling point, density, etc., and **chemical properties**, like composition, combustibility, reactivity with acids and bases, etc.

**Physical properties** can be measured or observed without changing the identity or the composition of the substance. The measurement or observation of **chemical properties** requires a chemical change to occur. Measurement of physical properties does not require occurrence of a chemical change. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility, etc. Chemists describe, interpret and predict the behaviour of substances on the basis of knowledge of their physical and chemical properties, which are determined by careful measurement and experimentation. In the following section, we

will learn about the measurement of physical properties.

### 1.3.2 Measurement of physical properties

Quantitative measurement of properties is required for scientific investigation. 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.

Earlier, 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. Late, need of a common standard system was felt by the scientific community. Such a system was established in 1960 and is discussed in detail below.

### 1.3.3 The International System of Units (SI)

The International System of Units (in French *Le Système International d'Unités* — abbreviated as SI) was established by the 11<sup>th</sup> General Conference on Weights and Measures (CGPM from *Conférence Générale des Poids et Mesures*). The CGPM is an inter-

### 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 industrialised 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 realise 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.

governmental treaty organisation created by a diplomatic treaty known as Metre 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.

**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

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 1.2 Definitions of SI Base Units**

<b>Unit of length</b>	<b>metre</b>	The <i>metre</i> , symbol m is the SI unit of length. It is defined by taking the fixed numerical value of the speed of light in vacuum c to be $299792458$ when expressed in the unit $\text{ms}^{-1}$ , where the second is defined in terms of the caesium frequency $\Delta V_{\text{Cs}}$ .
<b>Unit of mass</b>	<b>kilogram</b>	The <i>kilogram</i> , symbol kg, is the SI unit of mass. It is defined by taking the fixed numerical value of the Planck constant $h$ to be $6.62607015 \times 10^{-34}$ when expressed in the unit Js, which is equal to $\text{kgm}^2\text{s}^{-1}$ , where the metre and the second are defined in terms of c and $\Delta V_{\text{Cs}}$ .
<b>Unit of time</b>	<b>second</b>	The second symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency $\Delta V_{\text{Cs}}$ , the unperturbed ground-state hyperfine transition frequency of the caesium-133 atom, to be $9192631770$ when expressed in the unit Hz, which is equal to $\text{s}^{-1}$ .
<b>Unit of electric current</b>	<b>ampere</b>	The <i>ampere</i> , symbol A, is the SI unit of electric current. It is defined by taking the fixed numerical value of the elementary charge e to be $1.602176634 \times 10^{-19}$ when expressed in the unit C, which is equal to As, where the second is defined in terms of $\Delta V_{\text{Cs}}$ .
<b>Unit of thermodynamic temperature</b>	<b>kelvin</b>	The Kelvin, symbol k, is the SI unit of thermodynamic temperature. It is defined by taking the fixed numerical value of the Boltzmann constant $k$ to be $1.380649 \times 10^{-23}$ when expressed in the unit $\text{JK}^{-1}$ , which is equal to $\text{kgm}^2\text{s}^{-2}\text{k}^{-1}$ where the kilogram, metre and second are defined in terms of $h$ , $c$ and $\Delta V_{\text{Cs}}$ .
<b>Unit of amount of substance</b>	<b>mole</b>	The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, $N_A$ , when expressed in the unit $\text{mol}^{-1}$ and is called the Avogadro number. The amount of substance, symbol $n$ , of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.
<b>Unit of luminous Intensity</b>	<b>Candela</b>	The candela, symbol cd is the SI unit of luminous intensity in a given direction. It is defined by taking the fixed numerical value of the luminous efficacy of monochromatic radiation of frequency $540 \times 10^{12}$ Hz, $K_{\text{cd}}$ , to be 683 when expressed in the unit $\text{lm}\cdot\text{W}^{-1}$ , which is equal to $\text{cd}\cdot\text{sr}\cdot\text{W}^{-1}$ , or $\text{cd sr kg}^{-1}\text{m}^{-2}\text{s}^3$ , where the kilogram, metre and second are defined in terms of $h$ , $c$ and $\Delta V_{\text{Cs}}$ .

**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	$\mu$
$10^{-3}$	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

### 1.3.4 Mass and Weight

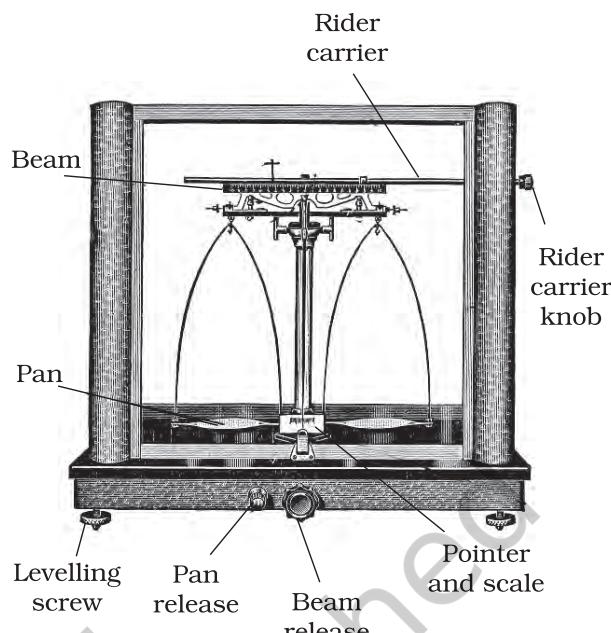
**Mass** of a substance is the amount of matter present in it, while **weight** is the force exerted by gravity on an object. The mass of a substance is constant, whereas, its weight may vary from one place to another due to change in gravity. You should be careful in using these terms.

The mass of a substance can be determined 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 named as gram ( $1 \text{ kg} = 1000 \text{ g}$ ), is used in laboratories due to the smaller amounts of chemicals used in chemical reactions.

### 1.3.5 Volume

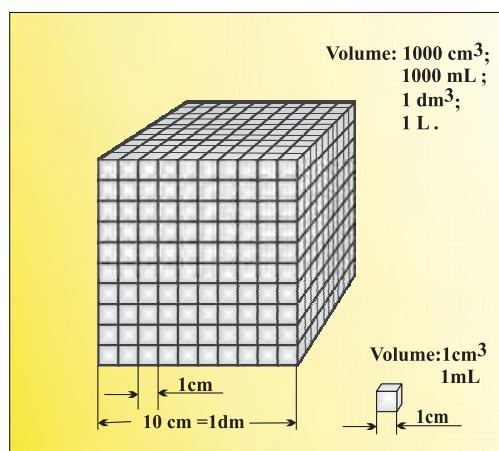
Volume is the amount of space occupied by a substance. It has the units of  $(\text{length})^3$ . So in

**Fig. 1.5** Analytical balance

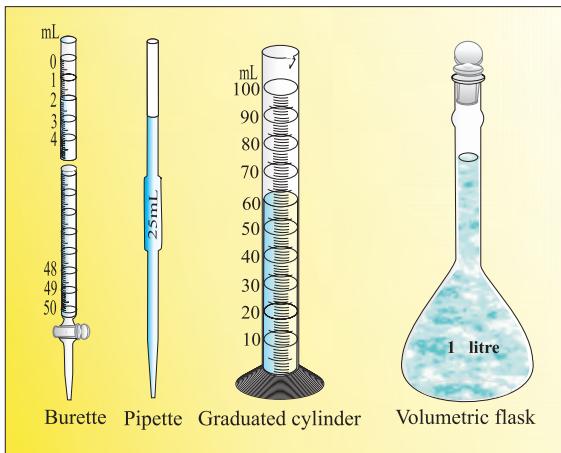
SI system, volume has units of  $\text{m}^3$ . But again, in chemistry laboratories, smaller volumes are used. Hence, volume is often denoted in  $\text{cm}^3$  or  $\text{dm}^3$  units.

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

$1 \text{ L} = 1000 \text{ mL}$ ,  $1000 \text{ cm}^3 = 1 \text{ dm}^3$   
Fig. 1.6 helps to visualise these relations.

**Fig. 1.6** Different units used to express volume

In the laboratory, the 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. 1.7** Some volume measuring devices

### 1.3.6 Density

The two properties — mass and volume discussed above are related as follows:

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

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

$$\begin{aligned}\text{SI unit of density} &= \frac{\text{SI unit of mass}}{\text{SI unit of volume}} \\ &= \frac{\text{kg}}{\text{m}^3} \text{ or kg m}^{-3}\end{aligned}$$

This unit is quite large and a chemist often expresses density in  $\text{g cm}^{-3}$ , where mass is expressed in gram and volume is expressed in  $\text{cm}^3$ . Density of a substance tells us about how closely its particles are packed. If density is more, it means particles are more closely packed.

### 1.3.7 Temperature

There are three common scales to measure temperature —  ${}^\circ\text{C}$  (degree celsius),  ${}^\circ\text{F}$  (degree

fahrenheit) and  $\text{K}$  (kelvin). Here,  $\text{K}$  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  $0^\circ$  to  $100^\circ$ , where these two temperatures are the freezing point and the boiling point of water, respectively. The fahrenheit scale is represented between  $32^\circ$  to  $212^\circ$ .

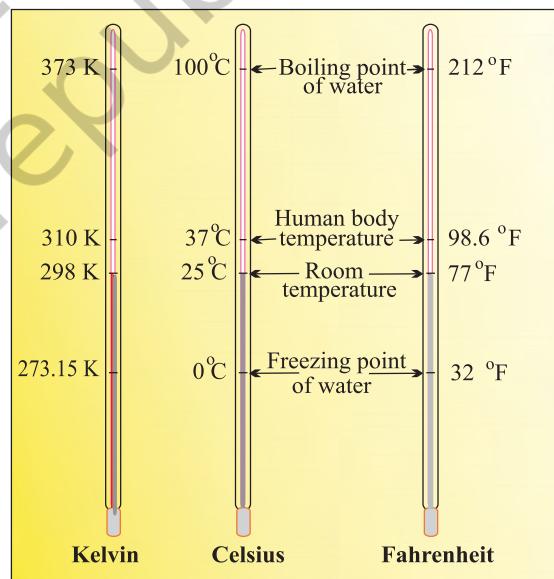
The temperatures on two scales are related to each other by the following relationship:

$${}^\circ\text{F} = \frac{9}{5}({}^\circ\text{C}) + 32$$

The kelvin scale is related to celsius scale as follows:

$$\text{K} = {}^\circ\text{C} + 273.15$$

It is interesting to note that temperature below  $0^\circ\text{C}$  (i.e., negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.



**Fig. 1.8** Thermometers using different temperature scales

## 1.4 UNCERTAINTY IN MEASUREMENT

Many a time 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

## 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  $1.65076373 \times 10^6$  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.

present the data realistically with certainty to the extent possible. These ideas are discussed below in detail.

### 1.4.1 Scientific Notation

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 as a 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  $N \times 10^n$ , where  $n$  is an exponent having positive or negative values and  $N$  is a number (called digit term) which varies between 1.000... and 9.999....

Thus, we can write 232.508 as  $2.32508 \times 10^2$  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  $1.6 \times 10^{-4}$ . Here, the decimal has to be moved four places to the right and (-4) is the exponent in the scientific notation.

While 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.

$$(5.6 \times 10^5) \times (6.9 \times 10^8) = (5.6 \times 6.9) (10^{5+8}) \\ = (5.6 \times 6.9) \times 10^{13} \\ = 38.64 \times 10^{13} \\ = 3.864 \times 10^{14}$$

$$(9.8 \times 10^{-2}) \times (2.5 \times 10^{-6}) = (9.8 \times 2.5) (10^{-2+(-6)}) \\ = (9.8 \times 2.5) (10^{-8}) \\ = 24.50 \times 10^{-8} \\ = 2.450 \times 10^{-7}$$

$$\frac{2.7 \times 10^{-3}}{5.5 \times 10^4} = (2.7 \div 5.5) (10^{-3-4}) = 0.4909 \times 10^{-7} \\ = 4.909 \times 10^{-8}$$

### Addition and Subtraction

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

Thus, for adding  $6.65 \times 10^4$  and  $8.95 \times 10^3$ , exponent is made same for both the numbers. Thus, we get  $(6.65 \times 10^4) + (0.895 \times 10^4)$

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

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

$$(2.5 \times 10^{-2}) - (4.8 \times 10^{-3}) \\ = (2.5 \times 10^{-2}) - (0.48 \times 10^{-2}) \\ = (2.5 - 0.48) \times 10^{-2} = 2.02 \times 10^{-2}$$

### 1.4.2 Significant Figures

Every experimental measurement has some amount of uncertainty associated with it because of limitation of measuring instrument and the skill of the person making the measurement. For example, mass of an object is obtained using a platform balance and it comes out to be 9.4g. On measuring the mass of this object on an analytical balance, the mass obtained is 9.4213g. The

mass obtained by an analytical balance is slightly higher than the mass obtained by using a platform balance. Therefore, digit 4 placed after decimal in the measurement by platform balance is uncertain.

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 plus one which is estimated or uncertain. 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  $\pm 1$  in the last digit. Unless otherwise stated, an uncertainty of  $\pm 1$  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 terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100 has three significant figures and 100.0 has four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as  $1 \times 10^2$  for one significant figure,  $1.0 \times 10^2$  for two significant figures and  $1.00 \times 10^2$  for three significant figures.

- (5) Counting the numbers of object, for example, 2 balls or 20 eggs, have 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  $20 = 20.000000$ .

In numbers written in scientific notation, all digits are significant e.g.,  $4.01 \times 10^2$  has three significant figures, and  $8.256 \times 10^{-3}$  has four significant figures.

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 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 'B' 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 the third student 'C' repeats these measurements and reports 2.01 g and 1.99 g 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

### 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.

12.11

18.0

1.012

31.122

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 in the measurement with the few significant figures.

$$2.5 \times 1.25 = 3.125$$

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

- 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.
- 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.
- 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 the 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?

### Solution

We know that 1 in = 2.54 cm

From this equivalence, we can write

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

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,

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

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.

### Example

A jug contains 2 L of milk. Calculate the volume of the milk in  $\text{m}^3$ .

### Solution

Since 1 L = 1000  $\text{cm}^3$

and 1 m = 100 cm, which gives

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

To get  $\text{m}^3$  from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 \Rightarrow \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = (1)^3 = 1$$

Now 2 L =  $2 \times 1000 \text{ cm}^3$

The above is multiplied by the unit factor

$$2 \times 1000 \text{ cm}^3 \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = \frac{2 \text{ m}^3}{10^3} = 2 \times 10^{-3} \text{ m}^3$$

### Example

How many seconds are there in 2 days?

### Solution

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

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

then, 1 h = 60 min

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

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:

$$\begin{aligned} 2 \text{ day} &\times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} \\ &= 2 \times 24 \times 60 \times 60 \text{ s} \\ &= 172800 \text{ s} \end{aligned}$$

## 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

This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions and reached to the conclusion that in all physical and chemical changes, there is no net change in mass during the process. Hence, he reached to the conclusion that matter can neither be created nor destroyed. This is called 'Law of Conservation of Mass'. 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. He found that the composition of elements present in it was same for both the samples as shown below:

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

Thus, he concluded that irrespective of the source, a given compound always contains same elements combined together in the same proportion by mass. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as **Law of Definite Composition.**

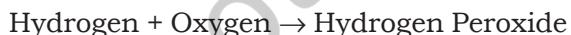
### 1.5.3 Law of Multiple Proportions

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.



$$2\text{g} \quad 16\text{g} \quad 18\text{g}$$



$$2\text{g} \quad 32\text{g} \quad 34\text{g}$$

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 the 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.



$$100 \text{ mL} \quad 50 \text{ mL} \quad 100 \text{ mL}$$

Thus, the volumes of hydrogen and oxygen which combine (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.

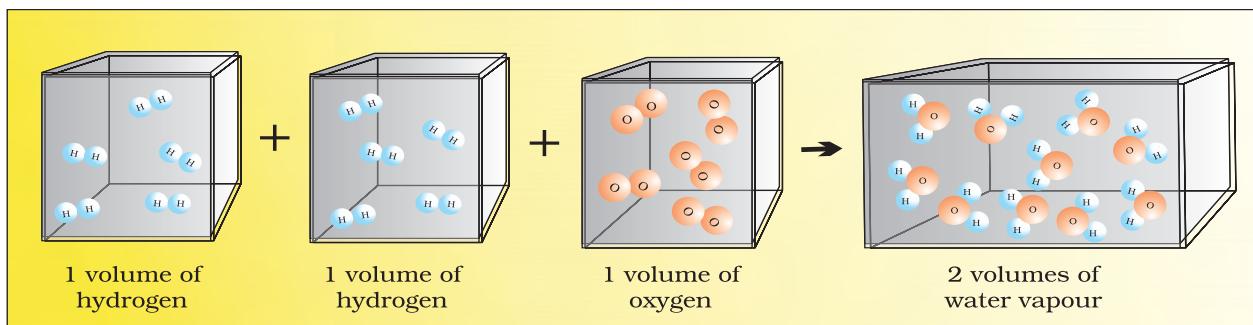
### 1.5.5 Avogadro's Law

In 1811, Avogadro proposed that *equal volumes of all 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 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.

Note that in the Fig. 1.9 (Page 16) each box contains equal number of molecules. In fact, Avogadro could explain the above result by considering the molecules to be **polyatomic**. If hydrogen 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



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



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

cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro's proposal was published in the French *Journal de Physique*. In spite of being correct, it did not gain much support.

After about 50 years, in 1860, the 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 on the importance of Avogadro's work.

## 1.6 DALTON'S ATOMIC THEORY

Although the origin of the 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 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.



John Dalton  
(1776–1884)

Dalton's theory could explain the laws of chemical combination. However, it could not explain the laws of gaseous volumes. It could not provide the reason for combining of atoms, which was answered later by other scientists.

## 1.7 ATOMIC AND MOLECULAR MASSES

After having some idea about the terms atoms and molecules, it is appropriate here to understand what do 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 the mass of one atom **relative** to another by experimental means, as has been mentioned earlier. Hydrogen, being the 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  $^{12}\text{C}$ . In this system,  $^{12}\text{C}$  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 of the mass of one carbon – 12 atom.

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

Mass of an atom of hydrogen

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

Thus, in terms of amu, the mass

$$\begin{aligned} \text{of hydrogen atom} &= \frac{1.6736 \times 10^{-24} \text{ g}}{1.66056 \times 10^{-24} \text{ g}} \\ &= 1.0078 \text{ amu} \\ &= 1.0080 \text{ amu} \end{aligned}$$

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

At present, '**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)
$^{12}\text{C}$	98.892	12
$^{13}\text{C}$	1.108	13.00335
$^{14}\text{C}$	$2 \times 10^{-10}$	14.00317

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

$$(0.98892) (12 \text{ u}) + (0.01108) (13.00335 \text{ u}) + (2 \times 10^{-10}) (14.00317 \text{ u}) = 12.011 \text{ u}$$

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

$$(\text{CH}_4) = (12.011 \text{ u}) + 4 (1.008 \text{ u})$$

$$= 16.043 \text{ u}$$

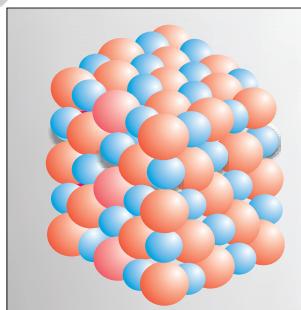
Similarly, molecular mass of water ( $\text{H}_2\text{O}$ )

$$\begin{aligned} &= 2 \times \text{atomic mass of hydrogen} + 1 \times \text{atomic mass of oxygen} \\ &= 2 (1.008 \text{ u}) + 16.00 \text{ u} \end{aligned}$$

$$= 18.02 \text{ u}$$

### 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 ion) and negative (chloride ion) entities are arranged in a three-dimensional structure, as shown in Fig. 1.10.



**Fig. 1.10** Packing of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in sodium chloride

It may be noted that in sodium chloride, one  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ion and *vice-versa*.

The formula, such as  $\text{NaCl}$ , 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, the formula mass of sodium chloride is  
atomic mass of sodium + atomic mass of chlorine  
 $= 23.0 \text{ u} + 35.5 \text{ u} = 58.5 \text{ u}$

### Problem 1.1

Calculate the molecular mass of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) molecule.

#### Solution

$$\begin{aligned}\text{Molecular mass of glucose } & (\text{C}_6\text{H}_{12}\text{O}_6) \\ &= 6(12.011 \text{ u}) + 12(1.008 \text{ u}) + 6(16.00 \text{ u}) \\ &= (72.066 \text{ u}) + (12.096 \text{ u}) + (96.00 \text{ u}) \\ &= 180.162 \text{ u}\end{aligned}$$

## 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 convenient 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.

The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly  $6.02214076 \times 10^{23}$  elementary entities. This number is the fixed numerical value of the Avogadro constant,  $N_A$ , when expressed in the unit  $\text{mol}^{-1}$  and is called the Avogadro number. The amount of substance, symbol  $n$ , of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. It may be emphasised that the mole of a substance always contains 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  $1.992648 \times 10^{-23}$  g. Knowing that one mole of carbon weighs 12 g, the number of atoms in it is equal to:

$$\begin{aligned}& \frac{12 \text{ g/mol } {}^{12}\text{C}}{1.992648 \times 10^{-23} \text{ g/}{}^{12}\text{C atom}} \\ &= 6.0221367 \times 10^{23} \text{ atoms/mol}\end{aligned}$$

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

6022136700000000000000000

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 =  $6.022 \times 10^{23}$  atoms

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

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

Having defined the mole, it is easier to know the mass of one mole of a 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 =  $18.02 \text{ g mol}^{-1}$

Molar mass of sodium chloride =  $58.5 \text{ g mol}^{-1}$

## 1.9 PERCENTAGE COMPOSITION

So far, we were dealing with the number of entities present in a given sample. But many a time, 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



**Fig. 1.11** One mole of various substances

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 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 ( $\text{H}_2\text{O}$ ). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows:

Mass % of an element =

$$\frac{\text{mass of that element in the compound}}{\text{molar mass of the compound}} \times 100$$

Molar mass of water = 18.02 g

$$\begin{aligned}\text{Mass \% of hydrogen} &= \frac{2 \times 1.008}{18.02} \times 100 \\ &= 11.18\end{aligned}$$

$$\begin{aligned}\text{Mass \% of oxygen} &= \frac{16.00}{18.02} \times 100 \\ &= 88.79\end{aligned}$$

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

Molecular formula of ethanol is:  $\text{C}_2\text{H}_5\text{OH}$   
Molar mass of ethanol is:

$$(2 \times 12.01 + 6 \times 1.008 + 16.00) \text{ g} = 46.068 \text{ g}$$

Mass per cent of carbon

$$= \frac{24.02 \text{ g}}{46.068 \text{ g}} \times 100 = 52.14\%$$

Mass per cent of hydrogen

$$= \frac{6.048 \text{ g}}{46.068 \text{ g}} \times 100 = 13.13\%$$

Mass per cent of oxygen

$$= \frac{16.00 \text{ g}}{46.068 \text{ g}} \times 100 = 34.73\%$$

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, 24.27g carbon and 71.65g chlorine are present.

##### Step 2. Convert into number moles of each element

Divide the masses obtained above by respective atomic masses of various elements. This gives the number of moles of constituent elements in the compound

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

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

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

**Step 3. Divide each of the mole values obtained above by the smallest number amongst them**

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 down the empirical formula by mentioning the numbers after writing the symbols of respective elements**

$\text{CH}_2\text{Cl}$  is, thus, the empirical formula of the above compound.

**Step 5. Writing molecular formula**

(a) Determine empirical formula mass by adding the atomic masses of various atoms present in the empirical formula.

$$\begin{aligned}\text{For } \text{CH}_2\text{Cl, empirical formula mass is} \\ 12.01 + (2 \times 1.008) + 35.453 \\ = 49.48 \text{ g}\end{aligned}$$

(b) Divide Molar mass by empirical formula mass

$$\begin{array}{rcl}\text{Molar mass} & = & 98.96 \text{ g} \\ \text{Empirical formula mass} & = & 49.48 \text{ g} \\ & = & 2 = (n)\end{array}$$

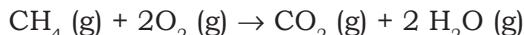
(c) Multiply empirical formula by  $n$  obtained above to get the molecular formula

Empirical formula =  $\text{CH}_2\text{Cl}$ ,  $n = 2$ . Hence molecular formula is  $\text{C}_2\text{H}_4\text{Cl}_2$ .

## 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 the products 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:



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 case of solids and liquids, (s) and (l) are written respectively.

The coefficients 2 for  $\text{O}_2$  and  $\text{H}_2\text{O}$  are called stoichiometric coefficients. Similarly the coefficient for  $\text{CH}_4$  and  $\text{CO}_2$  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  $\text{CH}_4(\text{g})$  reacts with two **moles** of  $\text{O}_2(\text{g})$  to give one **mole** of  $\text{CO}_2(\text{g})$  and two **moles** of  $\text{H}_2\text{O}(\text{g})$
- One **molecule** of  $\text{CH}_4(\text{g})$  reacts with 2 **molecules** of  $\text{O}_2(\text{g})$  to give one **molecule** of  $\text{CO}_2(\text{g})$  and 2 molecules of  $\text{H}_2\text{O}(\text{g})$
- 22.7 L of  $\text{CH}_4(\text{g})$  reacts with 45.4 L of  $\text{O}_2(\text{g})$  to give 22.7 L of  $\text{CO}_2(\text{g})$  and 45.4 L of  $\text{H}_2\text{O}(\text{g})$
- 16 g of  $\text{CH}_4(\text{g})$  reacts with  $2 \times 32$  g of  $\text{O}_2(\text{g})$  to give 44 g of  $\text{CO}_2(\text{g})$  and  $2 \times 18$  g of  $\text{H}_2\text{O}(\text{g})$ .

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

mass

mass  $\Leftarrow$  moles  $\Leftarrow$  no. of molecules

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

### 1.10.1 Limiting Reagent

Many a time, reactions are carried out with the amounts of reactants that are different than the amounts as required by a balanced chemical reaction. In such situations, one reactant is in more amount than the amount required by balanced chemical reaction. The

reactant which is present in the least amount gets consumed after sometime and after that further reaction does not take place whatever be the amount of the other reactant. Hence, the reactant, which gets consumed first, 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.

### 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 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.

#### 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



Equations (a) and (b) are balanced, since there are same number of metal and oxygen atoms on each side of the 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.



Now, let us take combustion of propane,  $\text{C}_3\text{H}_8$ . This equation can be balanced in steps.

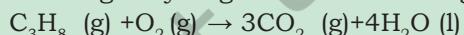
**Step 1** Write down the correct formulas of reactants and products. Here, propane and oxygen are reactants, and carbon dioxide and water are products.



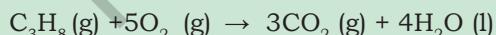
**Step 2 Balance the number of C atoms:** Since 3 carbon atoms are in the reactant, therefore, three  $\text{CO}_2$  molecules are required on the right side.



**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.



**Step 4 Balance the number of O atoms:** There are 10 oxygen atoms on the right side ( $3 \times 2 = 6$  in  $\text{CO}_2$  and  $4 \times 1 = 4$  in water). Therefore, five  $\text{O}_2$  molecules are needed to supply the required 10  $\text{CO}_2$  and  $4 \times 1 = 4$  in water). Therefore, five  $\text{O}_2$  molecules are needed to supply the required 10 oxygen atoms.



**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 10 oxygen atoms on each side.

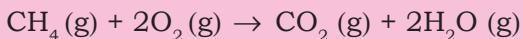
All equations that have correct formulas for all reactants and products can be balanced. Always remember that subscripts in formulas of reactants and products cannot be changed to balance an equation.

**Problem 1.3**

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

**Solution**

The balanced equation for the combustion of methane is :



(i) 16 g of  $\text{CH}_4$  corresponds to one mole.

(ii) From the above equation, 1 mol of  $\text{CH}_4$  (g) gives 2 mol of  $\text{H}_2\text{O}$  (g).

$$\begin{aligned} 2 \text{ mol of water } (\text{H}_2\text{O}) &= 2 \times (2+16) \\ &= 2 \times 18 = 36 \text{ g} \end{aligned}$$

$$1 \text{ mol H}_2\text{O} = 18 \text{ g H}_2\text{O} \Rightarrow \frac{18 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 1$$

$$\text{Hence, } 2 \text{ mol H}_2\text{O} \times \frac{18 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}$$

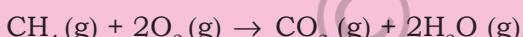
$$= 2 \times 18 \text{ g H}_2\text{O} = 36 \text{ g H}_2\text{O}$$

**Problem 1.4**

How many moles of methane are required to produce 22g  $\text{CO}_2$  (g) after combustion?

**Solution**

According to the chemical equation,



44g  $\text{CO}_2$  (g) is obtained from 16 g  $\text{CH}_4$  (g).

[∴ 1 mol  $\text{CO}_2$ (g) is obtained from 1 mol of  $\text{CH}_4$ (g)]

Number of moles of  $\text{CO}_2$  (g)

$$= 22 \text{ g CO}_2(\text{g}) \times \frac{1 \text{ mol CO}_2(\text{g})}{44 \text{ g CO}_2(\text{g})}$$

$$= 0.5 \text{ mol CO}_2(\text{g})$$

Hence, 0.5 mol  $\text{CO}_2$  (g) would be obtained from 0.5 mol  $\text{CH}_4$  (g) or 0.5 mol of  $\text{CH}_4$  (g) would be required to produce 22 g  $\text{CO}_2$  (g).

**Problem 1.5**

50.0 kg of  $\text{N}_2$  (g) and 10.0 kg of  $\text{H}_2$  (g) are mixed to produce  $\text{NH}_3$  (g). Calculate the amount of  $\text{NH}_3$  (g) formed. Identify

the limiting reagent in the production of  $\text{NH}_3$  in this situation.

**Solution**

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



Calculation of moles :

Number of moles of  $\text{N}_2$

$$= 50.0 \text{ kg N}_2 \times \frac{1000 \text{ g N}_2}{1 \text{ kg N}_2} \times \frac{1 \text{ mol N}_2}{28.0 \text{ g N}_2}$$

$$= 17.86 \times 10^2 \text{ mol}$$

Number of moles of  $\text{H}_2$

$$= 10.00 \text{ kg H}_2 \times \frac{1000 \text{ g H}_2}{1 \text{ kg H}_2} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2}$$

$$= 4.96 \times 10^3 \text{ mol}$$

According to the above equation, 1 mol  $\text{N}_2$  (g) requires 3 mol  $\text{H}_2$  (g), for the reaction. Hence, for  $17.86 \times 10^2$  mol of  $\text{N}_2$ , the moles of  $\text{H}_2$  (g) required would be

$$17.86 \times 10^2 \text{ mol N}_2 \times \frac{3 \text{ mol H}_2(\text{g})}{1 \text{ mol N}_2(\text{g})}$$

$$= 5.36 \times 10^3 \text{ mol H}_2$$

But we have only  $4.96 \times 10^3$  mol  $\text{H}_2$ . Hence, dihydrogen is the limiting reagent in this case. So,  $\text{NH}_3$ (g) would be formed only from that amount of available dihydrogen i.e.,  $4.96 \times 10^3$  mol

Since 3 mol  $\text{H}_2$ (g) gives 2 mol  $\text{NH}_3$ (g)

$$4.96 \times 10^3 \text{ mol H}_2(\text{g}) \times \frac{2 \text{ mol NH}_3(\text{g})}{3 \text{ mol H}_2(\text{g})}$$

$$= 3.30 \times 10^3 \text{ mol NH}_3(\text{g})$$

$3.30 \times 10^3$  mol  $\text{NH}_3$  (g) is obtained.

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

$$1 \text{ mol NH}_3(\text{g}) = 17.0 \text{ g NH}_3(\text{g})$$

$$3.30 \times 10^3 \text{ mol NH}_3(\text{g}) \times \frac{17.0 \text{ g NH}_3(\text{g})}{1 \text{ mol NH}_3(\text{g})}$$

$$\begin{aligned}
 &= 3.30 \times 10^3 \times 17 \text{ g NH}_3 \text{ (g)} \\
 &= 56.1 \times 10^3 \text{ g NH}_3 \\
 &= 56.1 \text{ kg NH}_3
 \end{aligned}$$

### 1. Mass per cent

It is obtained by using the following relation:

$$\text{Mass per cent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

#### 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

$$\begin{aligned}
 \text{Mass per cent of A} &= \frac{\text{Mass of A}}{\text{Mass of solution}} \times 100 \\
 &= \frac{2 \text{ g}}{2 \text{ g of A} + 18 \text{ g of water}} \times 100 \\
 &= \frac{2 \text{ g}}{20 \text{ g}} \times 100 \\
 &= 10\%
 \end{aligned}$$

### 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:

#### Mole fraction of A

$$\begin{aligned}
 &= \frac{\text{No. of moles of A}}{\text{No. of moles of solutions}} \\
 &= \frac{n_A}{n_A + n_B}
 \end{aligned}$$

#### Mole fraction of B

$$\begin{aligned}
 &= \frac{\text{No. of moles of B}}{\text{No. of moles of solutions}} \\
 &= \frac{n_B}{n_A + n_B}
 \end{aligned}$$

### 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,

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

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 dissolved in 1 litre solution.

Hence, for making 0.2M solution from 1M solution, we have to take that volume of 1M NaOH solution, which contains 0.2 mol of NaOH and dilute the solution with water 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 1L or 1000 mL solution

then, 0.2 mol is present in

$$\frac{1000 \text{ mL}}{1 \text{ mol}} \times 0.2 \text{ mol solution}$$

$$= 200 \text{ mL solution}$$

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,  $M_1 \times V_1 = M_2 \times V_2$  where M and V are molarity and volume, respectively, can be used. In this case,  $M_1$  is equal to 0.2M;  $V_1 = 1000$  mL and,  $M_2 = 1.0\text{M}$ ;  $V_2$  is to be calculated. Substituting the values in the formula:

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

$$\therefore V_2 = \frac{0.2 \text{ M} \times 1000 \text{ mL}}{1.0 \text{ M}} = 200 \text{ L}$$

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)

$$\begin{aligned} &= \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}} \\ &= \frac{\text{Mass of NaOH / Molar mass of NaOH}}{0.250\text{L}} \\ &= \frac{4\text{ g} / 40\text{ g}}{0.250\text{L}} = \frac{0.1\text{ mol}}{0.250\text{L}} \\ &= 0.4\text{ mol}^{-1} \\ &= 0.4\text{ M} \end{aligned}$$

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.

$$\text{Thus, Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

### Problem 1.8

The density of 3 M solution of NaCl is 1.25 g mL<sup>-1</sup>. Calculate the molality of the solution.

#### Solution

$$M = 3 \text{ mol L}^{-1}$$

$$\begin{aligned} \text{Mass of NaCl} \\ \text{in 1 L solution} &= 3 \times 58.5 = 175.5 \text{ g} \\ \text{Mass of} \\ 1\text{L solution} &= 1000 \times 1.25 = 1250 \text{ g} \\ (\text{since density} &= 1.25 \text{ g mL}^{-1}) \\ \text{Mass of water in solution} &= 1250 - 175.5 \\ &= 1074.5 \text{ g} \end{aligned}$$

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{3 \text{ mol}}{1.0745 \text{ kg}} = 2.79 \text{ m}$$

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 the molality of a solution does not change with temperature since mass remains unaffected with temperature.

### SUMMARY

Chemistry, as we understand it today is not a very old discipline. People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied the knowledge in various walks of life.

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, 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 Proportions**, **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  $^{12}\text{C}$  isotope of carbon, which has an exact value of 12u. 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** ( $6.022 \times 10^{23}$ ). 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 amount 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 molar mass of the following:  
 (i)  $\text{H}_2\text{O}$  (ii)  $\text{CO}_2$  (iii)  $\text{CH}_4$
- 1.2 Calculate the mass per cent of different elements present in sodium sulphate ( $\text{Na}_2\text{SO}_4$ ).
- 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 ( $\text{CH}_3\text{COONa}$ ) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is  $82.0245 \text{ g mol}^{-1}$ .

- 1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density,  $1.41 \text{ g mL}^{-1}$  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 ( $\text{CuSO}_4$ )?
- 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
$^{35}\text{Cl}$	75.77	34.9689
$^{37}\text{Cl}$	24.23	36.9659

- 1.10 In three moles of ethane ( $\text{C}_2\text{H}_6$ ), calculate the following:
- Number of moles of carbon atoms.
  - Number of moles of hydrogen atoms.
  - Number of molecules of ethane.
- 1.11 What is the concentration of sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) in mol  $\text{L}^{-1}$  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  $0.793 \text{ kg L}^{-1}$ , 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:  
 $1\text{Pa} = 1\text{N m}^{-2}$   
If mass of air at sea level is  $1034 \text{ g cm}^{-2}$ , 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,  $\text{CHCl}_3$ , supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).
- Express this in per cent by mass.
  - Determine the molality of chloroform in the water sample.
- 1.18 Express the following in the scientific notation:
- 0.0048
  - 234,000
  - 8008
  - 500.0
  - 6.0012
- 1.19 How many significant figures are present in the following?
- 0.0025
  - 208
  - 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:
- |       | <b>Mass of dinitrogen</b> | <b>Mass of dioxygen</b> |
|-------|---------------------------|-------------------------|
| (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<sup>3</sup>
- 1.22 If the speed of light is  $3.0 \times 10^8$  m s<sup>-1</sup>, 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  $2.00 \times 10^3$  g dinitrogen reacts with  $1.00 \times 10^3$  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<sub>2</sub>CO<sub>3</sub> and 0.50 M Na<sub>2</sub>CO<sub>3</sub> different?
- 1.26 If 10 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 the largest number of atoms?
- 1 g Au (s)
  - 1 g Na (s)
  - 1 g Li (s)
  - 1 g of Cl<sub>2</sub>(g)
- 1.29 Calculate the molarity of a solution of ethanol in water, in which the mole fraction of ethanol is 0.040 (assume the density of water to be one).
- 1.30 What will be the mass of one <sup>12</sup>C atom in g?
- 1.31 How many significant figures should be present in the answer of the following calculations?
- $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$
  - $5 \times 5.364$
  - $0.0125 + 0.7864 + 0.0215$
- 1.32 Use the data given in the following table to calculate the molar mass of naturally occurring argon isotopes:
- | Isotope          | Isotopic molar mass          | Abundance |
|------------------|------------------------------|-----------|
| <sup>36</sup> Ar | 35.96755 g mol <sup>-1</sup> | 0.337%    |
| <sup>38</sup> Ar | 37.96272 g mol <sup>-1</sup> | 0.063%    |
| <sup>40</sup> Ar | 39.9624 g mol <sup>-1</sup>  | 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<sub>2</sub> and CO<sub>2</sub> according to the reaction,  $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- What mass of CaCO<sub>3</sub> 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<sub>2</sub>) with aqueous hydrochloric acid according to the reaction
- $$4\text{HCl}(\text{aq}) + \text{MnO}_2(\text{s}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{MnCl}_2(\text{aq}) + \text{Cl}_2(\text{g})$$
- How many grams of HCl react with 5.0 g of manganese dioxide?



## UNIT 2

11082CH02

# 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; and
- 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 'uncut-able' 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). 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 get electrically charged.

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 are made of sub-atomic particles, i.e., electrons, protons and neutrons — a concept very different from that of Dalton.

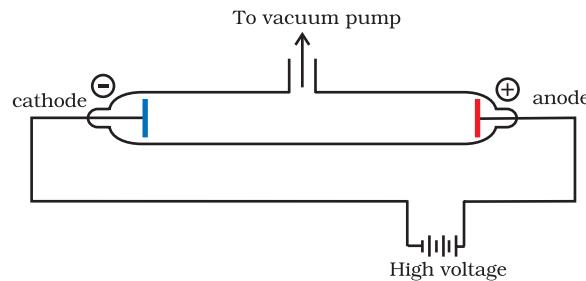
## 2.1 DISCOVERY OF SUB-ATOMIC PARTICLES

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”.

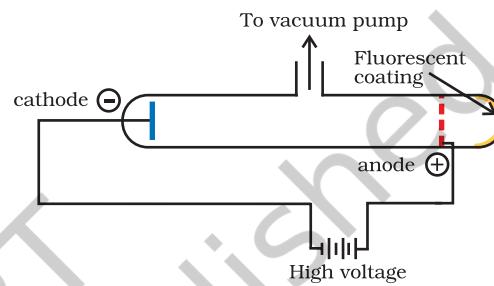
### 2.1.1 Discovery of Electron

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.

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 of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a 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 is developed on the coating [Fig. 2.1(b)].



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



**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). When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A (Fig. 2.2). 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 which is followed in the absence of electric or magnetic field and they hit the screen at point B. 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.

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:

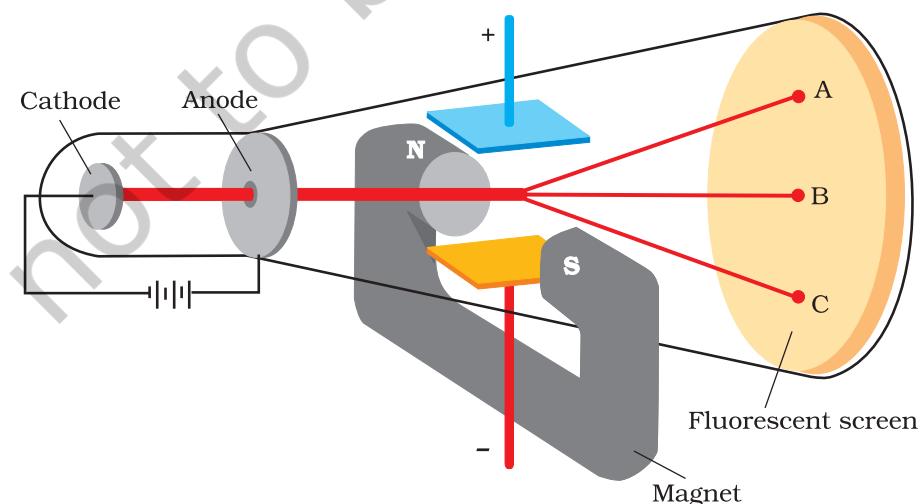
$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1} \quad (2.1)$$

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  $-e$ .

### 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 the charge on the electron to be  $-1.6 \times 10^{-19}$  C. The present accepted value of electrical charge is  $-1.602176 \times 10^{-19}$  C. The mass of the electron ( $m_e$ ) was determined by combining these results with Thomson's value of  $e/m_e$  ratio.

$$\begin{aligned} m_e &= \frac{e}{e/m_e} = \frac{1.602176 \times 10^{-19} \text{ C}}{1.758820 \times 10^{11} \text{ C kg}^{-1}} \\ &= 9.1094 \times 10^{-31} \text{ kg} \end{aligned} \quad (2.2)$$



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

### 2.1.4 Discovery of Protons and Neutrons

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

- (i) Unlike cathode rays, mass of positively charged particles depends 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 depends 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  $\alpha$ -particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as **neutrons**. The important properties of all these fundamental particles are given in Table 2.1.

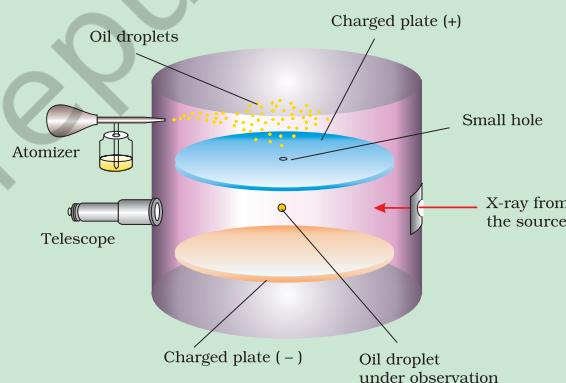
## 2.2 ATOMIC MODELS

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. The major problems before the scientists after the discovery of sub-atomic particles were:

- to account for the stability of atom,
- to compare the behaviour of elements in terms of both physical and chemical properties,

### 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  $n = 1, 2, 3 \dots$ .



**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.

- 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.

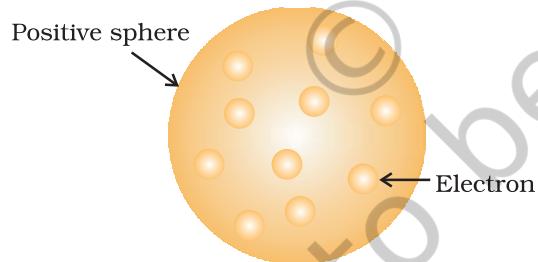
**Table 2.1 Properties of Fundamental Particles**

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	$-1.602176 \times 10^{-19}$	-1	$9.109382 \times 10^{-31}$	0.00054	0
Proton	p	$+1.602176 \times 10^{-19}$	+1	$1.6726216 \times 10^{-27}$	1.00727	1
Neutron	n	0	0	$1.674927 \times 10^{-27}$	1.00867	1

Different 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, one proposed by J.J. Thomson and the other proposed by 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.

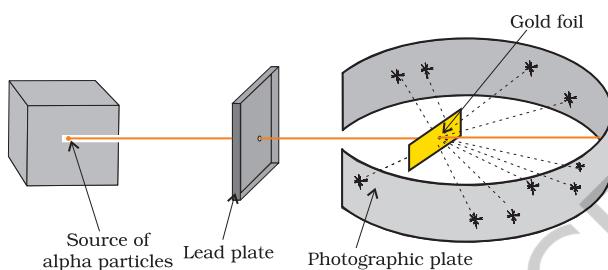
In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhelm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed 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 ( $\sim 0.1$  nm) and possess electro-magnetic character (Section 2.3.1).

Henri Becquerel (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, Pierre Curie, Rutherford and Frederick Soddy. It was observed that three kinds of rays i.e.,  $\alpha$ ,  $\beta$ - and  $\gamma$ -rays are emitted. Rutherford found that  $\alpha$ -rays consists of high energy particles carrying two units of positive charge and four unit of atomic mass. He concluded that  $\alpha$ - particles are helium nuclei as when  $\alpha$ - particles combined with two electrons yielded helium gas.  $\beta$ -rays are negatively charged

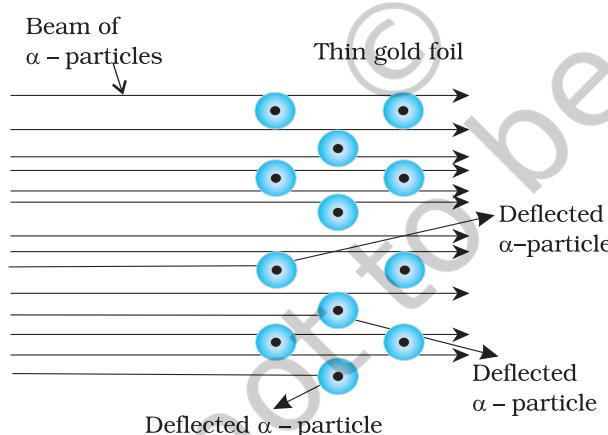
particles similar to electrons. The  $\gamma$ -rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power,  $\alpha$ -particles are the least, followed by  $\beta$ -rays (100 times that of  $\alpha$ -particles) and  $\gamma$ -rays (1000 times of that  $\alpha$ -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  $\alpha$ -particles. Rutherford's famous  **$\alpha$ -particle scattering experiment** is



**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 ( $\alpha$ ) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.

represented in Fig. 2.5. A stream of high energy  $\alpha$ -particles from a radioactive source was directed at a thin foil (thickness  $\sim 100$  nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever  $\alpha$ -particles struck the screen, a tiny flash of light was produced at that point.

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  $\alpha$ -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:

- most of the  $\alpha$ -particles passed through the gold foil undeflected.
- a small fraction of the  $\alpha$ -particles was deflected by small angles.
- a very few  $\alpha$ -particles ( $\sim 1$  in 20,000) bounced back, that is, were deflected by nearly  $180^\circ$ .

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

- Most of the space in the atom is empty as most of the  $\alpha$ -particles passed through the foil undeflected.
- A few positively charged  $\alpha$ -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  $\alpha$ -particles.
- 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. 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.

$$\begin{aligned} \text{Atomic number (Z)} &= \text{number of protons in} \\ &\quad \text{the nucleus of an atom} \\ &= \text{number of electrons} \\ &\quad \text{in a neutral atom} \quad (2.3) \end{aligned}$$

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.

$$\begin{aligned} \text{mass number (A)} &= \text{number of protons (Z)} \\ &+ \text{number of} \\ &\quad \text{neutrons (n)} \quad (2.4) \end{aligned}$$

### 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,  ${}^1_6 C$  and  ${}^1_7 N$ . 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 occurring 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  $^{80}_{35}\text{Br}$ .

**Solution**

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

$$\begin{aligned} \text{Number of protons} &= \text{number of electrons} \\ &= Z = 35 \end{aligned}$$

$$\text{Number of neutrons} = 80 - 35 = 45, \quad (\text{equation 2.4})$$

**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).

$$\begin{aligned} \text{Atomic mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= 16 + 16 = 32 \end{aligned}$$

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  $^{32}_{16}\text{S}^{2-}$ .

**Note :** Before using the notation  $^A_Z\text{X}$ , 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**

As you have learnt above, 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. When classical mechanics\* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets is given by the expression  $\left( G \cdot \frac{m_1 m_2}{r^2} \right)$  where  $m_1$  and  $m_2$  are the masses,  $r$  is the distance of separation of the masses and  $G$  is the gravitational constant. 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. Further, the coulomb force ( $kq_1 q_2 / r^2$  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. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit 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

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

around the nucleus. If the electrons were stationary, electrostatic attraction between 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 distribution of the electrons around the nucleus and 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.

First, we will discuss about the dual nature of electromagnetic radiations. Experimental results regarding atomic spectra will be discussed in Section 2.4.

#### 2.3.1 Wave Nature of Electromagnetic Radiation

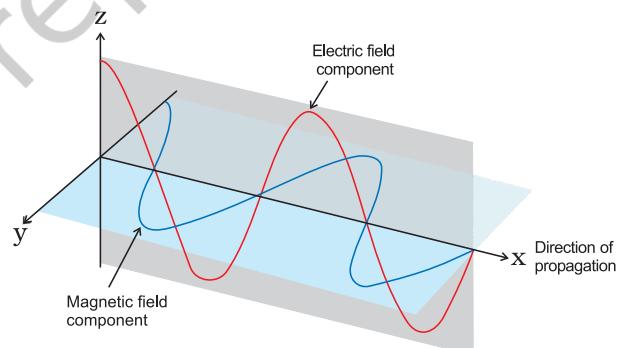
In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occurred in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles

was developed in the early 1870's by James Clerk Maxwell, which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations.

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 acceleration, 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 (corpuscles). 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).



**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.

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.

- (ii) Unlike sound waves or waves produced in water, 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.

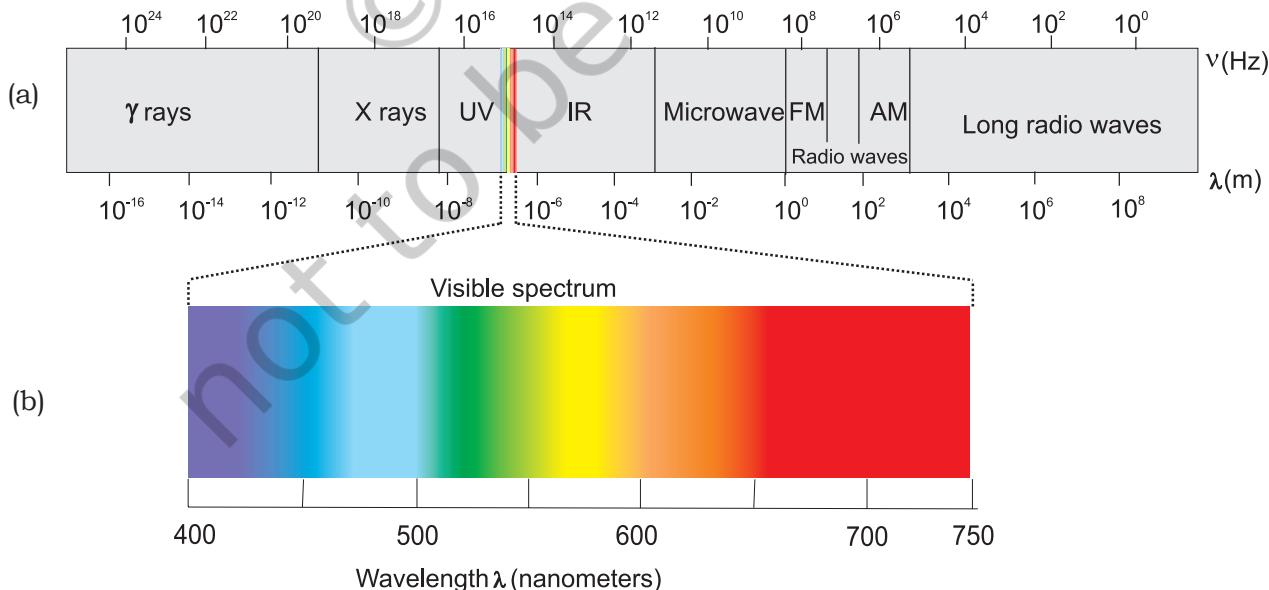
These radiations are characterised by the properties, namely, frequency ( $\nu$ ) and wavelength ( $\lambda$ ).

The SI unit for frequency ( $\nu$ ) 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 vacuum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e.,  $3.0 \times 10^8$  m  $s^{-1}$  ( $2.997925 \times 10^8$  ms $^{-1}$ , to be precise). This is called **speed of light** and is given the symbol 'c'. The frequency ( $\nu$ ), wavelength ( $\lambda$ ) and velocity of light (c) are related by the equation (2.5).

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



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

The other commonly used quantity specially in spectroscopy, is the **wavenumber** ( $\bar{v}$ ). 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,  $\lambda$ , is equal to  $c/v$ , where  $c$  is the speed of electromagnetic radiation in vacuum and  $v$  is the frequency. Substituting the given values, we have

$$\begin{aligned}\lambda &= \frac{c}{v} \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \text{ kHz}} \\ &= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} \\ &= 219.3 \text{ m}\end{aligned}$$

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). ( $1\text{nm} = 10^{-9}\text{m}$ )

#### Solution

Using equation 2.5, frequency of violet light

$$\begin{aligned}v &= \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} \\ &= 7.50 \times 10^{14} \text{ Hz}\end{aligned}$$

Frequency of red light

$$v = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} = 4.00 \times 10^{14} \text{ Hz}$$

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

### Problem 2.5

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

#### Solution

$$\begin{aligned}(a) \text{ Calculation of wavenumber } (\bar{v}) \\ \lambda &= 5800 \text{ Å} = 5800 \times 10^{-8} \text{ cm} \\ &= 5800 \times 10^{-10} \text{ m}\end{aligned}$$

$$\begin{aligned}\bar{v} &= \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10} \text{ m}} \\ &= 1.724 \times 10^6 \text{ m}^{-1} \\ &= 1.724 \times 10^4 \text{ cm}^{-1}\end{aligned}$$

$$(b) \text{ Calculation of the frequency } (v)$$

$$\bar{v} = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m s}^{-1}}{5800 \times 10^{-10} \text{ m}} = 5.172 \times 10^{14} \text{ s}^{-1}$$

### 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 electromagnetic 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

\* 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.

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

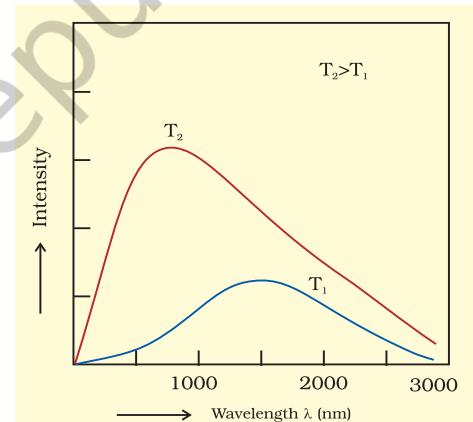
These phenomena indicate that the system can take energy only in discrete amounts. All possible energies cannot be taken up or radiated.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation mentioned above was given by Max Planck in 1900. Let us first try to understand this phenomenon, which is given below:

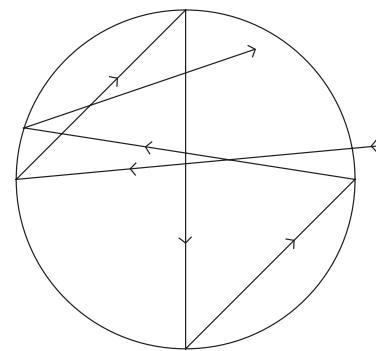
Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated. For example, when an iron 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. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature. This means intensities of radiations of different wavelengths emitted by hot body depend upon its temperature. By late 1850's it was known that objects made of different material and kept at different temperatures emit different amount of radiation. Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are as a rule imperfect absorbers of radiation. An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation. In practice, no such body exists. Carbon black approximates fairly closely to black body. A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray

entering the hole will be reflected by the cavity walls and will be eventually absorbed by the walls. A black body is also a perfect radiator of radiant energy. Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time. The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further increase of wavelength, as shown in Fig. 2.8. Also, as the temperature increases, maxima of the curve shifts to short wavelength. Several attempts were made to predict the intensity of radiation as a function of wavelength.

But the results of the above experiment could not be explained satisfactorily on the basis of the wave theory of light. Max Planck arrived at a satisfactory relationship



**Fig. 2.8** Wavelength-intensity relationship



**Fig. 2.8(a)** Black body

by making an assumption that absorption and emission of radiation arises from oscillator i.e., atoms in the wall of black body. Their frequency of oscillation is changed by interaction with oscillators of electromagnetic radiation. Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He 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 ( $\nu$ ) and is expressed by equation (2.6).

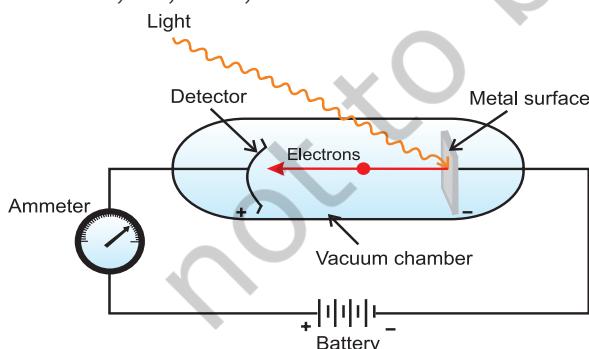
$$E = h\nu \quad (2.6)$$

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

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.

Quantisation has been compared to standing on a staircase. A person can stand on any step of a staircase, but it is not possible for him/her to stand in between the two steps. The energy can take any one of the values from the following set, but cannot take on any values between them.

$$E = 0, h\nu, 2h\nu, 3h\nu, \dots nh\nu, \dots$$



**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

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 **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,  $v_0$  (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency  $v > v_0$ , 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

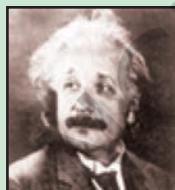
**Table 2.2 Values of Work Function ( $W_0$ ) for a Few Metals**

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

of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [ $\nu = (4.3 \text{ to } 4.6) \times 10^{14} \text{ Hz}$ ] 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 ( $\nu = 5.1\text{--}5.2 \times 10^{14} \text{ Hz}$ ) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency ( $\nu_0$ ) for potassium metal is  $5.0 \times 10^{14} \text{ Hz}$ .

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

*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.*



**Albert Einstein  
(1879–1955)**

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.

$$h\nu = h\nu_0 + \frac{1}{2}m_e v^2 \quad (2.7)$$

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 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  $5 \times 10^{14}$  Hz.

**Solution**

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

$$E = hv$$

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

$$v = 5 \times 10^{14} \text{ s}^{-1} \text{ (given)}$$

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

$$= 3.313 \times 10^{-19} \text{ J}$$

Energy of one mole of photons

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

$$= 199.51 \text{ kJ mol}^{-1}$$

**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

$$= 100 \text{ J s}^{-1}$$

Energy of one photon  $E = hv = hc/\lambda$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= 4.969 \times 10^{-19} \text{ J}$$

Number of photons emitted

$$\frac{100 \text{ J s}^{-1}}{4.969 \times 10^{-19} \text{ J}} = 2.012 \times 10^{20} \text{ s}^{-1}$$

**Problem 2.8**

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of  $1.68 \times 10^5 \text{ J mol}^{-1}$ . 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

$$hn = hc/\lambda$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}}$$

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

The energy of one mole of photons

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

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

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

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

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

The minimum energy for one electron

$$= \frac{2.31 \times 10^5 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ electrons mol}^{-1}}$$

$$= 3.84 \times 10^{-19} \text{ J}$$

This corresponds to the wavelength

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

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{3.84 \times 10^{-19} \text{ J}}$$

$$= 517 \text{ nm}$$

(This corresponds to green light)

**Problem 2.9**

The threshold frequency  $v_0$  for a metal is  $7.0 \times 10^{14} \text{ s}^{-1}$ . Calculate the kinetic energy of an electron emitted when radiation of frequency  $v = 1.0 \times 10^{15} \text{ s}^{-1}$  hits the metal.

**Solution**

According to Einstein's equation

$$\text{Kinetic energy} = \frac{1}{2} m_e v^2 = h(v - v_0)$$

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

$$= (6.626 \times 10^{-34} \text{ J s}) (10.0 \times 10^{14} \text{ s}^{-1} - 7.0 \times 10^{14} \text{ s}^{-1})$$

$$= (6.626 \times 10^{-34} \text{ J s}) \times (3.0 \times 10^{14} \text{ s}^{-1})$$

$$= 1.988 \times 10^{-19} \text{ J}$$

### 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  $7.50 \times 10^{14}$  Hz to red at  $4 \times 10^{14}$  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 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 page 45).

**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 fingerprints 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.

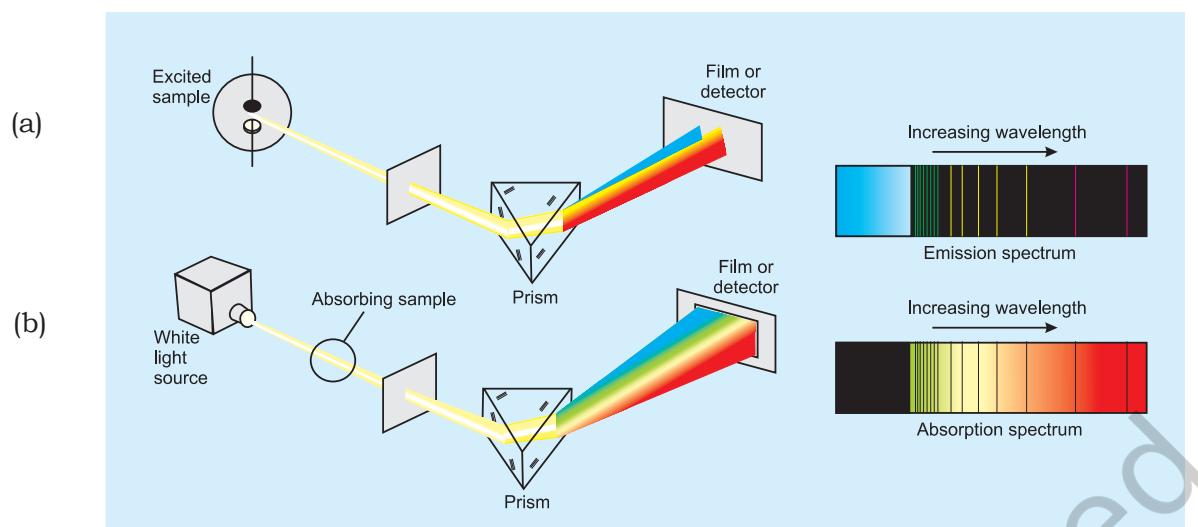
Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

#### 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

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



**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.

that if spectral lines are expressed in terms of wavenumber ( $\bar{v}$ ), then the visible lines of the hydrogen spectrum obey the following formula:

$$\bar{v} = 109,677 \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \text{ cm}^{-1} \quad (2.8)$$

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

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 :

$$\bar{v} = 109,677 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \quad (2.9)$$

where  $n_1 = 1, 2, \dots$

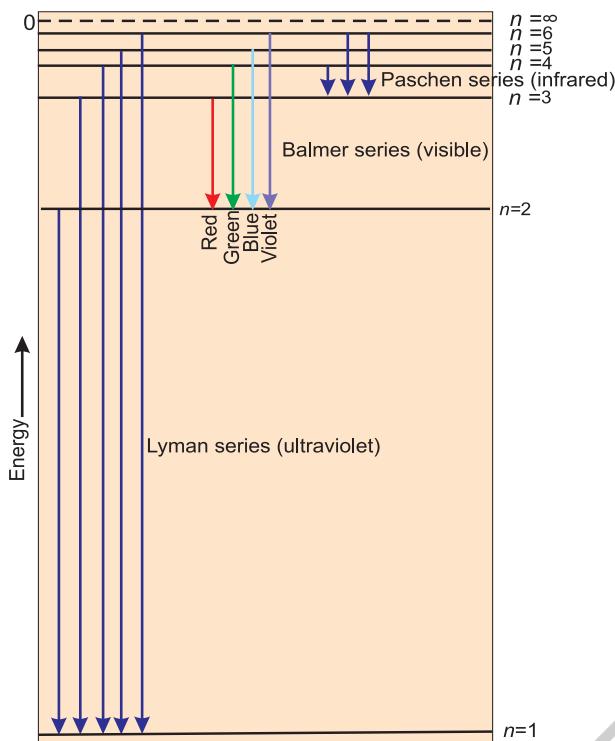
$n_2 = n_1 + 1, n_1 + 2, \dots$

The value  $109,677 \text{ cm}^{-1}$  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, Brackett and Pfund series, respectively, Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig. 2.11 (page, 46) 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

**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)

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 the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. 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:

- 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.
- The energy of an electron in the orbit does not change with time. However, the 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 ( $\omega$ ). For an electron of mass  $m_e$ , moving in a circular path of radius  $r$  around the nucleus,

$$\text{angular momentum} = I \times \omega$$

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

$$\therefore \text{angular momentum} = m_e r^2 \times v/r = m_e v r$$

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by  $\Delta E$ , is given by:

$$n = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \quad (2.10)$$

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.

- The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11)

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots \quad (2.11)$$

Where  $m_e$  is the mass of electron,  $v$  is the velocity and  $r$  is the radius of the orbit in which electron is moving.

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of  $h/2\pi$ . That means angular momentum is quantised. Radiation is emitted or absorbed only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here 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:

- The stationary states for electron are numbered  $n = 1, 2, 3, \dots$ . These integral numbers (Section 2.6.2) are known as **Principal quantum numbers**.
  - The radii of the stationary states are expressed as:
- $$r_n = n^2 a_0 \quad (2.12)$$
- where  $a_0 = 52.9$  pm. Thus the radius of the first stationary state, called the **Bohr orbit**, 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.
- The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

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

where  $R_H$  is called **Rydberg constant** and its value is  $2.18 \times 10^{-18}$  J. The energy of the lowest state, also called as the ground state, is

$$E_1 = -2.18 \times 10^{-18} \left( \frac{1}{1^2} \right) = -2.18 \times 10^{-18} \text{ J.}$$

The energy of the stationary state for  $n = 2$ , will

$$\text{be : } E_2 = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{2^2} \right) = -0.545 \times 10^{-18} \text{ J.}$$



**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.

Fig. 2.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

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  $= n = \infty$  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

#### 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  $E_\infty = 0$ . 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.

for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and  $n = \infty$ .

- d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  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.

$$E_n = -2.18 \times 10^{-18} \left( \frac{Z^2}{n^2} \right) \text{ J} \quad (2.14)$$

and radii by the expression

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

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)

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

Combining equations (2.13) and (2.16)

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

$$\Delta E = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.17)$$

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

$$\begin{aligned} v &= \frac{\Delta E}{h} = \frac{R_H}{h} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \end{aligned} \quad (2.18)$$

$$= 3.29 \times 10^{15} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ Hz} \quad (2.19)$$

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

$$\begin{aligned} \bar{v} &= \frac{v}{c} = \frac{R_H}{hc} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{3.29 \times 10^{15} \text{ s}^{-1}}{3 \times 10^8 \text{ m s}^{-1}} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 1.09677 \times 10^7 \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ m}^{-1} \end{aligned} \quad (2.20) \quad (2.21)$$

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  $n_i > n_f$ ,  $\Delta E$  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)

$$\begin{aligned}\Delta E &= 2.18 \times 10^{-18} J \left[ \frac{1}{5^2} - \frac{1}{2^2} \right] \\ &= -4.58 \times 10^{-19} J\end{aligned}$$

It is an emission energy

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

$$\begin{aligned}v &= \frac{\Delta E}{h} \\ &= \frac{4.58 \times 10^{-19} J}{6.626 \times 10^{-34} Js} \\ &= 6.91 \times 10^{14} Hz \\ \lambda &= \frac{c}{v} = \frac{3.0 \times 10^8 m s^{-1}}{6.91 \times 10^{14} Hz} = 434 nm\end{aligned}$$

**Problem 2.11**

Calculate the energy associated with the first orbit of  $\text{He}^+$ . What is the radius of this orbit?

**Solution**

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

For  $\text{He}^+$ ,  $n = 1$ ,  $Z = 2$

$$E_1 = -\frac{(2.18 \times 10^{-18} J)(2^2)}{1^2} = -8.72 \times 10^{-18} J$$

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

$$r_n = \frac{(0.0529 nm)n^2}{Z}$$

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

$$r_1 = \frac{(0.0529 nm)1^2}{2} = 0.02645 nm$$

**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,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , and so on). However, Bohr's model was too simple to account for the following points.

- 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).
- 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 ( $\lambda$ ) and momentum ( $p$ ) of a material particle.

**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 until his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929.



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

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.

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  $10 \text{ m s}^{-1}$ ?

**Solution**

According to de Broglie equation (2.22)

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ Js})}{(0.1 \text{ kg})(10 \text{ m s}^{-1})}$$

$$= 6.626 \times 10^{-34} \text{ m } (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

**Problem 2.13**

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

**Solution**

Since K.E. =  $\frac{1}{2} mv^2$

$$v = \left( \frac{2\text{K.E.}}{m} \right)^{1/2} = \left( \frac{2 \times 3.0 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

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

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(812 \text{ m s}^{-1})}$$

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

**Problem 2.14**

Calculate the mass of a photon with wavelength  $3.6 \text{ \AA}$ .

**Solution**

$$\lambda = 3.6 \text{ \AA} = 3.6 \times 10^{-10} \text{ m}$$

Velocity of photon = velocity of light

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34} \text{ Js}}{(3.6 \times 10^{-10} \text{ m})(3 \times 10^8 \text{ m s}^{-1})}$$

$$= 6.135 \times 10^{-29} \text{ kg}$$

**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).

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

$$\text{or } \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

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

where  $\Delta x$  is the uncertainty in position and  $\Delta p_x$  (or  $\Delta v_x$ ) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy ( $\Delta x$  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 ( $\Delta x$  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 ( $p = \frac{h}{\lambda}$ )

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

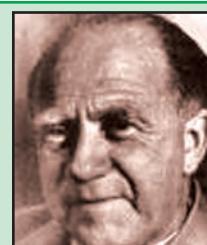
One of the important implications of the Heisenberg Uncertainty Principle is that **it rules out existence of definite paths or trajectories of electrons and other similar particles**. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is 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

$$\begin{aligned}\Delta v \cdot \Delta x &= \frac{h}{4\pi m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.1416 \times 10^{-6} \text{ kg}} \approx 10^{-28} \text{ m}^2 \text{ s}^{-1}\end{aligned}$$

*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.



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  $9.11 \times 10^{-31}$  kg., according to Heisenberg uncertainty principle

$$\begin{aligned}\Delta v \Delta x &= \frac{h}{4\pi m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.1416 \times 9.11 \times 10^{-31} \text{ kg}} \\ &= 10^{-4} \text{ m}^2 \text{s}^{-1}\end{aligned}$$

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  $\Delta v$  in velocity would be

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

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

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

$$\begin{aligned}\Delta v &= \frac{h}{4\pi \Delta x m} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 0.1 \times 10^{-10} \text{ m} \times 9.11 \times 10^{-31} \text{ kg}} \\ &= 0.579 \times 10^7 \text{ m s}^{-1} (1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}) \\ &= 5.79 \times 10^6 \text{ m s}^{-1}\end{aligned}$$

### 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.

#### Solution

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

$$45 \quad \frac{2}{100} = 0.9 \text{ m s}^{-1}$$

Using the equation (2.22)

$$\begin{aligned}\Delta x &= \frac{h}{4\pi m \Delta v} \\ &= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 40 \text{ g} \times 10^{-3} \text{ kg g}^{-1} (0.9 \text{ m s}^{-1})} \\ &= 1.46 \times 10^{-33} \text{ m}\end{aligned}$$

This is nearly  $\sim 10^{18}$  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.

### 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.*

*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.*



**Erwin Schrödinger  
(1887–1961)**

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.

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

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  $\psi$ .

### 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) ( $\psi$ ) 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 quantised 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  $\psi$  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  $\psi$  and quantum mechanics makes it possible to extract this information out of  $\psi$ .
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  $n = 1, 2, 3, \dots$ . The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species ( $\text{He}^+$ ,  $\text{Li}^{2+}$ , ... 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

$$n = 1 \quad 2 \quad 3 \quad 4 \quad \dots$$

$$\text{Shell} = \text{K L M N} \quad \dots$$

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 :  $l = 0, 1, 2, \dots, (n-1)$

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 s p d f g h ..... sub-shell

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**

<b>n</b>	<b>l</b>	<b>Subshell notation</b>
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 :  $m_l = -l, -(l-1), -(l-2) \dots 0, 1, \dots (l-2), (l-1), l$

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  $p$  subshell of the second shell. The following chart gives the relation between the subshell 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 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  $+1/2$  or  $-1/2$ . These are called the **two spin states of the electron** and are normally represented by two arrows,  $\uparrow$  (spin up) and  $\downarrow$  (spin down). Two electrons that have different  $m_s$  values (one  $+1/2$  and the other  $-1/2$ ) 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 :

- $n$  defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.
- There are  $n$  subshells in the  $n^{\text{th}}$  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.
- $m_l$  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

### 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  $\psi$  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.  $\psi$  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.

the number of orbitals is equal to the number of ways in which they are oriented.

- iv)  $m_s$  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

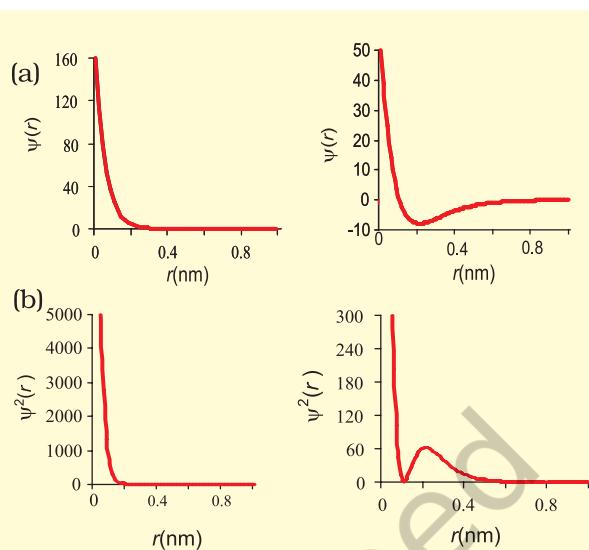
- (a)  $n = 2$ ,  $l = 1$ , (b)  $n = 4$ ,  $l = 0$ , (c)  $n = 5$ ,  $l = 3$ , (d)  $n = 3$ ,  $l = 2$

#### 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  $\psi$  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), gives such plots for  $1s$  ( $n = 1$ ,  $l = 0$ ) and  $2s$  ( $n = 2$ ,  $l = 0$ ) orbitals.



**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.

According to the German physicist, Max Born, the square of the wave function (i.e.,  $\psi^2$ ) at a point gives the probability density of the electron at that point. The variation of  $\psi^2$  as a function of  $r$  for  $1s$  and  $2s$  orbitals is given in Fig. 2.12(b). 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 away from it. On the other hand, for  $2s$  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  $2s$  orbital is one, two for  $3s$  and so on.

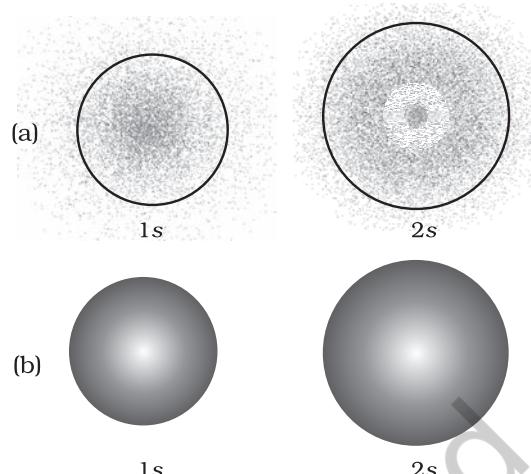
These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density

of the dots in a region represents electron probability density in that region.

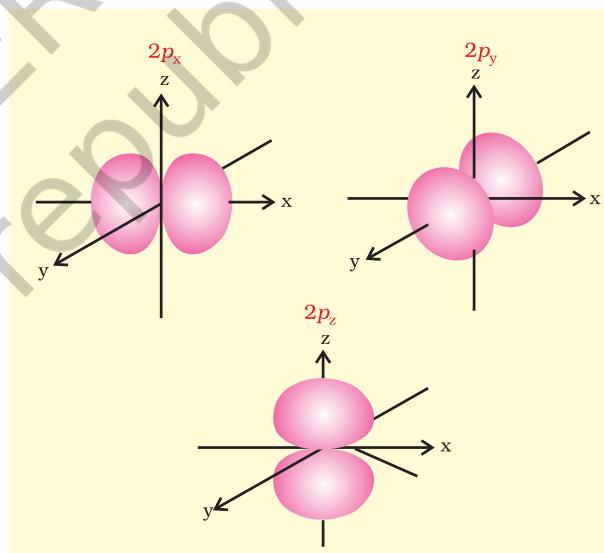
**Boundary surface diagrams** of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density  $|\psi|^2$  is 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 1s and 2s 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%.

Thus, we see that 1s and 2s 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,  $4s > 3s > 2s > 1s$  and the electron is located further away from the nucleus as the principal quantum number increases.

Boundary surface diagrams for three  $2p$  orbitals ( $l = 1$ ) are shown in Fig. 2.14. In



**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.

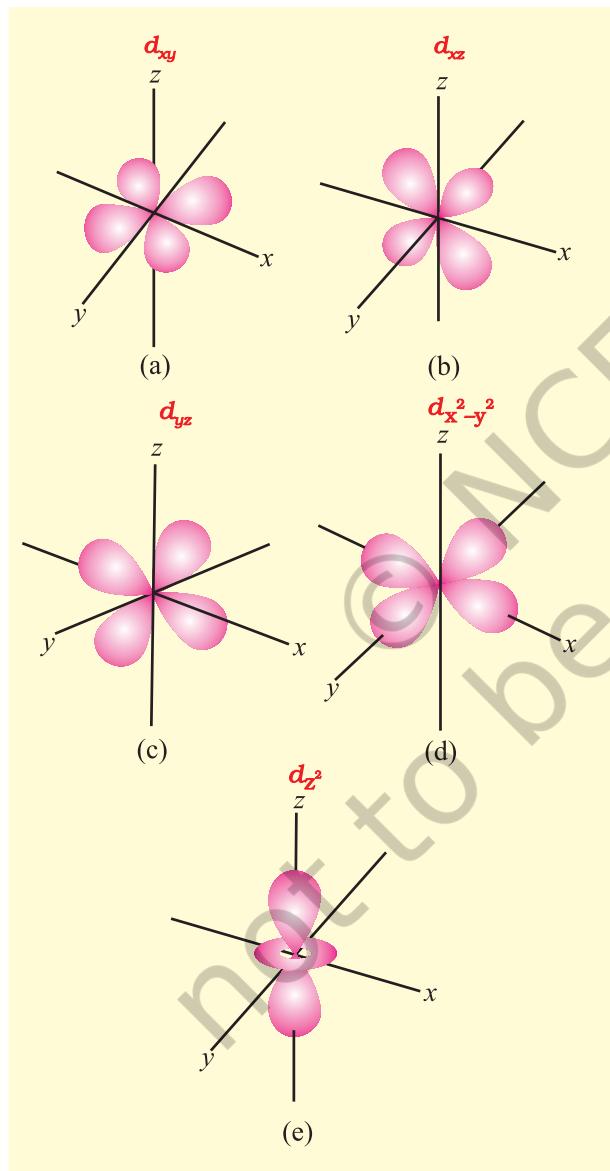


**Fig. 2.14** Boundary surface diagrams of the three 2p orbitals.

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

\* 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.

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,



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

it is sufficient to remember that, 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  $4p > 3p > 2p$ . 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  $3p$  orbital, two for  $4p$  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 diagrams of  $d$  orbitals are shown in Fig. 2.15.

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, whereas that of the fifth one,  $d_{z^2}$ , is different from others, but all five  $3d$  orbitals are equivalent in energy. The  $d$  orbitals for which  $n$  is greater than 3 ( $4d$ ,  $5d$ ...) also have shapes similar to  $3d$  orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the  $np$  and  $nd$  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.**

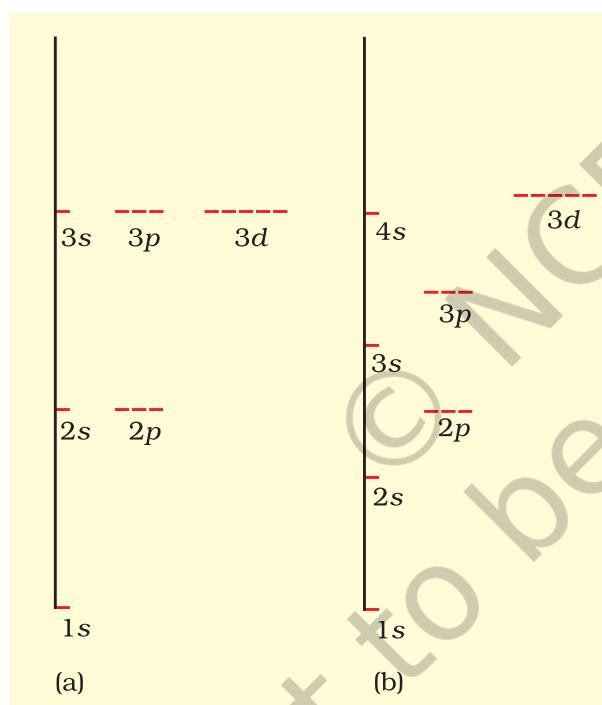
### 2.6.3 Energies of Orbitals

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

number. Thus the energy of the orbitals in hydrogen atom increases as follows :

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

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  $1s$  orbital in a hydrogen atom, as said earlier, corresponds to the most 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**.



**Fig. 2.16** Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electron 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.

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. Within a given principal quantum number, the energy of orbitals increases in the order  $s < p < d < f$ . For higher energy levels, these differences are sufficiently pronounced and staggering of orbital energy may result, e.g.,  $4s < 3d$  and  $6s < 5d$ ;  $4f < 6p$ . The main reason for having different energies of the subshells is the mutual repulsion among the electrons in 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 a 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 of the nucleus ( $Ze$ ). The effect 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 outer shell electrons from the nucleus by the inner shell electrons**, and the net positive charge experienced by the outer electrons is known as **effective nuclear charge** ( $Z_{\text{eff}} e$ ). Despite the shielding of the outer electrons from the nucleus by the inner shell electrons, the attractive force experienced by the outer shell electrons increases 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 electrons present in spherical shaped,  $s$  orbital shields the outer electrons from the nucleus more effectively as compared to electrons present in  $p$  orbital. Similarly electrons present in  $p$  orbitals shield the outer electrons from the nucleus more than the electrons present in  $d$  orbitals, even though all these orbitals are present in the same shell. Further within a shell, due to spherical shape of  $s$  orbital, the  $s$  orbital electron spends more time close to the nucleus in comparison to  $p$  orbital electron which spends more time in the vicinity of nucleus in comparison to  $d$  orbital electron. In other words, for a given shell (principal quantum number), the  $Z_{\text{eff}}$  experienced by the electron decreases with increase of azimuthal quantum number ( $l$ ), that is, the  $s$  orbital electron will be more tightly bound to the nucleus than  $p$  orbital electron which in turn will be better tightly bound than the  $d$  orbital electron. The energy of electrons in  $s$  orbital will be lower (more negative) than that of  $p$  orbital electron which will have less energy than that of  $d$  orbital electron and so on. Since the extent of shielding from the nucleus is different for electrons in different orbitals, it leads to the splitting of energy levels within the same shell (or same principal quantum number), that is, energy of electron in an 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, **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 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

**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 $(n + l)$	
<b>1s</b>	1	0	$1 + 0 = 1$	
<b>2s</b>	2	0	$2 + 0 = 2$	
<b>2p</b>	2	1	$2 + 1 = 3$	$2p \text{ } (n=2)$ has lower energy than
<b>3s</b>	3	0	$3 + 0 = 3$	$3s \text{ } (n=3)$
<b>3p</b>	3	1	$3 + 1 = 4$	$3p \text{ } (n=3)$ has lower energy than
<b>4s</b>	4	0	$4 + 0 = 4$	$4s \text{ } (n=4)$
<b>3d</b>	3	2	$3 + 2 = 5$	$3d \text{ } (n=3)$ has lower energy than
<b>4p</b>	4	1	$4 + 1 = 5$	$4p \text{ } (n=4)$

same energy. Lastly it may be mentioned here that **energies of the orbitals in the same subshell decrease with increase in the atomic number ( $Z_{\text{eff}}$ )**. 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,  $E_{2s}(\text{H}) > E_{2s}(\text{Li}) > E_{2s}(\text{Na}) > E_{2s}(\text{K})$ .

#### 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.

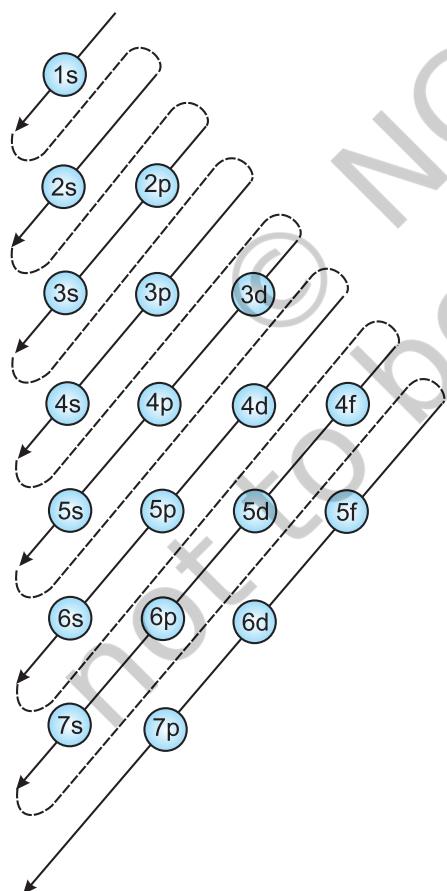
#### Aufbau Principle

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

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. As you have learnt above, energy of a given orbital depends upon effective nuclear charge and different type of orbitals are affected to different extent. Thus, there is no single ordering of energies of orbitals which will be universally correct for all atoms.

However, following order of energies of the orbitals is extremely useful:  
 $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s\dots$

The order may be remembered by using the method given in Fig. 2.17. Starting from



**Fig. 2.17 Order of filling of orbitals**

the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left. With respect to placement of outermost valence electrons, it is remarkably accurate for all atoms. For example, valence electron in potassium must choose between  $3d$  and  $4s$  orbitals and as predicted by this sequence, it is found in  $4s$  orbital. The above order should be assumed to be a rough guide to the filling of energy levels. In many cases, the orbitals are similar in energy and small changes in atomic structure may bring about a change in the order of filling. Even then, the above series is a useful guide to the building of the electronic structure of an atom provided that it is remembered that exceptions may occur.

#### **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 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)  $s^a p^b d^c \dots$  notation

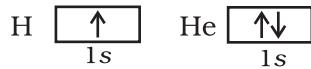
(ii) Orbital diagram



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 ( $\uparrow$ ) a positive spin or an arrow ( $\downarrow$ ) 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 1s. The electronic configuration of the hydrogen atom is  $1s^1$  meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the

1s 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 1s orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2s orbital. The electronic configuration of Li is  $1s^2 2s^1$ . The 2s orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore,  $1s^2 2s^2$  (see Table 2.6, page 66 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 2p orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows :

Li			
Be			
B			
C			
N			
O			
F			
Ne			
	1s	2s	2p

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<sup>1</sup>) to (Ar, [Ne] 3s<sup>2</sup>3p<sup>6</sup>). 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<sup>3</sup>, p<sup>6</sup>, d<sup>5</sup>, d<sup>10</sup>, f<sup>7</sup>, f<sup>4</sup> etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d<sup>5</sup> and d<sup>10</sup> 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 (page 66).

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<sup>5</sup> 4s<sup>1</sup> and 3d<sup>10</sup> 4s<sup>1</sup> respectively and not 3d<sup>4</sup> 4s<sup>2</sup> and 3d<sup>9</sup> 4s<sup>2</sup>. It has been found that there is extra stability associated with these electronic configurations.

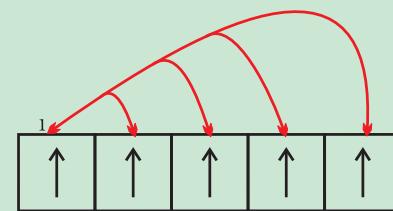
### Causes of Stability of Completely Filled and Half-filled Subshells

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

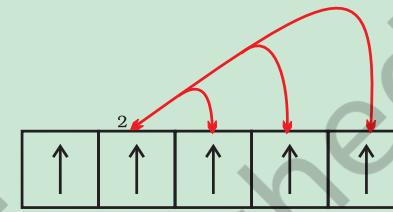
**1. Symmetrical distribution of electrons:** It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here  $3d$ ) have equal energy but different 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.

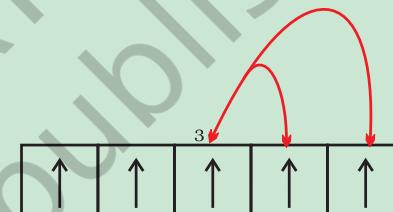
You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic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



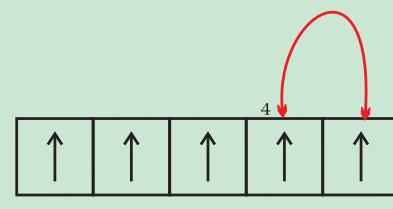
4 exchange by electron 1



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**

<b>Element Z</b>	<b>1s</b>	<b>2s</b>	<b>2p</b>	<b>3s</b>	<b>3p</b>	<b>3d</b>	<b>4s</b>	<b>4p</b>	<b>4d</b>	<b>4f</b>	<b>5s</b>	<b>5p</b>	<b>5d</b>	<b>5f</b>	<b>6s</b>	<b>6p</b>	<b>6d</b>	<b>7s</b>
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	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	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										
Sr 38	2	2	6	2	6	10	2	6										
Y 39	2	2	6	2	6	10	2	6	1									
Zr 40	2	2	6	2	6	10	2	6	2									
Nb*	41	2	2	6	2	6	10	2	6	4								
Mo*	42	2	2	6	2	6	10	2	6	5								
Tc 43	2	2	6	2	6	10	2	6	5									
Ru*	44	2	2	6	2	6	10	2	6	7								
Rh*	45	2	2	6	2	6	10	2	6	8								
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								
Sn 50	2	2	6	2	6	10	2	6	10	2								
Sb 51	2	2	6	2	6	10	2	6	10	2								
Te 52	2	2	6	2	6	10	2	6	10	2								
I 53	2	2	6	2	6	10	2	6	10	2								
Xe 54	2	2	6	2	6	10	2	6	10	2								

\* 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		1	2			
La* 57	2	2	6	2	6	10	2	6	10	2	2	6			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		1			
Au* 79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
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) ( $\psi$ ) (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  $m$** ) 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  $\text{He}^+$ ,  $\text{Li}^{2+}$  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  $^{14}\text{C}$ .  
 (Assume that mass of a neutron =  $1.675 \times 10^{-27}$  kg).  
 (iii) Find (a) the total number and (b) the total mass of protons in 34 mg of  $\text{NH}_3$  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 ?  
 $^{13}_{\text{6}}\text{C}$ ,  $^{16}_{\text{8}}\text{O}$ ,  $^{24}_{\text{12}}\text{Mg}$ ,  $^{56}_{\text{26}}\text{Fe}$ ,  $^{88}_{\text{38}}\text{Sr}$
- 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 ( $\lambda$ ) of 580 nm. Calculate the frequency ( $\nu$ ) and wavenumber ( $\bar{\nu}$ ) of the yellow light.
- 2.6 Find energy of each of the photons which
  - (i) correspond to light of frequency  $3 \times 10^{15}$  Hz.
  - (ii) have wavelength of 0.50 Å.
- 2.7 Calculate the wavelength, frequency and wavenumber of a light wave whose period is  $2.0 \times 10^{-10}$  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  $4 \times 10^{-7}$  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 =  $1.6020 \times 10^{-19}$  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<sup>-1</sup>.
- 2.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57 μm. 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 ( $v_0$ ) 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  $-2.18 \times 10^{-18}$  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  $-2.18 \times 10^{-11}$  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  $2.05 \times 10^7$  m s $^{-1}$ .
- 2.21 The mass of an electron is  $9.1 \times 10^{-31}$  kg. If its K.E. is  $3.0 \times 10^{-25}$  J, calculate its wavelength.
- 2.22 Which of the following are isoelectronic species i.e., those having the same number of electrons?  
 $\text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{S}^{2-}, \text{Ar}$
- 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) 3s1 (b) 2p3 and (c) 3p5 ?  
(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 ( $ml$  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) $n = 0,$ | $l = 0,$ | $m_l = 0,$ | $m_s = + \frac{1}{2}$ |
| (b) $n = 1,$ | $l = 0,$ | $ml = 0,$  | $ms = - \frac{1}{2}$  |
| (c) $n = 1,$ | $l = 1,$ | $m_l = 0,$ | $m_s = + \frac{1}{2}$ |
| (d) $n = 2,$ | $l = 1,$ | $m_l = 0,$ | $m_s = - \frac{1}{2}$ |

- (e)  $n = 3, l = 3, ml = -3, ms = + \frac{1}{2}$   
 (f)  $n = 3, l = 1, m_l = 0, m_s = + \frac{1}{2}$
- 2.31 How many electrons in an atom may have the following quantum numbers?  
 (a)  $n = 4, m_s = -\frac{1}{2}$       (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  $\text{He}^+$  spectrum?
- 2.34 Calculate the energy required for the process  
 $\text{He}^+(\text{g}) \rightarrow \text{He}^{2+}(\text{g}) + \text{e}^-$   
 The ionization energy for the H atom in the ground state is  $2.18 \times 10^{-18} \text{ J atom}^{-1}$
- 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  $2 \times 10^8$  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  $2.5 \times 10^{-16} \text{ C}$  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  $-1.282 \times 10^{-18} \text{ C}$ , 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  $\alpha$ -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  ${}^{79}_{35}\text{Br}$  and  ${}^{79}\text{Br}$  can be written, whereas symbols  ${}^{35}_{79}\text{Br}$  and  ${}^{35}\text{Br}$  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 contains 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  $5.6 \times 10^{24}$ , 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  $3.15 \times 10^{-18}$  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  $2.5 \times 10^{15}$ , calculate the energy of the source.
- 2.50 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate 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.
- |  |      |      |      |
|--|------|------|------|
| $\lambda$ (nm)                           | 500  | 450  | 400  |
| $v \times 10^{-5}$ (cm s <sup>-1</sup> ) | 2.55 | 4.35 | 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 its inner bound electrons is ejected out with a velocity of  $1.5 \times 10^7$  m s<sup>-1</sup>, 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 represented as  $v = 3.29 \times 10^{15}$  (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  $1.6 \times 10^6$  ms<sup>-1</sup>, 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  $2.19 \times 10^6$  ms<sup>-1</sup>, 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  $4.37 \times 10^5$  ms<sup>-1</sup>. If the hockey ball of mass 0.1 kg is moving with this velocity, calculate 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  $h/4\pi_m \times 0.05$  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 subshells are associated with  $n = 4$  ? (b) How many electrons will be present in the subshells having  $m_s$  value of  $-1/2$  for  $n = 4$  ?



## UNIT 3

11082CH03

# 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

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).

**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

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

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

**Table 3.2 Newlands' 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					

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 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)
<b>Atomic weight</b>	68	70	72	72.6
<b>Density/(g/cm<sup>3</sup>)</b>	5.9	5.94	5.5	5.36
<b>Melting point/K</b>	Low	302.93	High	1231
<b>Formula of oxide</b>	$\text{E}_2\text{O}_3$	$\text{Ga}_2\text{O}_3$	$\text{EO}_2$	$\text{GeO}_2$
<b>Formula of chloride</b>	$\text{E Cl}_3$	$\text{GaCl}_3$	$\text{ECl}_4$	$\text{GeCl}_4$

## PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES

SERIES	GROUPS OF ELEMENTS							
	0	I	II	III	IV	V	VI	VII
1	-	Hydrogen H 1.008	-	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Aluminium Al 27.0	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Silicon Si 28.4	-	-	-	-
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	Iron Fe 55.9
5	Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Arsenic As 75	Selenium Se 79	Nickel Co 59
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 Ru 101.7
7	Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127.6	Rhodium Rh 103.0
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	Palladium Pd 106.5
9	-	-	-	-	-	-	-	(Ag)
10	-	-	Mercury Hg 200.0	Ytterbium Yb 173	-	Lead Pb 206.9	Tantalum Ta 183	-
11	-	Gold Au 197.2	Thallium Tl 204.1	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	Tungsten W 184	Platinum Pt 194.9
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239	Osmium Os 191
	R	R <sub>2</sub> O	RO	R <sub>2</sub> O <sub>3</sub>	RO <sub>2</sub> RH <sub>4</sub>	HIGHER SALINE OXIDES R <sub>2</sub> O <sub>5</sub> HIGHER GASEOUS HYDROGEN COMPOUNDS RH <sub>2</sub>	R <sub>2</sub> O <sub>7</sub> RH <sub>3</sub>	RO <sub>4</sub>

**Fig. 3.1** Mendeleev's Periodic Table published earlier

### 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 20<sup>th</sup> 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  $\sqrt{v}$  (where  $v$  is frequency of X-rays emitted) against atomic number ( $Z$ ) gave a straight line and not the plot of  $\sqrt{v}$  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

\* Glenn T. Seaborg's work in the middle of the 20<sup>th</sup> 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.

GROUP NUMBER		Representative elements								Noble gases																																																																																																																																																																																																																																																																																																																																																											
		GROUP NUMBER		GROUP NUMBER		GROUP NUMBER		GROUP NUMBER																																																																																																																																																																																																																																																																																																																																																													
1 IA		2 IIA		3 IIIA		4 IV A		5 V A		6 VI A		7 VII A		8 VIII		d-Transition elements		f - Inner transition elements																																																																																																																																																																																																																																																																																																																																																			
2	Li	3	4 Be	5	6 Ca	7 Sc	8 Ti	9 V	10 Cr	21 Mn	25 Fe	26 Co	27 Ni	28 Cu	29 Zn	30 Ga	31 Ge	32 As	33 Se	34 Br	35 Kr																																																																																																																																																																																																																																																																																																																																																
11	Na	12	Mg	13	Al	14	Si	15 P	16 S	17 P	18 Cl	19 S	20 S	21 S	22 S	23 S	24 S	25 S	26 S	27 S	28 S	29 Ne																																																																																																																																																																																																																																																																																																																																															
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4	4s <sup>1</sup>	4s <sup>2</sup>	4s <sup>1</sup>	4s <sup>2</sup>	4s <sup>1</sup>	4s <sup>2</sup>	4s <sup>1</sup>	4s <sup>2</sup>	4s <sup>1</sup>	41 Cr	42 Ti	43 V	44 Mo	45 Nb	46 Ru	47 Rh	48 Cd	49 Ag	50 In	51 Te	52 I	53 Kr																																																																																																																																																																																																																																																																																																																																															
5	5s <sup>1</sup>	5s <sup>2</sup>	5s <sup>1</sup>	5s <sup>2</sup>	5s <sup>1</sup>	5s <sup>2</sup>	5s <sup>1</sup>	5s <sup>2</sup>	5s <sup>1</sup>	5d <sup>1</sup> 5s <sup>2</sup>	5d <sup>2</sup> 5s <sup>2</sup>	5d <sup>3</sup> 5s <sup>1</sup>	5d <sup>4</sup> 5s <sup>1</sup>	5d <sup>5</sup> 5s <sup>1</sup>	5d <sup>6</sup> 5s <sup>1</sup>	5d <sup>7</sup> 5s <sup>1</sup>	5d <sup>8</sup> 5s <sup>1</sup>	5s <sup>2</sup> 5p <sup>1</sup>	5s <sup>2</sup> 5p <sup>2</sup>	5s <sup>2</sup> 5p <sup>3</sup>	5s <sup>2</sup> 5p <sup>4</sup>	5s <sup>2</sup> 5p <sup>5</sup>	5s <sup>2</sup> 5p <sup>6</sup>																																																																																																																																																																																																																																																																																																																																														
55	5s <sup>2</sup>	56	57 La*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	87 Ra	88 Ac*	89 Rf	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Cf	98 Es	99 Fm	100 Md	101 No	102 Lr	103 Og																																																																																																																																																																																																																																																																																																																				
6	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>2</sup> 6s <sup>2</sup>	5d <sup>3</sup> 6s <sup>2</sup>	5d <sup>4</sup> 6s <sup>2</sup>	5d <sup>5</sup> 6s <sup>2</sup>	5d <sup>6</sup> 6s <sup>2</sup>	5d <sup>7</sup> 6s <sup>2</sup>	5d <sup>8</sup> 6s <sup>2</sup>	5d <sup>9</sup> 6s <sup>2</sup>	5d <sup>10</sup> 6s <sup>1</sup>	5d <sup>11</sup> 6s <sup>2</sup>	5d <sup>12</sup> 6s <sup>2</sup>	5d <sup>13</sup> 6s <sup>2</sup>	5d <sup>14</sup> 6s <sup>2</sup>	5d <sup>15</sup> 6s <sup>2</sup>	5d <sup>16</sup> 6s <sup>2</sup>	5d <sup>17</sup> 6s <sup>2</sup>	5d <sup>18</sup> 6s <sup>2</sup>	5d <sup>19</sup> 6s <sup>2</sup>	5d <sup>20</sup> 6s <sup>2</sup>	5d <sup>21</sup> 6s <sup>2</sup>	5d <sup>22</sup> 6s <sup>2</sup>	5d <sup>23</sup> 6s <sup>2</sup>	5d <sup>24</sup> 6s <sup>2</sup>	5d <sup>25</sup> 6s <sup>2</sup>	5d <sup>26</sup> 6s <sup>2</sup>	5d <sup>27</sup> 6s <sup>2</sup>	5d <sup>28</sup> 6s <sup>2</sup>	5d <sup>29</sup> 6s <sup>2</sup>	5d <sup>30</sup> 6s <sup>2</sup>	5d <sup>31</sup> 6s <sup>2</sup>	5d <sup>32</sup> 6s <sup>2</sup>	5d <sup>33</sup> 6s <sup>2</sup>	5d <sup>34</sup> 6s <sup>2</sup>	5d <sup>35</sup> 6s <sup>2</sup>	5d <sup>36</sup> 6s <sup>2</sup>	5d <sup>37</sup> 6s <sup>2</sup>	5d <sup>38</sup> 6s <sup>2</sup>	5d <sup>39</sup> 6s <sup>2</sup>	5d <sup>40</sup> 6s <sup>2</sup>	5d <sup>41</sup> 6s <sup>2</sup>	5d <sup>42</sup> 6s <sup>2</sup>	5d <sup>43</sup> 6s <sup>2</sup>	5d <sup>44</sup> 6s <sup>2</sup>	5d <sup>45</sup> 6s <sup>2</sup>	5d <sup>46</sup> 6s <sup>2</sup>	5d <sup>47</sup> 6s <sup>2</sup>	5d <sup>48</sup> 6s <sup>2</sup>	5d <sup>49</sup> 6s <sup>2</sup>	5d <sup>50</sup> 6s <sup>2</sup>	5d <sup>51</sup> 6s <sup>2</sup>	5d <sup>52</sup> 6s <sup>2</sup>	5d <sup>53</sup> 6s <sup>2</sup>	5d <sup>54</sup> 6s <sup>2</sup>	5d <sup>55</sup> 6s <sup>2</sup>	5d <sup>56</sup> 6s <sup>2</sup>	5d <sup>57</sup> 6s <sup>2</sup>	5d <sup>58</sup> 6s <sup>2</sup>	5d <sup>59</sup> 6s <sup>2</sup>	5d <sup>60</sup> 6s <sup>2</sup>	5d <sup>61</sup> 6s <sup>2</sup>	5d <sup>62</sup> 6s <sup>2</sup>	5d <sup>63</sup> 6s <sup>2</sup>	5d <sup>64</sup> 6s <sup>2</sup>	5d <sup>65</sup> 6s <sup>2</sup>	5d <sup>66</sup> 6s <sup>2</sup>	5d <sup>67</sup> 6s <sup>2</sup>	5d <sup>68</sup> 6s <sup>2</sup>	5d <sup>69</sup> 6s <sup>2</sup>	5d <sup>70</sup> 6s <sup>2</sup>	5d <sup>71</sup> 6s <sup>2</sup>	5d <sup>72</sup> 6s <sup>2</sup>	5d <sup>73</sup> 6s <sup>2</sup>	5d <sup>74</sup> 6s <sup>2</sup>	5d <sup>75</sup> 6s <sup>2</sup>	5d <sup>76</sup> 6s <sup>2</sup>	5d <sup>77</sup> 6s <sup>2</sup>	5d <sup>78</sup> 6s <sup>2</sup>	5d <sup>79</sup> 6s <sup>2</sup>	5d <sup>80</sup> 6s <sup>2</sup>	5d <sup>81</sup> 6s <sup>2</sup>	5d <sup>82</sup> 6s <sup>2</sup>	5d <sup>83</sup> 6s <sup>2</sup>	5d <sup>84</sup> 6s <sup>2</sup>	5d <sup>85</sup> 6s <sup>2</sup>	5d <sup>86</sup> 6s <sup>2</sup>	5d <sup>87</sup> 6s <sup>2</sup>	5d <sup>88</sup> 6s <sup>2</sup>	5d <sup>89</sup> 6s <sup>2</sup>	5d <sup>90</sup> 6s <sup>2</sup>	5d <sup>91</sup> 6s <sup>2</sup>	5d <sup>92</sup> 6s <sup>2</sup>	5d <sup>93</sup> 6s <sup>2</sup>	5d <sup>94</sup> 6s <sup>2</sup>	5d <sup>95</sup> 6s <sup>2</sup>	5d <sup>96</sup> 6s <sup>2</sup>	5d <sup>97</sup> 6s <sup>2</sup>	5d <sup>98</sup> 6s <sup>2</sup>	5d <sup>99</sup> 6s <sup>2</sup>	5d <sup>100</sup> 6s <sup>2</sup>	5d <sup>101</sup> 6s <sup>2</sup>	5d <sup>102</sup> 6s <sup>2</sup>	5d <sup>103</sup> 6s <sup>2</sup>	5d <sup>104</sup> 6s <sup>2</sup>	5d <sup>105</sup> 6s <sup>2</sup>	5d <sup>106</sup> 6s <sup>2</sup>	5d <sup>107</sup> 6s <sup>2</sup>	5d <sup>108</sup> 6s <sup>2</sup>	5d <sup>109</sup> 6s <sup>2</sup>	5d <sup>110</sup> 6s <sup>2</sup>	5d <sup>111</sup> 6s <sup>2</sup>	5d <sup>112</sup> 6s <sup>2</sup>	5d <sup>113</sup> 6s <sup>2</sup>	5d <sup>114</sup> 6s <sup>2</sup>	5d <sup>115</sup> 6s <sup>2</sup>	5d <sup>116</sup> 6s <sup>2</sup>	5d <sup>117</sup> 6s <sup>2</sup>	5d <sup>118</sup> 6s <sup>2</sup>	5d <sup>119</sup> 6s <sup>2</sup>	5d <sup>120</sup> 6s <sup>2</sup>	5d <sup>121</sup> 6s <sup>2</sup>	5d <sup>122</sup> 6s <sup>2</sup>	5d <sup>123</sup> 6s <sup>2</sup>	5d <sup>124</sup> 6s <sup>2</sup>	5d <sup>125</sup> 6s <sup>2</sup>	5d <sup>126</sup> 6s <sup>2</sup>	5d <sup>127</sup> 6s <sup>2</sup>	5d <sup>128</sup> 6s <sup>2</sup>	5d <sup>129</sup> 6s <sup>2</sup>	5d <sup>130</sup> 6s <sup>2</sup>	5d <sup>131</sup> 6s <sup>2</sup>	5d <sup>132</sup> 6s <sup>2</sup>	5d <sup>133</sup> 6s <sup>2</sup>	5d <sup>134</sup> 6s <sup>2</sup>	5d <sup>135</sup> 6s <sup>2</sup>	5d <sup>136</sup> 6s <sup>2</sup>	5d <sup>137</sup> 6s <sup>2</sup>	5d <sup>138</sup> 6s <sup>2</sup>	5d <sup>139</sup> 6s <sup>2</sup>	5d <sup>140</sup> 6s <sup>2</sup>	5d <sup>141</sup> 6s <sup>2</sup>	5d <sup>142</sup> 6s <sup>2</sup>	5d <sup>143</sup> 6s <sup>2</sup>	5d <sup>144</sup> 6s <sup>2</sup>	5d <sup>145</sup> 6s <sup>2</sup>	5d <sup>146</sup> 6s <sup>2</sup>	5d <sup>147</sup> 6s <sup>2</sup>	5d <sup>148</sup> 6s <sup>2</sup>	5d <sup>149</sup> 6s <sup>2</sup>	5d <sup>150</sup> 6s <sup>2</sup>	5d <sup>151</sup> 6s <sup>2</sup>	5d <sup>152</sup> 6s <sup>2</sup>	5d <sup>153</sup> 6s <sup>2</sup>	5d <sup>154</sup> 6s <sup>2</sup>	5d <sup>155</sup> 6s <sup>2</sup>	5d <sup>156</sup> 6s <sup>2</sup>	5d <sup>157</sup> 6s <sup>2</sup>	5d <sup>158</sup> 6s <sup>2</sup>	5d <sup>159</sup> 6s <sup>2</sup>	5d <sup>160</sup> 6s <sup>2</sup>	5d <sup>161</sup> 6s <sup>2</sup>	5d <sup>162</sup> 6s <sup>2</sup>	5d <sup>163</sup> 6s <sup>2</sup>	5d <sup>164</sup> 6s <sup>2</sup>	5d <sup>165</sup> 6s <sup>2</sup>	5d <sup>166</sup> 6s <sup>2</sup>	5d <sup>167</sup> 6s <sup>2</sup>	5d <sup>168</sup> 6s <sup>2</sup>	5d <sup>169</sup> 6s <sup>2</sup>	5d <sup>170</sup> 6s <sup>2</sup>	5d <sup>171</sup> 6s <sup>2</sup>	5d <sup>172</sup> 6s <sup>2</sup>	5d <sup>173</sup> 6s <sup>2</sup>	5d <sup>174</sup> 6s <sup>2</sup>	5d <sup>175</sup> 6s <sup>2</sup>	5d <sup>176</sup> 6s <sup>2</sup>	5d <sup>177</sup> 6s <sup>2</sup>	5d <sup>178</sup> 6s <sup>2</sup>	5d <sup>179</sup> 6s <sup>2</sup>	5d <sup>180</sup> 6s <sup>2</sup>	5d <sup>181</sup> 6s <sup>2</sup>	5d <sup>182</sup> 6s <sup>2</sup>	5d <sup>183</sup> 6s <sup>2</sup>	5d <sup>184</sup> 6s <sup>2</sup>	5d <sup>185</sup> 6s <sup>2</sup>	5d <sup>186</sup> 6s <sup>2</sup>	5d <sup>187</sup> 6s <sup>2</sup>	5d <sup>188</sup> 6s <sup>2</sup>	5d <sup>189</sup> 6s <sup>2</sup>	5d <sup>190</sup> 6s <sup>2</sup>	5d <sup>191</sup> 6s <sup>2</sup>	5d <sup>192</sup> 6s <sup>2</sup>	5d <sup>193</sup> 6s <sup>2</sup>	5d <sup>194</sup> 6s <sup>2</sup>	5d <sup>195</sup> 6s <sup>2</sup>	5d <sup>196</sup> 6s <sup>2</sup>	5d <sup>197</sup> 6s <sup>2</sup>	5d <sup>198</sup> 6s <sup>2</sup>	5d <sup>199</sup> 6s <sup>2</sup>	5d <sup>200</sup> 6s <sup>2</sup>	5d <sup>201</sup> 6s <sup>2</sup>	5d <sup>202</sup> 6s <sup>2</sup>	5d <sup>203</sup> 6s <sup>2</sup>	5d <sup>204</sup> 6s <sup>2</sup>	5d <sup>205</sup> 6s <sup>2</sup>	5d <sup>206</sup> 6s <sup>2</sup>	5d <sup>207</sup> 6s <sup>2</sup>	5d <sup>208</sup> 6s <sup>2</sup>	5d <sup>209</sup> 6s <sup>2</sup>	5d <sup>210</sup> 6s <sup>2</sup>	5d <sup>211</sup> 6s <sup>2</sup>	5d <sup>212</sup> 6s <sup>2</sup>	5d <sup>213</sup> 6s <sup>2</sup>	5d <sup>214</sup> 6s <sup>2</sup>	5d <sup>215</sup> 6s <sup>2</sup>	5d <sup>216</sup> 6s <sup>2</sup>	5d <sup>217</sup> 6s <sup>2</sup>	5d <sup>218</sup> 6s <sup>2</sup>	5d <sup>219</sup> 6s <sup>2</sup>	5d <sup>220</sup> 6s <sup>2</sup>	5d <sup>221</sup> 6s <sup>2</sup>	5d <sup>222</sup> 6s <sup>2</sup>	5d <sup>223</sup> 6s <sup>2</sup>	5d <sup>224</sup> 6s <sup>2</sup>	5d <sup>225</sup> 6s <sup>2</sup>	5d <sup>226</sup> 6s <sup>2</sup>	5d <sup>227</sup> 6s <sup>2</sup>	5d <sup>228</sup> 6s <sup>2</sup>	5d <sup>229</sup> 6s <sup>2</sup>	5d <sup>230</sup> 6s <sup>2</sup>	5d <sup>231</sup> 6s <sup>2</sup>	5d <sup>232</sup> 6s <sup>2</sup>	5d <sup>233</sup> 6s <sup>2</sup>	5d <sup>234</sup> 6s <sup>2</sup>	5d <sup>235</sup> 6s <sup>2</sup>	5d <sup>236</sup> 6s <sup>2</sup>	5d <sup>237</sup> 6s <sup>2</sup>	5d <sup>238</sup> 6s <sup>2</sup>	5d <sup>239</sup> 6s <sup>2</sup>	5d <sup>240</sup> 6s <sup>2</sup>	5d <sup>241</sup> 6s <sup>2</sup>	5d <sup>242</sup> 6s <sup>2</sup>	5d <sup>243</sup> 6s <sup>2</sup>	5d <sup>244</sup> 6s <sup>2</sup>	5d <sup>245</sup> 6s <sup>2</sup>	5d <sup>246</sup> 6s <sup>2</sup>	5d <sup>247</sup> 6s <sup>2</sup>	5d <sup>248</sup> 6s <sup>2</sup>	5d <sup>249</sup> 6s <sup>2</sup>	5d <sup>250</sup> 6s <sup>2</sup>	5d <sup>251</sup> 6s <sup>2</sup>	5d <sup>252</sup> 6s <sup>2</sup>	5d <sup>253</sup> 6s <sup>2</sup>	5d <sup>254</sup> 6s <sup>2</sup>	5d <sup>255</sup> 6s <sup>2</sup>	5d <sup>256</sup> 6s <sup>2</sup>	5d <sup>257</sup> 6s <sup>2</sup>	5d <sup>258</sup> 6s <sup>2</sup>	5d <sup>259</sup> 6s <sup>2</sup>	5d <sup>260</sup> 6s <sup>2</sup>	5d <sup>261</sup> 6s <sup>2</sup>	5d <sup>262</sup> 6s <sup>2</sup>	5d <sup>263</sup> 6s <sup>2</sup>	5d <sup>264</sup> 6s <sup>2</sup>	5d <sup>265</sup> 6s <sup>2</sup>	5d <sup>266</sup> 6s <sup>2</sup>	5d <sup>267</sup> 6s <sup>2</sup>	5d <sup>268</sup> 6s <sup>2</sup>	5d <sup>269</sup> 6s <sup>2</sup>	5d <sup>270</sup> 6s <sup>2</sup>	5d <sup>271</sup> 6s <sup>2</sup>	5d <sup>272</sup> 6s <sup>2</sup>	5d <sup>273</sup> 6s <sup>2</sup>	5d <sup>274</sup> 6s <sup>2</sup>	5d <sup>275</sup> 6s <sup>2</sup>	5d <sup>276</sup> 6s <sup>2</sup>	5d <sup>277</sup> 6s <sup>2</sup>	5d <sup>278</sup> 6s <sup>2</sup>	5d <sup>279</sup> 6s <sup>2</sup>	5d <sup>280</sup> 6s <sup>2</sup>	5d <sup>281</sup> 6s <sup>2</sup>	5d <sup>282</sup> 6s <sup>2</sup>	5d <sup>283</sup> 6s <sup>2</sup>	5d <sup>284</sup> 6s <sup>2</sup>	5d <sup>285</sup> 6s <sup>2</sup>	5d <sup>286</sup> 6s <sup>2</sup>	5d <sup>287</sup> 6s <sup>2</sup>	5d <sup>288</sup> 6s <sup>2</sup>	5d <sup>289</sup> 6s <sup>2</sup>	5d <sup>290</sup> 6s <sup>2</sup>	5d <sup>291</sup> 6s <sup>2</sup>	5d <sup>292</sup> 6s <sup>2</sup>	5d <sup>293</sup> 6s <sup>2</sup>	5d <sup>294</sup> 6s <sup>2</sup>	5d <sup>295</sup> 6s <sup>2</sup>	5d <sup>296</sup> 6s <sup>2</sup>	5d <sup>297</sup> 6s <sup>2</sup>	5d <sup>298</sup> 6s <sup>2</sup>	5d <sup>299</sup> 6s <sup>2</sup>	5d <sup>300</sup> 6s <sup>2</sup>	5d <sup>301</sup> 6s <sup>2</sup>	5d <sup>302</sup> 6s <sup>2</sup>	5d <sup>303</sup> 6s <sup>2</sup>	5d <sup>304</sup> 6s <sup>2</sup>	5d <sup>305</sup> 6s <sup>2</sup>	5d <sup>306</sup> 6s <sup>2</sup>	5d <sup>307</sup> 6s <sup>2</sup>	5d <sup>308</sup> 6s <sup>2</sup>	5d <sup>309</sup> 6s <sup>2</sup>	5d <sup>310</sup> 6s <sup>2</sup>	5d <sup>311</sup> 6s <sup>2</sup>	5d <sup>312</sup> 6s <sup>2</sup>	5d <sup>313</sup> 6s <sup>2</sup>	5d <sup>314</sup> 6s <sup>2</sup>	5d <sup>315</sup> 6s <sup>2</sup>	5d <sup>316</sup> 6s <sup>2</sup>	5d <sup>317</sup> 6s <sup>2</sup>	5d <sup>318</sup> 6s <sup>2</sup>	5d <sup>319</sup> 6s <sup>2</sup>	5d <sup>320</sup> 6s <sup>2</sup>	5d <sup>321</sup> 6s <sup>2</sup>	5d <sup>322</sup> 6s <sup>2</sup>	5d <sup>323</sup> 6s <sup>2</sup>	5d <sup>324</sup> 6s <sup>2</sup>	5d <sup>325</sup> 6s <sup>2</sup>	5d <sup>326</sup> 6s <sup>2</sup>	5d <sup>327</sup> 6s <sup>2</sup>	5d <sup>328</sup> 6s <sup>2</sup>	5d <sup>329</sup> 6s <sup>2</sup>	5d <sup>330</sup> 6s <sup>2</sup>	5d <sup>331</sup> 6s <sup>2</sup>	5d <sup>332</sup> 6s <sup>2</sup>	5d <sup>333</sup> 6s <sup>2</sup>	5d <sup>334</sup> 6s <sup>2</sup>	5d <sup>335</sup> 6s <sup>2</sup>	5d <sup>336</sup> 6s <sup>2</sup>	5d <sup>337</sup> 6s <sup>2</sup>	5d <sup>338</sup> 6s <sup>2</sup>	5d <sup>339</sup> 6s <sup>2</sup>	5d <sup>340</sup> 6s <sup>2</sup>	5d <sup>341</sup> 6s <sup>2</sup>	5d <sup>342</sup> 6s <sup>2</sup>	5d <sup>343</sup> 6s <sup>2</sup>	5d <sup>344</sup> 6s <sup>2</sup>	5d <sup>345</sup> 6s <sup>2</sup>	5d <sup>346</sup> 6s <sup>2</sup>	5d <sup>347</sup> 6s <sup>2</sup>	

a few atoms of them are obtained. Their synthesis and characterisation, therefore, require highly 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 recognised, 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 according to IUPAC nomenclature	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	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

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 118 have been discovered. Official names of all elements have been announced by IUPAC.

### 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  $1s^22s^2$ . Starting from the next element boron, the  $2p$  orbitals are filled with electrons when the  $L$  shell is completed at neon ( $2s^22p^6$ ). 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  $3d^14s^2$ . 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 4f- and 5f-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 5<sup>th</sup> 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 5<sup>th</sup> 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 <sup>1</sup>
11	Na	$1s^2 2s^2 2p^6 3s^1$ (or) [Ne]3s <sup>1</sup>
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ (or) [Ar]4s <sup>1</sup>
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ (or) [Kr]5s <sup>1</sup>
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 <sup>1</sup>
87	Fr	[Rn]7s <sup>1</sup>

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 only one 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  $ns^1$  and  $ns^2$  outermost electronic configuration belong to the **s-Block Elements**. They are all

s-BLOCK		p-BLOCK											
1s	2	H		He									
2s	Li Be	2p											
3s	Na Mg	3p											
4s	K Ca	Sc Ti V Cr Mn Fe Co Ni Cu Zn	4p										
5s	Rb Sr	Y Zr Nb Mo Tc Ru Rh Pd Ag Cd	5p										
6s	Cs Ba	La Hf Ta W Re Os Ir Pt Au Hg	6p										
7s	Fr Ra	Ac Rf Db Sg Bh Hs Mt Ds Rg Cn	7p										
d-BLOCK		f-BLOCK											
3d	Sc Ti V Cr Mn Fe Co Ni Cu Zn	Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	Lanthanoids 4f	Lanthanoids 4f									
4d	Y Zr Nb Mo Tc Ru Rh Pd Ag Cd	Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr	Actinoids 5f	Actinoids 5f									

**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 (blue), NON-METALS (green), and METALLOIDS (orange).

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 highly 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  $(n-1)d^{1-10}ns^{0-2}$  except for Pd where its electronic configuration is  $4d^{10}5s^0$ . 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  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ . 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  $[Rn]5f^46d^{10}7s^27p^5$ . 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 ( $\sim 1.2 \text{ \AA}$  i.e.,  $1.2 \times 10^{-10} \text{ m}$  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 ( $\text{Cl}_2$ ) 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.

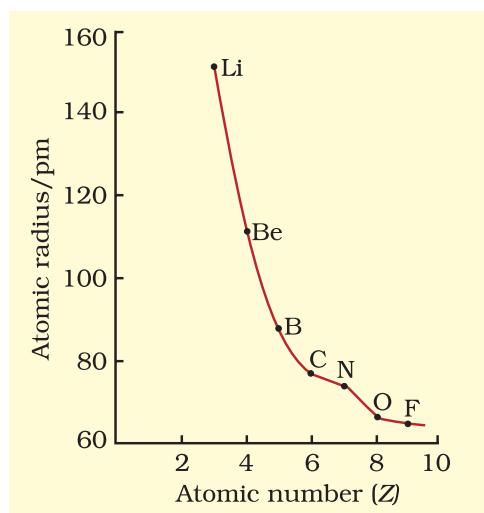
Note that the atomic radii of noble gases are not considered here. Being monoatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

**Table 3.6(a) Atomic Radii/pm Across the Periods**

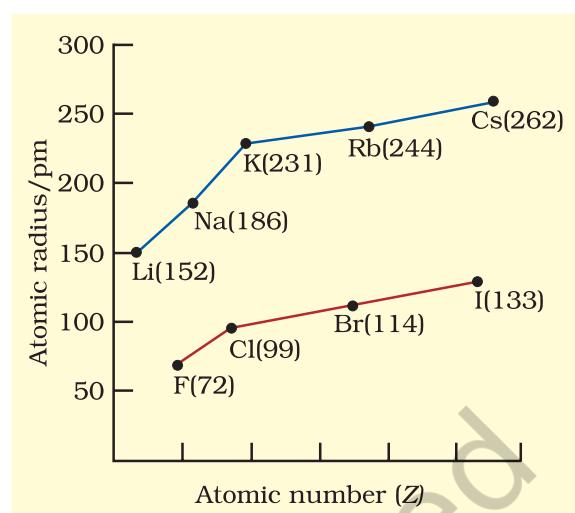
Atom (Period II)	Li	Be	B	C	N	O	F
<b>Atomic radius</b>	152	111	88	77	74	66	64
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
<b>Atomic radius</b>	186	160	143	117	110	104	99

**Table 3.6(b) Atomic Radii/pm Down a Family**

Atom (Group I)	Atomic Radius	Atom (Group 17)	Atomic Radius
Li	152	F	64
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 ( $\text{F}^-$ ) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for  $\text{Na}^+$ .

When we find some atoms and ions which contain the same number of electrons, we call them **isoelectronic species\***. For example,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  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?  
 $\text{Mg}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}$ ,  $\text{Al}^{3+}$ .

### 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  $\text{Mg}$ ; the smallest one is  $\text{Al}^{3+}$ .

### (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.

\* Two or more species with same number of atoms, same number of valence electrons and same structure, regardless of the nature of elements involved.

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.

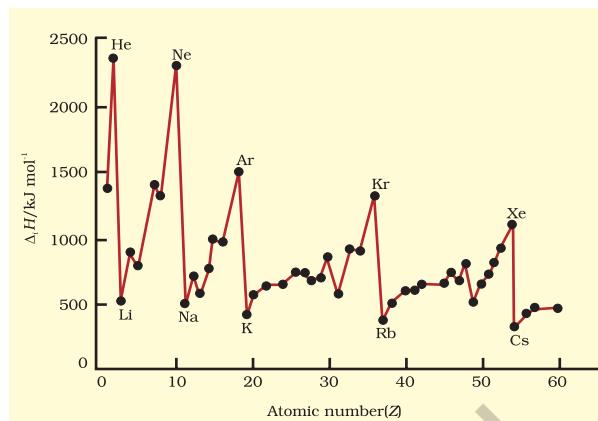
$$X(g) \rightarrow X^+(g) + e^- \quad (3.1)$$

The ionization enthalpy is expressed in units of  $\text{kJ mol}^{-1}$ . 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.



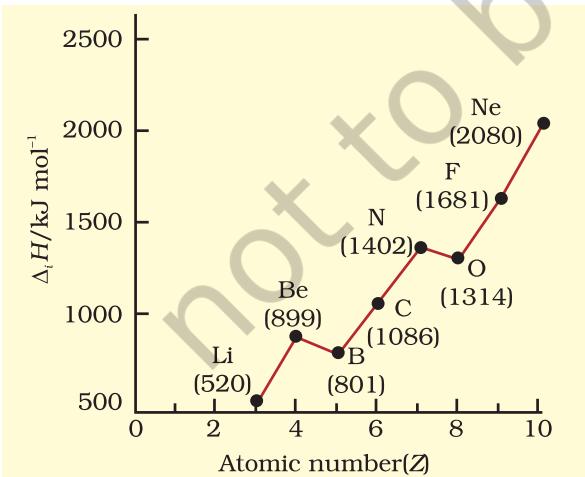
Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In 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

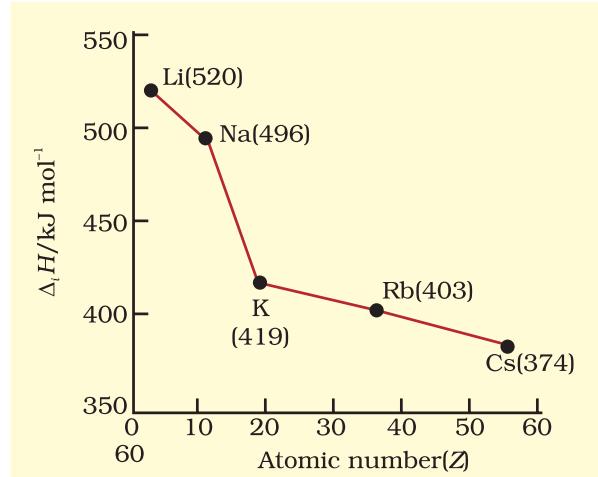


**Fig. 3.5** Variation of first ionization enthalpies ( $\Delta_i H$ ) with atomic number for elements with  $Z = 1$  to 60

can be correlated 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



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  $Z$ .

valence electron in an atom will be less than 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 2s electron in lithium is shielded from the nucleus by the inner core of 1s 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 single outermost ns-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 2s-electron to the nucleus is more than that of a 2p-electron; hence the 2p electron of boron is more shielded from the nucleus by the inner core of electrons than

the 2s electrons of beryllium. Therefore, it is easier to remove the 2p-electron from boron compared to the removal of a 2s-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 2p-electrons reside in different atomic orbitals (Hund’s rule) whereas in the oxygen atom, two of the four 2p-electrons must occupy the same 2p-orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2p-electron from oxygen than it is, to remove one of the three 2p-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<sup>-1</sup>. Predict whether the first  $\Delta_i H$  value for Al will be more close to 575 or 760 kJ mol<sup>-1</sup>? Justify your answer.

### Solution

It will be more close to 575 kJ mol<sup>-1</sup>. The value for Al should be lower than that of Mg because of effective shielding of 3p electrons from the nucleus by 3s-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.



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

**Table 3.7 Electron Gain Enthalpies\* / (kJ mol<sup>-1</sup>) of Some Main Group Elements**

<b>Group 1</b>	$\Delta_{eg}H$	<b>Group 16</b>	$\Delta_{eg}H$	<b>Group 17</b>	$\Delta_{eg}H$	<b>Group 0</b>	$\Delta_{eg}H$
<b>H</b>	- 73					<b>He</b>	+ 48
<b>Li</b>	- 60	<b>O</b>	- 141	<b>F</b>	- 328	<b>Ne</b>	+ 116
<b>Na</b>	- 53	<b>S</b>	- 200	<b>Cl</b>	- 349	<b>Ar</b>	+ 96
<b>K</b>	- 48	<b>Se</b>	- 195	<b>Br</b>	- 325	<b>Kr</b>	+ 96
<b>Rb</b>	- 47	<b>Te</b>	- 190	<b>I</b>	- 295	<b>Xe</b>	+ 77
<b>Cs</b>	- 46	<b>Po</b>	- 174	<b>At</b>	- 270	<b>Rn</b>	+ 68

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 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 negative 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  $2p$ -orbital leads to greater repulsion than adding an electron to the larger  $3p$ -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 measurable 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 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

\* 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  $\Delta_{eg}H = -A_e - 5/2 RT$ .

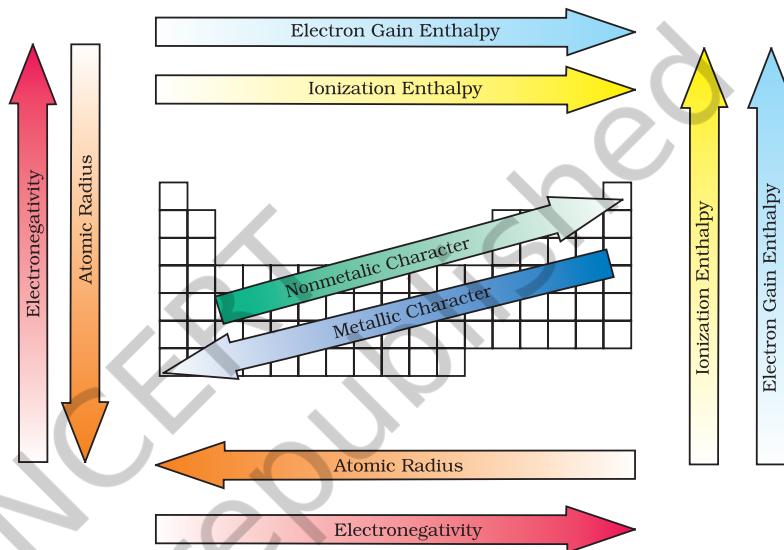
ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 3.8(a)

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? Non-metallic elements have strong tendency



**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
<b>Electronegativity</b>	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
<b>Electronegativity</b>	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

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:  $\text{OF}_2$  and  $\text{Na}_2\text{O}$ . The order of electronegativity of the three elements involved in these compounds is  $\text{F} > \text{O} > \text{Na}$ . Each of the atoms of fluorine,

with outer electronic configuration  $2s^22p^5$ , shares one electron with oxygen in the  $\text{OF}_2$  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  $2s^22p^4$  shares two electrons with fluorine atoms and thereby exhibits oxidation state  $+2$ . In  $\text{Na}_2\text{O}$ , 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

- 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  $\text{SiBr}_4$ .
- 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  $\text{Al}_2\text{S}_3$ .

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

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**

<b>Group</b>	<b>1</b>	<b>2</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>
Formula of hydride	LiH NaH KH	CaH <sub>2</sub>	B <sub>2</sub> H <sub>6</sub> AlH <sub>3</sub>	CH <sub>4</sub> SiH <sub>4</sub> GeH <sub>4</sub> SnH <sub>4</sub>	NH <sub>3</sub> PH <sub>3</sub> AsH <sub>3</sub>	H <sub>2</sub> O H <sub>2</sub> S H <sub>2</sub> Se H <sub>2</sub> Te	HF HCl HBr HI
Formula of oxide	Li <sub>2</sub> O Na <sub>2</sub> O K <sub>2</sub> O	MgO CaO SrO BaO	B <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> Ga <sub>2</sub> O <sub>3</sub> In <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub> SiO <sub>2</sub> GeO <sub>2</sub> SnO <sub>2</sub> PbO <sub>2</sub>	N <sub>2</sub> O <sub>3</sub> , N <sub>2</sub> O <sub>5</sub> P <sub>4</sub> O <sub>6</sub> , P <sub>4</sub> O <sub>10</sub> As <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>5</sub> Sb <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>5</sub> Bi <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub> SeO <sub>3</sub> TeO <sub>3</sub>	— Cl <sub>2</sub> O <sub>7</sub> —

this book. 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 (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s, 3p, 3d). 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

$[AlF_6]^{3-}$  forms). Furthermore, the first member of p-block elements displays greater ability to form  $p_{\pi} - p_{\pi}$  multiple bonds to itself (e.g.,  $C = C$ ,  $C \equiv C$ ,  $N = N$ ,  $N \equiv N$ ) and to other second period elements (e.g.,  $C = O$ ,  $C = N$ ,  $C \equiv N$ ,  $N = O$ ) compared to subsequent members of the same group.

<b>Property</b>	<b>Element</b>		
Metallic radius M/pm	<b>Li</b> 152	<b>Be</b> 111	<b>B</b> 88
	<b>Na</b> 186	<b>Mg</b> 160	<b>Al</b> 143
Ionic radius M <sup>+</sup> /pm	<b>Li</b> 76	<b>Be</b> 31	
	<b>Na</b> 102	<b>Mg</b> 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,

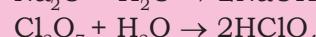
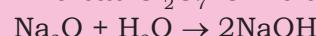
here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period. The chemical reactivity of an 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.



Their basic or acidic nature can be qualitatively tested with litmus paper.

Among transition metals ( $3d$  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 ( $4f$  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 1s 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 highest 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) $\text{F}^-$	(ii) $\text{Ar}$	(iii) $\text{Mg}^{2+}$	(iv) $\text{Rb}^+$
------------------	------------------	------------------------	--------------------
- 3.12 Consider the following species :  
 $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ 
  - (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  $-2.18 \times 10^{-18} \text{ J}$ . Calculate the ionization enthalpy of atomic hydrogen in terms of  $\text{J mol}^{-1}$ .  
**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  $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$ .  
 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  $\text{kJ mol}^{-1}$ ) 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?
- O or F
  - 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
- gains an electron
  - 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.
- Identify an element with five electrons in the outer subshell.
  - Identify an element that would tend to lose two electrons.
  - Identify an element that would tend to gain two electrons.
  - 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 > Cl > 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)  $(n-1)d^2ns^2$  for  $n=4$ , and (iii)  $(n-2)f^7(n-1)d^1ns^2$  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  $\text{kJ mol}^{-1}$ ) and the ( $\Delta_{eg} H$ ) electron gain enthalpy (in  $\text{kJ mol}^{-1}$ ) of a few elements are given below:

Elements	$\Delta H_1$	$\Delta H_2$	$\Delta_{eg} H$
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  $\text{MX}_2$  (X=halogen).
  - (f) the metal which can form a predominantly stable covalent halide of the formula  $\text{MX}$  (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

11082CH04

# 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.”**

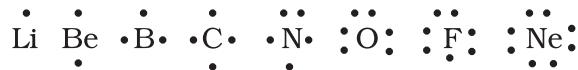
Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. 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 configuration 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  $\text{Na}^+$  and  $\text{Cl}^-$  ions. In the case of other molecules like  $\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{F}_2$ , 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:



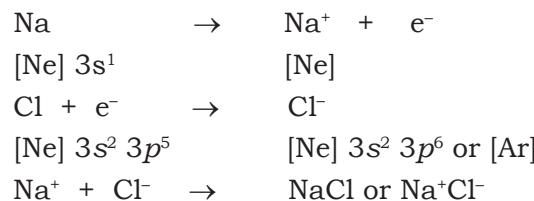
**Significance of Lewis Symbols :** The number of dots around the symbol represents

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.

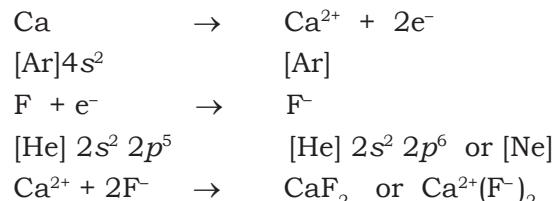
**Kössel, in relation to chemical bonding, drew attention to the following facts:**

- 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  $\text{NaCl}$  from sodium and chlorine, according to the above scheme, can be explained as:



Similarly the formation of  $\text{CaF}_2$  may be shown as:



**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.

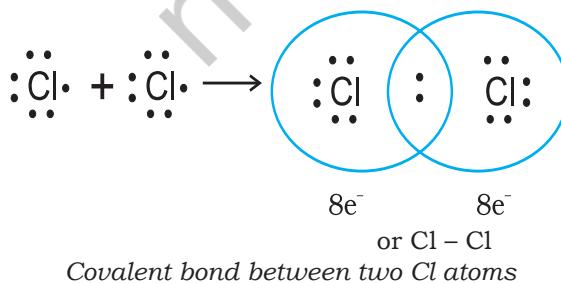
Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise 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,  $\text{Cl}_2$ . The Cl atom with electronic configuration,  $[\text{Ne}]3s^2 3p^5$ , is one electron short of the argon configuration. The formation of the  $\text{Cl}_2$  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

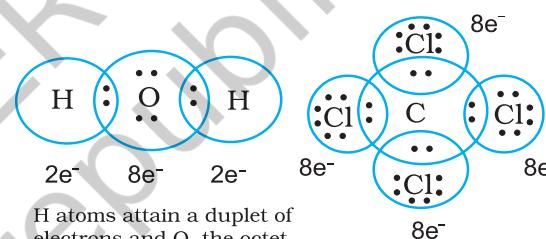


chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

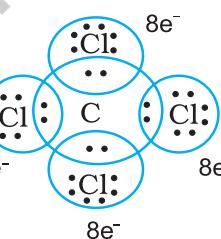
**The dots represent electrons. Such structures are referred to as Lewis dot structures.**

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:

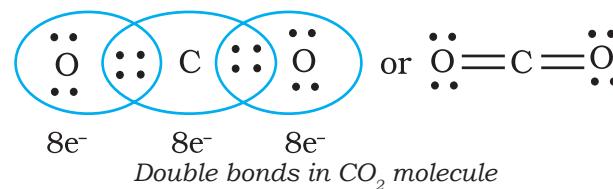


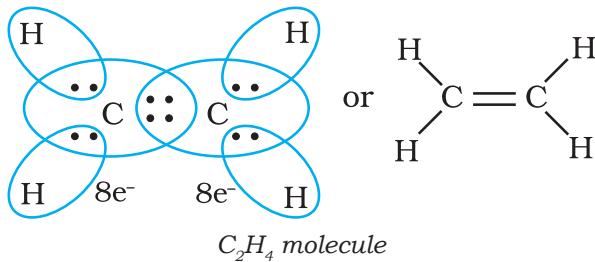
H atoms attain a duplet of electrons and O, the octet



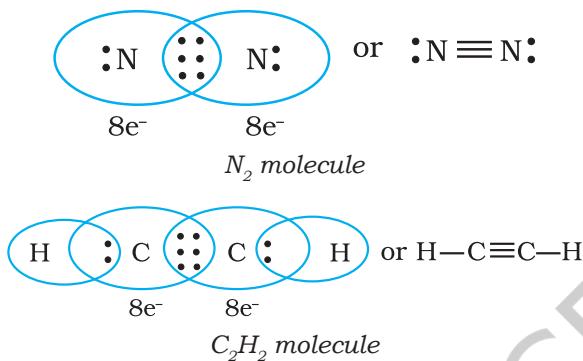
Each of the four Cl atoms along with the C atom attains octet of electrons

**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.





**When combining atoms share three electron pairs as in the case of two nitrogen atoms in the  $\text{N}_2$  molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.**



#### 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  $\text{CH}_4$  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  $\text{CO}_3^{2-}$  ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For  $\text{NH}_4^+$  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  $\text{NF}_3$  and  $\text{CO}_3^{2-}$ , 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	
$\text{H}_2$	$\text{H} : \text{H}^*$	$\text{H} - \text{H}$
$\text{O}_2$	$:\ddot{\text{O}}::\ddot{\text{O}}:$	$:\ddot{\text{O}}=\ddot{\text{O}}:$
$\text{O}_3$	$:\ddot{\text{O}}^+::\ddot{\text{O}}^-:$	$:\ddot{\text{O}}^+ \text{---} \ddot{\text{O}}^-:$
$\text{NF}_3$	$:\ddot{\text{F}}: \text{---} \text{N}(\ddot{\text{F}})_2$	$:\ddot{\text{F}}-\text{N}-\ddot{\text{F}}:$ $\vdots \ddot{\text{F}} \vdots$
$\text{CO}_3^{2-}$	$\left[ :\ddot{\text{O}}: \text{---} \text{C}(\ddot{\text{O}})_2 \right]^{2-}$	$\left[ :\ddot{\text{O}}: \text{---} \text{C}(\ddot{\text{O}})_2 \right]^{2-}$ $+\text{---}$
$\text{HNO}_3$	$:\ddot{\text{O}}^+ \text{---} \text{N}(\ddot{\text{O}}^-)_2 \text{---} \text{H}$	$:\ddot{\text{O}}^+ = \text{N}(\ddot{\text{O}}^-) \text{---} \text{H}$ $\vdots \ddot{\text{O}}^- \vdots$

\* Each H atom attains the configuration of helium (a duplet of electrons)

**Problem 4.1**

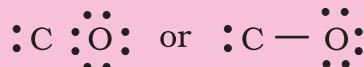
Write the Lewis dot structure of CO molecule.

**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,  $\text{NO}_2^-$ .

**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).

$$\text{N}(2s^2 2p^3), \text{O}(2s^2 2p^4)$$

$$5 + (2 \times 6) + 1 = 18 \text{ electrons}$$

**Step 2.** The skeletal structure of  $\text{NO}_2^-$  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 :

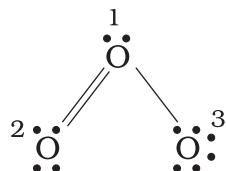
Formal charge (F.C.)  
on an atom in a Lewis  
structure

=

$$\left[ \begin{array}{c} \text{total number of valence} \\ \text{electrons in the free} \\ \text{atom} \end{array} \right] - \left[ \begin{array}{c} \text{total number of non} \\ \text{bonding (lone pair)} \\ \text{electrons} \end{array} \right] - (1/2) \left[ \begin{array}{c} \text{total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$

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 formal charge on:

- The central O atom marked 1

$$= 6 - 2 - \frac{1}{2} (6) = +1$$

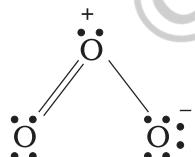
- The end O atom marked 2

$$= 6 - 4 - \frac{1}{2} (4) = 0$$

- 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**

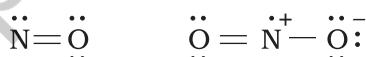
In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are  $LiCl$ ,  $BeH_2$  and  $BCl_3$ .



$Li$ ,  $Be$  and  $B$  have 1, 2 and 3 valence electrons only. Some other such compounds are  $AlCl_3$  and  $BF_3$ .

##### **Odd-electron molecules**

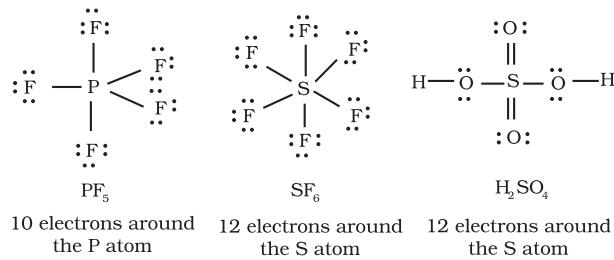
In molecules with an odd number of electrons like nitric oxide,  $NO$  and nitrogen dioxide,  $NO_2$ , the octet rule is not satisfied for all the atoms



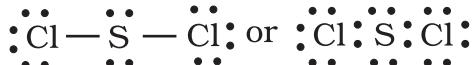
##### **The expanded octet**

Elements in and beyond the third period of the periodic table have, apart from  $3s$  and  $3p$  orbitals,  $3d$  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.



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**

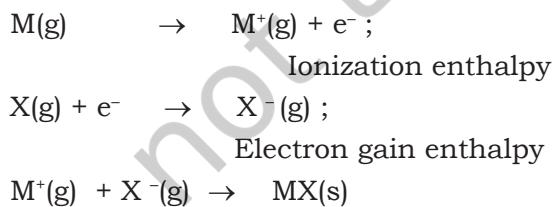
- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like  $\text{XeF}_2$ ,  $\text{KrF}_2$ ,  $\text{XeOF}_2$  etc.
- This theory does not account 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 Kossel 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.



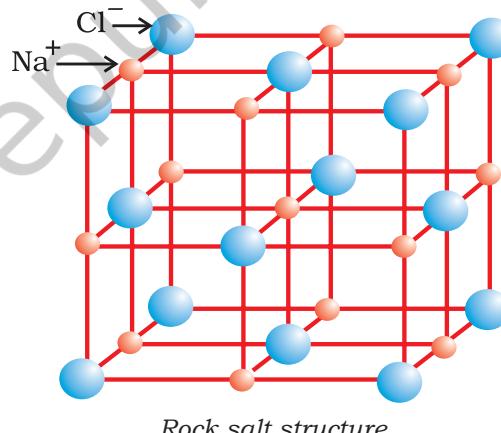
The **electron gain enthalpy**,  $\Delta_{eg} H$ , is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron

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,  $\text{NH}_4^+$  (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,  $\text{NaCl}$  (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  $\text{Na}^+(\text{g})$  formation from  $\text{Na}(\text{g})$  is  $495.8 \text{ kJ mol}^{-1}$ ; while the electron gain enthalpy for the change  $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$  is,  $-348.7 \text{ kJ mol}^{-1}$  only. The sum of the two,  $147.1 \text{ kJ mol}^{-1}$  is more than compensated for by the enthalpy of lattice formation of  $\text{NaCl}(\text{s})$  ( $-788 \text{ kJ mol}^{-1}$ ). Therefore, the energy released in the processes is more than

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<sup>-1</sup>. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na<sup>+</sup> (g) and one mole of Cl<sup>-</sup> (g) to an infinite distance.

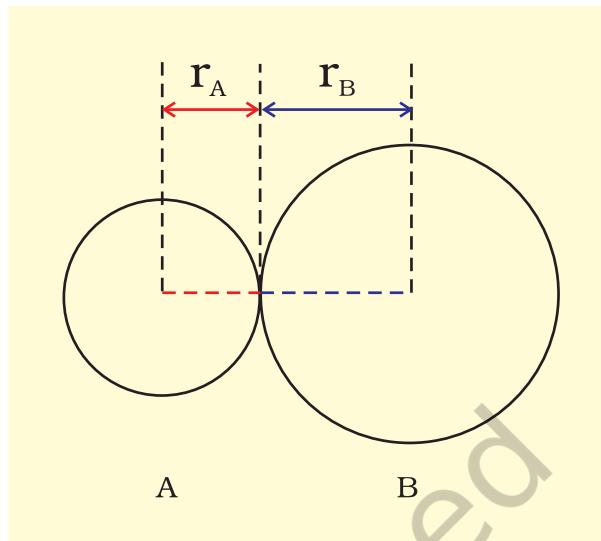
This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. 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.

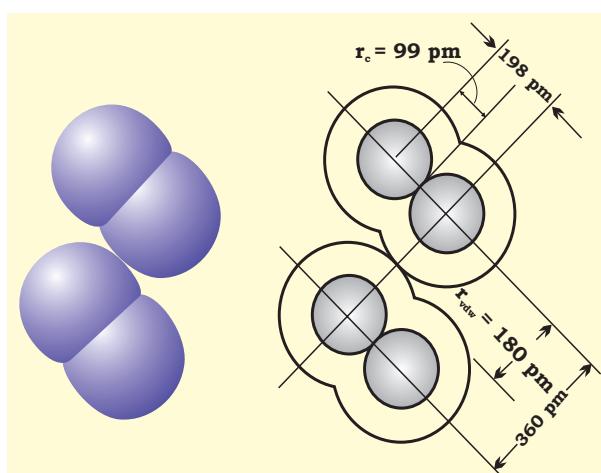
**The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.** The covalent radius is half of the distance between two similar atoms joined by a covalent bond



**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)

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.



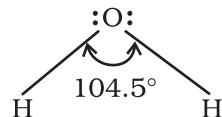
**Fig. 4.2** Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom ( $r_{vdw}$  and  $r_c$  are van der Waals and covalent radii respectively).

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 :

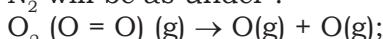


### 4.3.3 Bond Enthalpy

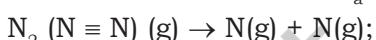
It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is  $\text{kJ mol}^{-1}$ . For example, the H–H bond enthalpy in hydrogen molecule is  $435.8 \text{ kJ mol}^{-1}$ .



Similarly the bond enthalpy for molecules containing multiple bonds, for example  $\text{O}_2$  and  $\text{N}_2$  will be as under :

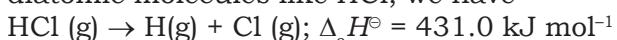


$$\Delta_a H^\ominus = 498 \text{ kJ mol}^{-1}$$



$$\Delta_a H^\ominus = 946.0 \text{ kJ mol}^{-1}$$

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



In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of  $\text{H}_2\text{O}$  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

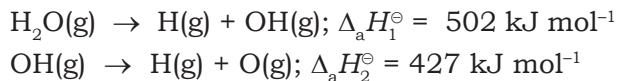
**Table 4.3 Bond Lengths in Some Common Molecules**

Molecule	Bond Length (pm)
$\text{H}_2$ (H–H)	74
$\text{F}_2$ (F–F)	144
$\text{Cl}_2$ (Cl–Cl)	199
$\text{Br}_2$ (Br–Br)	228
$\text{I}_2$ (I–I)	267
$\text{N}_2$ (N≡N)	109
$\text{O}_2$ (O=O)	121
HF (H–F)	92
HCl (H–Cl)	127
HBr (H–Br)	141
HI (H–I)	160

**Table 4.4 Covalent Radii,  $*r_{\text{cov}}$ /(pm)**

H	37				
C	77(1)	N	74 (1)	O	66(1)
	67 (2)		65(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).



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  $\text{C}_2\text{H}_5\text{OH}$  (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,

$$\begin{aligned}\text{Average bond enthalpy} &= \frac{502 + 427}{2} \\ &= 464.5 \text{ kJ mol}^{-1}\end{aligned}$$

#### 4.3.4 Bond Order

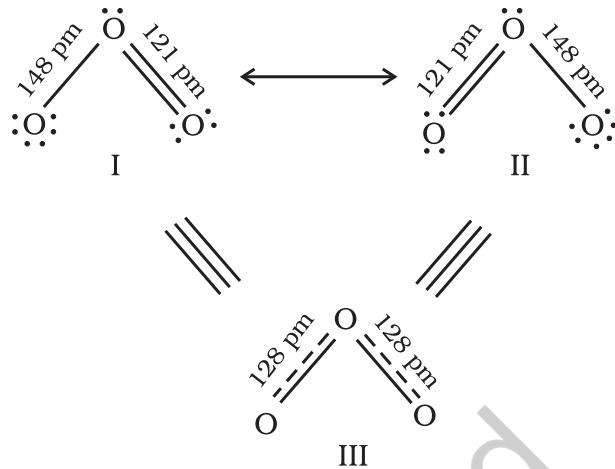
**In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule.** The bond order, for example in  $\text{H}_2$  (with a single shared electron pair), in  $\text{O}_2$  (with two shared electron pairs) and in  $\text{N}_2$  (with three shared electron pairs) is 1, 2, 3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For  $\text{N}_2$ , bond order is 3 and its  $\Delta_a H^\ominus$  is  $946 \text{ kJ mol}^{-1}$ ; being one of the highest for a diatomic molecule.

**Isoelectronic molecules and ions have identical bond orders; for example,  $\text{F}_2$  and  $\text{O}_2^{2-}$  have bond order 1.  $\text{N}_2$ , CO and  $\text{NO}^+$  have bond order 3.**

**A general correlation useful for understanding the stabilities 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,  $\text{O}_3$  molecule can be equally represented by the structures I and II shown below:



**Fig. 4.3** Resonance in the  $\text{O}_3$  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  $\text{O}_3$  molecule are same (128 pm). Thus the oxygen-oxygen bonds in the  $\text{O}_3$  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  $\text{O}_3$ . **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  $\text{O}_3$ , the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of  $\text{O}_3$  more accurately. This is also called **resonance hybrid**. Resonance is represented by a double headed arrow.

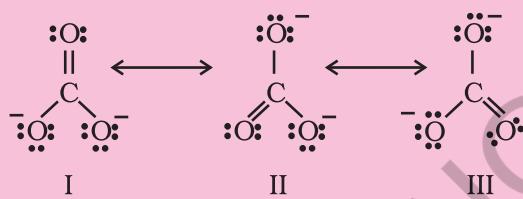
Some of the other examples of resonance structures are provided by the **carbonate ion** and the **carbon dioxide molecule**.

### Problem 4.3

Explain the structure of  $\text{CO}_3^{2-}$  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  $\text{CO}_3^{2-}$  are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.



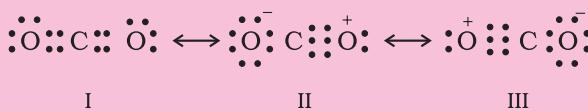
**Fig. 4.4** Resonance in  $\text{CO}_3^{2-}$ , I, II and III represent the three canonical forms.

### Problem 4.4

Explain the structure of  $\text{CO}_2$  molecule.

#### Solution

The experimentally determined carbon to oxygen bond length in  $\text{CO}_2$  is 115 pm. The lengths of a normal carbon to oxygen double bond ( $\text{C}=\text{O}$ ) and carbon to oxygen triple bond ( $\text{C}\equiv\text{O}$ ) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in  $\text{CO}_2$  (115 pm) lie between the values for  $\text{C}=\text{O}$  and  $\text{C}\equiv\text{O}$ . 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  $\text{CO}_2$  is best described as a hybrid of the canonical or resonance forms I, II and III.



**Fig. 4.5** Resonance in  $\text{CO}_2$  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 canonical structure; and,
- Resonance averages the bond characteristics as a whole.  
Thus the energy of the  $\text{O}_3$  resonance hybrid is lower than either of the two canonical forms I and II (Fig. 4.3).

Many **misconceptions** are associated with resonance and the same need to be dispelled. You should remember that :

- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.
- There is no such equilibrium between the canonical 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 canonical 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  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$  or  $\text{F}_2$ , 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 ' $\mu$ '. Mathematically, it is expressed as follows :

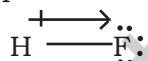
$$\text{Dipole moment } (\mu) = \text{charge } (Q) \times \text{distance of separation } (r)$$

Dipole moment is usually expressed in Debye units (D). The conversion factor is

$$1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$$

where C is coulomb and m is meter.

Further dipole moment is a vector quantity and by convention it is depicted by a small arrow with tail on the negative centre and head pointing towards the positive centre. But in chemistry presence of dipole moment is represented by the crossed arrow ( $\leftrightarrow$ ) put on Lewis structure of the molecule. The cross is on positive end and arrow head is on negative end. For example the dipole moment of HF may be represented as :

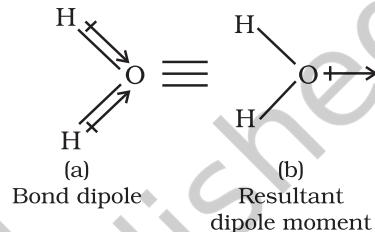


This arrow symbolises the direction of the shift of electron density in the molecule. Note that the direction of crossed arrow is opposite to the conventional direction of dipole moment vector.



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 Debye units in order to honour him.

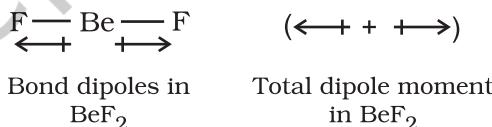
In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in  $\text{H}_2\text{O}$  molecule, which has a bent structure, the two O-H bonds are oriented at an angle of  $104.5^\circ$ . Net dipole moment of  $6.17 \times 10^{-30} \text{ C m}$  ( $1\text{D} = 3.33564 \times 10^{-30} \text{ C m}$ ) is the resultant of the dipole moments of two O-H bonds.



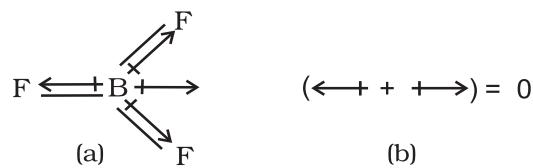
$$\text{Net Dipole moment, } \mu = 1.85 \text{ D}$$

$$= 1.85 \times 3.33564 \times 10^{-30} \text{ C m} = 6.17 \times 10^{-30} \text{ C m}$$

The dipole moment in case of  $\text{BeF}_2$  is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.



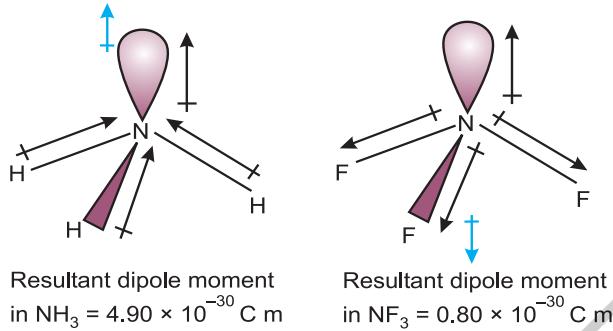
In tetra-atomic molecule, for example in  $\text{BF}_3$ , the dipole moment is zero although the B - F bonds are oriented at an angle of  $120^\circ$  to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third.



$\text{BF}_3$  molecule; representation of (a) bond dipoles and (b) total dipole moment

Let us study an interesting case of  $\text{NH}_3$  and  $\text{NF}_3$  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  $\text{NH}_3$  ( $4.90 \times 10^{-30}$  C m) is greater than that of  $\text{NF}_3$  ( $0.8 \times 10^{-30}$  C m). This is because, in case of  $\text{NH}_3$  the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in  $\text{NF}_3$  the orbital dipole is in 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  $\text{NF}_3$  as represented below :



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  $(n-1)d^n ns^0$ , 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, $\mu(\text{D})$	Geometry
<b>Molecule (AB)</b>	HF HCl HBr HI $\text{H}_2$	1.78 1.07 0.79 0.38 0	linear linear linear linear linear
<b>Molecule (AB<sub>2</sub>)</b>	$\text{H}_2\text{O}$ $\text{H}_2\text{S}$ $\text{CO}_2$	1.85 0.95 0	bent bent linear
<b>Molecule (AB<sub>3</sub>)</b>	$\text{NH}_3$ $\text{NF}_3$ $\text{BF}_3$	1.47 0.23 0	trigonal-pyramidal trigonal-pyramidal trigonal-planar
<b>Molecule (AB<sub>4</sub>)</b>	$\text{CH}_4$ $\text{CHCl}_3$ $\text{CCl}_4$	0 1.04 0	tetrahedral tetrahedral 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)

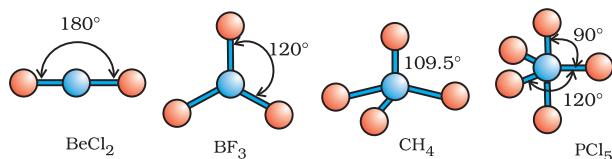
Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy 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 (page 114) 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 115) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 116) explains the reasons for the distortions in the geometry of the molecule.

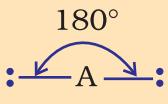
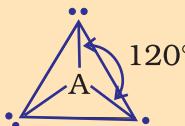
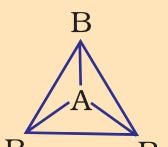
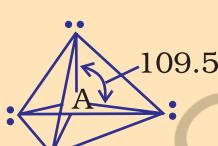
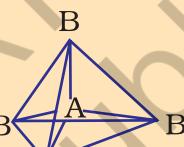
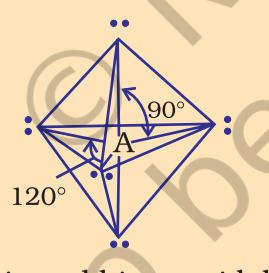
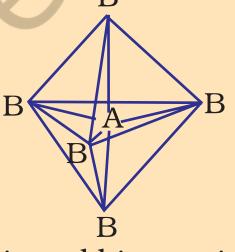
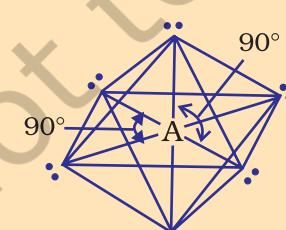
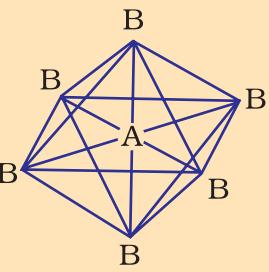
As depicted in Table 4.6, in the compounds of  $\text{AB}_2$ ,  $\text{AB}_3$ ,  $\text{AB}_4$ ,  $\text{AB}_5$  and  $\text{AB}_6$ , the arrangement of electron pairs and the B atoms around the central atom A are : **linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral**, respectively. Such arrangement can be seen in the molecules like  $\text{BF}_3$  ( $\text{AB}_3$ ),  $\text{CH}_4$  ( $\text{AB}_4$ ) and  $\text{PCl}_5$  ( $\text{AB}_5$ ) as depicted below by their ball and stick models.



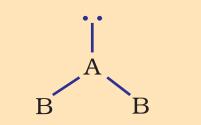
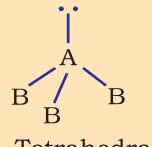
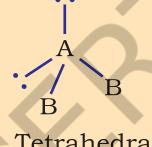
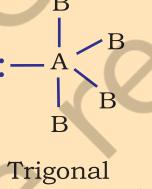
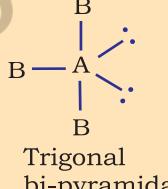
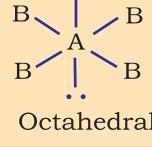
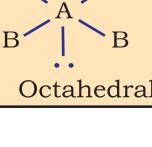
**Fig. 4.6** The shapes of molecules in which central atom has no lone pair

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**

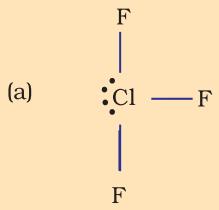
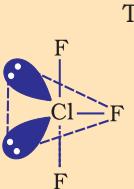
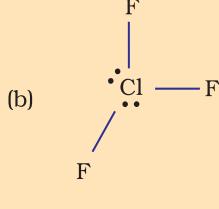
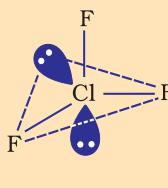
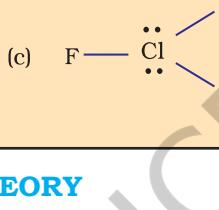
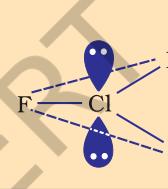
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B	BeCl <sub>2</sub> , HgCl <sub>2</sub>
3	 Trigonal planar	 Trigonal planar	BF <sub>3</sub>
4	 Tetrahedral	 Tetrahedral	CH <sub>4</sub> , NH <sub>4</sub> <sup>+</sup>
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl <sub>5</sub>
6	 Octahedral	 Octahedral	SF <sub>6</sub>

**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
$\text{AB}_2\text{E}$	2	1	 Trigonal planar	Bent	$\text{SO}^2\text{O}_3$
$\text{AB}_3\text{E}$	3	1	 Tetrahedral	Trigonal pyramidal	$\text{NH}_3$
$\text{AB}_3\text{E}_2$	2	2	 Tetrahedral	Bent	$\text{H}_2\text{O}$
$\text{AB}_4\text{E}$	4	1	 Trigonal bi-pyramidal	See saw	$\text{SF}_4$
$\text{AB}_3\text{E}_2$	3	2	 Trigonal bi-pyramidal	T-shape	$\text{ClF}_3$
$\text{AB}_5\text{E}$	5	1	 Octahedral	Square pyramid	$\text{BrF}_5$
$\text{AB}_4\text{E}_2$	4	2	 Octahedral	Square planer	$\text{XeF}_4$

**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
$\text{AB}_2\text{E}$	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°.
$\text{AB}_3\text{E}$	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°.
$\text{AB}_2\text{E}_2$	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°.
$\text{AB}_4\text{E}$	4	1	(a)	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.
			(b)	(More stable)	

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
$\text{AB}_3\text{E}_2$	3	2		T-shape	
			(a) 		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  $\text{H}_2$  ( $435.8 \text{ kJ mol}^{-1}$ ,  $74 \text{ pm}$ ) and  $\text{F}_2$  ( $155 \text{ kJ mol}^{-1}$ ,  $144 \text{ pm}$ ), 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:

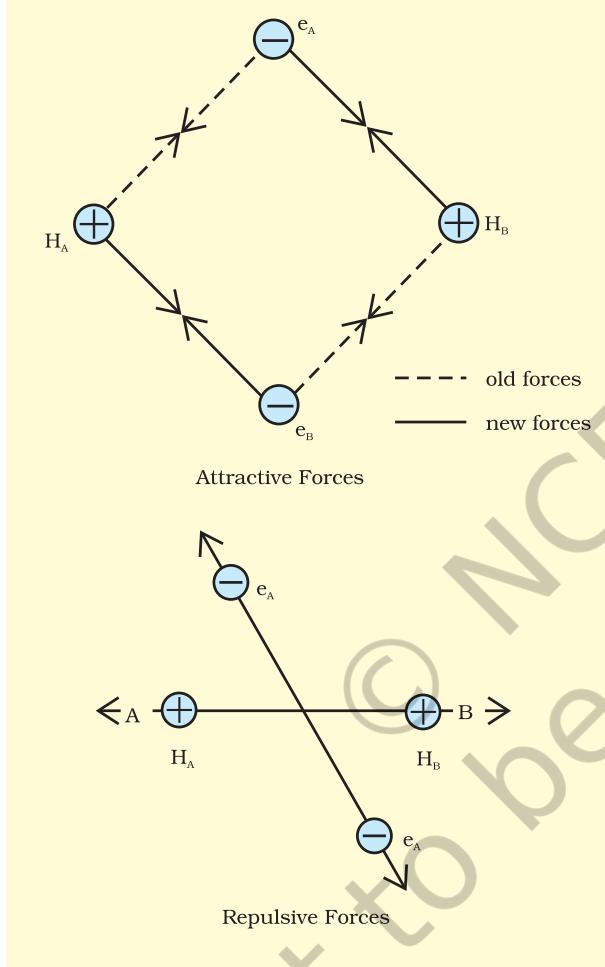
- (i) nucleus of one atom and its own electron that is  $N_A - e_A$  and  $N_B - e_B$ .

- (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).

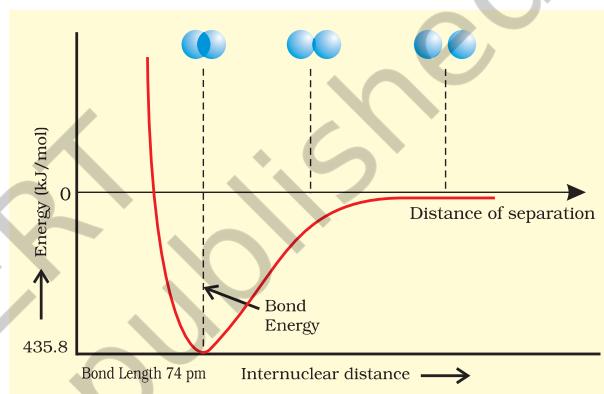
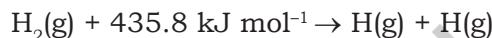


**Fig. 4.7** Forces of attraction and repulsion during the formation of  $H_2$  molecule

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.



**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 covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms.

In case of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , the geometry of the molecules is also important in addition to the bond formation. For example why is it so that  $\text{CH}_4$  molecule has tetrahedral shape and HCH bond angles are  $109.5^\circ$ ? Why is the shape of  $\text{NH}_3$  molecule pyramidal?

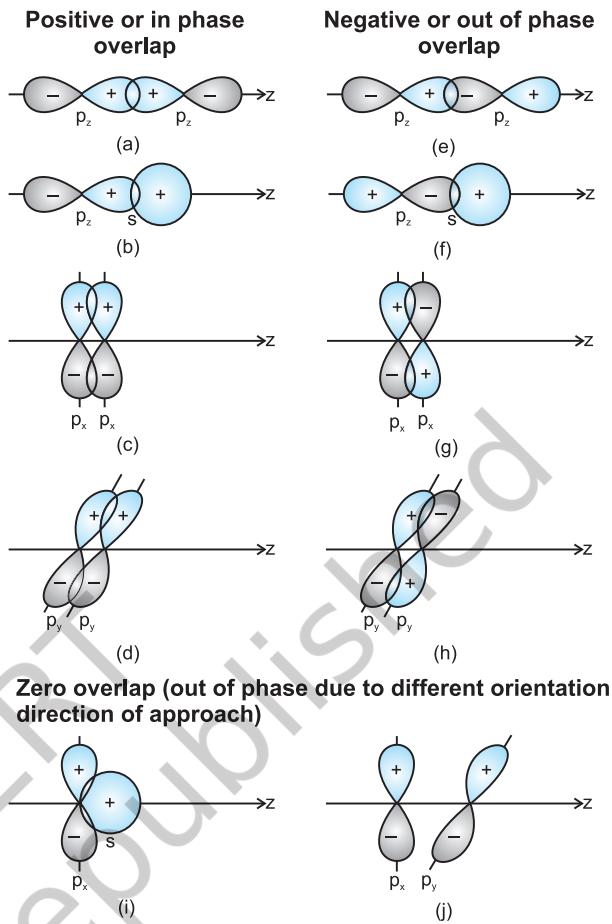
The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , etc. in terms of overlap and hybridisation of atomic orbitals.

#### 4.5.3 Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Fig. 4.9). Positive and negative sign on boundary surface diagrams in the Fig. 4.9 show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of s and p orbitals are depicted in Fig. 4.9.

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. We know that the shapes of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the  $\text{CH}_4$  (methane) molecule. The electronic configuration of carbon in its ground state is  $[\text{He}]2s^2 2p^2$  which in the excited state becomes  $[\text{He}]2s^1 2p_x^1 2p_y^1 2p_z^1$ . The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the



**Fig. 4.9** Positive, negative and zero overlaps of s and p atomic orbitals

hydrogen. The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s 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  $90^\circ$  to one another, the HCH angle for these will also be  $90^\circ$ . That is three C-H bonds will be oriented at  $90^\circ$  to one another. The 2s orbital of carbon and the 1s 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  $109.5^\circ$ . Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in  $\text{CH}_4$ . Using similar procedure and arguments, it can be seen that in the case of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules, the HNH

and HOH angles should be  $90^\circ$ . This is in disagreement with the actual bond angles of  $107^\circ$  and  $104.5^\circ$  in the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  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:

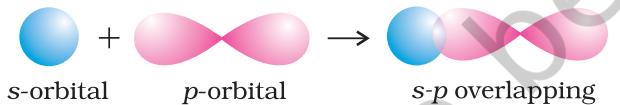
- (i) Sigma( $\sigma$ ) bond, and (ii) pi( $\pi$ ) bond

**(i) Sigma( $\sigma$ ) bond :** This type of covalent bond is formed by the end to end (head-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.

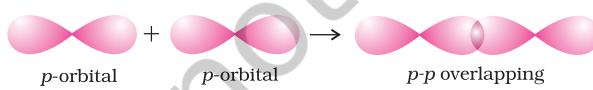
- **s-s overlapping :** In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



- **s-p overlapping:** This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.

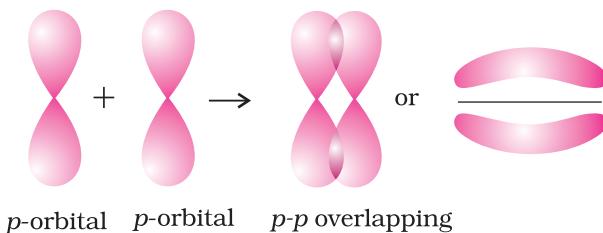


- **p-p overlapping :** This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



- (ii) **pi( $\pi$ ) bond :** In the formation of  $\pi$  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.



#### 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 in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

#### 4.6 HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  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 2s and three 2p-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:

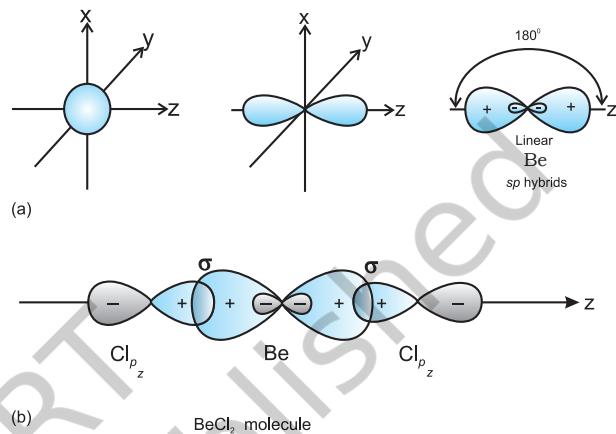
**(I)  $sp$  hybridisation:** This type of hybridisation involves the mixing of one  $s$  and one  $p$  orbital resulting in the formation of two equivalent  $sp$  hybrid orbitals. The suitable orbitals for  $sp$  hybridisation are  $s$  and  $p_z$ , if the hybrid orbitals are to lie along the  $z$ -axis. Each  $sp$  hybrid orbital 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

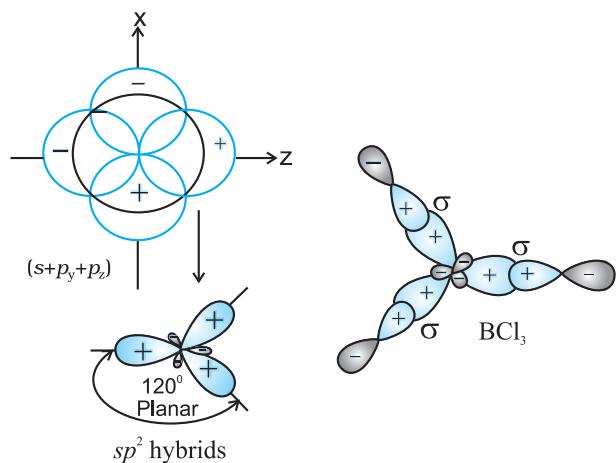
**BeCl<sub>2</sub>:** The ground state electronic configuration of Be is  $1s^22s^2$ . In the excited state one of the  $2s$ -electrons is promoted to

vacant  $2p$  orbital to account for its bivalence. One  $2s$  and one  $2p$ -orbital gets hybridised to form two  $sp$  hybridised orbitals. These two  $sp$  hybrid orbitals are oriented in opposite direction forming an angle of  $180^\circ$ . Each of the  $sp$  hybridised orbital overlaps with the  $2p$ -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  $\text{BeCl}_2$  molecule

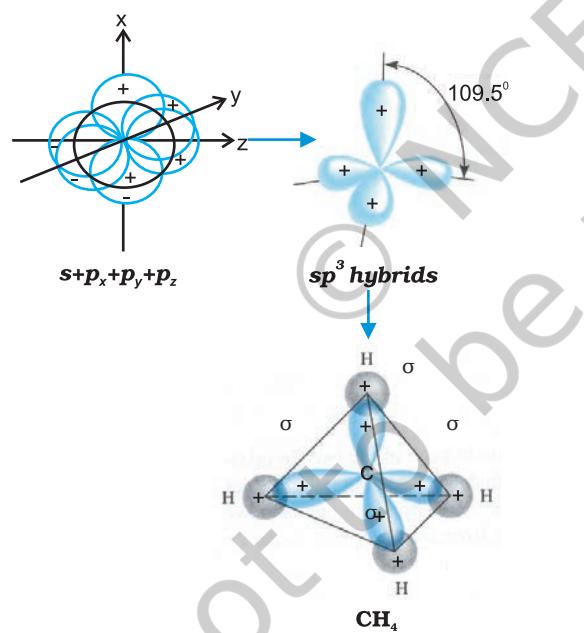
**(II)  $sp^2$  hybridisation :** In this hybridisation there is involvement of one  $s$  and two  $p$ -orbitals in order to form three equivalent  $sp^2$  hybridised orbitals. For example, in  $\text{BCl}_3$  molecule, the ground state electronic configuration of central boron atom is  $1s^22s^22p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbital as



**Fig. 4.11** Formation of  $sp^2$  hybrids and the  $\text{BCl}_3$  molecule

a result boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three  $sp^2$  hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p 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  $120^\circ$ .

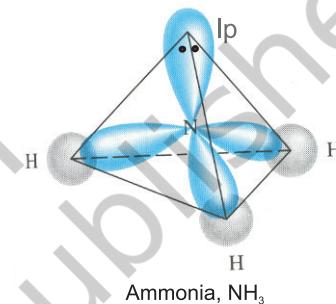
**(III)  $sp^3$  hybridisation:** This type of hybridisation can be explained by taking the example of  $CH_4$  molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four  $sp^3$  hybrid orbital of equivalent energies and shape. There is 25% s-character 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  $109.5^\circ$  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

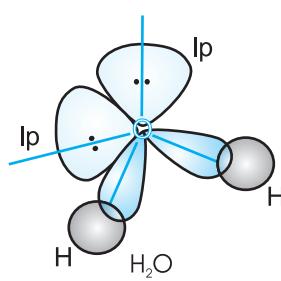
The structure of  $NH_3$  and  $H_2O$  molecules can also be explained with the help of  $sp^3$  hybridisation. In  $NH_3$ , the valence shell (outer) electronic configuration of nitrogen in the

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 1s 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  $107^\circ$  from  $109.5^\circ$ . 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 2s and three 2p) 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  $104.5^\circ$  from  $109.5^\circ$  (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry.



**Fig. 4.14** Formation of  $H_2O$  molecule

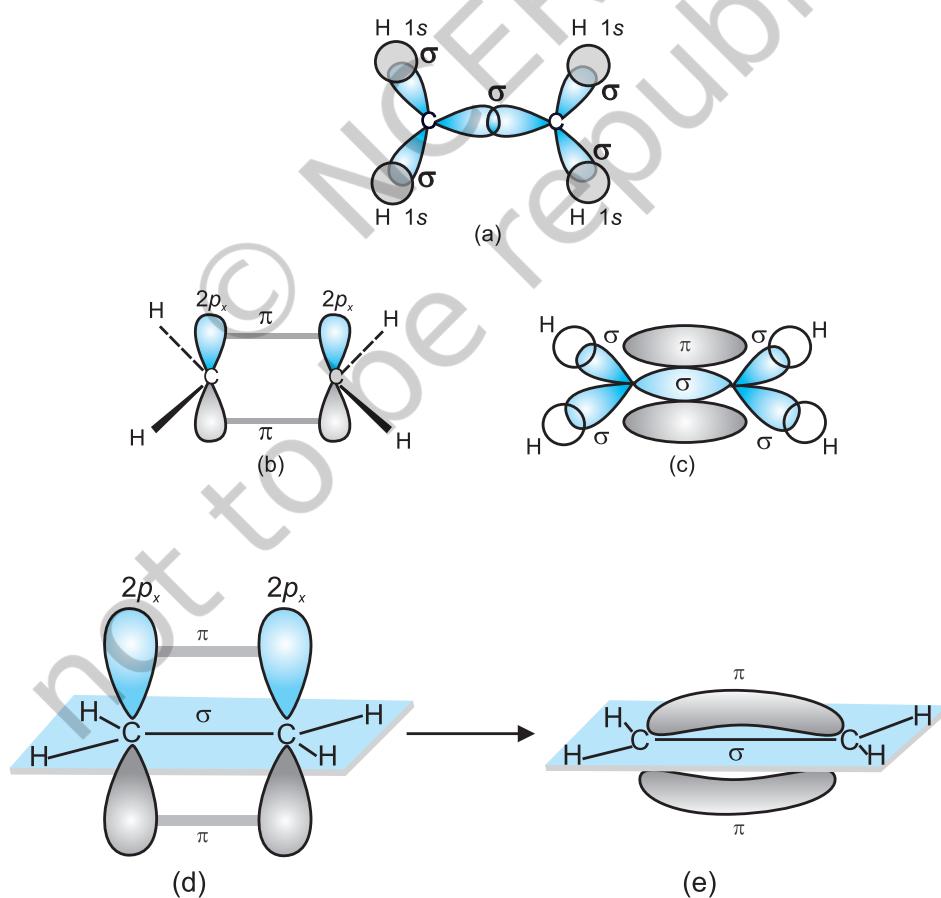
#### 4.6.2 Other Examples of $sp^3$ , $sp^2$ and $sp$ Hybridisation

**$sp^3$  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  $\pi$  bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms.

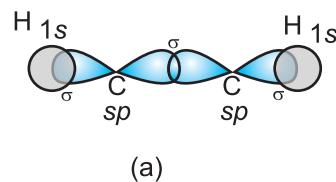
Thus, in ethene molecule, the carbon-carbon bond consists of one  $sp^2-sp^2$  sigma bond and one pi ( $\pi$ ) bond between  $p$  orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C-H bond is  $sp^2-s$  sigma with bond length 108 pm. The H-C-H bond angle is  $117.6^\circ$  while the H-C-C angle is  $121^\circ$ . The formation of sigma and pi bonds in ethene is shown in Fig. 4.15.



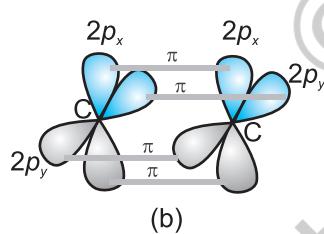
**Fig. 4.15** Formation of sigma and pi bonds in ethene

**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  $2p_x$ .

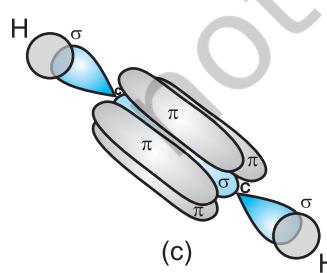
One  $sp$  hybrid orbital of one carbon atom overlaps axially with  $sp$  hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled  $s$  orbital of hydrogen atoms forming  $\sigma$  bonds. Each of the two unhybridised  $p$  orbitals of both the carbon atoms overlaps sidewise to form two  $\pi$  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.



(a)



(b)



(c)

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	$sp^3d^2$	$s+p(3)+d(2)$	$BrF_5$
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):

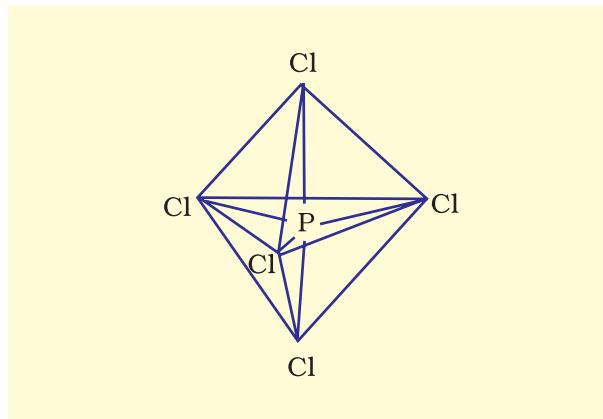
The ground state and the excited state outer electronic configurations of phosphorus ( $Z=15$ ) are represented below.

P (ground state)	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow\uparrow$	$\square\square\square\square\square$
	3s	3p	3d
P (excited state)	$\uparrow$	$\uparrow\uparrow\uparrow\uparrow$	$\uparrow\square\square\square\square$
PCl <sub>5</sub>	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\square\square\square\square$
	Cl	Cl Cl Cl Cl	Cl

**Fig. 4.16** Formation of sigma and pi bonds in ethyne

$sp^3d$  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.

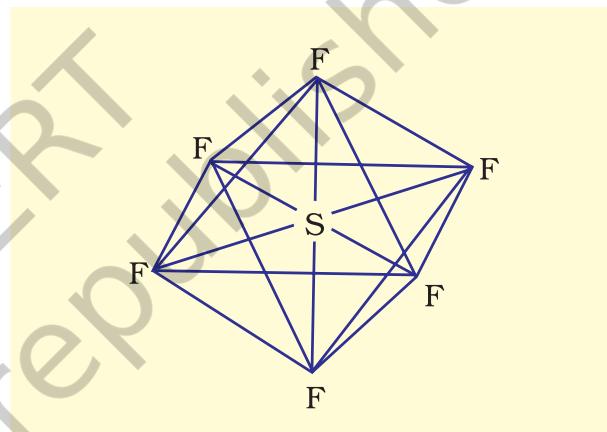
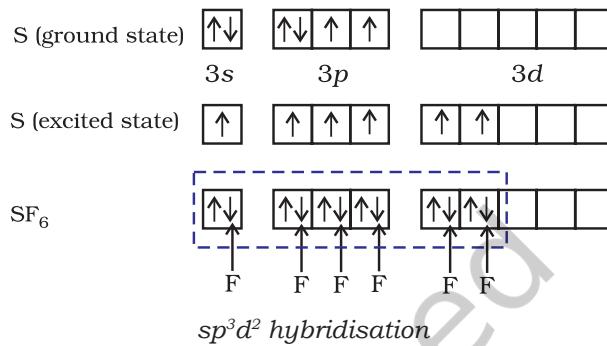


**Fig. 4.17** Trigonal bipyramidal geometry of  $PCl_5$  molecule

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  $120^\circ$  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  $90^\circ$  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  $3s^23p^4$ . In the excited 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 :

- The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- 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 ( $\psi$ '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  $1s$  orbital. The atomic orbitals of these atoms may be represented by the wave functions

$\psi_A$  and  $\psi_B$ . 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 :

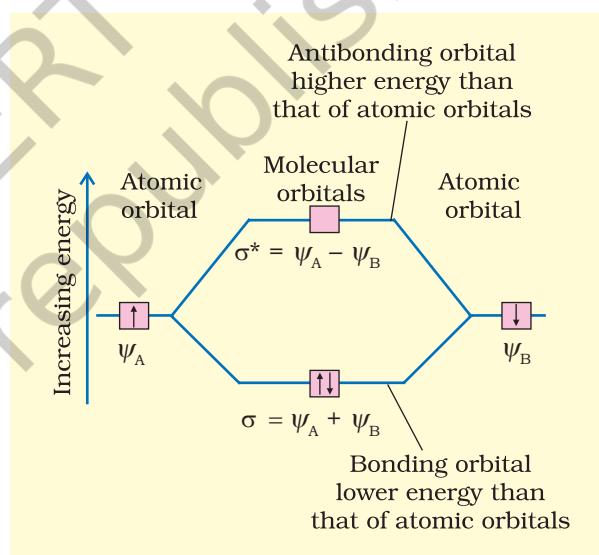
$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals  $\sigma$  and  $\sigma^*$  are formed as :

$$\sigma = \psi_A + \psi_B$$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called **antibonding molecular orbital** as depicted in Fig. 4.19.



**Fig.4.19** Formation of bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) molecular orbitals by the linear combination of atomic orbitals  $\psi_A$  and  $\psi_B$  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 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s 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

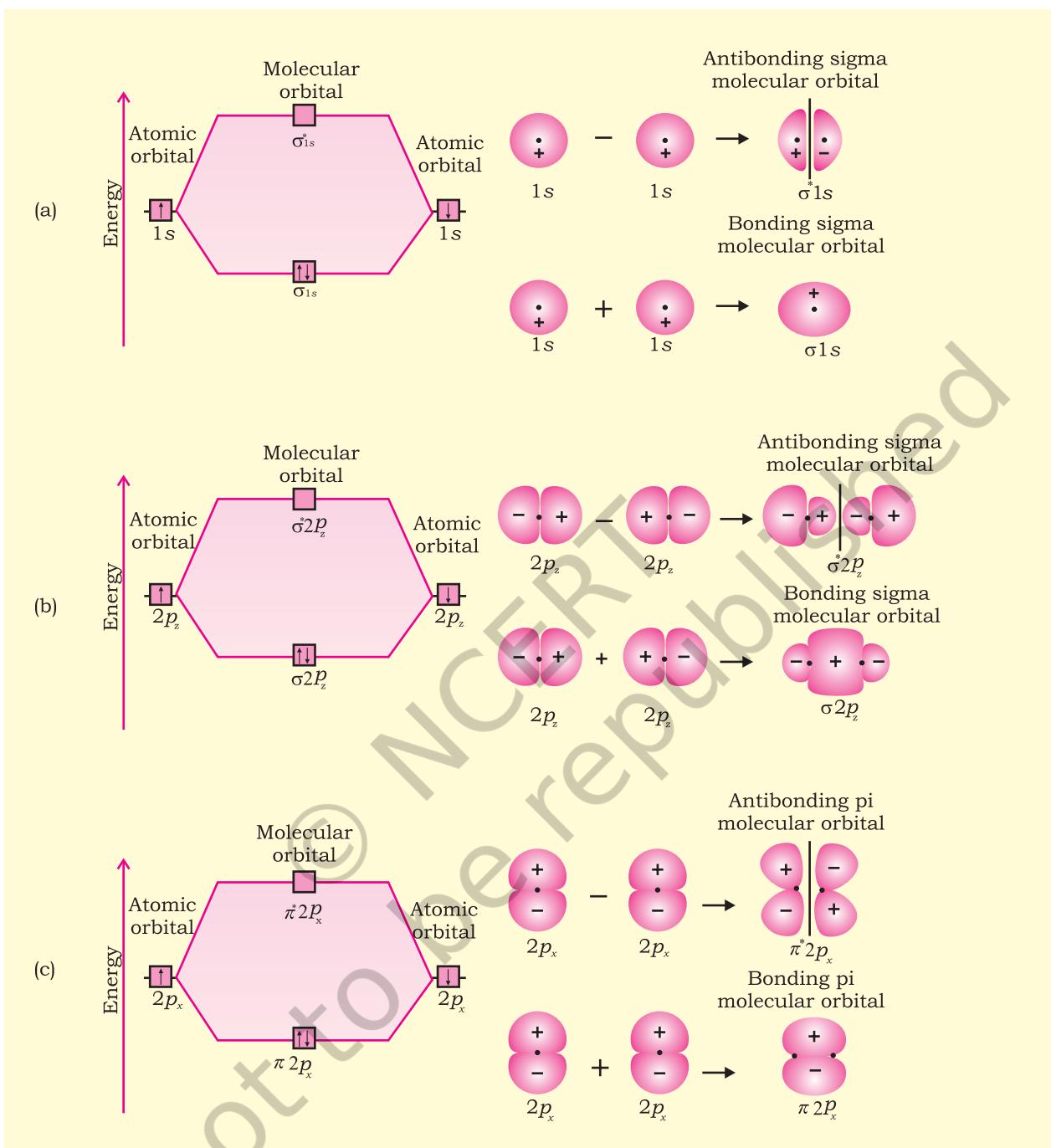
Molecular orbitals of diatomic molecules are designated as  $\sigma$  (sigma),  $\pi$  (pi),  $\delta$  (delta), etc.

In this nomenclature, the **sigma ( $\sigma$ ) molecular orbitals are symmetrical around the bond-axis while pi ( $\pi$ ) 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  $\sigma$  type and are designated as  $\sigma 1s$  and  $\sigma^* 1s$  [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  $\pi$  and  $=\pi^*$  [Fig. 4.20(c)]. A  $\pi$  bonding MO has larger electron density above and below the inter-nuclear axis. The  $\pi^*$  antibonding MO has a node between the nuclei.

#### 4.7.4 Energy Level Diagram for Molecular Orbitals

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as  $\sigma 1s$  and  $\sigma^* 1s$ . In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals



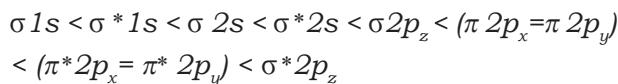
**Fig. 4.20** Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) 2p<sub>z</sub> atomic orbitals and (c) 2p<sub>x</sub> atomic orbitals.

on two atoms) give rise to the following eight molecular orbitals:

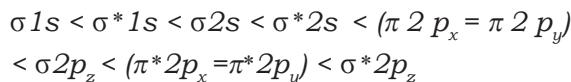
Antibonding MOs	$\sigma^* 2s$	$\sigma^* 2p_z$	$\pi^* 2p_x$	$\pi^* 2p_y$
Bonding MOs	$\sigma 2s$	$\sigma 2p_z$	$\pi 2p_x$	$\pi 2p_y$

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<sub>2</sub> and F<sub>2</sub> is given below:



However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>. For instance, it has been observed experimentally that for molecules such as B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, etc. the increasing order of energies of various molecular orbitals is



The important characteristic feature of this order is that the **energy of σ2p<sub>z</sub> molecular orbital is higher than that of π2p<sub>x</sub> and π2p<sub>y</sub> 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<sub>b</sub> is the number of electrons occupying bonding orbitals and N<sub>a</sub> the number occupying the antibonding orbitals, then

- (i) the molecule is stable if N<sub>b</sub> is greater than N<sub>a</sub>, and
- (ii) the molecule is unstable if N<sub>b</sub> is less than N<sub>a</sub>.

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.,**

$$\text{Bond order (b.o.)} = \frac{1}{2} (N_b - N_a)$$

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<sub>b</sub> > N<sub>a</sub>) means a stable molecule while a negative (i.e., N<sub>b</sub> < N<sub>a</sub>) or zero (i.e., N<sub>b</sub> = N<sub>a</sub>) 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.

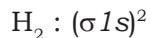
#### Magnetic nature

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<sub>2</sub> 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<sub>2</sub>):** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ1s molecular orbital. So electronic configuration of hydrogen molecule is



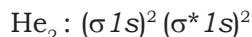
The bond order of H<sub>2</sub> molecule can be calculated as given below:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

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<sup>-1</sup> and bond length equal to 74 pm. Since no

unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

**2. Helium molecule ( $\text{He}_2$ ):** The electronic configuration of helium atom is  $1s^2$ . Each helium atom contains 2 electrons, therefore, in  $\text{He}_2$  molecule there would be 4 electrons. These electrons will be accommodated in  $\sigma 1s$  and  $\sigma^* 1s$  molecular orbitals leading to electronic configuration:

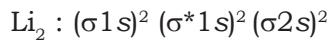


Bond order of  $\text{He}_2$  is  $\frac{1}{2}(2 - 2) = 0$

$\text{He}_2$  molecule is therefore unstable and does not exist.

Similarly, it can be shown that  $\text{Be}_2$  molecule  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$  also does not exist.

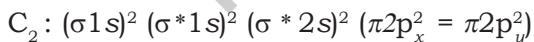
**3. Lithium molecule ( $\text{Li}_2$ ):** The electronic configuration of lithium is  $1s^2$ ,  $2s^1$ . There are six electrons in  $\text{Li}_2$ . The electronic configuration of  $\text{Li}_2$  molecule, therefore, is



The above configuration is also written as  $\text{KK}(\sigma 2s)^2$  where KK represents the closed K shell structure  $(\sigma 1s)^2 (\sigma^* 1s)^2$ .

From the electronic configuration of  $\text{Li}_2$  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  $\frac{1}{2}(4 - 2) = 1$ . It means that  $\text{Li}_2$  molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic  $\text{Li}_2$  molecules are known to exist in the vapour phase.

**4. Carbon molecule ( $\text{C}_2$ ):** The electronic configuration of carbon is  $1s^2$ ,  $2s^2$ ,  $2p^2$ . There are twelve electrons in  $\text{C}_2$ . The electronic configuration of  $\text{C}_2$  molecule, therefore, is

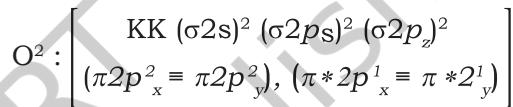
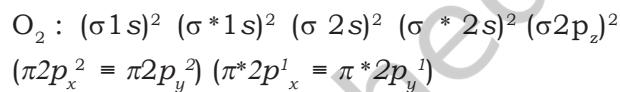


or  $\text{KK}(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$

The bond order of  $\text{C}_2$  is  $\frac{1}{2}(8 - 4) = 2$  and  $\text{C}_2$  should be diamagnetic. Diamagnetic  $\text{C}_2$  molecules have indeed been detected in

vapour phase. It is important to note that double bond in  $\text{C}_2$  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  $\text{N}_2$  molecule can be discussed.

**5. Oxygen molecule ( $\text{O}_2$ ):** The electronic configuration of oxygen atom is  $1s^2$ ,  $2s^2$ ,  $2p^4$ . Each oxygen atom has 8 electrons, hence, in  $\text{O}_2$  molecule there are 16 electrons. The electronic configuration of  $\text{O}_2$  molecule, therefore, is



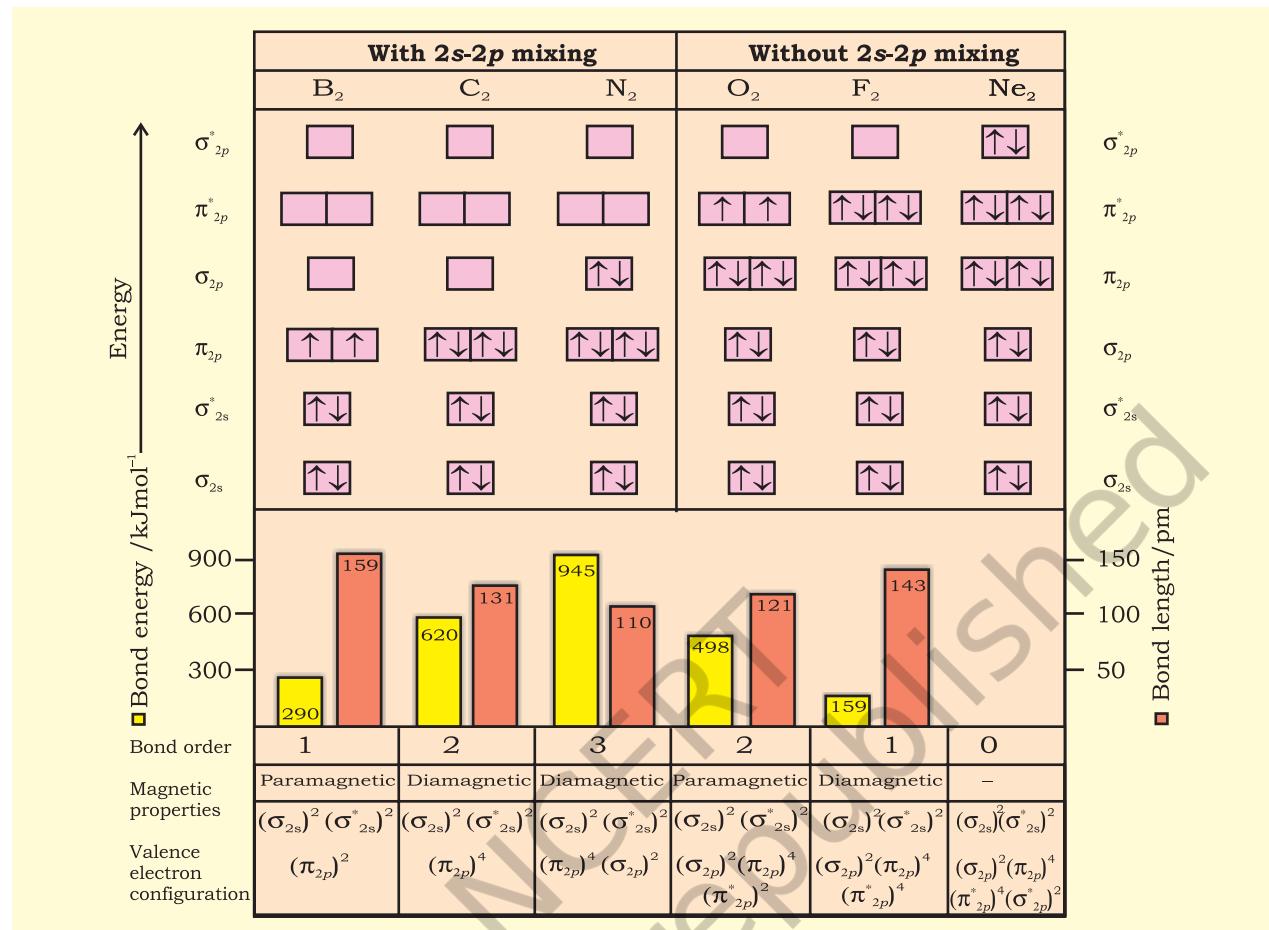
From the electronic configuration of  $\text{O}_2$  molecule it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2} [N_b - N_a] = \frac{1}{2} [10 - 6] = 2$$

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,  **$\text{O}_2$  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  $\text{B}_2$  through  $\text{Ne}_2$ . 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.

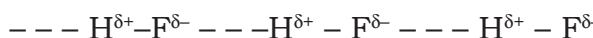
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**Fig. 4.21** MO occupancy and molecular properties for B<sub>2</sub> through Ne<sub>2</sub>.

## 4.9 HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the highly 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 :



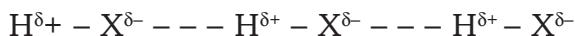
Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond.

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 ( $\delta^+$ ) while 'X' attains fractional negative

charge ( $\delta^-$ ). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as:



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

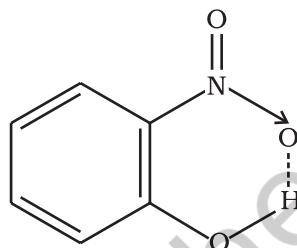
There are two types of H-bonds

- (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. 4.22** Intramolecular hydrogen bonding in *o*-nitrophenol molecule

#### SUMMARY

Kössel'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 1s 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 arrangement 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 electrons 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:  
 $\text{BeCl}_2$ ,  $\text{BCl}_3$ ,  $\text{SiCl}_4$ ,  $\text{AsF}_5$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$

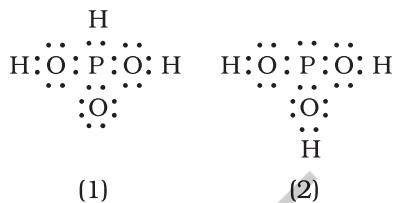
4.8 Although geometries of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

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  $\text{CO}_3^{2-}$  ion.

4.12  $\text{H}_3\text{PO}_3$  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  $\text{H}_3\text{PO}_3$ ? If not, give reasons for the same.



- 4.13 Write the resonance structures for  $\text{SO}_3$ ,  $\text{NO}_2$  and  $\text{NO}_3^-$ .

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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are triatomic molecules, the shape of  $\text{H}_2\text{O}$  molecule is bent while that of  $\text{CO}_2$  is linear. Explain this on the basis of dipole moment.

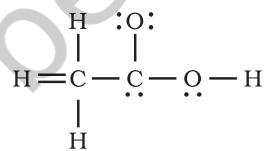
4.16 Write the significance/applications of dipole moment.

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:  $\text{LiF}$ ,  $\text{K}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{SO}_2$  and  $\text{ClF}_3$ .

4.20 The skeletal structure of  $\text{CH}_3\text{COOH}$  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  $\text{CH}_4$  is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why  $\text{CH}_4$  is not square planar ?

4.22 Explain why  $\text{BeH}_2$  molecule has a zero dipole moment although the Be-H bonds are polar.

4.23 Which out of  $\text{NH}_3$  and  $\text{NF}_3$  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.  
$$\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$$

- 4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction?  
 $\text{BF}_3 + \text{NH}_3 \rightarrow \text{F}_3\text{B.NH}_3$
- 4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  molecules.
- 4.28 What is the total number of sigma and pi bonds in the following molecules?  
(a)  $\text{C}_2\text{H}_2$  (b)  $\text{C}_2\text{H}_4$
- 4.29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) 1s and 1s (b) 1s and  $2p_x$ ; (c)  $2p_y$  and  $2p_y$  (d) 1s and 2s.
- 4.30 Which hybrid orbitals are used by carbon atoms in the following molecules?  
(a)  $\text{CH}_3-\text{CH}_3$ ; (b)  $\text{CH}_3-\text{CH}=\text{CH}_2$ ; (c)  $\text{CH}_3-\text{CH}_2-\text{OH}$ ; (d)  $\text{CH}_3-\text{CHO}$  (e)  $\text{CH}_3\text{COOH}$
- 4.31 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one example of each type.
- 4.32 Distinguish between a sigma and a pi bond.
- 4.33 Explain the formation of  $\text{H}_2$  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  $\text{Be}_2$  molecule does not exist.
- 4.36 Compare the relative stability of the following species and indicate their magnetic properties;  
 $\text{O}_2, \text{O}_2^+, \text{O}_2^-$  (superoxide),  $\text{O}_2^{2-}$  (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  $\text{PCl}_5$ . 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 :  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{O}_2^+$  and  $\text{O}_2^-$ .



## UNIT 5

11082CH06

# 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  $\Delta U$  and  $\Delta H$ ;
- measure experimentally  $\Delta U$  and  $\Delta H$ ;
- define standard states for  $\Delta H$ ;
- 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 ( $\Delta G$ ); and
- establish relationship between  $\Delta G$  and spontaneity,  $\Delta G$  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?*

## 5.1 THERMODYNAMIC TERMS

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

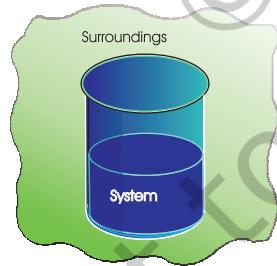
### 5.1.1 The System and the Surroundings

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. 5.1).



**Fig. 5.1** 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.

### 5.1.2 Types of the System

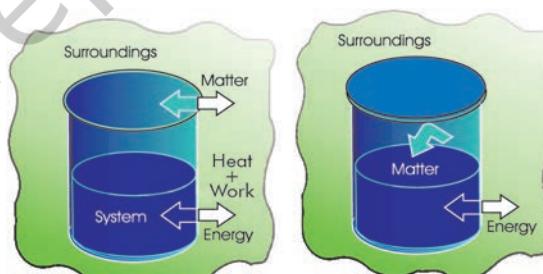
We, further classify the systems according to the movements of matter and energy in or out of the system.

#### 1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 5.2 (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.

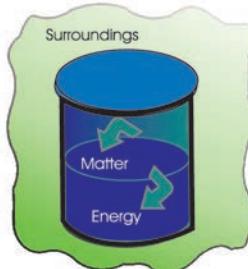
#### 2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 5.2 (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. 5.2** 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. 5.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

#### 5.1.3 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.

#### 5.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce

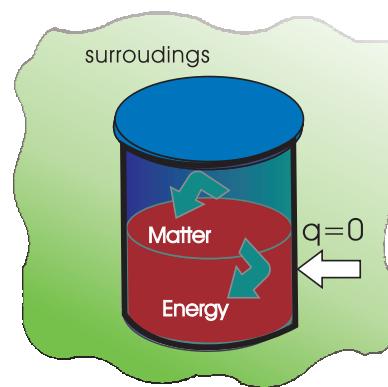
a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy,  $U$  of the system, which may change, when

- 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 5.1.2.

##### (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. 5.3).



**Fig. 5.3** 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,  $\Delta U$  i.e.,

$$\Delta U = U_2 - U_1 = w_{ad}$$

Therefore, internal energy,  $U$ , of the system is a state function.

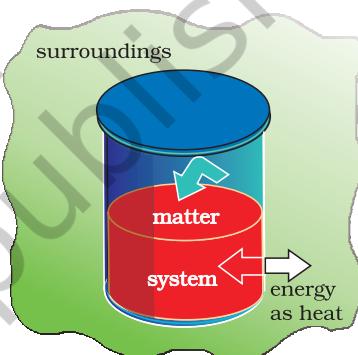
By conventions of IUPAC in chemical thermodynamics. The positive sign expresses that  $w_{ad}$  is positive when work is done **on** the system and the internal energy of system increases. Similarly, if the work is done **by** the system,  $w_{ad}$  will be negative because internal energy of the system decreases.

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  $25^\circ\text{C}$  to  $35^\circ\text{C}$ , the change in temperature is  $35^\circ\text{C} - 25^\circ\text{C} = +10^\circ\text{C}$ , whether we go straight up to  $35^\circ\text{C}$  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 5.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 5.4).



**Fig. 5.4** 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.

By conventions of IUPAC in chemical thermodynamics. The  $q$  is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and  $q$  is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system.

\* Earlier negative sign was assigned when the work is done on the system and positive sign when the work is done by the system. This is still followed in physics books, although IUPAC has recommended the use of new sign convention.

### (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:

$$\Delta U = q + w \quad (5.1)$$

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 5.1 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,  $\Delta U$  of the system.

### Problem 5.1

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.

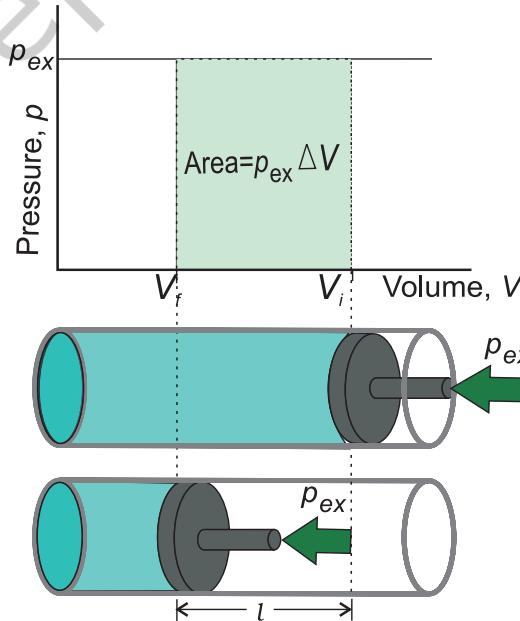
## 5.2 APPLICATIONS

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!

### 5.2.1 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



**Fig. 5.5 (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.

inside becomes equal to  $p_{ex}$ . Let this change 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. 5.5(a)].

$$\text{then, volume change} = l \times A = \Delta V = (V_f - V_i)$$

We also know, pressure =  $\frac{\text{force}}{\text{area}}$

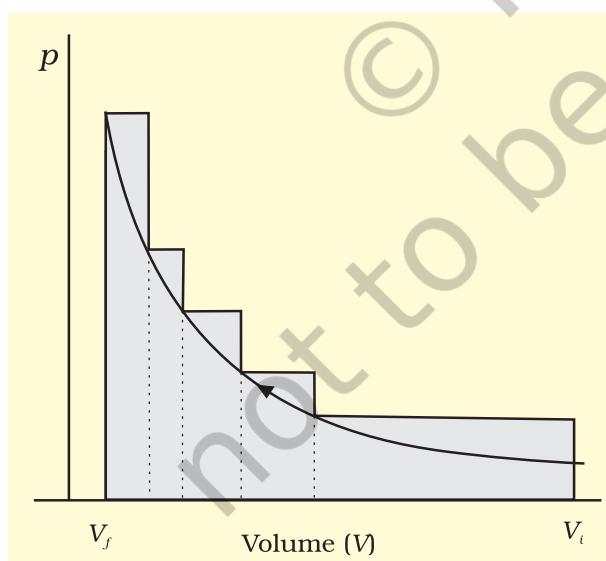
Therefore, force on the piston =  $p_{ex} \cdot A$

If  $w$  is the work done on the system by movement of the piston then

$$\begin{aligned} w &= \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l \\ &= p_{ex} \cdot (-\Delta V) = -p_{ex} \Delta V = -p_{ex} (V_f - V_i) \quad (5.2) \end{aligned}$$

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. 5.5 (b)]



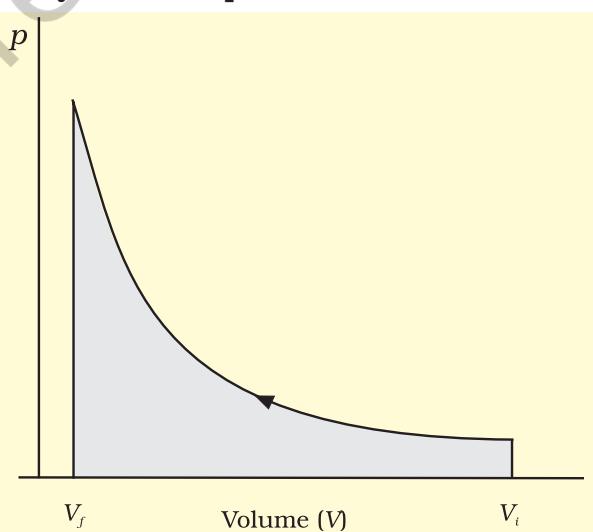
**Fig. 5.5 (b)** *pV-plot when pressure is not constant and changes in finite steps during compression from initial volume,  $V_i$  to final volume,  $V_f$ . Work done on the gas is represented by the shaded area.*

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

$$w = - \int_{V_i}^{V_f} p_{ex} dV \quad (5.3)$$

Here,  $p_{ex}$  at each stage is equal to  $(p_{in} + dp)$  in case of compression [Fig. 5.5(c)]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e.,  $p_{ex} = (p_{in} - dp)$ . 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.**



**Fig. 5.5 (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.*

**Processes 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 5.3 as follows:

$$w_{rev} = - \int_{V_i}^{V_f} p_{ex} dV = - \int_{V_i}^{V_f} (p_{in} \pm dp) dV$$

Since  $dp \times dV$  is very small we can write

$$w_{rev} = - \int_{V_i}^{V_f} p_{in} dV \quad (5.4)$$

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),

$$\begin{aligned} w_{rev} &= - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \\ &= -2.303 nRT \log \frac{V_f}{V_i} \end{aligned} \quad (5.5)$$

**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 5.2 and 5.3).

Now, we can write equation 5.1 in number of ways depending on the type of processes.

Let us substitute  $w = -p_{ex}\Delta V$  (eq. 5.2) in equation 5.1, 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 ( $T = \text{constant}$ ) 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 5.1,  $\Delta U = q + w$  can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

$$q = -w = p_{ex}(V_f - V_i)$$

2. For isothermal reversible change

$$q = -w = nRT \ln \frac{V_f}{V_i}$$

$$= 2.303 nRT \log \frac{V_f}{V_i}$$

For adiabatic change,  $q = 0$ ,

$$\Delta U = w_{ad}$$

**Problem 5.2**

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C 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 5.3**

Consider the same expansion, but this time against a constant external pressure of 1 atm.

**Solution**

We have  $q = -w = p_{ex}(8) = 8 \text{ litre-atm}$

**Problem 5.4**

Consider the expansion given in problem 5.2, for 1 mol of an ideal gas conducted reversibly.

**Solution**

$$\text{We have } q = -w = 2.303 nRT \log \frac{V_f}{V_i}$$

$$= 2.303 \times 1 \times 0.8206 \times 298 \times \log \frac{10}{2}$$

$$\begin{aligned}
 &= 2.303 \times 0.8206 \times 298 \times \log 5 \\
 &= 2.303 \times 0.8206 \times 298 \times 0.6990 \\
 &= 393.66 \text{ L atm}
 \end{aligned}$$

### 5.2.2 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 (5.1) 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

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \quad (5.6)$$

Now we can define another thermodynamic function, the enthalpy  $H$  [Greek word *enthalpien*, to warm or heat content] as :

$$H = U + pV \quad (5.7)$$

so, equation (5.6) 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,  $\Delta H$  is independent of path. Hence,  $q_p$  is also independent of path.

For finite changes at constant pressure, we can write equation 5.7 as

$$\Delta H = \Delta U + \Delta pV$$

Since  $p$  is constant, we can write

$$\Delta H = \Delta U + p\Delta V \quad (5.8)$$

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.

**$\Delta H$  is negative for exothermic reactions which evolve heat during the reaction and  $\Delta H$  is positive for endothermic reactions which absorb heat from the surroundings.**

At constant volume ( $\Delta V = 0$ ),  $\Delta U = q_v$ , therefore equation 5.8 becomes

$$\Delta H = \Delta U = q_v$$

The difference between  $\Delta H$  and  $\Delta U$  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,

$$pV_A = n_A RT$$

$$pV_B = n_B RT$$

$$\text{Thus, } pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A) RT$$

$$\text{or } p(V_B - V_A) = (n_B - n_A) RT$$

$$\text{or } p \Delta V = \Delta n_g RT \quad (5.9)$$

Here,  $\Delta n_g$  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 5.9 in equation 5.8, we get

$$\Delta H = \Delta U + \Delta n_g RT \quad (5.10)$$

The equation 5.10 is useful for calculating  $\Delta H$  from  $\Delta U$  and vice versa.

### Problem 5.5

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<sup>-1</sup>. Calculate the internal energy change, when

1 mol of water is vapourised at 1 bar pressure and 100°C.

### Solution

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

$$\Delta H = \Delta U + \Delta n g RT$$

or  $\Delta U = \Delta H - \Delta n_g RT$ , substituting the values, we get

$$\begin{aligned}\Delta U &= 41.00 \text{ kJ mol}^{-1} - 1 \\ &\quad \times 8.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 373 \text{ K} \\ &= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1} \\ &= 37.904 \text{ kJ mol}^{-1}\end{aligned}$$

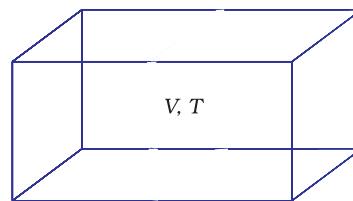
### (b) Extensive and Intensive Properties

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.

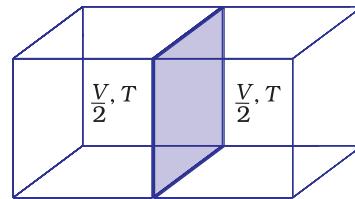
Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**. For example temperature, density, pressure etc. are intensive properties. A molar property,  $\chi_m$ , is the value of an extensive property  $\chi$  of the system for 1 mol of the substance. 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. 5.6(a)]. Let us make a partition such that volume is halved, each part [Fig. 5.6 (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. 5.6(a)** A gas at volume  $V$  and temperature  $T$



**Fig. 5.6 (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

$$q = \text{coeff} \times \Delta T$$

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,  $\Delta T$  as

$$q = c \times m \times \Delta T = C \Delta T \quad (5.11)$$

#### (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,  $\Delta H = \Delta U + \Delta(pV)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$$\therefore \Delta H = \Delta U + R\Delta T \quad (5.12)$$

On putting the values of  $\Delta H$  and  $\Delta U$ , we have

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

$$C_p = C_v + R$$

$$C_p - C_v = R \quad (5.13)$$

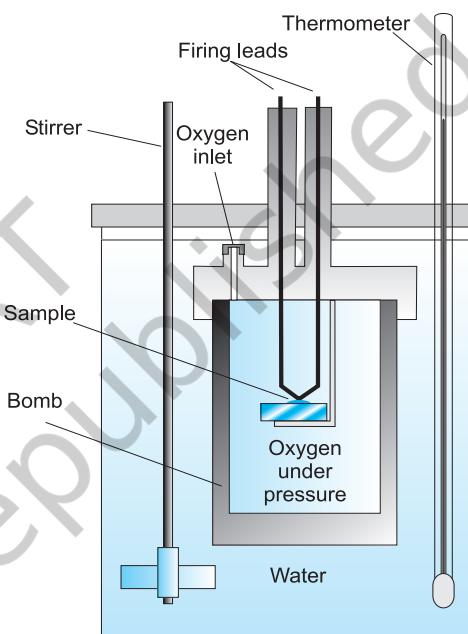
### 5.3 MEASUREMENT OF $\Delta U$ AND $\Delta H$ : CALORIMETRY

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) $\Delta U$ Measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Fig. 5.7). 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



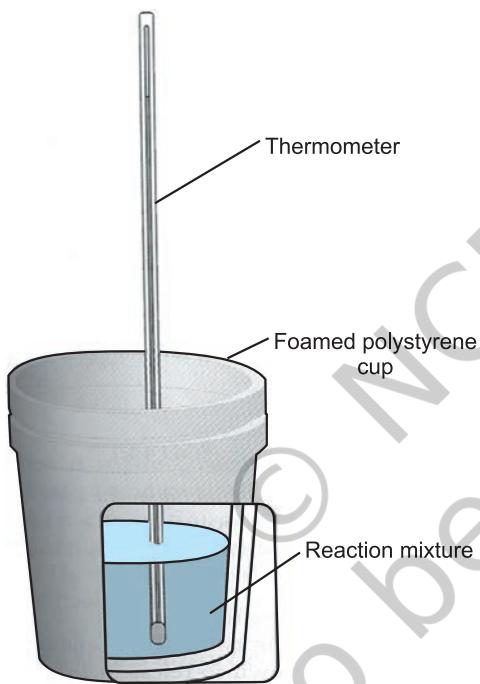
**Fig. 5.7** Bomb calorimeter

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 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 5.11.

### (B) $\Delta H$ Measurements

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig. 5.8. 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. 5.8** Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

#### Problem 5.6

1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation



During the reaction, temperature rises from 298 K to 299 K. If the heat capacity

of the bomb calorimeter is 20.7 kJ/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.

$$q = C_v \times \Delta T$$

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.

$$q = -C_v \times \Delta T = -20.7 \text{ kJ/K} \times (299 - 298) \text{ K} \\ = -20.7 \text{ kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus,  $\Delta U$  for the combustion of the 1g of graphite =  $-20.7 \text{ kJ K}^{-1}$

For combustion of 1 mol of graphite,

$$= \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}}$$

$$= -2.48 \times 10^2 \text{ kJ mol}^{-1}, \quad \text{Since } \Delta n_g = 0, \\ \Delta H = \Delta U = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

#### 5.4 ENTHALPY CHANGE, $\Delta_r H$ OF A REACTION – REACTION ENTHALPY

In a chemical reaction, reactants are converted into products and is represented by,



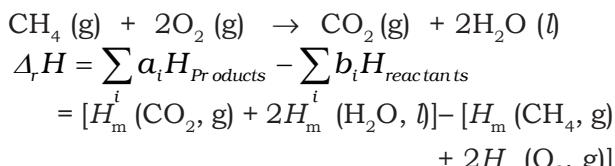
The enthalpy change accompanying a reaction is called the **reaction enthalpy**. The enthalpy change of a chemical reaction, is given by the symbol  $\Delta_r H$

$$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$$

$$= \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}} \quad (5.14)$$

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



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.**

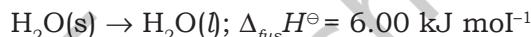
**The standard state of a substance at a specified temperature is its pure form at 1 bar.** For example, the standard state of liquid

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  $\ominus$  to the symbol  $\Delta H$ , e.g.,  $\Delta H^\ominus$

#### (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).



Here  $\Delta_{\text{fus}} H^\ominus$  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,  $\Delta_{\text{fus}} H^\ominus$ .**

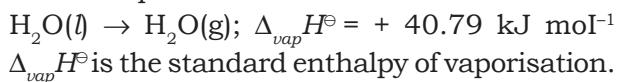
Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water

**Table 5.1 Standard Enthalpy Changes of Fusion and Vaporisation**

Substance	$T_f/\text{K}$	$\Delta_{\text{fus}} H^\ominus/(\text{kJ mol}^{-1})$	$T_b/\text{K}$	$\Delta_{\text{vap}} H^\ominus/(\text{kJ mol}^{-1})$
N <sub>2</sub>	63.15	0.72	77.35	5.59
NH <sub>3</sub>	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 <sub>3</sub> COCH <sub>3</sub>	177.8	5.72	329.4	29.1
CCl <sub>4</sub>	250.16	2.5	349.69	30.0
H <sub>2</sub> O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C <sub>6</sub> H <sub>6</sub>	278.65	9.83	353.25	30.8

( $T_f$  and  $T_b$  are melting and boiling points, respectively)

requires heat for evaporation. At constant temperature of its boiling point  $T_b$  and at constant pressure:



**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,  $\Delta_{vap} H^\ominus$ .**

Sublimation is direct conversion of a solid into its vapour. Solid CO<sub>2</sub> or 'dry ice' sublimes at 195K with  $\Delta_{sub} H^\ominus = 25.2 \text{ kJ mol}^{-1}$ ; naphthalene sublimes slowly and for this  $\Delta_{sub} H^\ominus = 73.0 \text{ kJ mol}^{-1}$ .

**Standard enthalpy of sublimation,  $\Delta_{sub} H^\ominus$  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 transformations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mol of acetone than it does to vaporise 1 mol of water. Table 5.1 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

### Problem 5.7

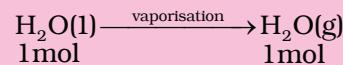
A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 298K.

$$\Delta_{vap} H^\ominus \text{ for water}$$

at 298K= 44.01kJ mol<sup>-1</sup>

### Solution

We can represent the process of evaporation as



No. of moles in 18 g H<sub>2</sub>O(l) is

$$= \frac{18\text{g}}{18\text{g mol}^{-1}} = 1 \text{ mol}$$

$$\begin{aligned} \text{Heat supplied to evaporate } 18\text{g water at} \\ 298 \text{ K} &= n \times \Delta_{vap} H^\ominus \\ &= (1 \text{ mol}) \times (44.01 \text{ kJ mol}^{-1}) \\ &= 44.01 \text{ kJ} \end{aligned}$$

(assuming steam behaving as an ideal gas).

$$\begin{aligned} \Delta_{vap} U &= \Delta_{vap} H^\ominus - p\Delta V = \Delta_{vap} H^\ominus - \Delta n_g RT \\ \Delta_{vap} H^\ominus - \Delta n_g RT &= 44.01 \text{ kJ} \\ -(1)(8.314 \text{ JK}^{-1}\text{mol}^{-1})(298\text{K})(10^{-3}\text{kJ J}^{-1}) \\ \Delta_{vap} U &= 44.01 \text{ kJ} - 2.48\text{kJ} \\ &= 41.53 \text{ kJ} \end{aligned}$$

### Problem 5.8

Assuming the water vapour to be a perfect gas, calculate the internal energy change when 1 mol of water at 100°C and 1 bar pressure is converted to ice at 0°C. Given the enthalpy of fusion of ice is 6.00 kJ mol<sup>-1</sup> heat capacity of water is 4.2 J/g°C

The change take place as follows:

Step - 1     1 mol H<sub>2</sub>O (l, 100°C)  $\rightarrow$  1 mol (l, 0°C) Enthalpy change  $\Delta H_1$

Step - 2     1 mol H<sub>2</sub>O (l, 0°C)  $\rightarrow$  1 mol H<sub>2</sub>O (S, 0°C) Enthalpy change  $\Delta H_2$

Total enthalpy change will be -

$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 \\ \Delta H_1 &= -(18 \times 4.2 \times 100) \text{ J mol}^{-1} \\ &= - 7560 \text{ J mol}^{-1} = - 7.56 \text{ kJ mol}^{-1} \\ \Delta H_2 &= - 6.00 \text{ kJ mol}^{-1} \end{aligned}$$

**Table 5.2 Standard Molar Enthalpies of Formation ( $\Delta_f H^\ominus$ ) at 298K of a Few Selected Substances**

Substance	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	Substance	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$
Al <sub>2</sub> O <sub>3</sub> (s)	-1675.7	HI(g)	+26.48
BaCO <sub>3</sub> (s)	-1216.3	KCl(s)	-436.75
Br <sub>2</sub> (l)	0	KBr(s)	-393.8
Br <sub>2</sub> (g)	+30.91	MgO(s)	-601.70
CaCO <sub>3</sub> (s)	-1206.92	Mg(OH) <sub>2</sub> (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 <sub>4</sub> (g)	-74.81	NaI(s)	-287.78
C <sub>2</sub> H <sub>4</sub> (g)	52.26	NH <sub>3</sub> (g)	-46.11
CH <sub>3</sub> OH(l)	-238.86	NO(g)	+90.25
C <sub>2</sub> H <sub>5</sub> OH(l)	-277.69	NO <sub>2</sub> (g)	+33.18
C <sub>6</sub> H <sub>6</sub> (l)	+49.0	PCl <sub>3</sub> (l)	-319.70
CO(g)	-110.53	PCl <sub>5</sub> (s)	-443.5
CO <sub>2</sub> (g)	-393.51	SiO <sub>2</sub> (s) (quartz)	-910.94
C <sub>2</sub> H <sub>6</sub> (g)	-84.68	SnCl <sub>2</sub> (s)	-325.1
Cl <sub>2</sub> (g)	0	SnCl <sub>4</sub> (l)	-511.3
C <sub>3</sub> H <sub>8</sub> (g)	-103.85	SO <sub>2</sub> (g)	-296.83
n-C <sub>4</sub> H <sub>10</sub> (g)	-126.15	SO <sub>3</sub> (g)	-395.72
HgS(s) red	-58.2	SiH <sub>4</sub> (g)	+34
H <sub>2</sub> (g)	0	SiCl <sub>4</sub> (g)	-657.0
H <sub>2</sub> O(g)	-241.82	C(g)	+716.68
H <sub>2</sub> O(l)	-285.83	H(g)	+217.97
HF(g)	-271.1	Cl(g)	+121.68
HCl(g)	-92.31	Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2
HBr(g)	-36.40		

Therefore,

$$\Delta H = -7.56 \text{ kJ mol}^{-1} + (-6.00 \text{ kJ mol}^{-1}) \\ = -13.56 \text{ kJ mol}^{-1}$$

There is negligible change in the volume during the change from liquid to solid state.

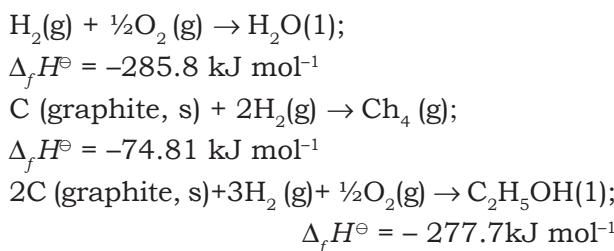
Therefore,  $p\Delta V = \Delta n g RT = 0$

$$\Delta H = \Delta U = -13.56 \text{ kJ mol}^{-1}$$

### (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

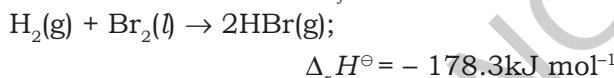
of aggregation (also known as reference states) is called **Standard Molar Enthalpy of Formation**. Its symbol is  $\Delta_f H^\ominus$ , where the subscript 'f' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of 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<sub>2</sub> gas and those of dioxygen, carbon and sulphur are O<sub>2</sub> gas, C<sub>graphite</sub> and S<sub>rhombic</sub> respectively. Some reactions with standard molar enthalpies of formation are as follows.



It is important to understand that a standard molar enthalpy of formation,  $\Delta_f H^\ominus$ , is just a special case of  $\Delta_r H^\ominus$ , 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:



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,  $\Delta_f H^\ominus$  for  $\text{HBr}(\text{g})$ .



Here two moles, instead of one mole of the product is formed from the elements, i.e.,

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus$$

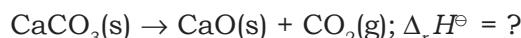
Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of  $\text{HBr}(\text{g})$  is written as  $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{HBr}(\text{g})$ ;

$$\Delta_f H^\ominus = -36.4 \text{ kJ mol}^{-1}$$

Standard enthalpies of formation of some common substances are given in Table 5.2.

By convention, standard enthalpy for formation,  $\Delta_f H^\ominus$ , 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.



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.

$$\Delta_r H^\ominus = \sum_i a_i \Delta_f H^\ominus (\text{products}) - \sum_i b_i \Delta_f H^\ominus (\text{reactants}) \quad (5.15)$$

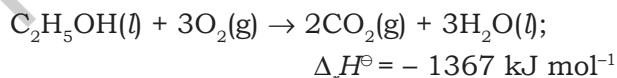
where  $a$  and  $b$  represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are 1 each. Therefore,

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus = [\text{CaO}(\text{s})] + \Delta_f H^\ominus [\text{CO}_2(\text{g})] \\ &\quad - \Delta_f H^\ominus = [\text{CaCO}_3(\text{s})] \\ &= 1(-635.1 \text{ kJ mol}^{-1}) + 1(-393.5 \text{ kJ mol}^{-1}) \\ &\quad - 1(-1206.9 \text{ kJ mol}^{-1}) \\ &= 178.3 \text{ kJ mol}^{-1} \end{aligned}$$

Thus, the decomposition of  $\text{CaCO}_3(\text{s})$  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:

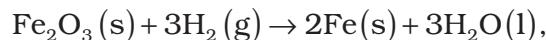


The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

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  $\Delta_r H^\ominus$  refers to the number of moles of substances specified by an equation. Standard enthalpy change  $\Delta_r H^\ominus$  will have units as  $\text{kJ mol}^{-1}$ .

To illustrate the concept, let us consider the calculation of heat of reaction for the following reaction :



From the Table (5.2) of standard enthalpy of formation ( $\Delta_f H^\ominus$ ), we find :

$$\Delta_f H^\ominus (\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ mol}^{-1};$$

$$\Delta_f H^\ominus (\text{Fe}_2\text{O}_3, \text{s}) = -824.2 \text{ kJ mol}^{-1};$$

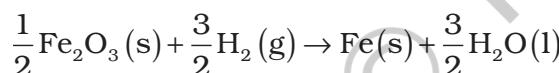
$$\text{Also } \Delta_f H^\ominus (\text{Fe}, \text{s}) = 0 \text{ and}$$

$$\Delta_f H^\ominus (\text{H}_2, \text{g}) = 0 \text{ as per convention}$$

Then,

$$\begin{aligned}\Delta_f H_1^\ominus &= 3(-285.83 \text{ kJ mol}^{-1}) \\ &\quad - 1(-824.2 \text{ kJ mol}^{-1}) \\ &= (-857.5 + 824.2) \text{ kJ mol}^{-1} \\ &= -33.3 \text{ kJ mol}^{-1}\end{aligned}$$

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for  $\Delta_r H^\ominus$  is  $\text{kJ mol}^{-1}$ , 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,



then this amount of reaction would be one mole of reaction and  $\Delta_r H^\ominus$  would be

$$\Delta_f H_2^\ominus = \frac{3}{2}(-285.83 \text{ kJ mol}^{-1})$$

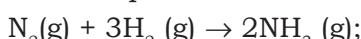
$$- \frac{1}{2}(-824.2 \text{ kJ mol}^{-1})$$

$$= (-428.7 + 412.1) \text{ kJ mol}^{-1}$$

$$= -16.6 \text{ kJ mol}^{-1} = \frac{1}{2} \Delta_r H_1^\ominus$$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of  $\Delta_r H^\ominus$  is reversed in sign. For example



$$\Delta_r H^\ominus = -91.8 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\ominus = +91.8 \text{ kJ mol}^{-1}$$

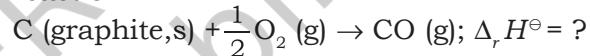
### (e) Hess's Law of Constant Heat Summation

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.**

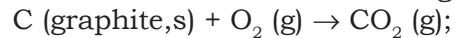
Let us understand the importance of this law with the help of an example.

Consider the enthalpy change for the reaction

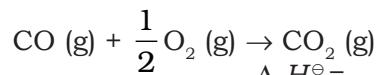


Although CO(g) is the major product, some CO<sub>2</sub> gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:



$$\Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1} \text{ (i)}$$



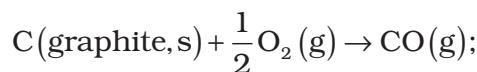
$$\Delta_r H^\ominus = -283.0 \text{ kJ mol}^{-1} \text{ (ii)}$$

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  $\Delta_r H^\ominus$  value



$$\Delta_r H^\ominus = +283.0 \text{ kJ mol}^{-1} \text{ (iii)}$$

Adding equation (i) and (iii), we get the desired equation,

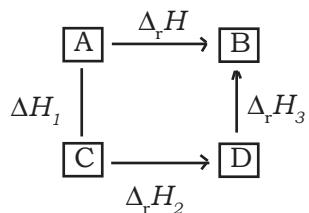


$$\text{for which } \Delta_r H^\ominus = (-393.5 + 283.0) \\ = -110.5 \text{ kJ mol}^{-1}$$

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

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \dots \quad (5.16)$$

It can be represented as:



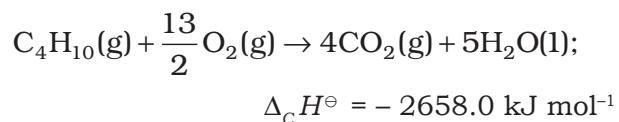
## 5.5 ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

It is convenient to give name to enthalpies specifying the types of reactions.

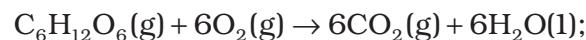
### (a) Standard Enthalpy of Combustion (symbol : $\Delta_c H^\ominus$ )

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 ( $\text{C}_4\text{H}_{10}$ ). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:



Similarly, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is :



$$\Delta_c H^\ominus = -2802.0 \text{ kJ mol}^{-1}$$

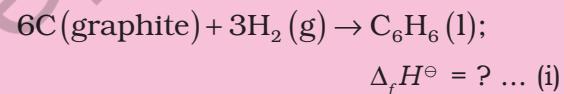
Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

### Problem 5.9

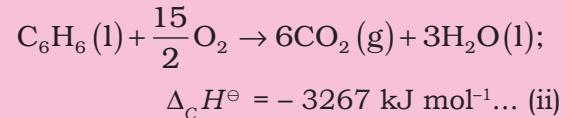
The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O(l)}$  are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation,  $\Delta_f H^\ominus$  of benzene. Standard enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O(l)}$  are  $-393.5 \text{ kJ mol}^{-1}$  and  $-285.83 \text{ kJ mol}^{-1}$  respectively.

### Solution

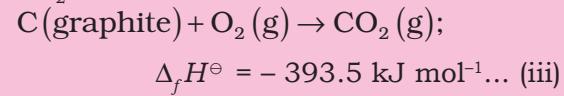
The formation reaction of benzene is given by :



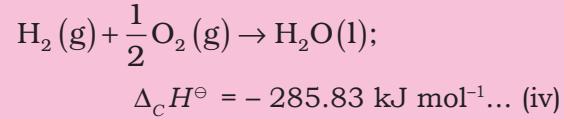
The enthalpy of combustion of 1 mol of benzene is :



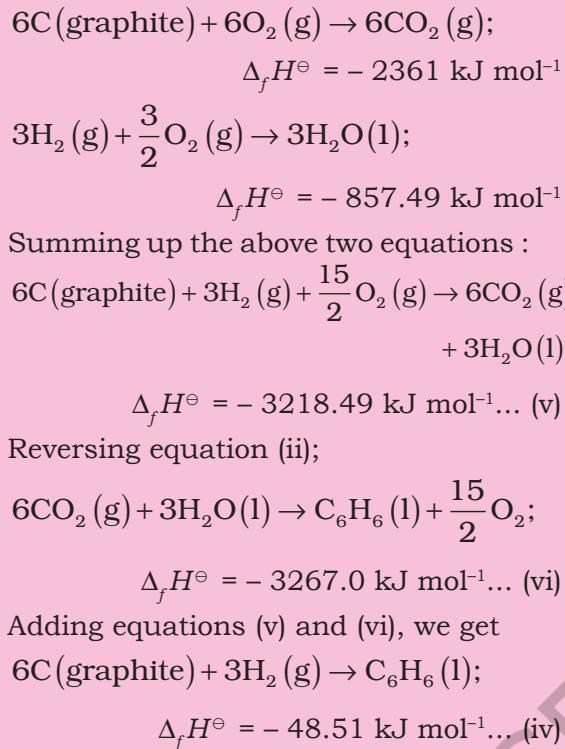
The enthalpy of formation of 1 mol of  $\text{CO}_2(\text{g})$  :



The enthalpy of formation of 1 mol of  $\text{H}_2\text{O(l)}$  is :



multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:



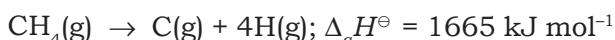
### (b) Enthalpy of Atomization (symbol: $\Delta_a H^\ominus$ )

Consider the following example of atomization of dihydrogen

$\text{H}_2(\text{g}) \rightarrow 2\text{H(g)}; \Delta_a H^\ominus = 435.0 \text{ kJ mol}^{-1}$

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,  $\Delta_a H^\ominus$ . 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



Note that the products are only **atoms** of C and H in gaseous phase. Now see the following reaction:



In this case, the enthalpy of atomization is same as the enthalpy of sublimation.

### (c) Bond Enthalpy (symbol: $\Delta_{\text{bond}} H^\ominus$ )

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.

**Diatomeric Molecules:** Consider the following process in which the bonds in one mole of dihydrogen gas ( $\text{H}_2$ ) are broken:



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:

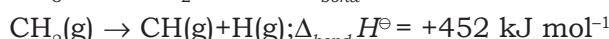
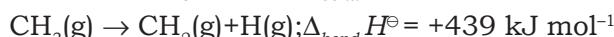
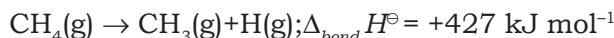


In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

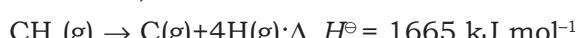
**Polyatomic Molecules:** Let us now consider a polyatomic molecule like methane,  $\text{CH}_4$ . The overall thermochemical equation for its atomization reaction is given below:



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 :



Therefore,



In such cases we use **mean bond enthalpy of C - H bond**.

For example in  $\text{CH}_4$ ,  $\Delta_{\text{C-H}} H^\ominus$  is calculated as:

$$\Delta_{\text{C-H}} H^\ominus = \frac{1}{4} (\Delta_a H^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1})$$

$$= 416 \text{ kJ mol}^{-1}$$

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  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{NO}_2$ , 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 5.3. 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,  $\Delta_r H^\ominus$  is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\Delta_r H^\ominus = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}} \quad (5.17)^{**}$$

This relationship is particularly more useful when the required values of  $\Delta_f H^\ominus$  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

**Table 5.3(a) Some Mean Single Bond Enthalpies in  $\text{kJ mol}^{-1}$  at 298 K**

H	C	N	O	F	Si	P	S	Cl	Br	I	
435.8	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
				155	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 5.3(b) Some Mean Multiple Bond Enthalpies in  $\text{kJ mol}^{-1}$  at 298 K**

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,  $(\Delta_f H^\ominus_{\text{bond}})$ , which is the enthalpy change when one mole of a particular type of bond is formed from gaseous atom, then  $\Delta_f H^\ominus = \sum \Delta_f H^\ominus_{\text{bonds of products}} - \sum \Delta_f H^\ominus_{\text{bonds of reactants}}$

(reactants and products) in the reaction are in gaseous state.

#### (d) 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.



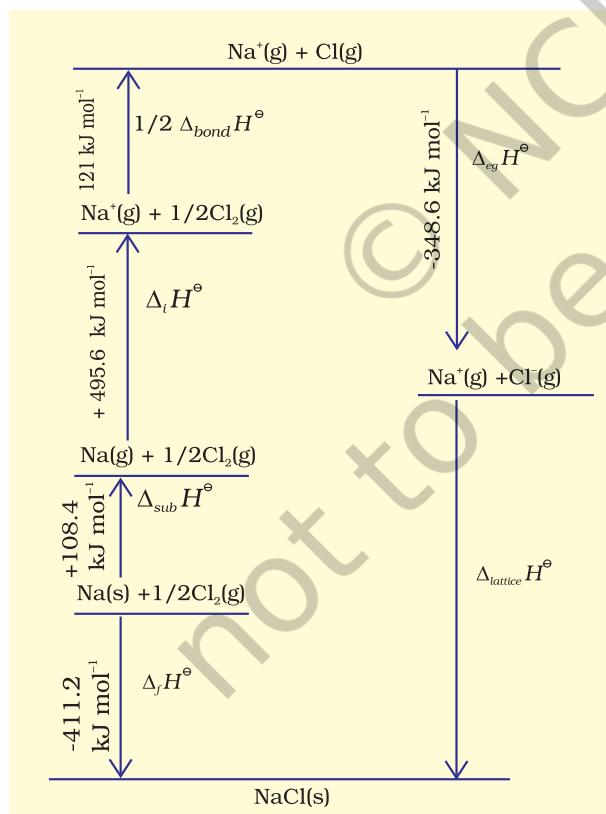
$$\Delta_{lattice}H^\ominus = +788 \text{ kJ mol}^{-1}$$

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. 5.9).

Let us now calculate the lattice enthalpy of  $\text{Na}^+\text{Cl}^-(\text{s})$  by following steps given below :

1.  $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$ , sublimation of sodium metal,  $\Delta_{sub}H^\ominus = 108.4 \text{ kJ mol}^{-1}$

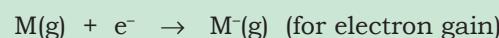
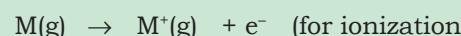
2.  $\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}^-(\text{g})$ , the ionization of sodium atoms, ionization enthalpy  
 $\Delta_iH^\ominus = 496 \text{ kJ mol}^{-1}$
3.  $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$ , the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy.  
 $\frac{1}{2}\Delta_{bond}H^\ominus = 121 \text{ kJ mol}^{-1}$
4.  $\text{Cl}(\text{g}) + \text{e}^-(\text{g}) \rightarrow \text{Cl}^-(\text{g})$  electron gained by chlorine atoms. The electron gain enthalpy,  $\Delta_{eg}H^\ominus = -348.6 \text{ kJ mol}^{-1}$ . 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).



**Fig. 5.9** Enthalpy diagram for lattice enthalpy of  $\text{NaCl}$

#### 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



at temperature,  $T$  is

$$\Delta_rH^\ominus(T) = \Delta_rH^\ominus(0) + \int_0^T \Delta_rC_p^\ominus dT$$

The value of  $C_p$  for each species in the above reaction is  $5/2 R$  ( $C_V = 3/2 R$ )

$$\text{So, } \Delta_rC_p^\ominus = +5/2 R \quad (\text{for ionization})$$

$$\Delta_rC_p^\ominus = -5/2 R \quad (\text{for electron gain})$$

Therefore,

$$\Delta_rH^\ominus \text{ (ionization enthalpy)}$$

$$= E_0 \text{ (ionization energy)} + 5/2 RT$$

$$\Delta_rH^\ominus \text{ (electron gain enthalpy)}$$

$$= -A \text{ (electron affinity)} - 5/2 RT$$

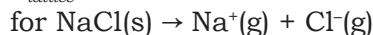
5.  $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{Na}^+\text{Cl}^-(\text{s})$

The sequence of steps is shown in Fig. 5.9, 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,

$$\Delta_{lattice}H^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{lattice}H^\ominus = + 788 \text{ kJ}$$



Internal energy is smaller by  $2RT$  (because  $\Delta n_g = 2$ ) and is equal to  $+ 783 \text{ kJ mol}^{-1}$ .

Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

$$\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$$

For one mole of  $\text{NaCl(s)}$ ,

$$\text{lattice enthalpy} = + 788 \text{ kJ mol}^{-1}$$

and  $\Delta_{hyd}H^\ominus = - 784 \text{ kJ mol}^{-1}$  (from the literature)

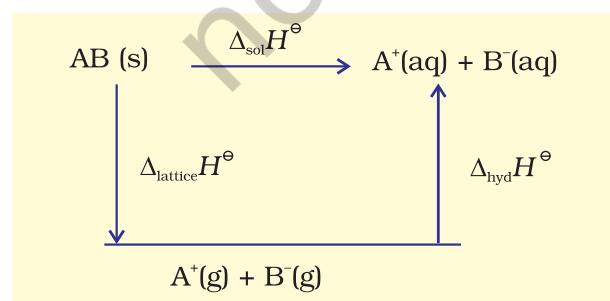
$$\begin{aligned}\Delta_{sol}H^\ominus &= + 788 \text{ kJ mol}^{-1} - 784 \text{ kJ mol}^{-1} \\ &= + 4 \text{ kJ mol}^{-1}\end{aligned}$$

The dissolution of  $\text{NaCl(s)}$  is accompanied by very little heat change.

### (e) Enthalpy of Solution (symbol : $\Delta_{sol}H^\ominus$ )

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves 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,  $\text{AB (s)}$



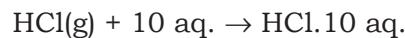
The enthalpy of solution of  $\text{AB(s)}$ ,  $\Delta_{sol}H^\ominus$ , in water is, therefore, determined by the selective values of the lattice enthalpy,  $\Delta_{lattice}H^\ominus$  and enthalpy of hydration of ions,  $\Delta_{hyd}H^\ominus$  as

$$\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$$

For most of the ionic compounds,  $\Delta_{sol}H^\ominus$  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).

### (f) Enthalpy of Dilution

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. for water



$$\Delta H = -69.01 \text{ kJ / mol}$$

Let us consider the following set of enthalpy changes:



$$\Delta H = -72.03 \text{ kJ / mol}$$



$$\Delta H = -72.79 \text{ kJ / mol}$$



$$\Delta H = -74.85 \text{ kJ / mol}$$

The values of  $\Delta H$  show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e., the value in infinitely dilute solution. For hydrochloric acid this value of  $\Delta H$  is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain—

$$\text{HCl.25 aq.} + 15 \text{ aq.} \rightarrow \text{HCl.40 aq.}$$

$$\Delta H = [ -72.79 - (-72.03)] \text{ kJ / mol}$$

$$= -0.76 \text{ kJ / mol}$$

This value ( $-0.76 \text{ kJ/mol}$ ) of  $\Delta H$  is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

## 5.6 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.

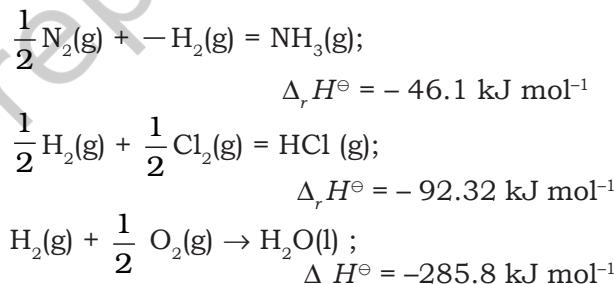
Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room 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 ?

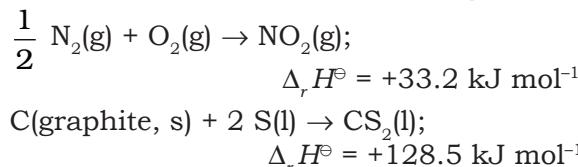
If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:

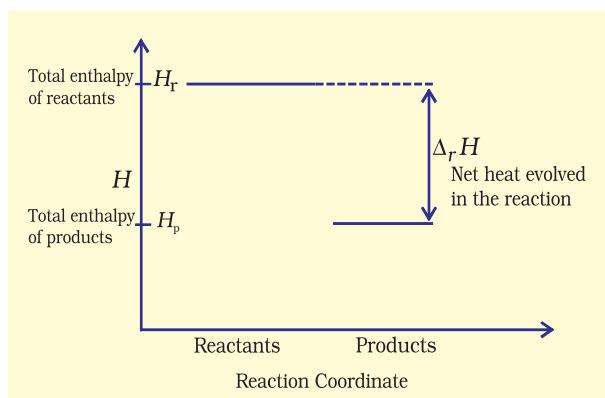


The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 5.10(a).

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 !

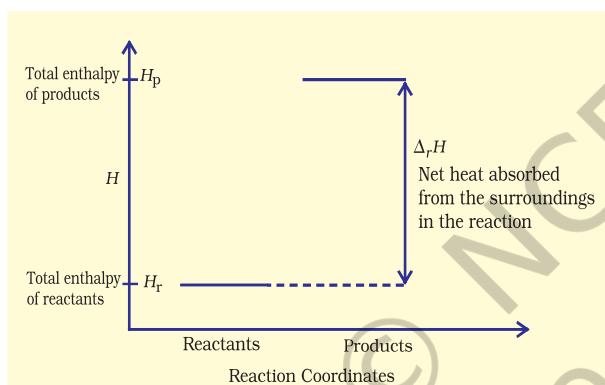
Now let us examine the following reactions:





**Fig. 5.10 (a)** Enthalpy diagram for exothermic reactions

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 5.10(b).



**Fig. 5.10 (b)** Enthalpy diagram for endothermic reactions

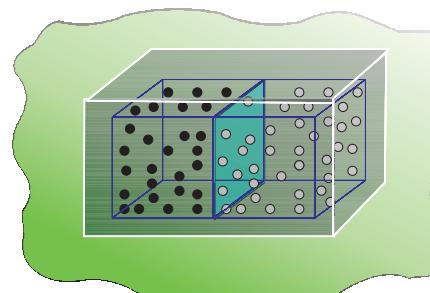
Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

### (b) Entropy and Spontaneity

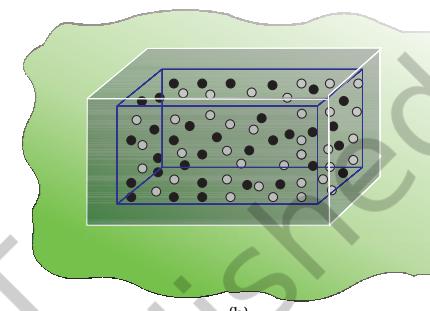
Then, what drives the spontaneous process in a given direction? Let us examine such a case in which  $\Delta H = 0$  i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 5.11.

The two gases, say, gas A and gas B are represented by black dots and white dots



(a)



(b)

**Fig. 5.11** Diffusion of two gases

respectively and separated by a movable partition [Fig. 5.11 (a)]. When the partition is withdrawn [Fig. 5.11(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  $\Delta S$  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  $\Delta S$  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.  $\Delta S$  is related with  $q$  and  $T$  for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \quad (5.18)$$

The total entropy change ( $\Delta S_{total}$ ) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surv} > 0 \quad (5.19)$$

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  $\Delta S_{total}$  i.e.,  $\Delta S_{sys} + \Delta S_{surv}$  is not zero for irreversible process. Thus,  $\Delta U$  does not discriminate between reversible and irreversible process, whereas  $\Delta S$  does.

### Problem 5.10

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)  $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- (iv)  $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$

### Solution

- (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.
- (ii) At 0 K, the constituent 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,  $\text{NaHCO}_3$  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 5.11

For oxidation of iron,



entropy change is  $-549.4 \text{ JK}^{-1} \text{ mol}^{-1}$  at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous?

$(\Delta_r H^\ominus$  for this reaction is  $-1648 \times 10^3 \text{ J mol}^{-1})$

### Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{total} (\Delta S_{sys} + \Delta S_{surr})$ . For calculating  $\Delta S_{surr}$ , we have to consider the heat absorbed by the surroundings which is equal to  $-\Delta_r H^\ominus$ . At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H^\ominus}{T} \text{ (at constant pressure)}$$

$$= -\frac{(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}}$$

$$= 5530 \text{ JK}^{-1} \text{ mol}^{-1}$$

Thus, total entropy change for this reaction

$$\Delta_r S_{total} = 5530 \text{ JK}^{-1} \text{ mol}^{-1} + (-549.4 \text{ JK}^{-1} \text{ mol}^{-1})$$

$$= 4980.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

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,  $\Delta S_{total}$  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

$$G = H - TS \quad (5.20)$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system,  $\Delta G_{sys}$  can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature,  $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \quad (5.21)$$

Thus, Gibbs energy change = enthalpy change – temperature  $\times$  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  $\Delta H$ ) and entropy ( $\Delta S$ , a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that  $\Delta G$  has units of energy because, both  $\Delta H$  and the  $T\Delta S$  are energy terms, since  $T\Delta S = (K) (J/K) = J$ .

Now let us consider how  $\Delta G$  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,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left( -\frac{\Delta H_{sys}}{T} \right)$$

Rearranging the above equation:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontaneous process,  $\Delta S_{total} > 0$ , so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Rightarrow -(\Delta H_{sys} - T\Delta S_{sys}) > 0$$

Using equation 5.21, the above equation can be written as

$$-\Delta G > 0$$

$$\Delta G = \Delta H - T\Delta S < 0 \quad (5.22)$$

$\Delta H_{sys}$  is the enthalpy change of a reaction,  $T\Delta S_{sys}$  is the energy which is not available to do useful work. So  $\Delta G$  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.

$\Delta G$  gives a criteria for spontaneity at constant pressure and temperature.

- (i) If  $\Delta G$  is negative ( $< 0$ ), the process is spontaneous.
- (ii) If  $\Delta G$  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  $\Delta H$ . 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 5.4 summarises the effect of temperature on spontaneity of reactions.

#### (d) Entropy and Second Law of Thermodynamics

We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

#### (e) Absolute Entropy and Third Law of Thermodynamics

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. **The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.**

This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can

be done by summing  $\frac{q_{rev}}{T}$  increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

### 5.7 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



$$\Delta_r G = 0$$

Gibbs energy for a reaction in which all reactants and products are in standard state,  $\Delta_r G^\ominus$  is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

$$\text{or } \Delta_r G^\ominus = -RT \ln K$$

$$\text{or } \Delta_r G^\ominus = -2.303 RT \log K \quad (5.23)$$

We also know that

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K \quad (5.24)$$

For strongly endothermic reactions, the value of  $\Delta_r H^\ominus$  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,  $\Delta_r H^\ominus$  is large and negative, and  $\Delta_r G^\ominus$  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.  $\Delta_r G^\ominus$  also depends upon  $\Delta_r S^\ominus$ , 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  $\Delta_r S^\ominus$  is positive or negative.

Using equation (5.24),

**Table 5.4 Effect of Temperature on Spontaneity of Reactions**

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
-	+	-	Reaction spontaneous at all temperatures
-	-	- (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.

- (i) It is possible to obtain an estimate of  $\Delta G^\ominus$  from the measurement of  $\Delta H^\ominus$  and  $\Delta S^\ominus$ , and then calculate  $K$  at any temperature for economic yields of the products.
- (ii) If  $K$  is measured directly in the laboratory, value of  $\Delta G^\ominus$  at any other temperature can be calculated.

Using equation (5.24),

### Problem 5.12

Calculate  $\Delta_r G^\ominus$  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  $2.47 \times 10^{-29}$ .

#### Solution

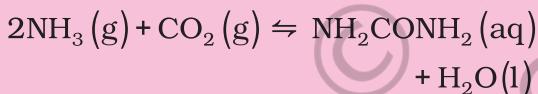
We know  $\Delta_r G^\ominus = -2.303 RT \log K_p$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\begin{aligned}\text{Therefore, } \Delta_r G^\ominus &= \\ &-2.303 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times (298 \text{ K}) (\log 2.47 \times 10^{-29})\end{aligned}$$

$$\begin{aligned}&= 163000 \text{ J mol}^{-1} \\ &= 163 \text{ kJ mol}^{-1}.\end{aligned}$$

### Problem 5.13

Find out the value of equilibrium constant for the following reaction at 298 K.



Standard Gibbs energy change,  $\Delta_r G^\ominus$  at the given temperature is  $-13.6 \text{ kJ mol}^{-1}$ .

#### Solution

$$\text{We know, } \log K = \frac{-\Delta_r G^\ominus}{2.303 RT}$$

$$\begin{aligned}&= \frac{(-13.6 \times 10^3 \text{ J mol}^{-1})}{2.303(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(298\text{K})} \\ &= 2.38\end{aligned}$$

Hence  $K = \text{antilog } 2.38 = 2.4 \times 10^2$ .

### Problem 5.14

At  $60^\circ\text{C}$ , dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

#### Solution



If  $\text{N}_2\text{O}_4$  is 50% dissociated, the mole fraction of both the substances is given by

$$x_{\text{N}_2\text{O}_4} = \frac{1 - 0.5}{1 + 0.5}; x_{\text{NO}_2} = \frac{2 \times 0.5}{1 + 0.5}$$

$$\begin{aligned}p_{\text{N}_2\text{O}_4} &= \frac{0.5}{1.5} \times 1 \text{ atm}, p_{\text{NO}_2} = \\ &\quad \frac{1}{1.5} \times 1 \text{ atm}.\end{aligned}$$

The equilibrium constant  $K_p$  is given by

$$K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{1.5}{(1.5)^2 (0.5)}$$

$$= 1.33 \text{ atm.}$$

Since

$$\Delta_r G^\ominus = -RT \ln K_p$$

$$\begin{aligned}\Delta_r G^\ominus &= (-8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (333 \text{ K}) \\ &\quad \times (2.303) \times (0.1239) \\ &= -763.8 \text{ kJ mol}^{-1}\end{aligned}$$

## 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  $\Delta U = q + w$ .  $\Delta U$ , 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

$$\Delta_r H = \sum_f (a_i \Delta_f H_{\text{products}}) - \sum_i (b_i \Delta_f H_{\text{reactions}})$$

and in gaseous state by

$$\Delta_r H^\ominus = \Sigma \text{ bond enthalpies of the reactants} - \Sigma \text{ bond enthalpies of the products}$$

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

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ for a reversible process. } \frac{q_{\text{rev}}}{T} \text{ is independent of path.}$$

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,  $\Delta G_{\text{sys}} < 0$  and at equilibrium,  $\Delta G_{\text{sys}} = 0$ .

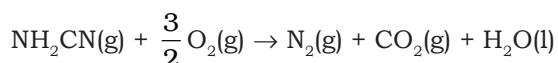
Standard Gibbs energy change is related to equilibrium constant by

$$\Delta_r G^\ominus = -RT \ln K.$$

$K$  can be calculated from this equation, if we know  $\Delta_r G^\ominus$  which can be found from  $\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$ . 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

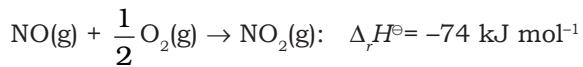
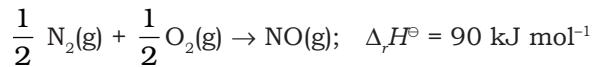
- 5.1 Choose the correct answer. A thermodynamic state function is a quantity  
 (i) used to determine heat changes  
 (ii) whose value is independent of path  
 (iii) used to determine pressure volume work  
 (iv) whose value depends on temperature only.
- 5.2 For the process to occur under adiabatic conditions, the correct condition is:  
 (i)  $\Delta T = 0$   
 (ii)  $\Delta p = 0$   
 (iii)  $q = 0$   
 (iv)  $w = 0$
- 5.3 The enthalpies of all elements in their standard states are:  
 (i) unity  
 (ii) zero  
 (iii)  $< 0$   
 (iv) different for each element
- 5.4  $\Delta U^\ominus$  of combustion of methane is  $-X \text{ kJ mol}^{-1}$ . The value of  $\Delta H^\ominus$  is  
 (i)  $= \Delta U^\ominus$   
 (ii)  $> \Delta U^\ominus$   
 (iii)  $< \Delta U^\ominus$   
 (iv)  $= 0$
- 5.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are,  $-890.3 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$ , and  $-285.8 \text{ kJ mol}^{-1}$  respectively. Enthalpy of formation of  $\text{CH}_4(\text{g})$  will be  
 (i)  $-74.8 \text{ kJ mol}^{-1}$       (ii)  $-52.27 \text{ kJ mol}^{-1}$   
 (iii)  $+74.8 \text{ kJ mol}^{-1}$       (iv)  $+52.26 \text{ kJ mol}^{-1}$ .
- 5.6 A reaction,  $A + B \rightarrow C + D + q$  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
- 5.7 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?
- 5.8 The reaction of cyanamide,  $\text{NH}_2\text{CN}$  (s), with dioxygen was carried out in a bomb calorimeter, and  $\Delta U$  was found to be  $-742.7 \text{ kJ mol}^{-1}$  at 298 K. Calculate enthalpy change for the reaction at 298 K.



- 5.9 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  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ .
- 5.10 Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C.  $\Delta_{fus}H = 6.03 \text{ kJ mol}^{-1}$  at 0°C.  
 $C_p [\text{H}_2\text{O(l)}] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$   
 $C_p [\text{H}_2\text{O(s)}] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$
- 5.11 Enthalpy of combustion of carbon to  $\text{CO}_2$  is  $-393.5 \text{ kJ mol}^{-1}$ . Calculate the heat released upon formation of 35.2 g of  $\text{CO}_2$  from carbon and dioxygen gas.
- 5.12 Enthalpies of formation of  $\text{CO(g)}$ ,  $\text{CO}_2(\text{g})$ ,  $\text{N}_2\text{O(g)}$  and  $\text{N}_2\text{O}_4(\text{g})$  are  $-110$ ,  $-393$ ,  $81$  and  $9.7 \text{ kJ mol}^{-1}$  respectively. Find the value of  $\Delta_fH$  for the reaction:  
 $\text{N}_2\text{O}_4(\text{g}) + 3\text{CO(g)} \rightarrow \text{N}_2\text{O(g)} + 3\text{CO}_2(\text{g})$
- 5.13 Given  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) ; \Delta_fH^\ominus = -92.4 \text{ kJ mol}^{-1}$   
What is the standard enthalpy of formation of  $\text{NH}_3$  gas?
- 5.14 Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH(l)}$  from the following data:  
 $\text{CH}_3\text{OH(l)} + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(l)} ; \Delta_fH^\ominus = -726 \text{ kJ mol}^{-1}$   
 $\text{C(graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) ; \Delta_cH^\ominus = -393 \text{ kJ mol}^{-1}$   
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)} ; \Delta_fH^\ominus = -286 \text{ kJ mol}^{-1}$ .
- 5.15 Calculate the enthalpy change for the process  
 $\text{CCl}_4(\text{g}) \rightarrow \text{C(g)} + 4\text{Cl(g)}$   
and calculate bond enthalpy of C – Cl in  $\text{CCl}_4(\text{g})$ .  
 $\Delta_{vap}H^\ominus(\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}$ .  
 $\Delta_fH^\ominus(\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$ .  
 $\Delta_aH^\ominus(\text{C}) = 715.0 \text{ kJ mol}^{-1}$ , where  $\Delta_aH^\ominus$  is enthalpy of atomisation  
 $\Delta_aH^\ominus(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$
- 5.16 For an isolated system,  $\Delta U = 0$ , what will be  $\Delta S$  ?
- 5.17 For the reaction at 298 K,  
 $2\text{A} + \text{B} \rightarrow \text{C}$   
 $\Delta H = 400 \text{ kJ mol}^{-1}$  and  $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$   
At what temperature will the reaction become spontaneous considering  $\Delta H$  and  $\Delta S$  to be constant over the temperature range.
- 5.18 For the reaction,  
 $2\text{Cl(g)} \rightarrow \text{Cl}_2(\text{g})$ , what are the signs of  $\Delta H$  and  $\Delta S$  ?
- 5.19 For the reaction  
 $2\text{A(g)} + \text{B(g)} \rightarrow 2\text{D(g)}$   
 $\Delta U^\ominus = -10.5 \text{ kJ}$  and  $\Delta S^\ominus = -44.1 \text{ JK}^{-1}$ .  
Calculate  $\Delta G^\ominus$  for the reaction, and predict whether the reaction may occur spontaneously.

- 5.20 The equilibrium constant for a reaction is 10. What will be the value of  $\Delta G^\ominus$ ?  
 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $T = 300 \text{ K}$ .

- 5.21 Comment on the thermodynamic stability of  $\text{NO(g)}$ , given



- 5.22 Calculate the entropy change in surroundings when 1.00 mol of  $\text{H}_2\text{O(l)}$  is formed under standard conditions.  $\Delta_f H^\ominus = -286 \text{ kJ mol}^{-1}$ .



## UNIT 6

11082CH07

# EQUILIBRIUM

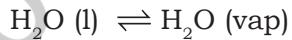
## Objectives

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 dual 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



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 to reach the state of **chemical equilibrium**, these 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**.

## 6.1 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.,



### 6.1.1 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

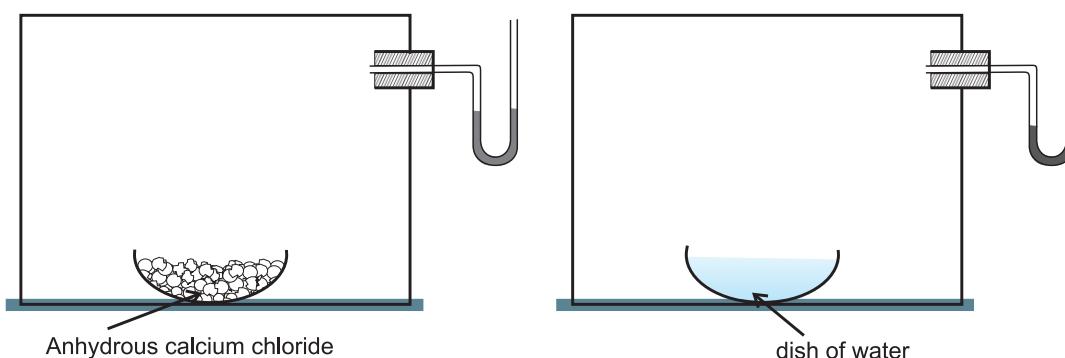
characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere 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.

### 6.1.2 Liquid-Vapour Equilibrium

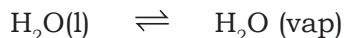
This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one 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. 6.1). 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 molecules into the gaseous phase inside the box. The rate of evaporation is constant.



**Fig. 6.1** Measuring equilibrium vapour pressure of water at a constant temperature

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.,

$$\text{rate of evaporation} = \text{rate of condensation}$$



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.

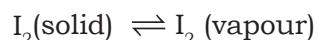
If we expose three watch glasses containing separately 1mL each of acetone, ethyl alcohol, and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation 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.

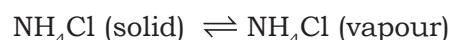
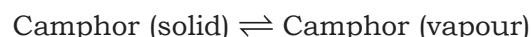
Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid. Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases.

### 6.1.3 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,



Other examples showing this kind of equilibrium are,



### 6.1.4 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 exists between the solute molecules in the solid state and in the solution:

$\text{Sugar (solution)} \rightleftharpoons \text{Sugar (solid)}$ , 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.,



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  $\rightleftharpoons$  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  $\rightleftharpoons$  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 6.1

**Table 6.1 Some Features of Physical Equilibria**

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (g)}$	$p_{\text{H}_2\text{O}}$ constant at given temperature
Solid $\rightleftharpoons$ Liquid $\text{H}_2\text{O (s)} \rightleftharpoons \text{H}_2\text{O (l)}$	Melting point is fixed at constant pressure
Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature
Gas(g) $\rightleftharpoons$ Gas (aq) $\text{CO}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(aq)}$	$[\text{gas(aq)}]/[\text{gas(g)}]$ is constant at a given temperature $[\text{CO}_2\text{(aq)}]/[\text{CO}_2\text{(g)}]$ is constant at a given temperature

### 6.1.5 General Characteristics of Equilibria Involving Physical Processes

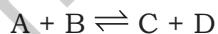
For the physical processes discussed above, following characteristics are common to the system at equilibrium:

- Equilibrium is possible only in a closed system at a given temperature.
- Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- All measurable properties of the system remain constant.
- When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 6.1 lists such quantities.
- The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

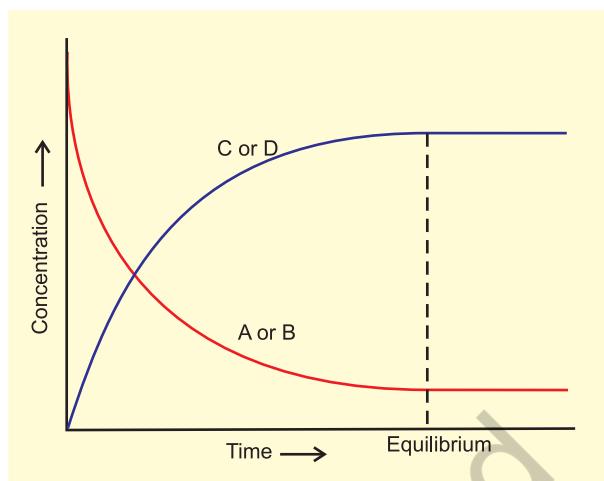
## 6.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

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,



With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 6.2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction,



**Fig. 6.2** Attainment of chemical equilibrium.

Eventually, the two reactions occur at the same rate and the system reaches a state of 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. 6.4 (page 174) 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

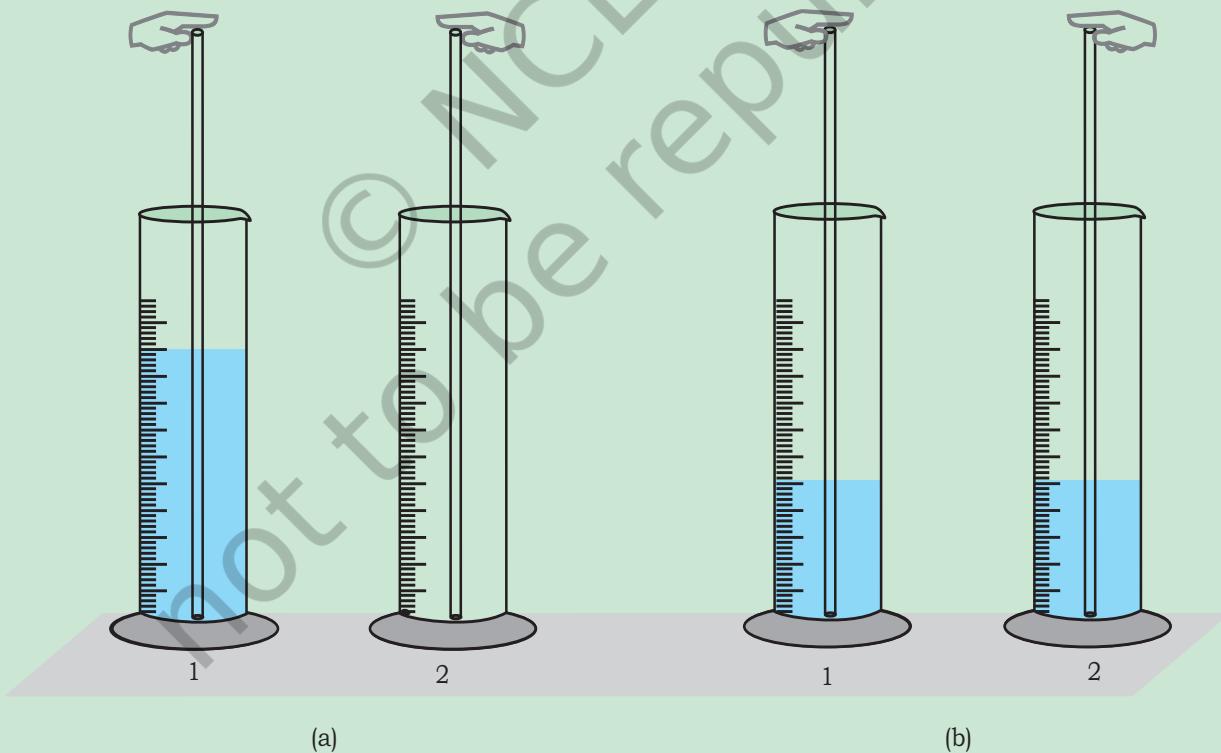
### Dynamic Equilibrium – A Student's Activity

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.

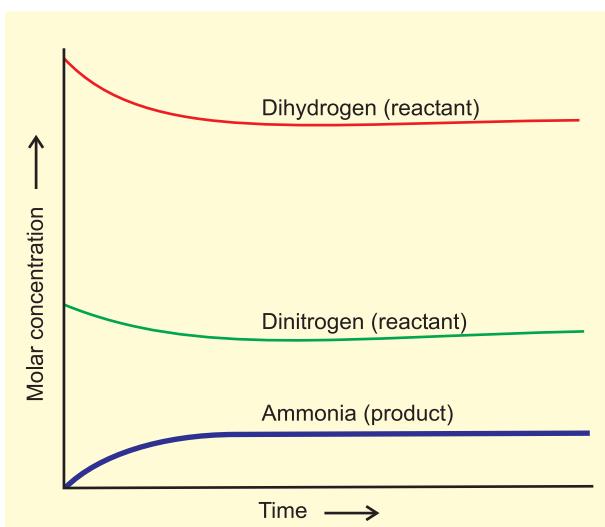
Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and 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 2<sup>nd</sup> 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.

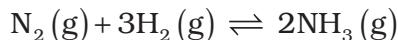
If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process 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.6.3** Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.



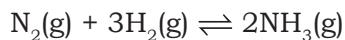
**Fig. 6.4** Depiction of equilibrium for the reaction



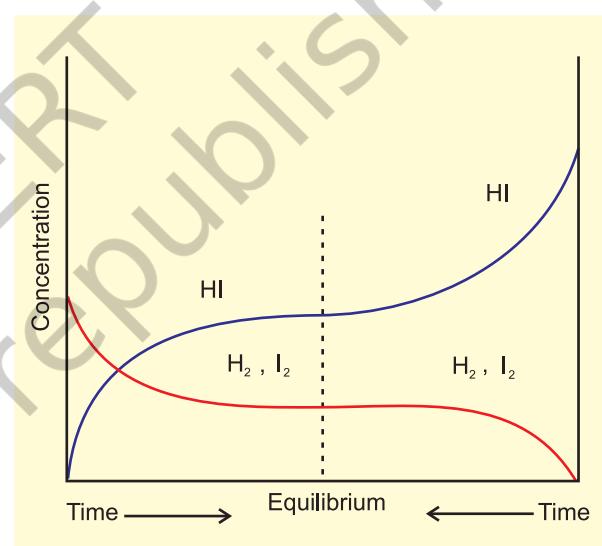
equilibrium is attained, these two mixtures ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{D}_2$ ,  $\text{N}_2$ ,  $\text{ND}_3$ ) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia ( $\text{NH}_3$ ,  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$  and  $\text{ND}_3$ ) and dihydrogen and its deuterated forms ( $\text{H}_2$ ,  $\text{HD}$  and  $\text{D}_2$ ) 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,  $\text{H}_2(\text{g})$  and  $\text{N}_2(\text{g})$  and get  $\text{NH}_3(\text{g})$  or by taking  $\text{NH}_3(\text{g})$  and decomposing it into  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$ .



Similarly let us consider the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ . If we start with equal initial concentration of  $\text{H}_2$  and  $\text{I}_2$ , the reaction proceeds in the forward direction and the concentration of  $\text{H}_2$  and  $\text{I}_2$  decreases while that of  $\text{HI}$  increases, until all of these become constant at equilibrium (Fig. 6.5). We can also start with  $\text{HI}$  alone and make the reaction to proceed in the reverse direction; the concentration of  $\text{HI}$  will decrease and concentration of  $\text{H}_2$  and  $\text{I}_2$  will increase until they all become constant when equilibrium is reached (Fig. 6.5). 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. 6.5** Chemical equilibrium in the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  can be attained from either direction

### 6.3 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<sub>2</sub>, NH<sub>3</sub>, CaO etc.

To answer these questions, let us consider a general reversible reaction:

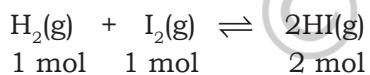


where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximilian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following **equilibrium equation**,

$$K_c = \frac{[C][D]}{[A][B]} \quad (6.1)$$

(6.1) where K<sub>c</sub> 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<sub>2</sub> and I<sub>2</sub> carried out in a sealed vessel at 731K.



Six sets of experiments with varying initial conditions were performed, starting with only gaseous H<sub>2</sub> and I<sub>2</sub> 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<sub>2</sub> and / or I<sub>2</sub>, 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 6.2.

It is evident from the experiments 1, 2, 3 and 4 that number of moles of dihydrogen reacted = number of moles of iodine reacted =  $\frac{1}{2}$  (number of moles of HI formed). Also, experiments 5 and 6 indicate that,

$$[\text{H}_2(\text{g})]_{\text{eq}} = [\text{I}_2(\text{g})]_{\text{eq}}$$

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,

$$[\text{HI}(\text{g})]_{\text{eq}} / [\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}$$

It can be seen from Table 6.3 that if we put the equilibrium concentrations of the reactants and products, the above expression

**Table 6.2 Initial and Equilibrium Concentrations of H<sub>2</sub>, I<sub>2</sub> and HI**

<b>Experiment number</b>	<b>Initial concentration/mol L<sup>-1</sup></b>			<b>Equilibrium concentration/mol L<sup>-1</sup></b>		
	[ H <sub>2</sub> (g) ]	[ I <sub>2</sub> (g) ]	[ HI(g) ]	[ H <sub>2</sub> (g) ]	[ I <sub>2</sub> (g) ]	[ HI(g) ]
1	$2.4 \times 10^{-2}$	$1.38 \times 10^{-2}$	0	$1.14 \times 10^{-2}$	$0.12 \times 10^{-2}$	$2.52 \times 10^{-2}$
2	$2.4 \times 10^{-2}$	$1.68 \times 10^{-2}$	0	$0.92 \times 10^{-2}$	$0.20 \times 10^{-2}$	$2.96 \times 10^{-2}$
3	$2.44 \times 10^{-2}$	$1.98 \times 10^{-2}$	0	$0.77 \times 10^{-2}$	$0.31 \times 10^{-2}$	$3.34 \times 10^{-2}$
4	$2.46 \times 10^{-2}$	$1.76 \times 10^{-2}$	0	$0.92 \times 10^{-2}$	$0.22 \times 10^{-2}$	$3.08 \times 10^{-2}$
5	0	0	$3.04 \times 10^{-2}$	$0.345 \times 10^{-2}$	$0.345 \times 10^{-2}$	$2.35 \times 10^{-2}$
6	0	0	$7.58 \times 10^{-2}$	$0.86 \times 10^{-2}$	$0.86 \times 10^{-2}$	$5.86 \times 10^{-2}$

**Table 6.3 Expression Involving the Equilibrium Concentration of Reactants**



Experiments Number	$\frac{[\text{HI}(\text{g})]_{\text{eq}}}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$	$\frac{[\text{HI}(\text{g})]_{\text{eq}}^2}{[\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}}$
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,

$$[\text{HI}(\text{g})]_{\text{eq}}^2 / [\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}}$$

we find that this expression gives constant value (as shown in Table 6.3) 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  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , following equation 6.1, the equilibrium constant  $K_c$  is written as,

$$K_c = [\text{HI}(\text{g})]_{\text{eq}}^2 / [\text{H}_2(\text{g})]_{\text{eq}} [\text{I}_2(\text{g})]_{\text{eq}} \quad (6.2)$$

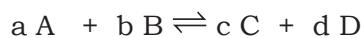
Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for  $K_c$  are equilibrium values. We, therefore, write,

$$K_c = [\text{HI}(\text{g})]^2 / [\text{H}_2(\text{g})] [\text{I}_2(\text{g})] \quad (6.3)$$

The subscript 'c' indicates that  $K_c$  is expressed in concentrations of  $\text{mol L}^{-1}$ .

**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,

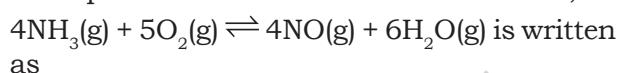


is expressed as,

$$K_c = [\text{C}]^c [\text{D}]^d / [\text{A}]^a [\text{B}]^b \quad (6.4)$$

where  $[\text{A}]$ ,  $[\text{B}]$ ,  $[\text{C}]$  and  $[\text{D}]$  are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,



$$K_c = [\text{NO}]^4 [\text{H}_2\text{O}]^6 / [\text{NH}_3]^4 [\text{O}_2]^5$$

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,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  (6.5)

$$\text{as, } K_c = [\text{HI}]^2 / [\text{H}_2] [\text{I}_2] = x \quad (6.6)$$

The equilibrium constant for the reverse reaction,  $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ , at the same temperature is,

$$K_c' = [\text{H}_2] [\text{I}_2] / [\text{HI}]^2 = 1/x = 1/K_c \quad (6.7)$$

$$\text{Thus, } K_c' = 1/K_c \quad (6.8)$$

**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 (6.5) is written as,

$$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{g}) \rightleftharpoons \text{HI}(\text{g}) \quad (6.9)$$

the equilibrium constant for the above reaction is given by

$$\begin{aligned} K_c'' &= [\text{HI}] / [\text{H}_2]^{1/2} [\text{I}_2]^{1/2} = \{[\text{HI}]^2 / [\text{H}_2][\text{I}_2]\}^{1/2} \\ &= x^{1/2} = K_c^{1/2} \end{aligned} \quad (6.10)$$

On multiplying the equation (6.5) by n, we get



Therefore, equilibrium constant for the reaction is equal to  $K_c^n$ . These findings are summarised in Table 6.4. It should be noted that because the equilibrium constants  $K_c$  and  $K_c^n$  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 6.4 Relations between Equilibrium Constants for a General Reaction and its Multiples.**

Chemical equation	Equilibrium constant
$a A + b B \rightleftharpoons c C + d D$	$K_c$
$c C + d D \rightleftharpoons a A + b B$	$K'_c = (1/K_c)$
$na A + nb B \rightleftharpoons ncC + ndD$	$K''_c = (K_c^n)$

### Problem 6.1

The following concentrations were obtained for the formation of  $NH_3$  from  $N_2$  and  $H_2$  at equilibrium at 500K.  $[N_2] = 1.5 \times 10^{-2} M$ ,  $[H_2] = 3.0 \times 10^{-2} M$  and  $[NH_3] = 1.2 \times 10^{-2} M$ . Calculate equilibrium constant.

#### Solution

The equilibrium constant for the reaction,  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  can be written as,

$$\begin{aligned} K_c &= \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \\ &= \frac{(1.2 \times 10^{-2})^2}{(1.5 \times 10^{-2})(3.0 \times 10^{-2})^3} \\ &= 0.355 \times 10^3 = 3.55 \times 10^2 \end{aligned}$$

### Problem 6.2

At equilibrium, the concentrations of  $N_2 = 3.0 \times 10^{-3} M$ ,  $O_2 = 4.2 \times 10^{-3} M$  and  $NO = 2.8 \times 10^{-3} M$  in a sealed vessel at 800K. What will be  $K_c$  for the reaction



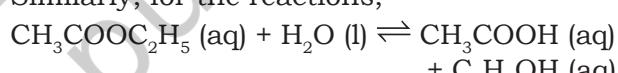
#### Solution

For the reaction equilibrium constant,  $K_c$  can be written as,

$$\begin{aligned} K_c &= \frac{[NO]^2}{[N_2][O_2]} \\ &= \frac{(2.8 \times 10^{-3} M)^2}{(3.0 \times 10^{-3} M)(4.2 \times 10^{-3} M)} \\ &= 0.622 \end{aligned}$$

## 6.4 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction,  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ , reactants and products are in the homogeneous phase. Similarly, for the reactions,



and,  $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq})$  all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

### 6.4.1 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,  
 $pV = nRT$

$$\Rightarrow p = \frac{n}{V} RT$$

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<sup>3</sup>

If concentration  $c$ , is in mol/L or mol/dm<sup>3</sup>, and  $p$  is in bar then

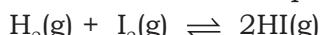
$$p = cRT$$

We can also write  $p = [\text{gas}]RT$ .

Here,  $R = 0.0831 \text{ bar litre/mol K}$

At constant temperature, the pressure of the gas is proportional to its concentration i.e.,  $p \propto [\text{gas}]$

For reaction in equilibrium



We can write either

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

$$\text{or } K_c = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} \quad (6.12)$$

Further, since  $p_{\text{HI}} = [\text{HI}(\text{g})]RT$

$$p_{\text{I}_2} = [\text{I}_2(\text{g})]RT$$

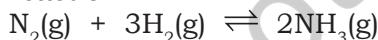
$$p_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

Therefore,

$$K_p = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{[\text{HI}(\text{g})]^2[RT]^2}{[\text{H}_2(\text{g})]RT \cdot [\text{I}_2(\text{g})]RT}$$

$$= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c \quad (6.13)$$

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



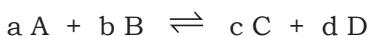
$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3}$$

$$= \frac{[\text{NH}_3(\text{g})]^2[RT]^2}{[\text{N}_2(\text{g})]RT \cdot [\text{H}_2(\text{g})]^3(RT)^3}$$

$$= \frac{[\text{NH}_3(\text{g})]^2[RT]^{-2}}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = K_c (RT)^{-2}$$

$$\text{or } K_p = K_c (RT)^{-2} \quad (6.14)$$

Similarly, for a general reaction



$$K_p = \frac{(p_{\text{C}}^c)(p_{\text{D}}^d)}{(p_{\text{A}}^a)(p_{\text{B}}^b)} = \frac{[\text{C}]^c[\text{D}]^d(RT)^{(c+d)}}{[\text{A}]^a[\text{B}]^b(RT)^{(a+b)}}$$

$$= \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}(RT)^{(c+d)-(a+b)}$$

$$= \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}(RT)^{\Delta n} = K_c (RT)^{\Delta n} \quad (6.15)$$

where  $\Delta n$  = (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 because standard state for pressure is 1 bar. We know from Unit 1 that:

1 pascal, Pa = 1 N m<sup>-2</sup>, and 1 bar =  $10^5$  Pa

$K_p$  values for a few selected reactions at different temperatures are given in Table 6.5

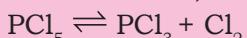
**Table 6.5 Equilibrium Constants,  $K_p$  for a Few Selected Reactions**

Reaction	Temperature/K	$K_p$
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	298	$6.8 \times 10^5$
	400	41
	500	$3.6 \times 10^{-2}$
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	298	$4.0 \times 10^{24}$
	500	$2.5 \times 10^{10}$
	700	$3.0 \times 10^4$
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	298	0.98
	400	47.9
	500	1700

### Problem 6.3

$\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  are at equilibrium at 500 K and having concentration 1.59 M  $\text{PCl}_3$ , 1.59 M  $\text{Cl}_2$  and 1.41 M  $\text{PCl}_5$ .

Calculate  $K_c$  for the reaction,



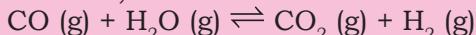
### Solution

The equilibrium constant  $K_c$  for the above reaction can be written as,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(1.59)^2}{(1.41)} = 1.79$$

### Problem 6.4

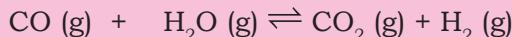
The value of  $K_c = 4.24$  at 800K for the reaction,



Calculate equilibrium concentrations of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  at 800 K, if only  $\text{CO}$  and  $\text{H}_2\text{O}$  are present initially at concentrations of 0.10M each.

### Solution

For the reaction,



Initial concentration:

$$0.1\text{M} \quad 0.1\text{M} \quad 0 \quad 0$$

Let  $x$  mole per litre of each of the product be formed.

At equilibrium:

$$(0.1-x)\text{M} \quad (0.1-x)\text{M} \quad x\text{M} \quad x\text{M}$$

where  $x$  is the amount of  $\text{CO}_2$  and  $\text{H}_2$  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  $ax^2 + bx + c = 0$ ,

$$x = \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$x = 0.848 \pm \sqrt{(0.848)^2 - 4(3.24)(0.0424)} / (3.24 \times 2)$$

$$x = (0.848 \pm 0.4118) / 6.48$$

$$x_1 = (0.848 - 0.4118) / 6.48 = 0.067$$

$$x_2 = (0.848 + 0.4118) / 6.48 = 0.194$$

the value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.

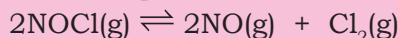
Hence the equilibrium concentrations are,

$$[\text{CO}_2] = [\text{H}_2] = x = 0.067 \text{ M}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.1 - 0.067 = 0.033 \text{ M}$$

### Problem 6.5

For the equilibrium,



the value of the equilibrium constant,  $K_c$  is  $3.75 \times 10^{-6}$  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,

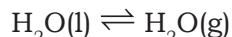
$$\Delta n = (2+1) - 2 = 1$$

$$K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)$$

$$K_p = 0.033$$

## 6.5 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.



In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,  $\text{Ca(OH)}_2 (\text{s}) + (\text{aq}) \rightleftharpoons \text{Ca}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq})$  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  $[\text{X(s)}]$  and  $[\text{X(l)}]$  are constant, whatever the amount of 'X' is taken. Contrary to this,  $[\text{X(g)}]$  and  $[\text{X(aq)}]$  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.



On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{[\text{CaO}(\text{s})][\text{CO}_2(\text{g})]}{[\text{CaCO}_3(\text{s})]}$$

Since  $[\text{CaCO}_3(\text{s})]$  and  $[\text{CaO}(\text{s})]$  are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K' = [\text{CO}_2(\text{g})] \quad (6.17)$$

$$\text{or } K_p = P_{\text{CO}_2} \quad (6.18)$$

### 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,

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}$ ,  $K_c$  and  $K_p$  have no unit.

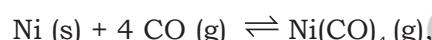
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ,  $K_c$  has unit mol/L and  $K_p$  has unit bar

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 1 bar. 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  $\text{CO}_2$  in equilibrium with  $\text{CaO}(\text{s})$  and  $\text{CaCO}_3(\text{s})$ . Experimentally it has been found that at 1100 K, the pressure of  $\text{CO}_2$  in equilibrium with  $\text{CaCO}_3(\text{s})$  and  $\text{CaO}(\text{s})$ , is  $2.0 \times 10^5$  Pa. Therefore, equilibrium constant at 1100 K for the above reaction is:

$$K_p = P_{\text{CO}_2} = 2 \times 10^5 \text{ Pa} / 10^5 \text{ Pa} = 2.00$$

Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),



the equilibrium constant is written as

$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$

It must be remembered that for the existence of heterogeneous equilibrium pure solids or liquids must also be present (however small the amount may be) at equilibrium, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction,  
 $\text{Ag}_2\text{O}(\text{s}) + 2\text{HNO}_3(\text{aq}) \rightleftharpoons 2\text{AgNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$K_c = \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2}$$

### Problem 6.6

The value of  $K_p$  for the reaction,  $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$  is 3.0 at 1000 K. If initially  $P_{\text{CO}_2} = 0.48$  bar and  $P_{\text{CO}} = 0$  bar and pure graphite is present, calculate the equilibrium partial pressures of CO and  $\text{CO}_2$ .

#### Solution

For the reaction,

let 'x' be the decrease in pressure of  $\text{CO}_2$ , then



Initial		
pressure: 0.48 bar		0

At equilibrium:

$$(0.48 - x)\text{bar} \quad 2x \text{ bar}$$

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

$$K_p = (2x)^2 / (0.48 - x) = 3$$

$$4x^2 = 3(0.48 - x)$$

$$4x^2 = 1.44 - x$$

$$4x^2 + 3x - 1.44 = 0$$

$$a = 4, b = 3, c = -1.44$$

$$x = \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$= [-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}]/2 \times 4$$

$$= (-3 \pm 5.66)/8$$

$= (-3 + 5.66)/8$  (as value of  $x$  cannot be negative hence we neglect that value)

$$x = 2.66/8 = 0.33$$

The equilibrium partial pressures are,

$$p_{CO_2} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

$$p_{CO} = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

## 6.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows:

1. Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at 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.

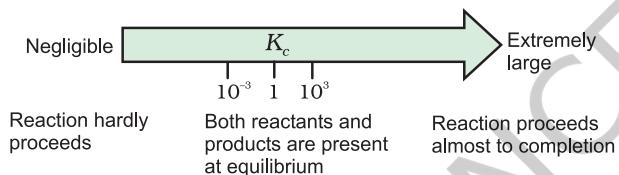
### 6.6.1 Predicting the Extent of a Reaction

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 constant 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,  $K_c = 2.4 \times 10^{47}$ .
  - (b)  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$  at 300 K has  $K_c = 4.0 \times 10^{31}$ .
  - (c)  $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$  at 300 K,  $K_c = 5.4 \times 10^{18}$
- 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  $\text{H}_2\text{O}$  into  $\text{H}_2$  and  $\text{O}_2$  at 500 K has a very small equilibrium constant,  $K_c = 4.1 \times 10^{-48}$
- (b)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ , at 298 K has  $K_c = 4.8 \times 10^{-31}$ .
- 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  $\text{H}_2$  with  $\text{I}_2$  to give  $\text{HI}$ ,  $K_c = 57.0$  at 700 K.
- (b) Also, gas phase decomposition of  $\text{N}_2\text{O}_4$  to  $\text{NO}_2$  is another reaction with a value of  $K_c = 4.64 \times 10^{-3}$  at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ .
- These generalisations are illustrated in Fig. 6.6



**Fig. 6.6** Dependence of extent of reaction on  $K_c$

### 6.6.2 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:



$$Q_c = [\text{C}]^c[\text{D}]^d / [\text{A}]^a[\text{B}]^b \quad (6.20)$$

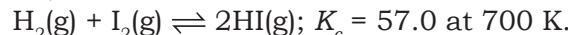
Then,

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  $\text{H}_2$  with  $\text{I}_2$ ,



Suppose we have molar concentrations  $[\text{H}_2]_t = 0.10 \text{ M}$ ,  $[\text{I}_2]_t = 0.20 \text{ M}$  and  $[\text{HI}]_t = 0.40 \text{ M}$ . (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

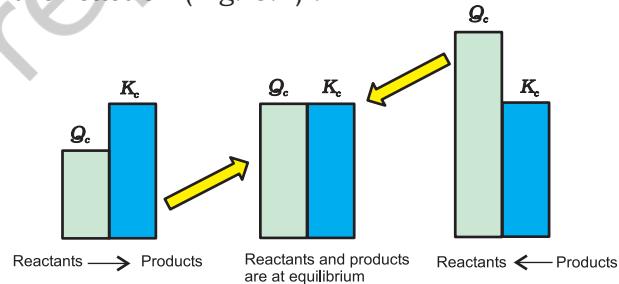
Thus, the reaction quotient,  $Q_c$  at this stage of the reaction is given by,

$$Q_c = [\text{HI}]_t^2 / [\text{H}_2]_t [\text{I}_2]_t = (0.40)^2 / (0.10) \times (0.20) \\ = 8.0$$

Now, in this case,  $Q_c$  (8.0) does not equal  $K_c$  (57.0), so the mixture of  $\text{H}_2(\text{g})$ ,  $\text{I}_2(\text{g})$  and  $\text{HI}(\text{g})$  is not at equilibrium; that is, more  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  will react to form more  $\text{HI}(\text{g})$  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. 6.7) :



**Fig. 6.7** 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 6.7

The value of  $K_c$  for the reaction  $2\text{A} \rightleftharpoons \text{B} + \text{C}$  is  $2 \times 10^{-3}$ . At a given time, the composition of reaction mixture is  $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4} \text{ M}$ . 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  $[A] = [B] = [C] = 3 \times 10^{-4} \text{ M}$   

$$Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$
  
as  $Q_c > K_c$  so the reaction will proceed in the reverse direction.

### 6.6.3 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 6.8

13.8g of  $\text{N}_2\text{O}_4$  was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium



The total pressure at equilibrium was found to be 9.15 bar. Calculate  $K_c$ ,  $K_p$  and partial pressure at equilibrium.

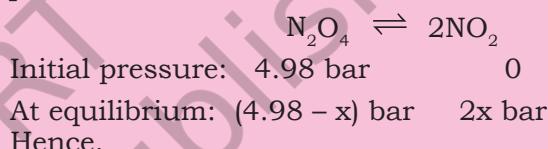
**Solution**

We know  $pV = nRT$   
Total volume ( $V$ ) = 1 L  
Molecular mass of  $\text{N}_2\text{O}_4$  = 92 g  
Number of moles = 13.8g/92 g = 0.15  
of the gas ( $n$ )  
Gas constant ( $R$ ) = 0.083 bar L mol $^{-1}$ K $^{-1}$   
Temperature ( $T$ ) = 400 K  
 $pV = nRT$   

$$p \times 1\text{L} = 0.15 \text{ mol} \times 0.083 \text{ bar L mol}^{-1}\text{K}^{-1}$$
  

$$\times 400 \text{ K}$$

$$p = 4.98 \text{ bar}$$



$$\begin{aligned} p_{\text{total}} \text{ at equilibrium} &= p_{\text{N}_2\text{O}_4} + p_{\text{NO}_2} \\ 9.15 &= (4.98 - x) + 2x \\ 9.15 &= 4.98 + x \\ x &= 9.15 - 4.98 = 4.17 \text{ bar} \end{aligned}$$

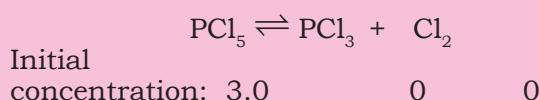
Partial pressures at equilibrium are,

$$\begin{aligned} p_{\text{N}_2\text{O}_4} &= 4.98 - 4.17 = 0.81 \text{ bar} \\ p_{\text{NO}_2} &= 2x = 2 \times 4.17 = 8.34 \text{ bar} \\ K_p &= (p_{\text{NO}_2})^2 / p_{\text{N}_2\text{O}_4} \\ &= (8.34)^2 / 0.81 = 85.87 \end{aligned}$$

$$\begin{aligned} K_p &= K_c(RT)^{\Delta n} \\ 85.87 &= K_c(0.083 \times 400)^1 \\ K_c &= 2.586 = 2.6 \end{aligned}$$

#### Problem 6.9

3.00 mol of  $\text{PCl}_5$  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**

Let  $x$  mol per litre of  $\text{PCl}_5$  be dissociated,  
At equilibrium:

$$\begin{array}{ccc} (3-x) & x & x \\ K_c = [\text{PCl}_3][\text{Cl}_2]/[\text{PCl}_5] \\ 1.8 = x^2 / (3 - x) \\ x^2 + 1.8x - 5.4 = 0 \\ x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]/2 \\ x = [-1.8 \pm \sqrt{3.24 + 21.6}]/2 \\ x = [-1.8 \pm 4.98]/2 \\ x = [-1.8 + 4.98]/2 = 1.59 \\ [\text{PCl}_5] = 3.0 - x = 3 - 1.59 = 1.41 \text{ M} \\ [\text{PCl}_3] = [\text{Cl}_2] = x = 1.59 \text{ M} \end{array}$$

### 6.7 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 5, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy,  $\Delta G$ . If,

- $\Delta G$  is negative, then the reaction is spontaneous and proceeds in the forward direction.
- $\Delta G$  is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative  $\Delta G$ , the products of the forward reaction shall be converted to the reactants.
- $\Delta G$  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:

$$\Delta G = \Delta G^\ominus + RT \ln Q \quad (6.21)$$

where,  $G^\ominus$  is standard Gibbs energy.

At equilibrium, when  $\Delta G = 0$  and  $Q = K_c$ , the equation (6.21) becomes,

$$\Delta G = \Delta G^\ominus + RT \ln K = 0$$

$$\Delta G^\ominus = -RT \ln K \quad (6.22)$$

$$\ln K = -\Delta G^\ominus / RT$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^\ominus / RT} \quad (6.23)$$

Hence, using the equation (6.23), the reaction spontaneity can be interpreted in terms of the value of  $\Delta G^\ominus$ .

- If  $\Delta G^\ominus < 0$ , then  $-\Delta G^\ominus / RT$  is positive, and  $e^{-\Delta G^\ominus / RT} > 1$ , 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  $\Delta G^\ominus > 0$ , then  $-\Delta G^\ominus / RT$  is negative, and  $e^{-\Delta G^\ominus / RT} < 1$ , 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 6.10

The value of  $\Delta G^\ominus$  for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of  $K_c$  at 298 K.

#### Solution

$$\Delta G^\ominus = 13.8 \text{ kJ/mol} = 13.8 \times 10^3 \text{ J/mol}$$

$$\text{Also, } \Delta G^\ominus = -RT \ln K_c$$

$$\text{Hence, } \ln K_c = -13.8 \times 10^3 \text{ J/mol} / (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K})$$

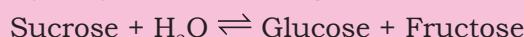
$$\ln K_c = -5.569$$

$$K_c = e^{-5.569}$$

$$K_c = 3.81 \times 10^{-3}$$

#### Problem 6.11

Hydrolysis of sucrose gives,



Equilibrium constant  $K_c$  for the reaction is  $2 \times 10^{13}$  at 300K. Calculate  $\Delta G^\ominus$  at 300K.

#### Solution

$$\Delta G^\ominus = -RT \ln K_c$$

$$\Delta G^\ominus = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times$$

$$300 \text{ K} \times \ln(2 \times 10^{13})$$

$$\Delta G^\ominus = -7.64 \times 10^4 \text{ J mol}^{-1}$$

### 6.8 FACTORS AFFECTING EQUILIBRIA

One of the principal goals of chemical synthesis is to maximise the conversion of the

reactants to products while minimising 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 fertilisers.

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.

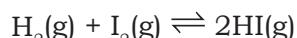
### 6.8.1 Effect of Concentration Change

In general, when equilibrium is disturbed by the addition/removal of any reactant/products, Le Chatelier's principle predicts that:

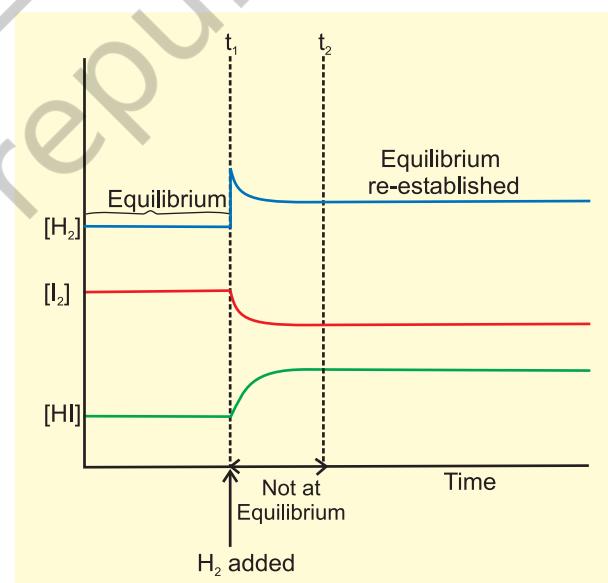
- The concentration stress of an *added* reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a *removed* reactant/product is relieved by net reaction in the direction that *replenishes* the removed substance.  
or in other words,

*"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,



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. 6.8). 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. 6.8** Effect of addition of  $H_2$  on change of concentration for the reactants and products in the reaction,  
 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

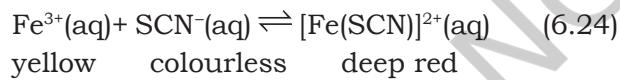
The same point can be explained in terms of the reaction quotient,  $Q_c$ ,

$$Q_c = [HI]^2 / [H_2][I_2]$$

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  $\text{CaCO}_3$ , constant removal of  $\text{CO}_2$  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:



$$K_c = \frac{[\text{Fe}(\text{SCN})]^{2+}(\text{aq})}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^-(\text{aq})]} \quad (6.25)$$

A reddish colour appears on adding two drops of 0.002 M potassium thiocyanate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of  $[\text{Fe}(\text{SCN})]^{2+}$ . 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  $\text{Fe}^{3+}$  or  $\text{SCN}^-$  ions. For example, oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), reacts with  $\text{Fe}^{3+}$  ions to form the stable complex ion  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , thus decreasing the concentration of free  $\text{Fe}^{3+}(\text{aq})$ . In accordance with the Le Chatelier's principle, the concentration stress of removed  $\text{Fe}^{3+}$  is relieved by dissociation of  $[\text{Fe}(\text{SCN})]^{2+}$  to replenish the  $\text{Fe}^{3+}$  ions. Because the

concentration of  $[\text{Fe}(\text{SCN})]^{2+}$  decreases, the intensity of red colour decreases.

Addition of aq.  $\text{HgCl}_2$  also decreases red colour because  $\text{Hg}^{2+}$  reacts with  $\text{SCN}^-$  ions to form stable complex ion  $[\text{Hg}(\text{SCN})_4]^{2-}$ . Removal of free  $\text{SCN}^-$  (aq) shifts the equilibrium in equation (6.24) from right to left to replenish  $\text{SCN}^-$  ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

### **6.8.2 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,



Here, 4 mol of gaseous reactants ( $\text{CO} + 3\text{H}_2$ ) become 2 mol of gaseous products ( $\text{CH}_4 + \text{H}_2\text{O}$ ). 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  $pV = \text{constant}$ ). 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  $[\text{CO}]$ ,  $[\text{H}_2]$ ,  $[\text{CH}_4]$  and  $[\text{H}_2\text{O}]$  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.

$$Q_c = \frac{[\text{CH}_4(\text{g})][\text{H}_2\text{O}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^3}$$

As  $Q_c < K_c$ , the reaction proceeds in the forward direction.

In reaction  $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO(g)}$ , when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

### 6.8.3 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.

### 6.8.4 Effect of Temperature Change

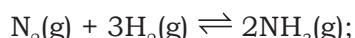
Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient,  $Q_c$  no longer equals the equilibrium constant,  $K_c$ . However, when a change in temperature occurs, the value of equilibrium constant,  $K_c$  is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of  $\Delta H$  for the reaction.

- The equilibrium constant for an exothermic reaction (negative  $\Delta H$ ) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive  $\Delta H$ ) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reactions.

Production of ammonia according to the reaction,



$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

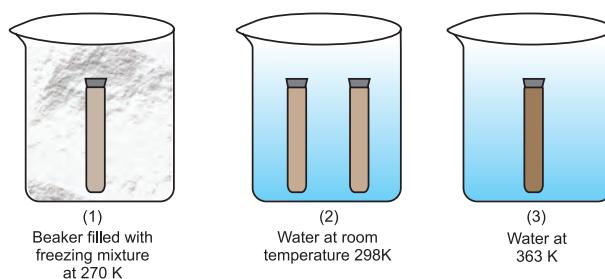
is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

### Effect of Temperature – An experiment

Effect of temperature on equilibrium can be demonstrated by taking  $\text{NO}_2$  gas (brown in colour) which dimerises into  $\text{N}_2\text{O}_4$  gas (colourless).



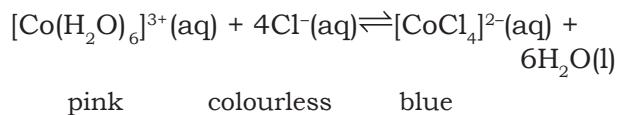
$\text{NO}_2$  gas prepared by addition of Cu turnings to conc.  $\text{HNO}_3$  is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freezing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 6.9). 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  $\text{N}_2\text{O}_4$  is preferred, as reaction is exothermic, and thus, intensity of brown colour due to  $\text{NO}_2$  decreases. While in beaker 3, high temperature favours the reverse reaction of



**Fig. 6.9** Effect of temperature on equilibrium for the reaction,  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

formation of  $\text{NO}_2$  and thus, the brown colour intensifies.

Effect of temperature can also be seen in an endothermic reaction,



At room temperature, the equilibrium mixture is blue due to  $[\text{CoCl}_4]^{2-}$ . When cooled in a freezing mixture, the colour of the mixture turns pink due to  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ .

#### 6.8.5 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  $\text{NH}_3$  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 catalyses the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of  $\text{NH}_3$  is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of  $\text{NH}_3$  can be improved by increasing the pressure.

Optimum conditions of temperature and pressure for the synthesis of  $\text{NH}_3$  using catalyst are around  $500^\circ\text{C}$  and 200 atm.

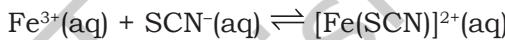
Similarly, in manufacture of sulphuric acid by *contact process*,

$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ ;  $K_c = 1.7 \times 10^{26}$  though the value of  $K$  is suggestive of reaction going to completion, but practically the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is very slow. Thus, platinum or divanadium penta-oxide ( $\text{V}_2\text{O}_5$ ) 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.

#### 6.9 IONIC EQUILIBRIUM IN SOLUTION

Under the effect of change of concentration on the direction of equilibrium, you have incidentally come across with the following equilibrium which involves ions:



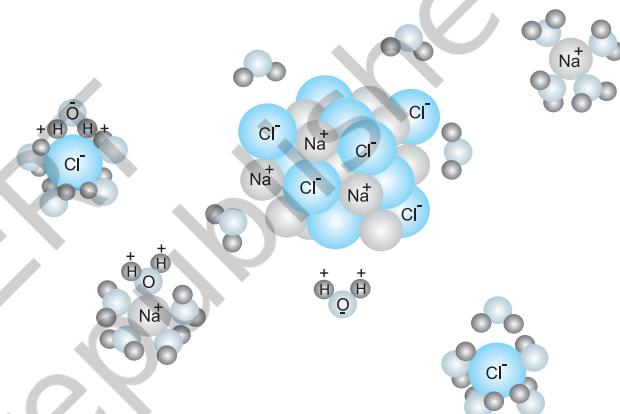
There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the 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 hydronium ions. 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.

### 6.10 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 some 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.6.10). 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.6.10** Dissolution of sodium chloride in water.  $\text{Na}^+$  and  $\text{Cl}^-$  ions are stabilised 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

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.

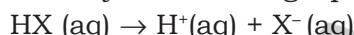


Michael Faraday  
(1791–1867)

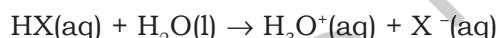
molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used 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.

### 6.10.1 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:



or



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.

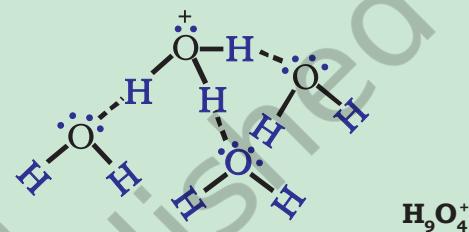
Similarly, a base molecule like  $MOH$  ionizes in aqueous solution according to the equation:



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

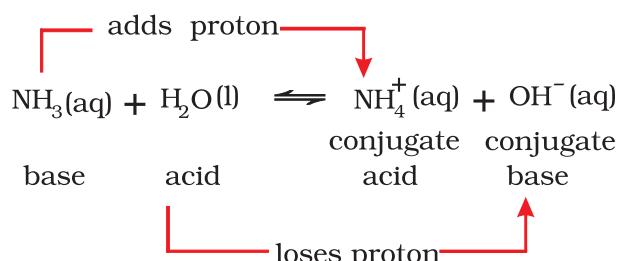
Hydrogen ion by itself is a bare proton with very small size ( $\sim 10^{-15} \text{ m radius}$ ) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving  $H_3O^+$ . This species has been detected in many compounds (e.g.,  $H_3O^+Cl^-$ ) in 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.



### 6.10.2 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:



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



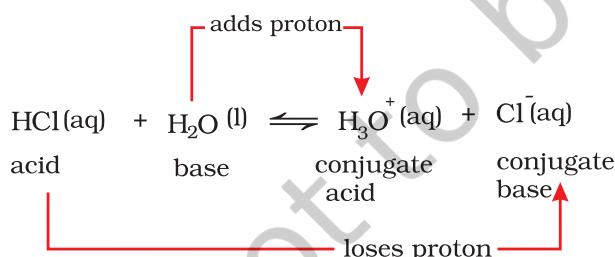
*Svante Arrhenius*  
(1859-1927)

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,  $\text{H}^+$  is transferred from  $\text{NH}_4^+$  to  $\text{OH}^-$ . In this case,  $\text{NH}_4^+$  acts as a Brønsted acid while  $\text{OH}^-$  acted as a Brønsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore,  $\text{OH}^-$  is called the conjugate base of an acid  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$  is called conjugate acid of the base  $\text{NH}_3$ . If Brønsted 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<sub>2</sub>O molecule which acts as a base.



It can be seen in the above equation, that water acts as a base because it accepts the proton. The species  $\text{H}_3\text{O}^+$  is produced when water accepts a proton from HCl. Therefore,  $\text{Cl}^-$  is a conjugate base of HCl and HCl is the conjugate acid of base  $\text{Cl}^-$ . Similarly,  $\text{H}_2\text{O}$  is a conjugate base of an acid  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+$  is a conjugate acid of base  $\text{H}_2\text{O}$ .

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 6.12

What will be the conjugate bases for the following Brönsted acids: HF, H<sub>2</sub>SO<sub>4</sub> and HCO<sub>3</sub><sup>-</sup>?

### Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are:  $\text{F}^-$ ,  $\text{HSO}_4^-$  and  $\text{CO}_3^{2-}$  respectively.

### Problem 6.13

Write the conjugate acids for the following Brønsted bases:  $\text{NH}_3^-$ ,  $\text{NH}_2$  and  $\text{HCOO}^-$ .

### Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are:  $\text{NH}_3^+$ ,  $\text{NH}_4^+$  and  $\text{HCOOH}$  respectively.

**Problem 6.14**

The species:  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$  and  $\text{NH}_3$  can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

### Solution

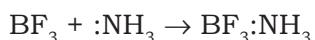
The answer is given in the following Table:

<b>Species</b>	<b>Conjugate acid</b>	<b>Conjugate base</b>
$\text{H}_2\text{O}$	$\text{H}_3\text{O}^+$	$\text{OH}^-$
$\text{HCO}_3^-$	$\text{H}_2\text{CO}_3$	$\text{CO}_3^{2-}$
$\text{HSO}_4^-$	$\text{H}_2\text{SO}_4$	$\text{SO}_4^{2-}$
$\text{NH}_3$	$\text{NH}_4^+$	$\text{NH}_2^-$

### 6.10.3 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  $\text{BF}_3$  with  $\text{NH}_3$ .

$\text{BF}_3$  does not have a proton but still acts as an acid and reacts with  $\text{NH}_3$  by accepting its lone pair of electrons. The reaction can be represented by,



Electron deficient species like  $\text{AlCl}_3$ ,  $\text{Co}^{3+}$ ,  $\text{Mg}^{2+}$ , etc. can act as Lewis acids while species like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$  etc. which can donate a pair of electrons, can act as Lewis bases.

#### Problem 6.15

Classify the following species into Lewis acids and Lewis bases and show how these act as such:

- (a)  $\text{HO}^-$       (b)  $\text{F}^-$       (c)  $\text{H}^+$       (d)  $\text{BCl}_3$

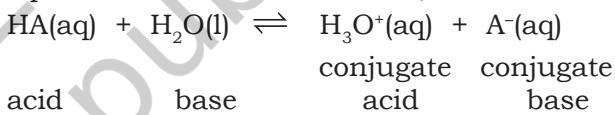
#### Solution

- (a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ( $:\text{OH}^-$ ).
- (b) Fluoride 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)  $\text{BCl}_3$  acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

### 6.11 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

( $\text{HClO}_4$ ), hydrochloric acid ( $\text{HCl}$ ), hydrobromic acid ( $\text{HBr}$ ), hydriodic acid ( $\text{HI}$ ), nitric acid ( $\text{HNO}_3$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) are termed strong because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton ( $\text{H}^+$ ) donors. Similarly, strong bases like lithium hydroxide ( $\text{LiOH}$ ), sodium hydroxide ( $\text{NaOH}$ ), potassium hydroxide ( $\text{KOH}$ ), caesium hydroxide ( $\text{CsOH}$ ) and barium hydroxide ( $\text{Ba(OH)}_2$ ) are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions,  $\text{OH}^-$ . According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  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,

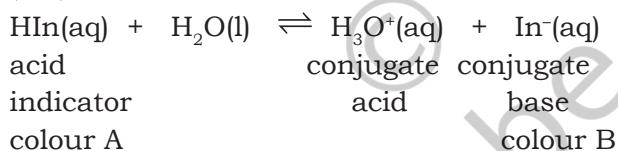


In section 6.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In 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  $\text{H}_3\text{O}^+$  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  $\text{H}_3\text{O}^+$ , then HA will donate protons and not  $\text{H}_3\text{O}^+$ , and the solution will mainly contain  $\text{A}^-$  and  $\text{H}_3\text{O}^+$  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 ( $\text{HClO}_4$ ), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid ( $\text{HNO}_3$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) will give conjugate base ions  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$  and  $\text{HSO}_4^-$ , which are much weaker bases than  $\text{H}_2\text{O}$ . 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 ( $\text{HNO}_2$ ), hydrofluoric acid (HF) and acetic acid ( $\text{CH}_3\text{COOH}$ ). It should be noted that the *weak acids have very strong conjugate bases.* For example,  $\text{NH}_2^-$ ,  $\text{O}^{2-}$  and  $\text{H}^-$  are very good proton acceptors and thus, much stronger bases than  $\text{H}_2\text{O}$ .

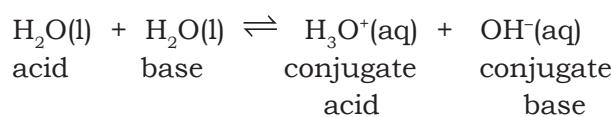
Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid ( $\text{HIn}$ ) and conjugate base ( $\text{In}^-$ ) forms.



Such compounds are useful as indicators in acid-base titrations, and finding out  $\text{H}^+$  ion concentration.

### 6.11.1 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 6.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base,  $\text{B}^-$  it acts as an acid by donating a proton. In pure water, one  $\text{H}_2\text{O}$  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:



The dissociation constant is represented by,

$$K = [\text{H}_3\text{O}^+] [\text{OH}^-] / [\text{H}_2\text{O}] \quad (6.26)$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant.  $[\text{H}_2\text{O}]$  is incorporated within the equilibrium constant to give a new constant,  $K_w$ , which is called the **ionic product of water.**

$$K_w = [\text{H}^+][\text{OH}^-] \quad (6.27)$$

The concentration of  $\text{H}^+$  has been found out experimentally as  $1.0 \times 10^{-7} \text{ M}$  at 298 K. And, as dissociation of water produces equal number of  $\text{H}^+$  and  $\text{OH}^-$  ions, the concentration of hydroxyl ions,  $[\text{OH}^-] = [\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$ . Thus, the value of  $K_w$  at 298K,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2 \quad (6.28)$$

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,

$[\text{H}_2\text{O}] = (1000 \text{ g / L})(1 \text{ mol / 18.0 g}) = 55.55 \text{ M}$ . Therefore, the ratio of dissociated water to that of undissociated water can be given as:  $10^{-7} / (55.55) = 1.8 \times 10^{-9}$  or  $\sim 2$  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  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentrations:

Acidic:  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

Neutral:  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

Basic :  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

### 6.11.2 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 ( $a_{\text{H}^+}$ ) of hydrogen

ion. In dilute solutions ( $< 0.01 \text{ M}$ ), activity of hydrogen ion ( $\text{H}^+$ ) is equal in magnitude to molarity represented by  $[\text{H}^+]$ . It should be noted that activity has no units and is defined as:

$$a_{\text{H}^+} = [\text{H}^+] / \text{mol L}^{-1}$$

From the definition of pH, the following can be written,

$$\text{pH} = -\log a_{\text{H}^+} = -\log \{[\text{H}^+] / \text{mol L}^{-1}\}$$

Thus, an acidic solution of HCl ( $10^{-2} \text{ M}$ ) will have a pH = 2. Similarly, a basic solution of NaOH having  $[\text{OH}^-] = 10^{-4} \text{ M}$  and  $[\text{H}_3\text{O}^+] = 10^{-10} \text{ M}$  will have a pH = 10. At  $25^\circ\text{C}$ , pure water has a concentration of hydrogen ions,  $[\text{H}^+] = 10^{-7} \text{ M}$ . Hence, the pH of pure water is given as:

$$\text{pH} = -\log(10^{-7}) = 7$$

Acidic solutions possess a concentration of hydrogen ions,  $[\text{H}^+] > 10^{-7} \text{ M}$ , while basic solutions possess a concentration of hydrogen ions,  $[\text{H}^+] < 10^{-7} \text{ M}$ . 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 (6.28) at  $298 \text{ K}$

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14}$$

Taking negative logarithm on both sides of equation, we obtain

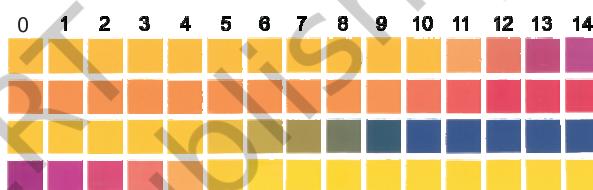
$$\begin{aligned} -\log K_w &= -\log \{[\text{H}_3\text{O}^+] [\text{OH}^-]\} \\ &= -\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-] \\ &= -\log 10^{-14} \\ pK_w &= \text{pH} + \text{pOH} = 14 \end{aligned} \quad (6.29)$$

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  $[\text{H}^+]$  by a factor of 10. Similarly,

when the hydrogen ion concentration,  $[\text{H}^+]$  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. 6.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of  $\sim 0.5$  using pH paper.



**Fig. 6.11** 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 6.5 (page 195).

### Problem 6.16

The concentration of hydrogen ion in a sample of soft drink is  $3.8 \times 10^{-3} \text{ M}$ . what is its pH ?

### Solution

$$\begin{aligned} \text{pH} &= -\log[3.8 \times 10^{-3}] \\ &= -\{\log[3.8] + \log[10^{-3}]\} \\ &= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42 \\ \text{Therefore, the pH of the soft drink is } 2.42 \text{ and it can be inferred that it is acidic.} \end{aligned}$$

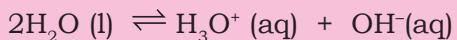
### Problem 6.17

Calculate pH of a  $1.0 \times 10^{-8} \text{ M}$  solution of HCl.

**Table 6.5 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



$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+]$$

$$= 10^{-14}$$

Let,  $x = [\text{OH}^-] = [\text{H}_3\text{O}^+]$  from  $\text{H}_2\text{O}$ . The  $\text{H}_3\text{O}^+$  concentration is generated (i) from the ionization of HCl dissolved i.e.,

$\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ , and (ii) from ionization of  $\text{H}_2\text{O}$ . In these very dilute solutions, both sources of  $\text{H}_3\text{O}^+$  must be considered:

$$[\text{H}_3\text{O}^+] = 10^{-8} + x$$

$$K_w = (10^{-8} + x)(x) = 10^{-14}$$

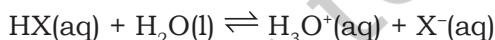
$$\text{or } x^2 + 10^{-8}x - 10^{-14} = 0$$

$$[\text{OH}^-] = x = 9.5 \times 10^{-8}$$

$$\text{So, pOH} = 7.02 \text{ and pH} = 6.98$$

### 6.11.3 Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:



Initial

concentration (M)

c	0	0
---	---	---

Let  $\alpha$  be the extent of ionization

Change (M)

- $c\alpha$	$+c\alpha$	$+c\alpha$
-------------	------------	------------

Equilibrium concentration (M)

c - $c\alpha$	$c\alpha$	$c\alpha$
---------------	-----------	-----------

Here,  $c$  = initial concentration of the undissociated acid, HX at time,  $t = 0$ .  $\alpha$  = 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,

$$K_a = [\text{H}^+][\text{X}^-] / [\text{HX}] \quad (6.30)$$

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 6.6.

**Table 6.6 The Ionization Constants of Some Selected Weak Acids (at 298K)**

Acid	Ionization Constant, $K_a$
Hydrofluoric Acid (HF)	$3.5 \times 10^{-4}$
Nitrous Acid ( $\text{HNO}_2$ )	$4.5 \times 10^{-4}$
Formic Acid ( $\text{HCOOH}$ )	$1.8 \times 10^{-4}$
Niacin ( $\text{C}_5\text{H}_4\text{NCOOH}$ )	$1.5 \times 10^{-5}$
Acetic Acid ( $\text{CH}_3\text{COOH}$ )	$1.74 \times 10^{-5}$
Benzoic Acid ( $\text{C}_6\text{H}_5\text{COOH}$ )	$6.5 \times 10^{-5}$
Hypochlorous Acid ( $\text{HClO}$ )	$3.0 \times 10^{-8}$
Hydrocyanic Acid (HCN)	$4.9 \times 10^{-10}$
Phenol ( $\text{C}_6\text{H}_5\text{OH}$ )	$1.3 \times 10^{-10}$

The pH scale for the hydrogen ion concentration has been so useful that besides  $\text{pK}_w$ , it has been extended to other species and

quantities. Thus, we have:

$$\text{p}K_a = -\log(K_a) \quad (6.31)$$

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  $\alpha$ , degree of ionization.
- (c) Equilibrium concentration.

**Step 5.** Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for  $\alpha$ .

**Step 6.** Calculate the concentration of species in principal reaction.

**Step 7.** Calculate  $\text{pH} = -\log[\text{H}_3\text{O}^+]$

The above mentioned methodology has been elucidated in the following examples.

### Problem 6.18

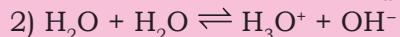
The ionization constant of HF is  $3.2 \times 10^{-4}$ . Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present ( $\text{H}_3\text{O}^+$ ,  $\text{F}^-$  and HF) in the solution and its pH.

### Solution

The following proton transfer reactions are possible:



$$K_a = 3.2 \times 10^{-4}$$



$$K_w = 1.0 \times 10^{-14}$$

As  $K_a \gg K_w$ , [1] is the principle reaction.



Initial

concentration (M)

$$0.02 \quad 0 \quad 0$$

Change (M)

$$-0.02\alpha$$

$$+0.02\alpha \quad +0.02\alpha$$

Equilibrium

concentration (M)

$$0.02 - 0.02\alpha \quad 0.02\alpha \quad 0.02\alpha$$

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$$K_a = (0.02\alpha)^2 / (0.02 - 0.02\alpha)$$

$$= 0.02\alpha^2 / (1 - \alpha) = 3.2 \times 10^{-4}$$

We obtain the following quadratic equation:  
 $\alpha^2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0$

The quadratic equation in  $\alpha$  can be solved and the two values of the roots are:

$$\alpha = +0.12 \text{ and } -0.12$$

The negative root is not acceptable and hence,

$$\alpha = 0.12$$

This means that the degree of ionization,  $\alpha = 0.12$ , then equilibrium concentrations of other species viz., HF,  $\text{F}^-$  and  $\text{H}_3\text{O}^+$  are given by:

$$[\text{H}_3\text{O}^+] = [\text{F}^-] = c\alpha = 0.02 \times 0.12 \\ = 2.4 \times 10^{-3} \text{ M}$$

$$[\text{HF}] = c(1 - \alpha) = 0.02(1 - 0.12)$$

$$= 17.6 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(2.4 \times 10^{-3}) = 2.62$$

### Problem 6.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species  $\text{H}^+$ ,  $\text{A}^-$

and HA at equilibrium. Also, determine the value of  $K_a$  and  $pK_a$  of the monobasic acid.

### Solution

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{Therefore, } [\text{H}^+] = 10^{-\text{pH}} = 10^{-4.50}$$

$$= 3.16 \times 10^{-5}$$

$$[\text{H}^+] = [\text{A}^-] = 3.16 \times 10^{-5}$$

$$\text{Thus, } K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$$

$$[\text{HA}]_{\text{eqbm}} = 0.1 - (3.16 \times 10^{-5}) \approx 0.1$$

$$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$$

$$pK_a = -\log(10^{-8}) = 8$$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

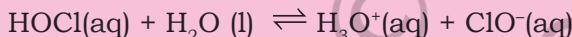
Percent dissociation

$$= [\text{HA}]_{\text{dissociated}} / [\text{HA}]_{\text{initial}} \times 100\% \quad (6.32)$$

### Problem 6.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is  $2.5 \times 10^{-5}$ . Determine the percent dissociation of HOCl.

### Solution



Initial concentration (M)

$$\begin{array}{ccc} 0.08 & 0 & 0 \end{array}$$

Change to reach

equilibrium concentration

(M)

$$\begin{array}{ccc} -x & +x & +x \end{array}$$

equilibrium concentration (M)

$$\begin{array}{ccc} 0.08-x & x & x \end{array}$$

$$K_a = \{[\text{H}_3\text{O}^+][\text{ClO}^-]\} / [\text{HOCl}]$$

$$= x^2 / (0.08-x)$$

As  $x \ll 0.08$ , therefore  $0.08-x \approx 0.08$

$$x^2 / 0.08 = 2.5 \times 10^{-5}$$

$$x^2 = 2.0 \times 10^{-6}, \text{ thus, } x = 1.41 \times 10^{-3}$$

$$[\text{H}^+] = 1.41 \times 10^{-3} \text{ M.}$$

Therefore,

Percent dissociation

$$= \{[\text{HOCl}]_{\text{dissociated}} / [\text{HOCl}]_{\text{initial}}\} \times 100$$

$$= 1.41 \times 10^{-3} \times 10^2 / 0.08 = 1.76 \%$$

$$\text{pH} = -\log(1.41 \times 10^{-3}) = 2.85.$$

### 6.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:



In a weak base there is partial ionization of MOH into  $\text{M}^+$  and  $\text{OH}^-$ , 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:

$$K_b = [\text{M}^+][\text{OH}^-] / [\text{MOH}] \quad (6.33)$$

Alternatively, if  $c$  = initial concentration of base and  $\alpha$  = 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:

$$K_b = (c\alpha)^2 / c(1-\alpha) = c\alpha^2 / (1-\alpha)$$

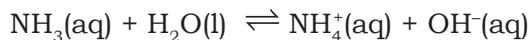
The values of the ionization constants of some selected weak bases,  $K_b$  are given in Table 6.7.

**Table 6.7 The Values of the Ionization Constant of Some Weak Bases at 298 K**

Base	$K_b$
Dimethylamine, $(\text{CH}_3)_2\text{NH}$	$5.4 \times 10^{-4}$
Triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$	$6.45 \times 10^{-5}$
Ammonia, $\text{NH}_3$ or $\text{NH}_4\text{OH}$	$1.77 \times 10^{-5}$
Quinine, (A plant product)	$1.10 \times 10^{-6}$
Pyridine, $\text{C}_5\text{H}_5\text{N}$	$1.77 \times 10^{-9}$
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	$4.27 \times 10^{-10}$
Urea, $\text{CO}(\text{NH}_2)_2$	$1.3 \times 10^{-14}$

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  $\text{OH}^-$  in aqueous solution:



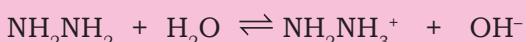
The pH scale for the hydrogen ion concentration has been extended to get:

$$\text{p}K_b = -\log(K_b) \quad (6.34)$$

### Problem 6.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant  $K_b$  and  $\text{p}K_b$ .

#### Solution



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:

$$\begin{aligned} [\text{H}^+] &= \text{antilog}(-\text{pH}) \\ &= \text{antilog}(-9.7) = 1.67 \times 10^{-10} \\ [\text{OH}^-] &= K_w / [\text{H}^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10} \\ &= 5.98 \times 10^{-5} \end{aligned}$$

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,

$$\begin{aligned} K_b &= [\text{NH}_2\text{NH}_3^+][\text{OH}^-] / [\text{NH}_2\text{NH}_2] \\ &= (5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7} \\ \text{p}K_b &= -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04. \end{aligned}$$

### Problem 6.22

Calculate the pH of the solution in which 0.2M  $\text{NH}_4\text{Cl}$  and 0.1M  $\text{NH}_3$  are present. The  $\text{p}K_b$  of ammonia solution is 4.75.

#### Solution



The ionization constant of  $\text{NH}_3$ ,

$$K_b = \text{antilog}(-\text{p}K_b) \text{ i.e.}$$

$K_b = 10^{-4.75} = 1.77 \times 10^{-5} \text{ M}$		
$\text{NH}_3 + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$		
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
$K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3]$		
$= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$		
As $K_b$ is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,		
$[\text{OH}^-] = x = 0.88 \times 10^{-5}$		
Therefore, $[\text{H}^+] = 1.12 \times 10^{-9}$		
$\text{pH} = -\log[\text{H}^+] = 8.95.$		

### 6.11.5 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  $\text{NH}_4^+$  and  $\text{NH}_3$  we see,

$$\begin{aligned} \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O(l)} &\rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \\ K_a &= [\text{H}_3\text{O}^+][\text{NH}_3] / [\text{NH}_4^+] = 5.6 \times 10^{-10} \\ \text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)} &\rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \\ K_b &= [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3] = 1.8 \times 10^{-5} \\ \text{Net: } 2 \text{ H}_2\text{O(l)} &\rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \\ K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M} \end{aligned}$$

Where,  $K_a$  represents the strength of  $\text{NH}_4^+$  as an acid and  $K_b$  represents the strength of  $\text{NH}_3$  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,

$$\begin{aligned} K_a \times K_b &= \{[\text{H}_3\text{O}^+][\text{NH}_3] / [\text{NH}_4^+]\} \times \{[\text{NH}_4^+] \\ &\quad [\text{OH}^-] / [\text{NH}_3]\} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \\ &= (5.6 \times 10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14} \text{ M} \end{aligned}$$

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:**

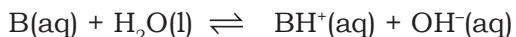
$$K_{\text{NET}} = K_1 \times K_2 \times \dots \quad (6.35)$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \quad (6.36)$$

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  $K_w = K_a \times K_b$ , can also be obtained by considering the base-dissociation equilibrium reaction:



$$K_b = [\text{BH}^+][\text{OH}^-] / [\text{B}]$$

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  $[\text{H}^+]$ , we get:

$$\begin{aligned} K_b &= [\text{BH}^+][\text{OH}^-][\text{H}^+] / [\text{B}][\text{H}^+] \\ &= \{\text{OH}^-\}\{\text{H}^+\} \{[\text{BH}^+] / [\text{B}][\text{H}^+\}] \\ &= K_w / K_a \end{aligned}$$

$$\text{or } K_a \times K_b = K_w$$

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:

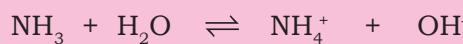
$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14 \text{ (at 298K)}$$

### Problem 6.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 6.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

#### Solution

The ionization of  $\text{NH}_3$  in water is represented by equation:



We use equation (6.33) to calculate hydroxyl ion concentration,

$$[\text{OH}^-] = c \alpha = 0.05 \alpha$$

$$K_b = 0.05 \alpha^2 / (1 - \alpha)$$

The value of  $\alpha$  is small, therefore the quadratic equation can be simplified by neglecting  $\alpha$  in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$$\begin{aligned} K_b &= c \alpha^2 \text{ or } \alpha = \sqrt{(1.77 \times 10^{-5}) / 0.05} \\ &= 0.018. \end{aligned}$$

$$[\text{OH}^-] = c \alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4} \text{ M.}$$

$$\begin{aligned} [\text{H}^+] &= K_w / [\text{OH}^-] = 10^{-14} / (9.4 \times 10^{-4}) \\ &= 1.06 \times 10^{-11} \end{aligned}$$

$$\text{pH} = -\log(1.06 \times 10^{-11}) = 10.97.$$

Now, using the relation for conjugate acid-base pair,

$$K_a \times K_b = K_w$$

using the value of  $K_b$  of  $\text{NH}_3$  from Table 6.7.

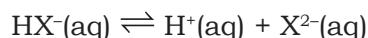
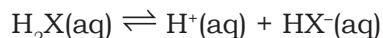
We can determine the concentration of conjugate acid  $\text{NH}_4^+$

$$\begin{aligned} K_a &= K_w / K_b = 10^{-14} / 1.77 \times 10^{-5} \\ &= 5.64 \times 10^{-10}. \end{aligned}$$

### 6.11.6 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*  $\text{H}_2\text{X}$  are represented by the equations:



And the corresponding equilibrium constants are given below:

$$K_{a_1} = \{[\text{H}^+][\text{HX}^-]\} / [\text{H}_2\text{X}] \text{ and}$$

$$K_{a_2} = \{[H^+][X^{2-}]\} / [HX^-]$$

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 6.8.

**Table 6.8 The Ionization Constants of Some Common Polyprotic Acids (298K)**

Acid	$K_{a_1}$	$K_{a_2}$	$K_{a_3}$
Oxalic Acid	$5.9 \times 10^{-2}$	$6.4 \times 10^{-5}$	
Ascorbic Acid	$7.4 \times 10^{-4}$	$1.6 \times 10^{-12}$	
Sulphurous Acid	$1.7 \times 10^{-2}$	$6.4 \times 10^{-8}$	
Sulphuric Acid	Very large	$1.2 \times 10^{-2}$	
Carbonic Acid	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Citric Acid	$7.4 \times 10^{-4}$	$1.7 \times 10^{-5}$	$4.0 \times 10^{-7}$
Phosphoric Acid	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.2 \times 10^{-13}$

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  $H_2PO_4^-$ .

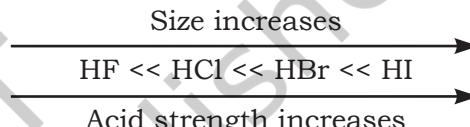
Polyprotic acid solutions contain a mixture of acids like  $H_2A$ ,  $HA^-$  and  $A^{2-}$  in case of a diprotic acid.  $H_2A$  being a strong acid, the primary reaction involves the dissociation of  $H_2A$ , and  $H_3O^+$  in the solution comes mainly from the first dissociation step.

### 6.11.7 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.

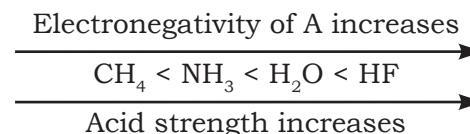
In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage 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,



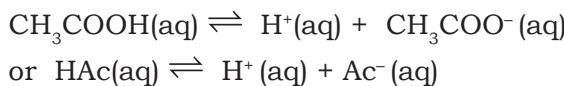
Similarly,  $H_2S$  is stronger acid than  $H_2O$ .

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,



### 6.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

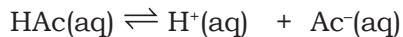


$$K_a = [H^+][Ac^-] / [HAc]$$

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 6.8.

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,



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,

$$K_a = [\text{H}^+][\text{Ac}^-]/[\text{HAc}] = \{(0.05+x)(x)\}/(0.05-x)$$

As  $K_a$  is small for a very weak acid,  $x \ll 0.05$ .

Hence,  $(0.05 + x) \approx (0.05 - x) \approx 0.05$

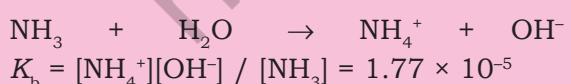
Thus,

$$\begin{aligned} 1.8 \times 10^{-5} &= (x)(0.05 + x) / (0.05 - x) \\ &= x(0.05) / (0.05) = x = [\text{H}^+] = 1.8 \times 10^{-5} \text{ M} \\ \text{pH} &= -\log(1.8 \times 10^{-5}) = 4.74 \end{aligned}$$

### Problem 6.24

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,  $K_b = 1.77 \times 10^{-5}$

#### Solution



Before neutralization,

$$[\text{NH}_4^+] = [\text{OH}^-] = x$$

$$[\text{NH}_3] = 0.10 - x \approx 0.10$$

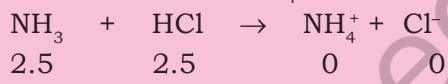
$$x^2 / 0.10 = 1.77 \times 10^{-5}$$

$$\text{Thus, } x = 1.33 \times 10^{-3} = [\text{OH}^-]$$

$$\text{Therefore, } [\text{H}^+] = K_w / [\text{OH}^-] = 10^{-14} / (1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$$

$$\text{pH} = -\log(7.51 \times 10^{-12}) = 11.12$$

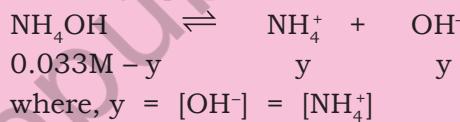
On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of  $\text{NH}_3$ ), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of  $\text{NH}_3$  molecules and 2.5 mmol of  $\text{NH}_4^+$ .



At equilibrium



The resulting 75 mL of solution contains 2.5 mmol of  $\text{NH}_4^+$  ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of unneutralised  $\text{NH}_3$  molecules. This  $\text{NH}_3$  exists in the following equilibrium:



The final 75 mL solution after neutralisation already contains 2.5 m mol  $\text{NH}_4^+$  ions (i.e. 0.033M), thus total concentration of  $\text{NH}_4^+$  ions is given as:

$$[\text{NH}_4^+] = 0.033 + y$$

As  $y$  is small,  $[\text{NH}_4\text{OH}] \approx 0.033 \text{ M}$  and  $[\text{NH}_4^+] \approx 0.033 \text{ M}$ .

We know,

$$\begin{aligned} K_b &= [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_4\text{OH}] \\ &= y(0.033)/(0.033) = 1.77 \times 10^{-5} \text{ M} \end{aligned}$$

$$\text{Thus, } y = 1.77 \times 10^{-5} = [\text{OH}^-]$$

$$[\text{H}^+] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$$

$$\text{Hence, pH} = 9.24$$

### 6.11.9 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.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , etc.) of strong bases and anions (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  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.

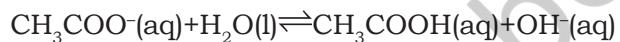
We now consider the hydrolysis of the salts of the following types :

- salts of weak acid and strong base e.g.,  $\text{CH}_3\text{COONa}$ .
- salts of strong acid and weak base e.g.,  $\text{NH}_4\text{Cl}$ , and
- salts of weak acid and weak base, e.g.,  $\text{CH}_3\text{COONH}_4$ .

In the first case,  $\text{CH}_3\text{COONa}$  being a salt of weak acid,  $\text{CH}_3\text{COOH}$  and strong base,  $\text{NaOH}$  gets completely ionised in aqueous solution.



Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and  $\text{OH}^-$  ions

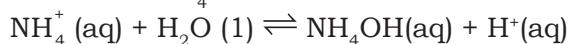


Acetic acid being a weak acid ( $K_a = 1.8 \times 10^{-5}$ ) remains mainly unionised in solution. This results in increase of  $\text{OH}^-$  ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly,  $\text{NH}_4\text{Cl}$  formed from weak base,  $\text{NH}_4\text{OH}$  and strong acid,  $\text{HCl}$ , in water dissociates completely.



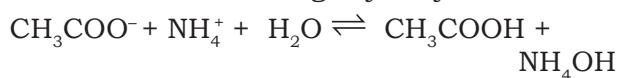
Ammonium ions undergo hydrolysis with water to form  $\text{NH}_4\text{OH}$  and  $\text{H}^+$  ions



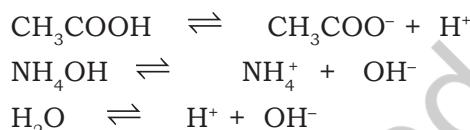
Ammonium hydroxide is a weak base ( $K_b = 1.77 \times 10^{-5}$ ) and therefore remains almost unionised in solution. This results in

increased of  $\text{H}^+$  ion concentration in solution making the solution acidic. Thus, the pH of  $\text{NH}_4\text{Cl}$  solution in water is less than 7.

Consider the hydrolysis of  $\text{CH}_3\text{COONH}_4$  salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:



$\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$ , also remain into partially dissociated form:



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:

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b) \quad (6.38)$$

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 6.25

The  $\text{p}K_a$  of acetic acid and  $\text{p}K_b$  of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

### Solution

$$\begin{aligned} \text{pH} &= 7 + \frac{1}{2} [\text{p}K_a - \text{p}K_b] \\ &= 7 + \frac{1}{2} [4.76 - 4.75] \\ &= 7 + \frac{1}{2} [0.01] = 7 + 0.005 = 7.005 \end{aligned}$$

## 6.12 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

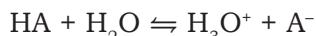
solutions of known pH can be prepared from the knowledge of  $pK_a$  of the acid or  $pK_b$  of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

### 6.12.1 Designing Buffer Solution

Knowledge of  $pK_a$ ,  $pK_b$  and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

#### Preparation of Acidic Buffer

To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant,  $K_a$  of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionises in water,



For which we can write the expression

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]}$$

Rearranging the expression we have,

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

Taking logarithm on both the sides and rearranging the terms we get —

$$pK_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Or

$$\text{pH} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (6.39)$$

$$\text{pH} = pK_a + \log \frac{[\text{Conjugate base, A}^-]}{[\text{Acid, HA}]} \quad (6.40)$$

The expression (6.40) is known as **Henderson-Hasselbalch equation**. The

quantity  $\frac{[\text{A}^-]}{[\text{HA}]}$  is the ratio of concentration of conjugate base (anion) of the acid and the

acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base,  $[\text{A}^-]$ , comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (6.40) takes the form:

$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

In the equation (6.39), if the concentration of  $[\text{A}^-]$  is equal to the concentration of [HA], then  $\text{pH} = pK_a$  because value of  $\log 1$  is zero. Thus if we take molar concentration of acid and salt (conjugate base) same, the pH of the buffer solution will be equal to the  $pK_a$  of the acid. So for preparing the buffer solution of the required pH we select that acid whose  $pK_a$  is close to the required pH. For acetic acid  $pK_a$  value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result,

$$\text{pOH} = pK_b + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]} \quad (6.41)$$

pH of the buffer solution can be calculated by using the equation  $\text{pH} + \text{pOH} = 14$ .

We know that  $\text{pH} + \text{pOH} = pK_w$  and  $pK_a + pK_b = pK_w$ . On putting these values in equation (6.41) it takes the form as follows:

$$pK_w - \text{pH} = pK_w - pK_a + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

or

$$\text{pH} = pK_a + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]} \quad (6.42)$$

If molar concentration of base and its conjugate acid (cation) is same then pH of the buffer solution will be same as  $pK_a$  for the base.  $pK_a$  value for ammonia is 9.25; therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium

chloride solution of same molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation (6.42) becomes:

$$\text{pH} = 9.25 + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

### 6.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

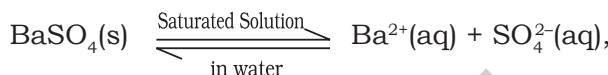
We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly 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.

#### 6.13.1 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:



The equilibrium constant is given by the equation:

$$K = \{\text{[Ba}^{2+}\text{][SO}_4^{2-}\}\} / [\text{BaSO}_4]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{\text{sp}} = K[\text{BaSO}_4] = \text{[Ba}^{2+}\text{][SO}_4^{2-}\] \quad (6.43)$$

We call  $K_{\text{sp}}$  the *solubility product constant* or simply *solubility product*. The experimental value of  $K_{\text{sp}}$  in above equation at 298K is  $1.1 \times 10^{-10}$ . 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

$$1.1 \times 10^{-10} = (\text{S})(\text{S}) = \text{S}^2$$

or  $\text{S} = 1.05 \times 10^{-5}$ .

Thus, molar solubility of barium sulphate will be equal to  $1.05 \times 10^{-5} \text{ mol L}^{-1}$ .

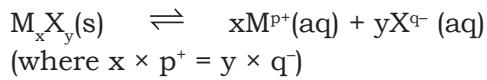
A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula  $(\text{Zr}^{4+})_3(\text{PO}_4^{3-})_4$ . It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge -3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$$[\text{Zr}^{4+}] = 3\text{S} \text{ and } [\text{PO}_4^{3-}] = 4\text{S}$$

$$\text{and } K_{\text{sp}} = (3\text{S})^3 (4\text{S})^4 = 6912 (\text{S})^7$$

$$\text{or } \text{S} = \{K_{\text{sp}} / (3^3 \times 4^4)\}^{1/7} = (K_{\text{sp}} / 6912)^{1/7}$$

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:



And its solubility product constant is given by:

$$K_{sp} = [M^{p+}]^x [X^{q-}]^y = (xS)^x (yS)^y \quad (6.44)$$

$$= x^x \cdot y^y \cdot S^{(x+y)}$$

$$S^{(x+y)} = K_{sp} / x^x \cdot y^y \quad (6.45)$$

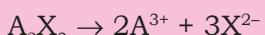
$$S = (K_{sp} / x^x \cdot y^y)^{1/(x+y)}$$

The term  $K_{sp}$  in equation is given by  $Q_{sp}$  (section 6.6.2) 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 6.9.

### Problem 6.26

Calculate the solubility of  $A_2X_3$  in pure water, assuming that neither kind of ion reacts with water. The solubility product of  $A_2X_3$ ,  $K_{sp} = 1.1 \times 10^{-23}$ .

#### Solution



$$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = 1.1 \times 10^{-23}$$

If S = solubility of  $A_2X_3$ , then

$$[A^{3+}] = 2S; [X^{2-}] = 3S$$

$$\text{therefore, } K_{sp} = (2S)^2 (3S)^3 = 108S^5 \\ = 1.1 \times 10^{-23}$$

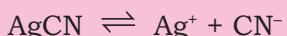
$$\text{thus, } S^5 = 1 \times 10^{-25}$$

$$S = 1.0 \times 10^{-5} \text{ mol/L.}$$

### Problem 6.27

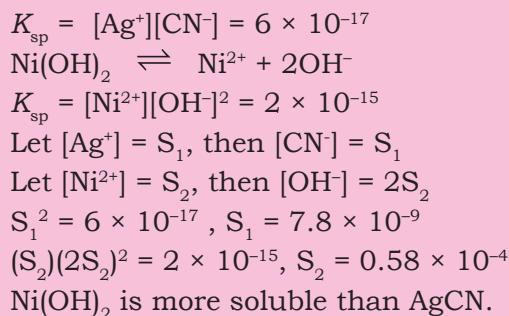
The values of  $K_{sp}$  of two sparingly soluble salts  $Ni(OH)_2$  and  $AgCN$  are  $2.0 \times 10^{-15}$  and  $6 \times 10^{-17}$  respectively. Which salt is more soluble? Explain.

#### Solution



**Table 6.9 The Solubility Product Constants,  $K_{sp}$  of Some Common Ionic Salts at 298K.**

Name of the Salt	Formula	$K_{sp}$
Silver Bromide	AgBr	$5.0 \times 10^{-13}$
Silver Carbonate	Ag <sub>2</sub> CO <sub>3</sub>	$8.1 \times 10^{-12}$
Silver Chromate	Ag <sub>2</sub> CrO <sub>4</sub>	$1.1 \times 10^{-12}$
Silver Chloride	AgCl	$1.8 \times 10^{-10}$
Silver Iodide	AgI	$8.3 \times 10^{-17}$
Silver Sulphate	Ag <sub>2</sub> SO <sub>4</sub>	$1.4 \times 10^{-5}$
Aluminium Hydroxide	Al(OH) <sub>3</sub>	$1.3 \times 10^{-33}$
Barium Chromate	BaCrO <sub>4</sub>	$1.2 \times 10^{-10}$
Barium Fluoride	BaF <sub>2</sub>	$1.0 \times 10^{-6}$
Barium Sulphate	BaSO <sub>4</sub>	$1.1 \times 10^{-10}$
Calcium Carbonate	CaCO <sub>3</sub>	$2.8 \times 10^{-9}$
Calcium Fluoride	CaF <sub>2</sub>	$5.3 \times 10^{-9}$
Calcium Hydroxide	Ca(OH) <sub>2</sub>	$5.5 \times 10^{-6}$
Calcium Oxalate	CaC <sub>2</sub> O <sub>4</sub>	$4.0 \times 10^{-9}$
Calcium Sulphate	CaSO <sub>4</sub>	$9.1 \times 10^{-6}$
Cadmium Hydroxide	Cd(OH) <sub>2</sub>	$2.5 \times 10^{-14}$
Cadmium Sulphide	CdS	$8.0 \times 10^{-27}$
Chromic Hydroxide	Cr(OH) <sub>3</sub>	$6.3 \times 10^{-31}$
Cuprous Bromide	CuBr	$5.3 \times 10^{-9}$
Cupric Carbonate	CuCO <sub>3</sub>	$1.4 \times 10^{-10}$
Cuprous Chloride	CuCl	$1.7 \times 10^{-6}$
Cupric Hydroxide	Cu(OH) <sub>2</sub>	$2.2 \times 10^{-20}$
Cuprous Iodide	CuI	$1.1 \times 10^{-12}$
Cupric Sulphide	CuS	$6.3 \times 10^{-36}$
Ferrous Carbonate	FeCO <sub>3</sub>	$3.2 \times 10^{-11}$
Ferrous Hydroxide	Fe(OH) <sub>2</sub>	$8.0 \times 10^{-16}$
Ferric Hydroxide	Fe(OH) <sub>3</sub>	$1.0 \times 10^{-38}$
Ferrous Sulphide	FeS	$6.3 \times 10^{-18}$
Mercurous Bromide	Hg <sub>2</sub> Br <sub>2</sub>	$5.6 \times 10^{-23}$
Mercurous Chloride	Hg <sub>2</sub> Cl <sub>2</sub>	$1.3 \times 10^{-18}$
Mercurous Iodide	Hg <sub>2</sub> I <sub>2</sub>	$4.5 \times 10^{-29}$
Mercurous Sulphate	Hg <sub>2</sub> SO <sub>4</sub>	$7.4 \times 10^{-7}$
Mercuric Sulphide	HgS	$4.0 \times 10^{-53}$
Magnesium Carbonate	MgCO <sub>3</sub>	$3.5 \times 10^{-8}$
Magnesium Fluoride	MgF <sub>2</sub>	$6.5 \times 10^{-9}$
Magnesium Hydroxide	Mg(OH) <sub>2</sub>	$1.8 \times 10^{-11}$
Magnesium Oxalate	MgC <sub>2</sub> O <sub>4</sub>	$7.0 \times 10^{-7}$
Manganese Carbonate	MnCO <sub>3</sub>	$1.8 \times 10^{-11}$
Manganese Sulphide	MnS	$2.5 \times 10^{-13}$
Nickel Hydroxide	Ni(OH) <sub>2</sub>	$2.0 \times 10^{-15}$
Nickel Sulphide	NiS	$4.7 \times 10^{-5}$
Lead Bromide	PbBr <sub>2</sub>	$4.0 \times 10^{-5}$
Lead Carbonate	PbCO <sub>3</sub>	$7.4 \times 10^{-14}$
Lead Chloride	PbCl <sub>2</sub>	$1.6 \times 10^{-5}$
Lead Fluoride	PbF <sub>2</sub>	$7.7 \times 10^{-8}$
Lead Hydroxide	Pb(OH) <sub>2</sub>	$1.2 \times 10^{-15}$
Lead Iodide	PbI <sub>2</sub>	$7.1 \times 10^{-9}$
Lead Sulphate	PbSO <sub>4</sub>	$1.6 \times 10^{-8}$
Lead Sulphide	PbS	$8.0 \times 10^{-28}$
Stannous Hydroxide	Sn(OH) <sub>2</sub>	$1.4 \times 10^{-28}$
Stannous Sulphide	SnS	$1.0 \times 10^{-25}$
Strontium Carbonate	SrCO <sub>3</sub>	$1.1 \times 10^{-10}$
Strontium Fluoride	SrF <sub>2</sub>	$2.5 \times 10^{-9}$
Strontium Sulphate	SrSO <sub>4</sub>	$3.2 \times 10^{-7}$
Thallous Bromide	TlBr	$3.4 \times 10^{-6}$
Thallous Chloride	TlCl	$1.7 \times 10^{-4}$
Thallous Iodide	TlI	$6.5 \times 10^{-8}$
Zinc Carbonate	ZnCO <sub>3</sub>	$1.4 \times 10^{-11}$
Zinc Hydroxide	Zn(OH) <sub>2</sub>	$1.0 \times 10^{-15}$
Zinc Sulphide	ZnS	$1.6 \times 10^{-24}$



### 6.13.2 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 6.28

Calculate the molar solubility of  $Ni(OH)_2$  in 0.10 M NaOH. The ionic product of  $Ni(OH)_2$  is  $2.0 \times 10^{-15}$ .

#### 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.

$$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}][OH^-]^2 \\ = (S)(0.10 + 2S)^2$$

As  $K_{sp}$  is small,  $2S \ll 0.10$ ,  
 thus,  $(0.10 + 2S) \approx 0.10$

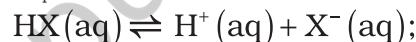
Hence,

$$2.0 \times 10^{-15} = S(0.10)^2$$

$$S = 2.0 \times 10^{-13} \text{ M} = [Ni^{2+}]$$

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.,

$$K_{sp} = [M^+][X^-]$$



$$K_a = \frac{[H^+(aq)][X^-(aq)]}{[HX(aq)]}$$

$$[X^-]/[HX] = K_a/[H^+]$$

Taking inverse of both side and adding 1 we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

$$\frac{[HX] + [H^-]}{[X^-]} = \frac{[H^+] + K_a}{K_a}$$

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

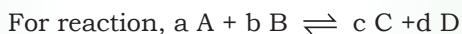
$$K_{sp} = [S][fS] = S^2 \{K_a/(K_a + [H^+])\} \text{ and}$$

$$S = \{K_{sp}([H^+] + K_a)/K_a\}^{1/2} \quad (6.46)$$

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.



$$K_c = [C]^c[D]^d/[A]^a[B]^b$$

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.

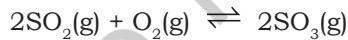
All substances that conduct electricity in aqueous solutions are called **electrolytes**. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the **dissociation or ionization of electrolytes** in aqueous solution. 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** ( $\text{pH} = -\log[\text{H}^+]$ ) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities ( $\text{pOH} = -\log[\text{OH}^-]$ ;  $\text{p}K_a = -\log[K_a]$ ;  $\text{p}K_b = -\log[K_b]$ ; and  $\text{p}K_w = -\log[K_w]$  etc.). The ionization of water has been considered and we note that the equation:  $\text{pH} + \text{pOH} = \text{p}K_w$  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 **solvability 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

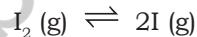
- (a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available.
- (b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these 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

- 6.1 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?
- 6.2 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  $[SO_3] = 1.90M$  ?



- 6.3 At a certain temperature and total pressure of  $10^5\text{Pa}$ , iodine vapour contains 40% by volume of I atoms



Calculate  $K_p$  for the equilibrium.

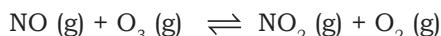
- 6.4 Write the expression for the equilibrium constant,  $K_c$  for each of the following reactions:

- (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)  $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

- 6.5 Find out the value of  $K_c$  for each of the following equilibria from the value of  $K_p$ :

- (i)  $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g); K_p = 1.8 \times 10^{-2}$  at  $500\text{ K}$
- (ii)  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g); K_p = 167$  at  $1073\text{ K}$

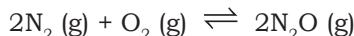
- 6.6 For the following equilibrium,  $K_c = 6.3 \times 10^{14}$  at 1000 K



Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is  $K_c$ , for the reverse reaction?

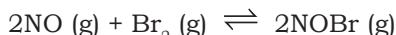
- 6.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

- 6.8 Reaction between  $\text{N}_2$  and  $\text{O}_{2-}$  takes place as follows:



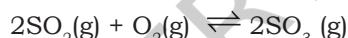
If a mixture of 0.482 mol  $\text{N}_2$  and 0.933 mol of  $\text{O}_{2-}$  is placed in a 10 L reaction vessel and allowed to form  $\text{N}_2\text{O}$  at a temperature for which  $K_c = 2.0 \times 10^{-37}$ , determine the composition of equilibrium mixture.

- 6.9 Nitric oxide reacts with  $\text{Br}_2$  and gives nitrosyl bromide as per reaction given below:



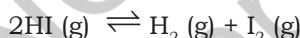
When 0.087 mol of NO and 0.0437 mol of  $\text{Br}_2$  are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and  $\text{Br}_2$ .

- 6.10 At 450K,  $K_p = 2.0 \times 10^{10}$ /bar for the given reaction at equilibrium.



What is  $K_c$  at this temperature ?

- 6.11 A sample of  $\text{HI(g)}$  is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of  $\text{HI(g)}$  is 0.04 atm. What is  $K_p$  for the given equilibrium ?



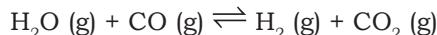
- 6.12 A mixture of 1.57 mol of  $\text{N}_2$ , 1.92 mol of  $\text{H}_2$  and 8.13 mol of  $\text{NH}_3$  is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant,  $K_c$  for the reaction  $\text{N}_2 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightleftharpoons 2\text{NH}_3 \text{ (g)}$  is  $1.7 \times 10^2$ . Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

- 6.13 The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

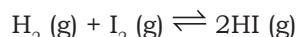
Write the balanced chemical equation corresponding to this expression.

- 6.14 One mole of  $\text{H}_2\text{O}$  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,



Calculate the equilibrium constant for the reaction.

- 6.15 At 700 K, equilibrium constant for the reaction:



is 54.8. If 0.5 mol  $\text{L}^{-1}$  of  $\text{HI(g)}$  is present at equilibrium at 700 K, what are the concentration of  $\text{H}_2\text{(g)}$  and  $\text{I}_2\text{(g)}$  assuming that we initially started with  $\text{HI(g)}$  and allowed it to reach equilibrium at 700K?

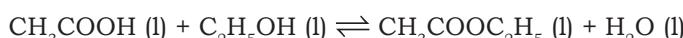
- 6.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of  $\text{ICl}$  was 0.78 M?



- 6.17  $K_p = 0.04$  atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of  $\text{C}_2\text{H}_6$  when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?



- 6.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:



- (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?
- 6.19 A sample of pure  $\text{PCl}_5$  was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of  $\text{PCl}_5$  was found to be  $0.5 \times 10^{-1}$  mol L<sup>-1</sup>. If value of  $K_c$  is  $8.3 \times 10^{-3}$ , what are the concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  at equilibrium?



- 6.20 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  $\text{CO}_2$ .



What are the equilibrium partial pressures of CO and  $\text{CO}_2$  at 1050 K if the initial partial pressures are:  $p_{\text{CO}} = 1.4$  atm and  $p_{\text{CO}_2} = 0.80$  atm?

- 6.21 Equilibrium constant,  $K_c$  for the reaction



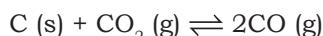
At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L<sup>-1</sup>  $\text{N}_2$ , 2.0 mol L<sup>-1</sup>  $\text{H}_2$  and 0.5 mol L<sup>-1</sup>  $\text{NH}_3$ . Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

- 6.22 Bromine monochloride,  $\text{BrCl}$  decomposes into bromine and chlorine and reaches the equilibrium:



for which  $K_c = 32$  at 500 K. If initially pure  $\text{BrCl}$  is present at a concentration of  $3.3 \times 10^{-3}$  mol L<sup>-1</sup>, what is its molar concentration in the mixture at equilibrium?

- 6.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and  $\text{CO}_2$  in equilibrium with solid carbon has 90.55% CO by mass



Calculate  $K_c$  for this reaction at the above temperature.

- 6.24 Calculate a)  $\Delta G^\ominus$  and b) the equilibrium constant for the formation of  $\text{NO}_2$  from  $\text{NO}$  and  $\text{O}_2$  at 298K



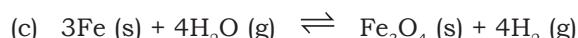
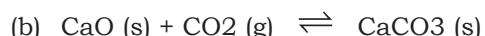
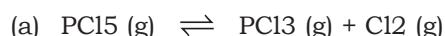
where

$$\Delta_f G^\ominus (\text{NO}_2) = 52.0 \text{ kJ/mol}$$

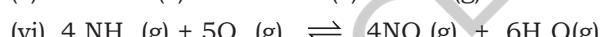
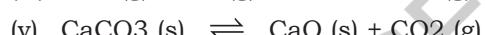
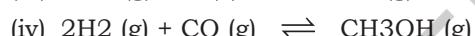
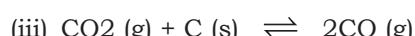
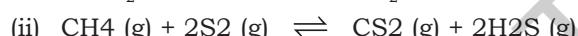
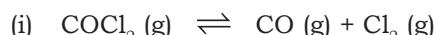
$$\Delta_f G^\ominus (\text{NO}) = 87.0 \text{ kJ/mol}$$

$$\Delta_f G^\ominus (\text{O}_2) = 0 \text{ kJ/mol}$$

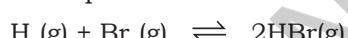
- 6.25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?



- 6.26 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.

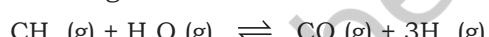


- 6.27 The equilibrium constant for the following reaction is  $1.6 \times 10^5$  at 1024K



Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

- 6.28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:



(a) Write an 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?

- 6.29 Describe the effect of:

- a) addition of  $\text{H}_2$
- b) addition of  $\text{CH}_3\text{OH}$
- c) removal of  $\text{CO}$
- d) removal of  $\text{CH}_3\text{OH}$

on the equilibrium of the reaction:



- 6.30 At 473 K, equilibrium constant  $K_c$  for decomposition of phosphorus pentachloride,  $\text{PCl}_5$  is  $8.3 \times 10^{-3}$ . If decomposition is depicted as,

- $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \quad \Delta_r H^\ominus = 124.0 \text{ kJ mol}^{-1}$
- write an expression for  $K_c$  for the reaction.
  - what is the value of  $K_c$  for the reverse reaction at the same temperature?
  - what would be the effect on  $K_c$  if (i) more  $\text{PCl}_5$  is added (ii) pressure is increased (iii) the temperature is increased ?
- 6.31 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  $\text{H}_2$ . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,
- $$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$$
- If a reaction vessel at  $400^\circ\text{C}$  is charged with an equimolar mixture of CO and steam such that  $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 4.0 \text{ bar}$ , what will be the partial pressure of  $\text{H}_2$  at equilibrium?  $K_p = 10.1$  at  $400^\circ\text{C}$
- 6.32 Predict which of the following reaction will have appreciable concentration of reactants and products:
- $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g}) \quad K_c = 5 \times 10^{-39}$
  - $\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g}) \quad K_c = 3.7 \times 10^8$
  - $\text{Cl}_2(\text{g}) + 2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}_2\text{Cl}(\text{g}) \quad K_c = 1.8$
- 6.33 The value of  $K_c$  for the reaction  $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$  is  $2.0 \times 10^{-50}$  at  $25^\circ\text{C}$ . If the equilibrium concentration of  $\text{O}_2$  in air at  $25^\circ\text{C}$  is  $1.6 \times 10^{-2}$ , what is the concentration of  $\text{O}_3$ ?
- 6.34 The reaction,  $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$  is at equilibrium at  $1300 \text{ K}$  in a  $1\text{L}$  flask. It also contain  $0.30 \text{ mol}$  of CO,  $0.10 \text{ mol}$  of  $\text{H}_2$  and  $0.02 \text{ mol}$  of  $\text{H}_2\text{O}$  and an unknown amount of  $\text{CH}_4$  in the flask. Determine the concentration of  $\text{CH}_4$  in the mixture. The equilibrium constant,  $K_c$  for the reaction at the given temperature is  $3.90$ .
- 6.35 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:
- HNO<sub>2</sub>, CN<sup>-</sup>, HClO<sub>4</sub>, F<sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and S<sup>2-</sup>
- 6.36 Which of the followings are Lewis acids? H<sub>2</sub>O, BF<sub>3</sub>, H<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>
- 6.37 What will be the conjugate bases for the Brönsted acids: HF, H<sub>2</sub>SO<sub>4</sub> and HCO<sub>3</sub><sup>-</sup>?
- 6.38 Write the conjugate acids for the following Brönsted bases: NH<sub>2</sub><sup>-</sup>, NH<sub>3</sub> and HCOO<sup>-</sup>.
- 6.39 The species: H<sub>2</sub>O, HCO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and NH<sub>3</sub> can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.
- 6.40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH<sup>-</sup> (b) F<sup>-</sup> (c) H<sup>+</sup> (d) BCl<sub>3</sub>.
- 6.41 The concentration of hydrogen ion in a sample of soft drink is  $3.8 \times 10^{-3} \text{ M}$ . What is its pH?
- 6.42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.
- 6.43 The ionization constant of HF, HCOOH and HCN at 298K are  $6.8 \times 10^{-4}$ ,  $1.8 \times 10^{-4}$  and  $4.8 \times 10^{-9}$  respectively. Calculate the ionization constants of the corresponding conjugate base.

- 6.44 The ionization constant of phenol is  $1.0 \times 10^{-10}$ . 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?

6.45 The first ionization constant of  $\text{H}_2\text{S}$  is  $9.1 \times 10^{-8}$ . Calculate the concentration of  $\text{HS}^-$  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  $\text{H}_2\text{S}$  is  $1.2 \times 10^{-13}$ , calculate the concentration of  $\text{S}^{2-}$  under both conditions.

6.46 The ionization constant of acetic acid is  $1.74 \times 10^{-5}$ . 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.

6.47 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  $\text{p}K_a$ .

6.48 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

6.49 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  $\text{Ca}(\text{OH})_2$  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.

6.50 The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the  $\text{p}K_a$  of bromoacetic acid.

6.51 The pH of 0.005M codeine ( $\text{C}_{18}\text{H}_{21}\text{NO}_3$ ) solution is 9.95. Calculate its ionization constant and  $\text{p}K_b$ .

6.52 What is the pH of 0.001M aniline solution? The ionization constant of aniline can be taken from Table 6.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

6.53 Calculate the degree of ionization of 0.05M acetic acid if its  $\text{p}K_a$  value is 4.74. How is the degree of dissociation affected when its solution also contains  
(a) 0.01M (b) 0.1M in HCl ?

6.54 The ionization constant of dimethylamine is  $5.4 \times 10^{-4}$ . 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?

6.55 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.

6.56 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.

6.57 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?

6.58 The solubility of  $\text{Sr}(\text{OH})_2$  at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

- 6.59 The ionization constant of propanoic acid is  $1.32 \times 10^{-5}$ . 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?
- 6.60 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.
- 6.61 The ionization constant of nitrous acid is  $4.5 \times 10^{-4}$ . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.
- 6.62 A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.
- 6.63 Predict if the solutions of the following salts are neutral, acidic or basic:  
NaCl, KBr, NaCN,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_2$  and KF
- 6.64 The ionization constant of chloroacetic acid is  $1.35 \times 10^{-3}$ . What will be the pH of 0.1M acid and its 0.1M sodium salt solution?
- 6.65 Ionic product of water at 310 K is  $2.7 \times 10^{-14}$ . What is the pH of neutral water at this temperature?
- 6.66 Calculate the pH of the resultant mixtures:
- 10 mL of 0.2M  $\text{Ca}(\text{OH})_2$  + 25 mL of 0.1M HCl
  - 10 mL of 0.01M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.01M  $\text{Ca}(\text{OH})_2$
  - 10 mL of 0.1M  $\text{H}_2\text{SO}_4$  + 10 mL of 0.1M KOH
- 6.67 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 6.9. Determine also the molarities of individual ions.
- 6.68 The solubility product constant of  $\text{Ag}_2\text{CrO}_4$  and AgBr are  $1.1 \times 10^{-12}$  and  $5.0 \times 10^{-13}$  respectively. Calculate the ratio of the molarities of their saturated solutions.
- 6.69 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  $K_{sp} = 7.4 \times 10^{-8}$ ).
- 6.70 The ionization constant of benzoic acid is  $6.46 \times 10^{-5}$  and  $K_{sp}$  for silver benzoate is  $2.5 \times 10^{-13}$ . How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?
- 6.71 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,  $K_{sp} = 6.3 \times 10^{-18}$ ).
- 6.72 What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate,  $K_{sp}$  is  $9.1 \times 10^{-6}$ ).
- 6.73 The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is  $1.0 \times 10^{-19}$  M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following:  $\text{FeSO}_4$ ,  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2$ , in which of these solutions precipitation will take place?



## UNIT 7

J1083CH08

# 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.

### 7.1 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:



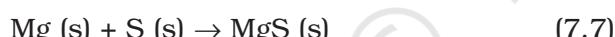
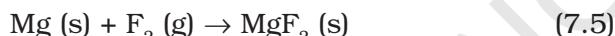
In reactions (7.1) and (7.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.



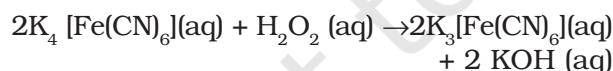
A careful examination of reaction (7.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.



As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (7.1 to 7.4), 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 :



Incorporating the reactions (7.5 to 7.7) 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 :

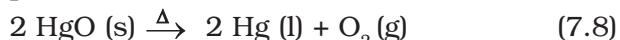


is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term "**oxidation**" is defined as the **addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance**.

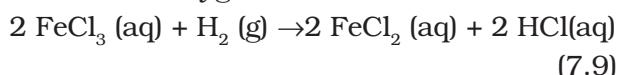
In the beginning, reduction was considered as removal of oxygen from a compound. However, the term **reduction** has been

broadened these days to include **removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance**.

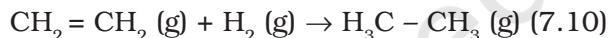
According to the definition given above, the following are the examples of reduction processes:



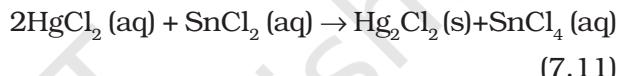
(removal of oxygen from mercuric oxide )



(removal of electronegative element, chlorine from ferric chloride)



(addition of hydrogen)

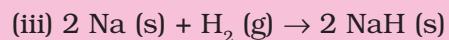
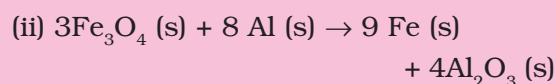
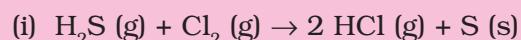


(addition of mercury to mercuric chloride)

In reaction (7.11) 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 7.1

In the reactions given below, identify the species undergoing oxidation and reduction:



### Solution

(i)  $\text{H}_2\text{S}$  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

$(\text{Fe}_3\text{O}_4)$  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.

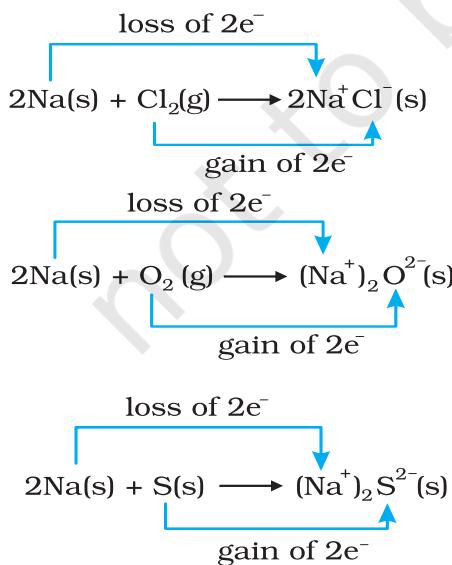
Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

## 7.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

We have already learnt that the reactions



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  $\text{Na}^+\text{Cl}^-(\text{s})$ ,  $(\text{Na}^+)_2\text{O}^{2-}(\text{s})$ , and  $(\text{Na}^+)_2\text{S}^{2-}(\text{s})$ . Development of charges on the species produced suggests us to rewrite the reactions (7.12 to 7.14) in the following manner :



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.



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 :



Reactions 7.12 to 7.14 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 (7.12 to 7.14) 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

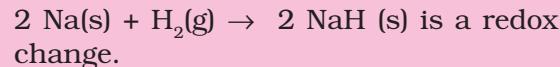
**Oxidation** : Loss of electron(s) by any species.

**Reduction** : Gain of electron(s) by any species.

**Oxidising agent** : Acceptor of electron(s).

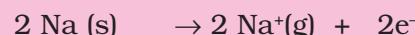
**Reducing agent** : Donor of electron(s).

### Problem 7.2 Justify that the reaction:

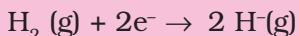


### Solution

Since in the above reaction the compound formed is an ionic compound, which may also be represented as  $\text{Na}^+\text{H}^-(\text{s})$ , this suggests that one half reaction in this process is :



and the other half reaction is:

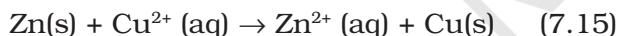


This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.

### 7.2.1 Competitive Electron Transfer Reactions

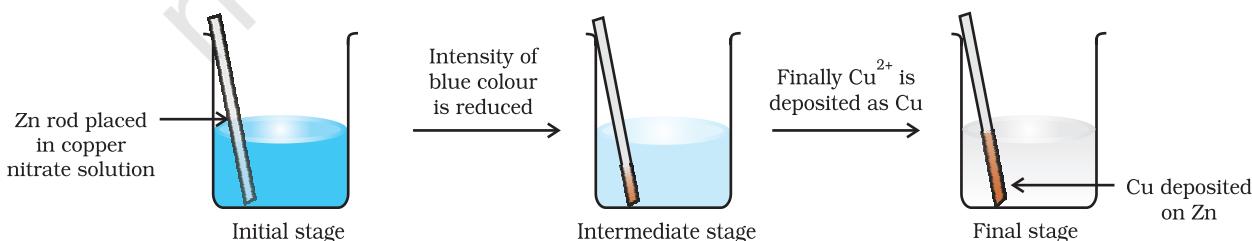
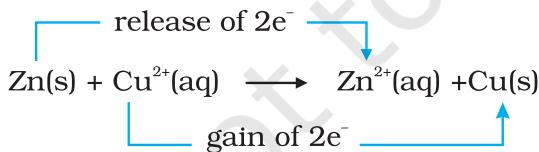
Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 7.1, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of  $\text{Zn}^{2+}$  ions among the products can easily be judged when the blue colour of the solution due to  $\text{Cu}^{2+}$  has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing  $\text{Zn}^{2+}$  ions, appearance of white zinc sulphide,  $\text{ZnS}$  can be seen on making the solution alkaline with ammonia.

The reaction between metallic zinc and the aqueous solution of copper nitrate is :



In reaction (7.15), zinc has lost electrons to form  $\text{Zn}^{2+}$  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.

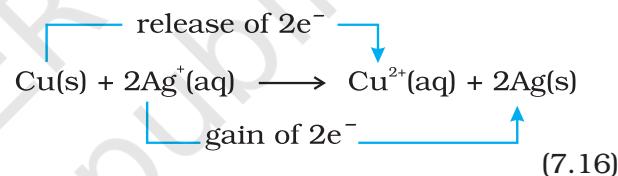
Reaction (7.15) may be rewritten as :



**Fig. 7.1** Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.

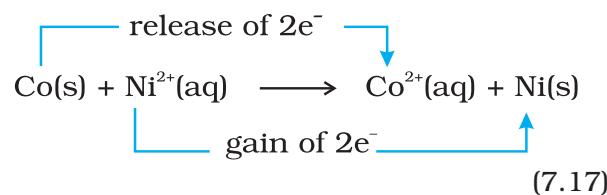
At this stage we may investigate the state of equilibrium for the reaction represented by equation (7.15). For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of  $\text{Cu}^{2+}$  ions by passing  $\text{H}_2\text{S}$  gas through the solution to produce the black colour of cupric sulphide,  $\text{CuS}$ , does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of  $\text{Cu}^{2+}$  formed cannot be detected. We thus conclude that the state of equilibrium for the reaction (7.15) greatly favours the products over the reactants.

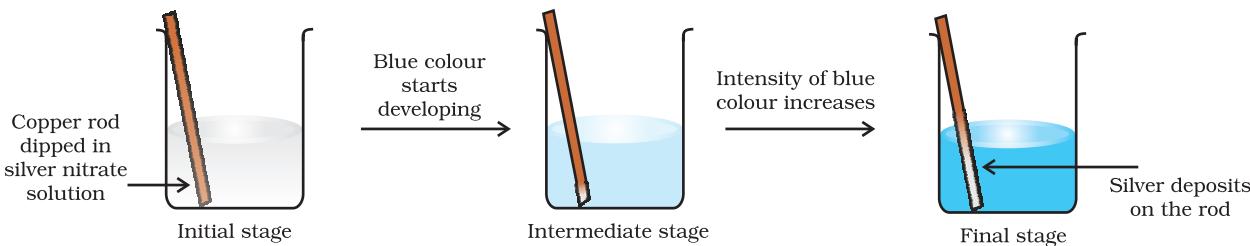
Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 7.2. The solution develops blue colour due to the formation of  $\text{Cu}^{2+}$  ions on account of the reaction:



Here,  $\text{Cu(s)}$  is oxidised to  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Ag}^+(\text{aq})$  is reduced to  $\text{Ag(s)}$ . Equilibrium greatly favours the products  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Ag(s)}$ .

By way of contrast, let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs here is :





**Fig. 7.2** Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.

At equilibrium, chemical tests reveal that both  $\text{Ni}^{2+}(\text{aq})$  and  $\text{Co}^{2+}(\text{aq})$  are present at moderate concentrations. In this case, neither the reactants [ $\text{Co(s)}$ ] and  $\text{Ni}^{2+}(\text{aq})$ ] nor the products [ $\text{Co}^{2+}(\text{aq})$  and  $\text{Ni(s)}$ ] 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:  $\text{Zn} > \text{Cu} > \text{Ag}$ . 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.

### 7.3 OXIDATION NUMBER

A less obvious example of electron transfer is realised when hydrogen combines with oxygen to form water by the reaction:



Though not simple in its approach, yet we can visualise the H atom as going from a neutral (zero) state in  $\text{H}_2$  to a positive state in  $\text{H}_2\text{O}$ , the O atom goes from a zero state in  $\text{O}_2$  to a dinegative state in  $\text{H}_2\text{O}$ . It is assumed that there is an electron transfer from H to O and consequently  $\text{H}_2$  is oxidised and  $\text{O}_2$  is reduced.

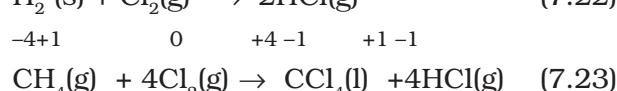
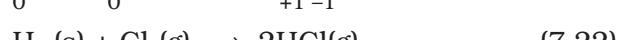
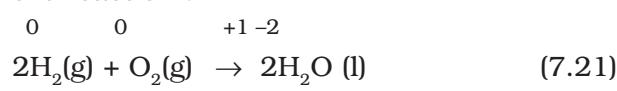
However, as we shall see later, the charge transfer is only partial and is perhaps better described as an electron shift rather than a complete loss of electron by H and gain by O. What has been said here with respect to equation (7.18) may be true for a good number of other reactions involving covalent compounds. Two such examples of this class of the reactions are:



and,



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 electronegative atom. For example, we rewrite equations (7.18 to 7.20) to show charge on each of the atoms forming part of the reaction :



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 pair**

**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  $\text{Na}_2\text{S}_2\text{O}_3/\text{Cr}_2\text{O}_7^{2-}$ , 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  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{P}_4$ ,  $\text{S}_8$ ,  $\text{Na}$ ,  $\text{Mg}$ ,  $\text{Al}$  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  $\text{Na}^+$  ion has an oxidation number of +1,  $\text{Mg}^{2+}$  ion, +2,  $\text{Fe}^{3+}$  ion, +3,  $\text{Cl}^-$  ion, -1,  $\text{O}^{2-}$  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.,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ ), each oxygen atom is assigned an oxidation number of -1, in superoxides (e.g.,  $\text{KO}_2$ ,  $\text{RbO}_2$ ) each oxygen atom is assigned an oxidation number of  $-(\frac{1}{2})$ . The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride ( $\text{OF}_2$ ) and dioxygen difluoride ( $\text{O}_2\text{F}_2$ ), 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  $\text{LiH}$ ,  $\text{NaH}$ , and  $\text{CaH}_2$ , 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,  $(\text{CO}_3)^{2-}$  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  $\text{CO}_2$ , 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 <sub>4</sub>	AlF <sub>3</sub>	SiCl <sub>4</sub>	P <sub>4</sub> O <sub>10</sub>	SF <sub>6</sub>	HClO
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<sub>3</sub>. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl<sub>2</sub> and Sn(IV)Cl<sub>4</sub>. 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<sub>2</sub>(I)Cl<sub>2</sub> is the reduced form of Hg(II) Cl<sub>2</sub>.

### Problem 7.3

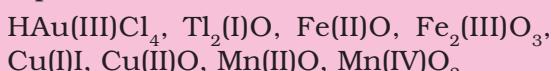
Using Stock notation, represent the following compounds :HAuCl<sub>4</sub>, Tl<sub>2</sub>O, FeO, Fe<sub>2</sub>O<sub>3</sub>, CuI, CuO, MnO and MnO<sub>2</sub>.

#### 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 <sub>4</sub>	→	Au has 3
Tl <sub>2</sub> O	→	Tl has 1
FeO	→	Fe has 2
Fe <sub>2</sub> O <sub>3</sub>	→	Fe has 3
CuI	→	Cu has 1
CuO	→	Cu has 2
MnO	→	Mn has 2
MnO <sub>2</sub>	→	Mn has 4

Therefore, these compounds may be represented as:



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.

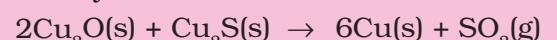
**Oxidising agent:** A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as **oxidants** also.

**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 7.4

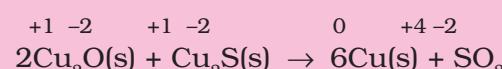
Justify that the reaction:



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:



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,  $\text{Cu}_2\text{O}$  helps sulphur in  $\text{Cu}_2\text{S}$  to increase its oxidation number, therefore,  $\text{Cu}(\text{l})$  is an oxidant; and sulphur of  $\text{Cu}_2\text{S}$  helps copper both in  $\text{Cu}_2\text{S}$  itself and  $\text{Cu}_2\text{O}$  to decrease its oxidation number; therefore, sulphur of  $\text{Cu}_2\text{S}$  is reductant.

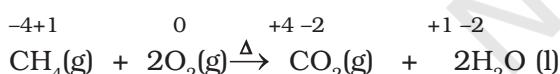
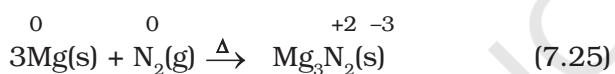
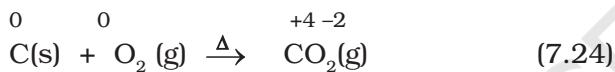
### 7.3.1 Types of Redox Reactions

#### 1. Combination reactions

A combination reaction may be denoted in the manner:

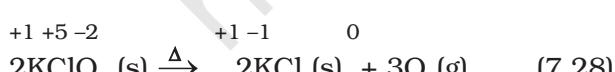
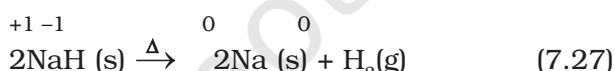
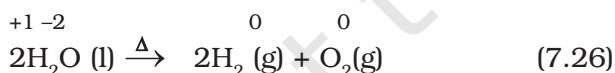


Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions. Some important examples of this category are:



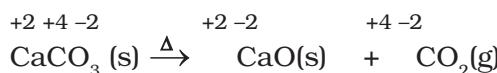
#### 2. Decomposition reactions

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:



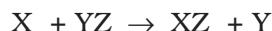
It may carefully be noted that there is no change in the oxidation number of hydrogen in methane under combination reactions and that of potassium in potassium chlorate in reaction (7.28). This may also be noted

here that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.



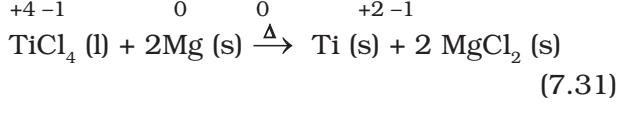
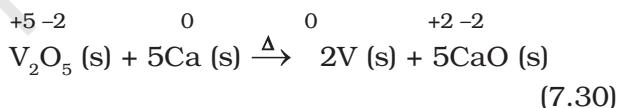
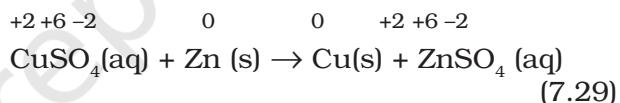
#### 3. Displacement reactions

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:



Displacement reactions fit into two categories: metal displacement and non-metal displacement.

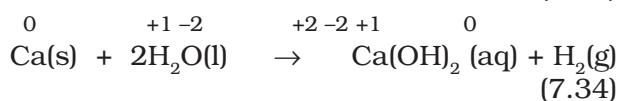
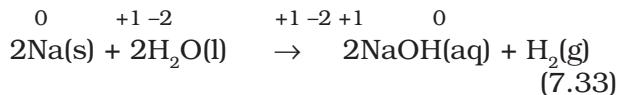
**(a) Metal displacement:** A metal in a compound can be displaced by another metal in the uncombined state. We have already discussed about this class of the reactions under section 7.2.1. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are:



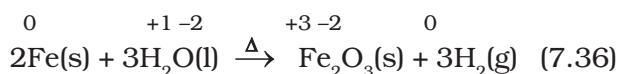
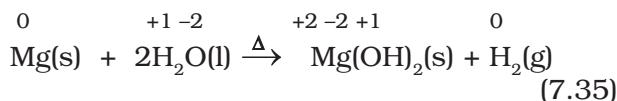
In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

**(b) Non-metal displacement:** The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

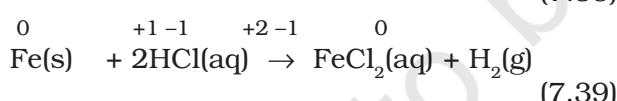
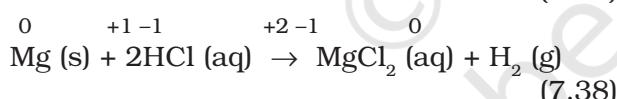
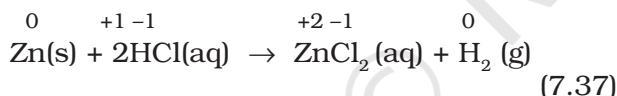
All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.



Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:



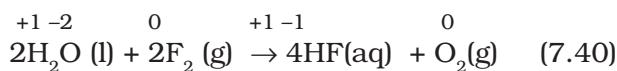
Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are:



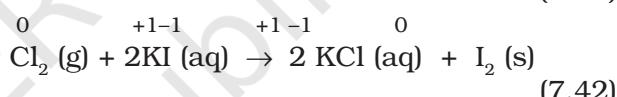
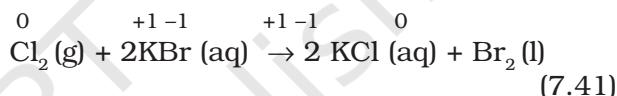
Reactions (7.37 to 7.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.

In section (7.2.1) 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>

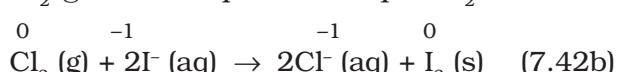
Cu>Ag. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :



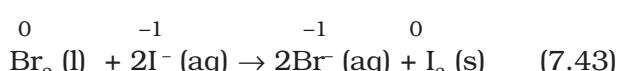
It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:



As Br<sub>2</sub> and I<sub>2</sub> are coloured and dissolve in CCl<sub>4</sub>, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:



Reactions (7.41) and (7.42) form the basis of identifying Br<sup>-</sup> and I<sup>-</sup> 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:



The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

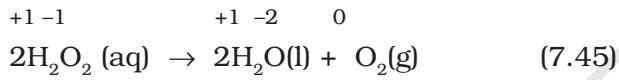


here X denotes a halogen element. Whereas chemical means are available to oxidise Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>, as fluorine is the strongest oxidising

agent; there is no way to convert  $\text{F}^-$  ions to  $\text{F}_2$  by chemical means. The only way to achieve  $\text{F}_2$  from  $\text{F}^-$  is to oxidise electrolytically, the details of which you will study at a later stage.

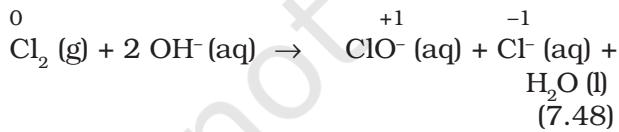
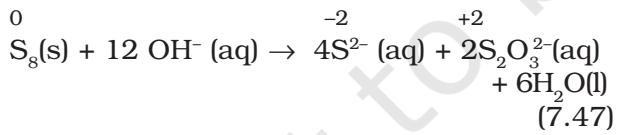
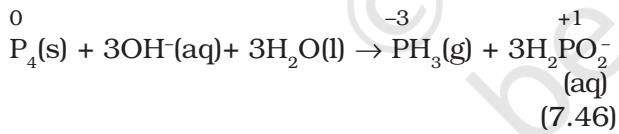
#### 4. Disproportionation reactions

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.



Here the oxygen of peroxide, which is present in  $-1$  state, is converted to zero oxidation state in  $\text{O}_2$  and decreases to  $-2$  oxidation state in  $\text{H}_2\text{O}$ .

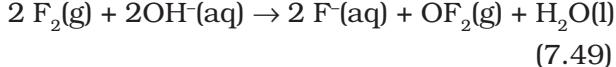
Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :



The reaction (7.48) describes the formation of household bleaching agents. The hypochlorite ion ( $\text{ClO}^-$ ) 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 (7.48),

fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows:



(It is to be noted with care that fluorine in reaction (7.49) 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 7.5

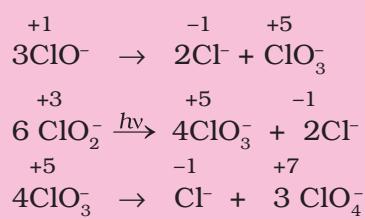
Which of the following species, do not show disproportionation reaction and why ?



Also write reaction for each of the species that disproportionate.

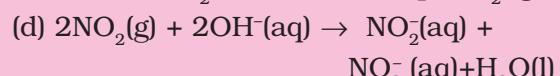
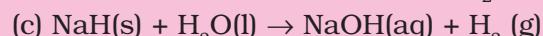
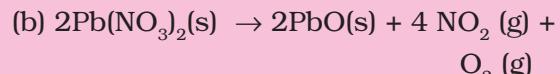
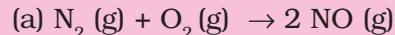
#### Solution

Among the oxoanions of chlorine listed above,  $\text{ClO}_4^-$  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:



#### Problem 7.6

Suggest a scheme of classification of the following redox reactions



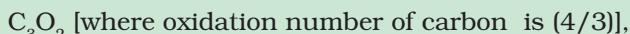
**Solution**

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

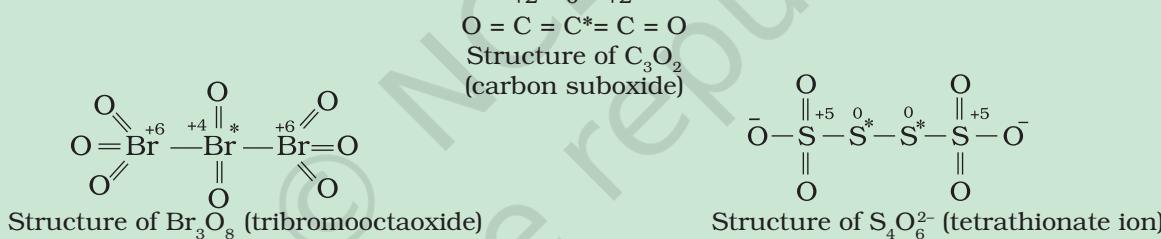
reaction (c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of  $\text{NO}_2$  (+4 state) into  $\text{NO}_2^-$  (+3 state) and  $\text{NO}_3^-$  (+5 state). Therefore 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:



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  $\text{C}_3\text{O}_2$ ,  $\text{Br}_3\text{O}_8$  and  $\text{S}_4\text{O}_6^{2-}$  reveal the following bonding situations:

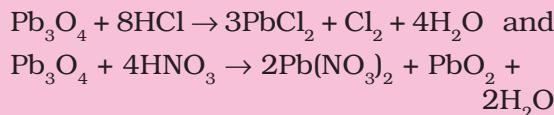


The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in  $\text{C}_3\text{O}_2$ , two carbon atoms are present in +2 oxidation state each, whereas the third 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  $\text{Br}_3\text{O}_8$ , 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  $\text{S}_4\text{O}_6^{2-}$ , 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  $\text{S}_4\text{O}_6^{2-}$  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.  $\text{Fe}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Pb}_3\text{O}_4$  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  $\text{O}_2^+$  and  $\text{O}_2^-$  where it is  $+1/2$  and  $-1/2$  respectively.

### Problem 7.7

Why do the following reactions proceed differently?

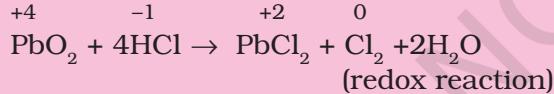
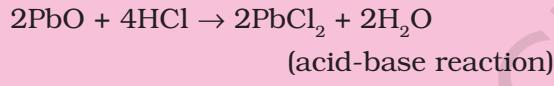


#### Solution

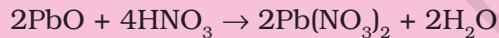
$\text{Pb}_3\text{O}_4$  is actually a stoichiometric mixture of 2 mol of  $\text{PbO}$  and 1 mol of  $\text{PbO}_2$ . In  $\text{PbO}_2$ , lead is present in +4 oxidation state, whereas the stable oxidation state of lead in  $\text{PbO}$  is +2.  $\text{PbO}_2$  thus can act as an oxidant (oxidising agent) and, therefore, can oxidise  $\text{Cl}^-$  ion of  $\text{HCl}$  into chlorine. We may also keep in mind that  $\text{PbO}$  is a basic oxide. Therefore, the reaction



can be splitted into two reactions namely:



Since  $\text{HNO}_3$  itself is an oxidising agent therefore, it is unlikely that the reaction may occur between  $\text{PbO}_2$  and  $\text{HNO}_3$ . However, the acid-base reaction occurs between  $\text{PbO}$  and  $\text{HNO}_3$  as:



It is the passive nature of  $\text{PbO}_2$  against  $\text{HNO}_3$  that makes the reaction different from the one that follows with  $\text{HCl}$ .

### 7.3.2 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 number 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  $\text{H}^+$  or  $\text{OH}^-$  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  $\text{H}^+$  ions in the equation; if in basic solution, use  $\text{OH}^-$  ions.

**Step 5 :** Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water ( $\text{H}_2\text{O}$ ) 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.

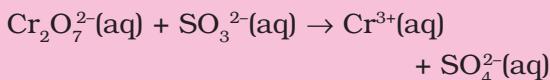
Let us now explain the steps involved in the method with the help of a few problems given below:

### Problem 7.8

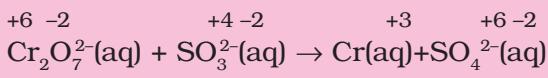
Write the net ionic equation for the reaction of potassium dichromate(VI),  $\text{K}_2\text{Cr}_2\text{O}_7$  with sodium sulphite,  $\text{Na}_2\text{SO}_3$ , in an acid solution to give chromium(III) ion and the sulphate ion.

**Solution**

**Step 1:** The skeletal ionic equation is:

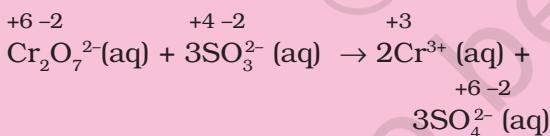


**Step 2:** Assign oxidation numbers for Cr and S

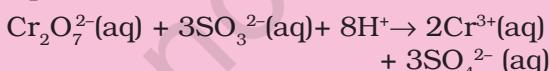


This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

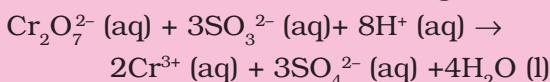
**Step 3:** Calculate the increase and decrease of oxidation number, and make them equal: from step-2 we can notice that there is change in oxidation state of chromium and sulphur. Oxidation state of chromium changes from +6 to +3. There is decrease of +3 in oxidation state of chromium on right hand side of the equation. Oxidation state of sulphur changes from +4 to +6. There is an increase of +2 in the oxidation state of sulphur on right hand side. To make the increase and decrease of oxidation state equal, place numeral 2 before chromium ion on right hand side and numeral 3 before sulphate ion on right hand side and balance the chromium and sulphur atoms on both the sides of the equation. Thus we get



**Step 4:** As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add  $8\text{H}^+$  on the left to make ionic charges equal



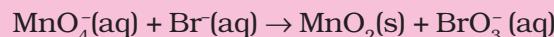
**Step 5:** Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e.,  $4\text{H}_2\text{O}$ ) on the right to achieve balanced redox change.

**Problem 7.9**

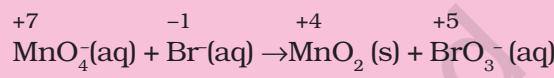
Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

**Solution**

**Step 1:** The skeletal ionic equation is :

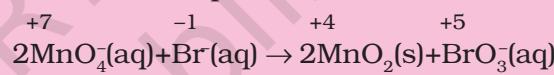


**Step 2:** Assign oxidation numbers for Mn and Br

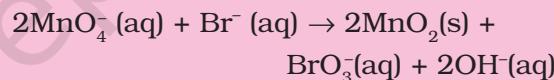


This indicates that permanganate ion is the oxidant and bromide ion is the reductant.

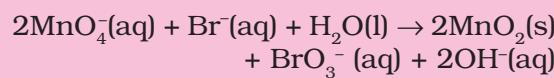
**Step 3:** Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.



**Step 4:** As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add  $2\text{OH}^-$  ions on the right to make ionic charges equal.



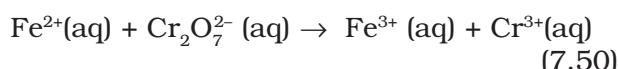
**Step 5:** Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one  $\text{H}_2\text{O}$  molecule) on the left side to achieve balanced redox change.



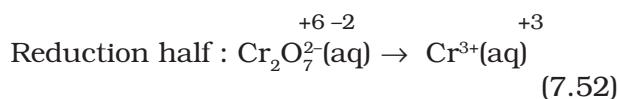
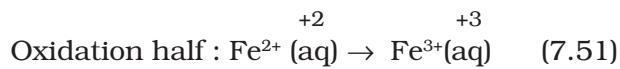
**(b) Half Reaction Method:** In this method, the two half equations are balanced separately and then added together to give balanced equation.

Suppose we are to balance the equation showing the oxidation of  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions by dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) in acidic medium, wherein,  $\text{Cr}_2\text{O}_7^{2-}$  ions are reduced to  $\text{Cr}^{3+}$  ions. The following steps are involved in this task.

**Step 1:** Produce unbalanced equation for the reaction in ionic form :



**Step 2:** Separate the equation into half-reactions:

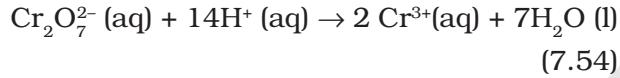


**Step 3:** Balance the atoms other than O and H in each half reaction individually. Here the oxidation half reaction is already balanced with respect to Fe atoms. For the reduction half reaction, we multiply the  $\text{Cr}^{3+}$  by 2 to balance Cr atoms.



**Step 4:** For reactions occurring in acidic medium, add  $\text{H}_2\text{O}$  to balance O atoms and  $\text{H}^+$  to balance H atoms.

Thus, we get :

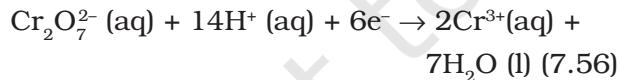


**Step 5:** Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate number.

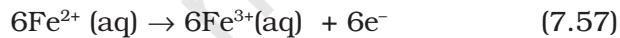
The oxidation half reaction is thus rewritten to balance the charge:



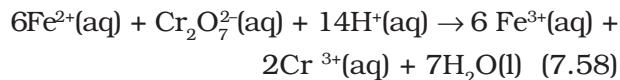
Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.



To equalise the number of electrons in both the half reactions, we multiply the oxidation half reaction by 6 and write as :



**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 :



**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.

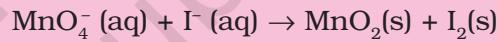
For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each  $\text{H}^+$  ion, add an equal number of  $\text{OH}^-$  ions to both sides of the equation. Where  $\text{H}^+$  and  $\text{OH}^-$  appear on the same side of the equation, combine these to give  $\text{H}_2\text{O}$ .

### Problem 7.10

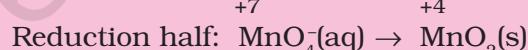
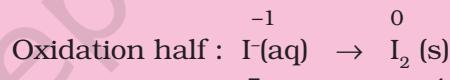
Permanganate(VII) ion,  $\text{MnO}_4^-$  in basic solution oxidises iodide ion,  $\text{I}^-$  to produce molecular iodine ( $\text{I}_2$ ) and manganese (IV) oxide ( $\text{MnO}_2$ ). Write a balanced ionic equation to represent this redox reaction.

#### Solution

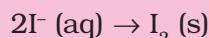
**Step 1:** First we write the skeletal ionic equation, which is



**Step 2:** The two half-reactions are:



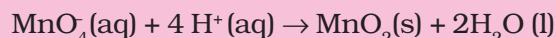
**Step 3:** To balance the I atoms in the oxidation half reaction, we rewrite it as:



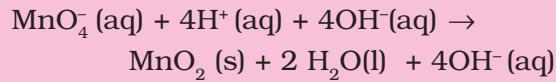
**Step 4:** To balance the O atoms in the reduction half reaction, we add two water molecules on the right:



To balance the H atoms, we add four  $\text{H}^+$  ions on the left:

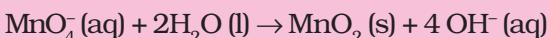


As the reaction takes place in a basic solution, therefore, for four  $\text{H}^+$  ions, we add four  $\text{OH}^-$  ions to both sides of the equation:

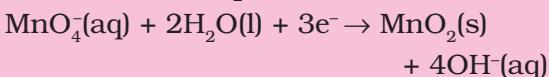
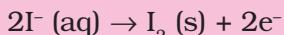


Replacing the  $\text{H}^+$  and  $\text{OH}^-$  ions with water,

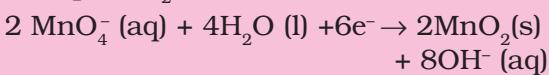
the resultant equation is:



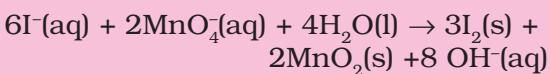
**Step 5 :** In this step we balance the charges of the two half-reactions in the manner depicted as:



Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.



**Step 6:** Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.



**Step 7:** A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

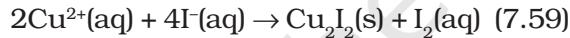
### 7.3.3 Redox Reactions as the Basis for Titrations

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:

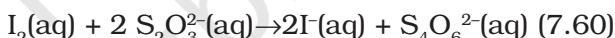
- (i) In one situation, the reagent itself is intensely coloured, e.g., permanganate ion,  $\text{MnO}_4^-$ . Here  $\text{MnO}_4^-$  acts as the self indicator. The visible end point in this case is achieved after the last of the reductant ( $\text{Fe}^{2+}$  or  $\text{C}_2\text{O}_4^{2-}$ ) is oxidised and the first lasting tinge of pink colour appears at  $\text{MnO}_4^-$  concentration as low as  $10^{-6} \text{ mol dm}^{-3}$  ( $10^{-6} \text{ mol L}^{-1}$ ). 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  $\text{MnO}_4^-$  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  $\text{Cr}_2\text{O}_7^{2-}$ , 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  $\text{I}^-$  ions, say, for example,  $\text{Cu}(\text{II})$ :



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 ( $\text{S}_2\text{O}_3^{2-}$ ), which too is a redox reaction:



$\text{I}_2$ , though insoluble in water, remains in solution containing  $\text{KI}$  as  $\text{KI}_3$ .

On addition of starch after the liberation of iodine from the reaction of  $\text{Cu}^{2+}$  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.

### 7.3.4 Limitations of Concept of Oxidation Number

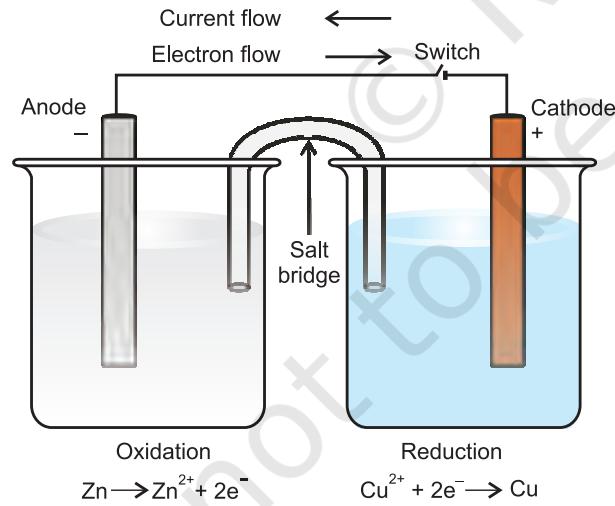
As you have observed in the above discussion, the concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

## 7.4 REDOX REACTIONS AND ELECTRODE PROCESSES

The experiment corresponding to reaction (7.15), 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



**Fig. 7.3** 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.

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. 7.3). 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. 7.3 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:

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 ( $E^\circ$ ) 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  $E^\circ$  means that the redox couple is a stronger

reducing agent than the  $\text{H}^+/\text{H}_2$  couple. A positive  $E^\ominus$  means that the redox couple is a weaker reducing agent than the  $\text{H}^+/\text{H}_2$  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 7.1. You will learn more about electrode reactions and cells in Class XII.

**Table 7.1 The Standard Electrode Potentials at 298 K**

Ions are present as aqueous species and  $\text{H}_2\text{O}$  as liquid; gases and solids are shown by g and s respectively.

Reaction (Oxidised form + $ne^-$ )	→ Reduced form)	$E^\ominus / \text{V}$
$\text{F}_2(\text{g}) + 2e^-$	→ $2\text{F}^-$	2.87
$\text{Co}^{3+} + e^-$	→ $\text{Co}^{2+}$	1.81
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^-$	→ $2\text{H}_2\text{O}$	1.78
$\text{MnO}_4^- + 8\text{H}^+ + 5e^-$	→ $\text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{Au}^{3+} + 3e^-$	→ $\text{Au}(\text{s})$	1.40
$\text{Cl}_2(\text{g}) + 2e^-$	→ $2\text{Cl}^-$	1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^-$	→ $2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4e^-$	→ $2\text{H}_2\text{O}$	1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2e^-$	→ $\text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{Br}_2 + 2e^-$	→ $2\text{Br}^-$	1.09
$\text{NO}_3^- + 4\text{H}^+ + 3e^-$	→ $\text{NO}(\text{g}) + 2\text{H}_2\text{O}$	0.97
$2\text{Hg}^{2+} + 2e^-$	→ $\text{Hg}_2^{2+}$	0.92
$\text{Ag}^+ + e^-$	→ $\text{Ag}(\text{s})$	0.80
$\text{Fe}^{3+} + e^-$	→ $\text{Fe}^{2+}$	0.77
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2e^-$	→ $\text{H}_2\text{O}_2$	0.68
$\text{I}_2(\text{s}) + 2e^-$	→ $2\text{I}^-$	0.54
$\text{Cu}^+ + e^-$	→ $\text{Cu}(\text{s})$	0.52
$\text{Cu}^{2+} + 2e^-$	→ $\text{Cu}(\text{s})$	0.34
$\text{AgCl}(\text{s}) + e^-$	→ $\text{Ag}(\text{s}) + \text{Cl}^-$	0.22
$\text{AgBr}(\text{s}) + e^-$	→ $\text{Ag}(\text{s}) + \text{Br}^-$	0.10
<b><math>2\text{H}^+ + 2e^-</math></b>	→ <b><math>\text{H}_2(\text{g})</math></b>	<b>0.00</b>
$\text{Pb}^{2+} + 2e^-$	→ $\text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+} + 2e^-$	→ $\text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+} + 2e^-$	→ $\text{Ni}(\text{s})$	-0.25
$\text{Fe}^{2+} + 2e^-$	→ $\text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+} + 3e^-$	→ $\text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+} + 2e^-$	→ $\text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O} + 2e^-$	→ $\text{H}_2(\text{g}) + 2\text{OH}^-$	-0.83
$\text{Al}^{3+} + 3e^-$	→ $\text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+} + 2e^-$	→ $\text{Mg}(\text{s})$	-2.36
$\text{Na}^+ + e^-$	→ $\text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+} + 2e^-$	→ $\text{Ca}(\text{s})$	-2.87
$\text{K}^+ + e^-$	→ $\text{K}(\text{s})$	-2.93
$\text{Li}^+ + e^-$	→ $\text{Li}(\text{s})$	-3.05

- A negative  $E^\ominus$  means that the redox couple is a stronger reducing agent than the  $\text{H}^+/\text{H}_2$  couple.
- A positive  $E^\ominus$  means that the redox couple is a weaker reducing agent than the  $\text{H}^+/\text{H}_2$  couple.

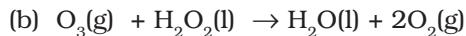
## SUMMARY

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.

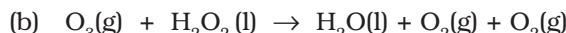
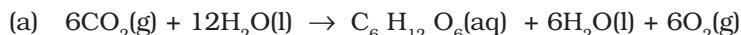
## EXERCISES

- 7.1 Assign oxidation number to the underlined elements in each of the following species:
  - (a)  $\underline{\text{NaH}_2\text{PO}_4}$
  - (b)  $\text{NaHSO}_4$
  - (c)  $\text{H}_4\underline{\text{P}_2}\text{O}_7$
  - (d)  $\text{K}_2\underline{\text{MnO}}_4$
  - (e)  $\text{Ca}\underline{\text{O}}_2$
  - (f)  $\text{Na}\underline{\text{BH}}_4$
  - (g)  $\text{H}_2\underline{\text{S}_2}\text{O}_7$
  - (h)  $\text{KAl}(\underline{\text{SO}}_4)_2 \cdot 12 \text{H}_2\text{O}$
- 7.2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ?
  - (a)  $\text{KI}_3$
  - (b)  $\text{H}_2\underline{\text{S}_4}\text{O}_6$
  - (c)  $\underline{\text{Fe}}_3\text{O}_4$
  - (d)  $\text{CH}_3\underline{\text{CH}_2}\text{OH}$
  - (e)  $\text{CH}_3\underline{\text{COOH}}$
- 7.3 Justify that the following reactions are redox reactions:
  - (a)  $\text{CuO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\text{O(g)}$
  - (b)  $\text{Fe}_2\text{O}_3\text{(s)} + 3\text{CO(g)} \rightarrow 2\text{Fe(s)} + 3\text{CO}_2\text{(g)}$
  - (c)  $4\text{BCl}_3\text{(g)} + 3\text{LiAlH}_4\text{(s)} \rightarrow 2\text{B}_2\text{H}_6\text{(g)} + 3\text{LiCl(s)} + 3\text{AlCl}_3\text{(s)}$
  - (d)  $2\text{K(s)} + \text{F}_2\text{(g)} \rightarrow 2\text{K}^+\text{F}^-(\text{s})$
  - (e)  $4\text{NH}_3\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(g)}$
- 7.4 Fluorine reacts with ice and results in the change:  
 $\text{H}_2\text{O(s)} + \text{F}_2\text{(g)} \rightarrow \text{HF(g)} + \text{HOF(g)}$   
 Justify that this reaction is a redox reaction.
- 7.5 Calculate the oxidation number of sulphur, chromium and nitrogen in  $\text{H}_2\text{SO}_5$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{NO}_3^-$ . Suggest structure of these compounds. Count for the fallacy.
- 7.6 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
- 7.7 Suggest a list of the substances where carbon can exhibit oxidation states from  $-4$  to  $+4$  and nitrogen from  $-3$  to  $+5$ .
- 7.8 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 ?
- 7.9 Consider the reactions:
  - (a)  $6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6\text{(aq)} + 6\text{O}_2\text{(g)}$



Why it is more appropriate to write these reactions as :



Also suggest a technique to investigate the path of the above (a) and (b) redox reactions.

7.10 The compound  $AgF_2$  is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ?

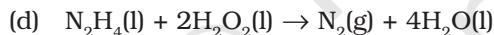
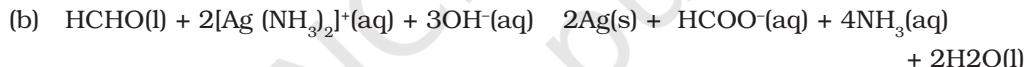
7.11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

7.12 How do you count for the following observations ?

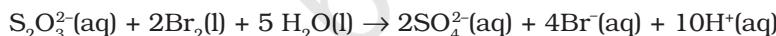
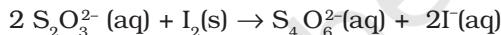
(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction.

(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 ?

7.13 Identify the substance oxidised reduced, oxidising agent and reducing agent for each of the following reactions:



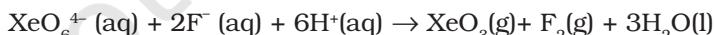
7.14 Consider the reactions :



Why does the same reductant, thiosulphate react differently with iodine and bromine ?

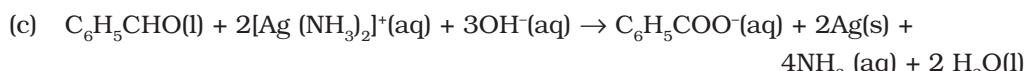
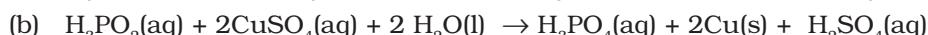
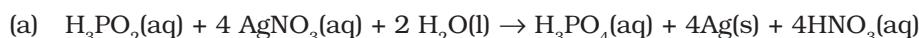
7.15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

7.16 Why does the following reaction occur ?



What conclusion about the compound  $Na_4XeO_6$  (of which  $XeO_6^{4-}$  is a part) can be drawn from the reaction.

7.17 Consider the reactions:



What inference do you draw about the behaviour of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  from these reactions?

- 7.18 Balance the following redox reactions by ion – electron method :
- $\text{MnO}_4^- (\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{MnO}_2 (\text{s}) + \text{I}_2 (\text{s})$  (in basic medium)
  - $\text{MnO}_4^- (\text{aq}) + \text{SO}_2 (\text{g}) \rightarrow \text{Mn}^{2+} (\text{aq}) + \text{HSO}_4^- (\text{aq})$  (in acidic solution)
  - $\text{H}_2\text{O}_2 (\text{aq}) + \text{Fe}^{2+} (\text{aq}) \rightarrow \text{Fe}^{3+} (\text{aq}) + \text{H}_2\text{O} (\text{l})$  (in acidic solution)
  - $\text{Cr}_2\text{O}_7^{2-} + \text{SO}_2 (\text{g}) \rightarrow \text{Cr}^{3+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq})$  (in acidic solution)
- 7.19 Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.
- $\text{P}_4 (\text{s}) + \text{OH}^- (\text{aq}) \rightarrow \text{PH}_3 (\text{g}) + \text{HPO}_4^{2-} (\text{aq})$
  - $\text{N}_2\text{H}_4 (\text{l}) + \text{ClO}_3^- (\text{aq}) \rightarrow \text{NO} (\text{g}) + \text{Cl}^- (\text{g})$
  - $\text{Cl}_2\text{O}_7 (\text{g}) + \text{H}_2\text{O}_2 (\text{aq}) \rightarrow \text{ClO}_4^- (\text{aq}) + \text{O}_2 (\text{g}) + \text{H}^+$
- 7.20 What sorts of informations can you draw from the following reaction ?
- $$(\text{CN})_2 (\text{g}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{CN}^- (\text{aq}) + \text{CNO}^- (\text{aq}) + \text{H}_2\text{O} (\text{l})$$
- 7.21 The  $\text{Mn}^{3+}$  ion is unstable in solution and undergoes disproportionation to give  $\text{Mn}^{2+}$ ,  $\text{MnO}_2$ , and  $\text{H}^+$  ion. Write a balanced ionic equation for the reaction.
- 7.22 Consider the elements :
- Cs, Ne, I and F
- Identify the element that exhibits only negative oxidation state.
  - Identify the element that exhibits only positive oxidation state.
  - Identify the element that exhibits both positive and negative oxidation states.
  - Identify the element which exhibits neither the negative nor does the positive oxidation state.
- 7.23 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.
- 7.24 Refer to the periodic table given in your book and now answer the following questions:
- Select the possible non metals that can show disproportionation reaction.
  - Select three metals that can show disproportionation reaction.
- 7.25 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 ?
- 7.26 Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible:
- $\text{Fe}^{3+} (\text{aq})$  and  $\text{I}^- (\text{aq})$
  - $\text{Ag}^+ (\text{aq})$  and  $\text{Cu} (\text{s})$
  - $\text{Fe}^{3+} (\text{aq})$  and  $\text{Cu} (\text{s})$
  - $\text{Ag} (\text{s})$  and  $\text{Fe}^{3+} (\text{aq})$
  - $\text{Br}_2 (\text{aq})$  and  $\text{Fe}^{2+} (\text{aq})$ .

- 7.27 Predict the products of electrolysis in each of the following:
- (i) An aqueous solution of  $\text{AgNO}_3$  with silver electrodes
  - (ii) An aqueous solution  $\text{AgNO}_3$  with platinum electrodes
  - (iii) A dilute solution of  $\text{H}_2\text{SO}_4$  with platinum electrodes
  - (iv) An aqueous solution of  $\text{CuCl}_2$  with platinum electrodes.
- 7.28 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.
- 7.29 Given the standard electrode potentials,  
 $\text{K}^+/\text{K} = -2.93\text{V}$ ,  $\text{Ag}^+/\text{Ag} = 0.80\text{V}$ ,  
 $\text{Hg}^{2+}/\text{Hg} = 0.79\text{V}$   
 $\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$ .  $\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$   
arrange these metals in their increasing order of reducing power.
- 7.30 Depict the galvanic cell in which the reaction  $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$  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 8

11083CH12

# ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

## Objectives

After studying this unit, you will be able to

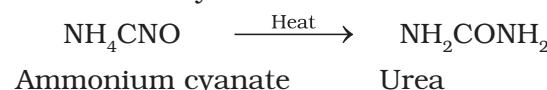
- understand reasons for tetravalence of carbon and shapes of organic molecules;
- write structures of organic molecules in various ways;
- classify the organic compounds;
- name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;
- understand 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.

### 8.1 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 compounds 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.



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.

## 8.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

### 8.2.1 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 ( $\text{CH}_4$ ), ethene ( $\text{C}_2\text{H}_4$ ), ethyne ( $\text{C}_2\text{H}_2$ ) 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 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.

### 8.2.2 Some Characteristic Features of $\pi$ Bonds

In a  $\pi$  (pi) bond formation, parallel orientation of the two *p* orbitals on adjacent atoms is necessary for a proper sideways overlap.

Thus, in  $\text{H}_2\text{C}=\text{CH}_2$  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  $\text{CH}_2$  fragment with respect to other interferes with maximum overlap of *p* orbitals and, therefore, such rotation about carbon-carbon double bond ( $\text{C}=\text{C}$ ) is restricted. The electron charge cloud of the  $\pi$  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,  $\pi$  bonds provide the most reactive centres in the molecules containing multiple bonds.

### Problem 8.1

How many  $\sigma$  and  $\pi$  bonds are present in each of the following molecules?

- (a)  $\text{HC}\equiv\text{CCH}=\text{CHCH}_3$  (b)  $\text{CH}_2=\text{C}=\text{CHCH}_3$

### Solution

- (a)  $\sigma_{\text{C}-\text{C}}: 4$ ;  $\sigma_{\text{C}-\text{H}}: 6$ ;  $\pi_{\text{C}=\text{C}}: 1$ ;  $\pi \text{C}\equiv\text{C}: 2$   
 (b)  $\sigma_{\text{C}-\text{C}}: 3$ ;  $\sigma_{\text{C}-\text{H}}: 6$ ;  $\pi_{\text{C}=\text{C}}: 2$ .

### Problem 8.2

What is the type of hybridisation of each carbon in the following compounds?

- (a)  $\text{CH}_3\text{Cl}$ , (b)  $(\text{CH}_3)_2\text{CO}$ , (c)  $\text{CH}_3\text{CN}$ ,  
 (d)  $\text{HCONH}_2$ , (e)  $\text{CH}_3\text{CH}=\text{CHCN}$

### 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 8.3

Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

- (a)  $\text{H}_2\text{C}=\text{O}$ , (b)  $\text{CH}_3\text{F}$ , (c)  $\text{HC}\equiv\text{N}$ .

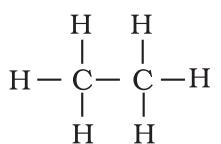
### Solution

- (a)  $sp^2$  hybridised carbon, trigonal planar;  
 (b)  $sp^3$  hybridised carbon, tetrahedral; (c)  $sp$  hybridised carbon, linear.

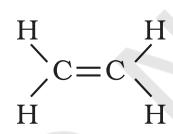
### 8.3 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

#### 8.3.1 Complete, Condensed and Bond-line Structural Formulas

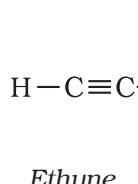
Structures of organic compounds are represented in several ways. The *Lewis structure* or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond 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*.



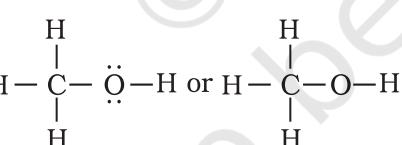
Ethane



Ethene



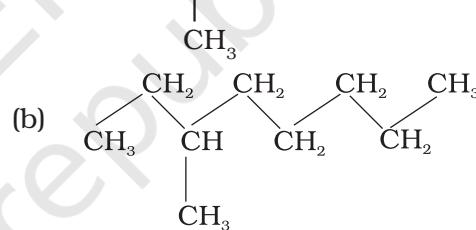
Ethyne



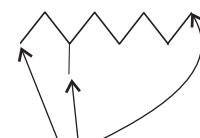
Methanol

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:

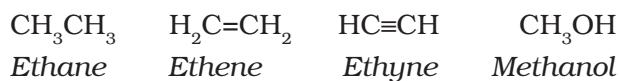
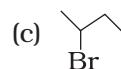
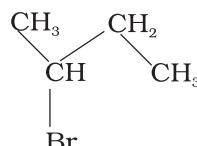
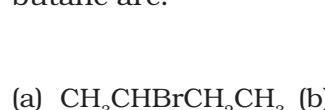


(c)

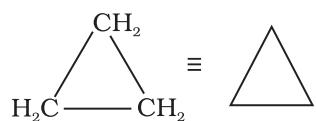


Terminals represent methyl group

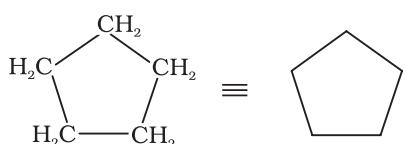
(ii) Various ways of representing 2-bromo butane are:



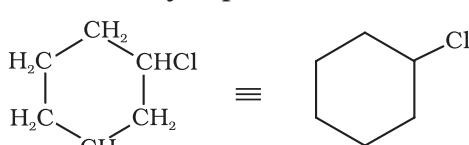
In cyclic compounds, the bond-line formulas may be given as follows:



## Cyclopropane



### Cyclopentane



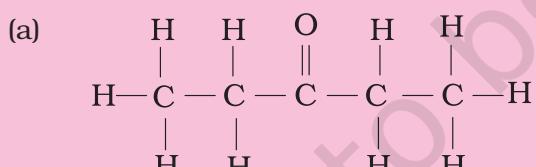
### chlorocyclohexane

### Problem 8.4

Expand each of the following condensed formulas into their complete structural formulas.

- (a)  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$   
 (b)  $\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$

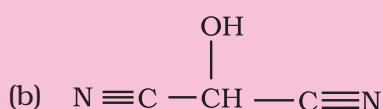
### Solution



### Problem 8.5

For each of the following compounds, write a condensed formula and also their bond-line formula.

- (a) HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH(CH<sub>3</sub>)CH<sub>2</sub>



### Solution

Condensed formula:

- (a) HO(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>3</sub>)CH(CH<sub>3</sub>)<sub>2</sub>  
 (b) HOCH(CN)<sub>2</sub>

Bond-line formula:

- (a)

(b)

### Problem 8.6

Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen.

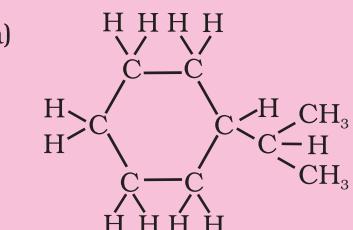
- (a)  A skeletal structure of a cyclohexane ring with a methyl group branch at the second carbon.

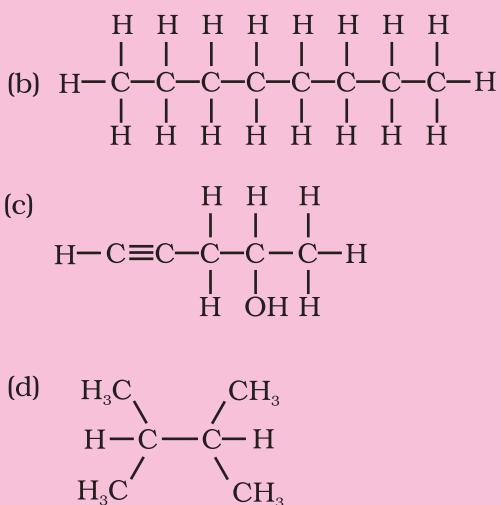
(b)  A skeletal structure of a six-carbon saturated hydrocarbon chain.

(c)  A skeletal structure of propanoic acid, showing a carboxylic acid group (-COOH) attached to the third carbon of a three-carbon chain. The first carbon has two methyl groups, and the second carbon has one methyl group.

(d)  A skeletal structure of 2,2-dimethylpropane, showing a central carbon atom bonded to four methyl groups.

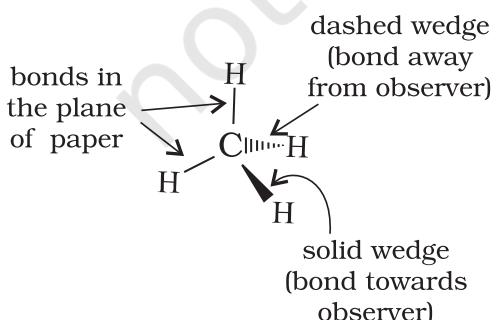
### Solution





### 8.3.2 Three-Dimensional Representation of Organic Molecules

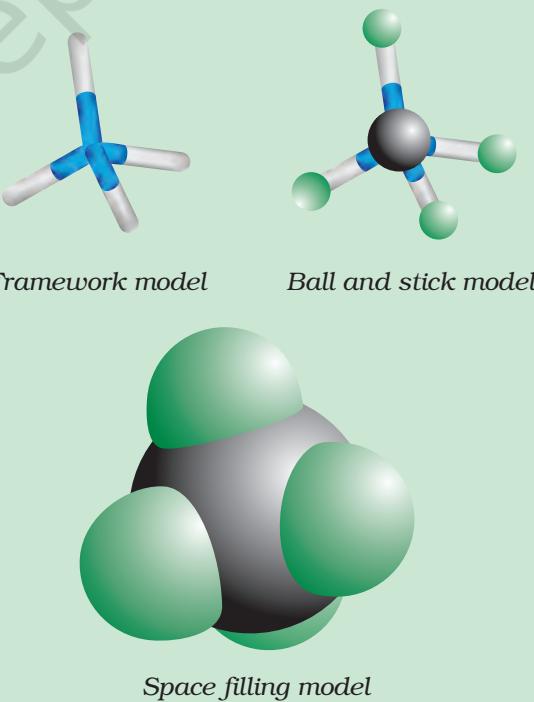
The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid (—) and dashed (·····) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used 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. 8.1



**Fig. 8.1** Wedge-and-dash representation of  $\text{CH}_4$

### Molecular Models

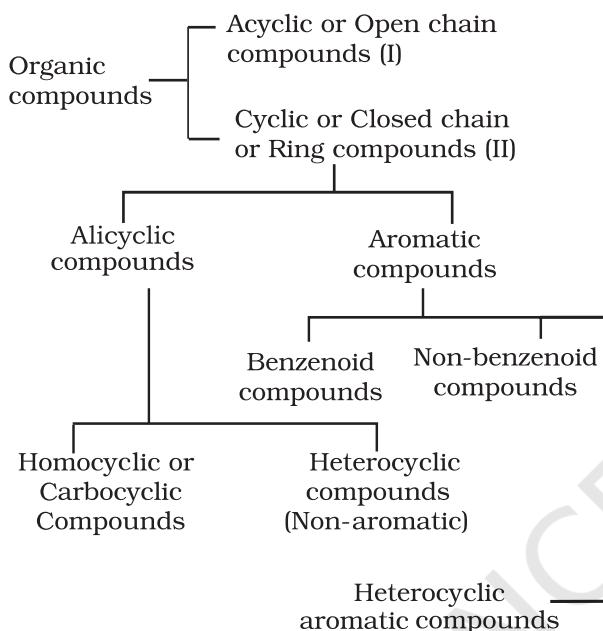
Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) *Framework model*, (2) *Ball-and-stick 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  $\text{C}=\text{C}$  (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.



**Fig. 8.2**

## 8.4 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:

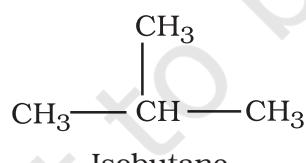


### I. Acyclic or open chain compounds

These compounds are also called as **aliphatic** compounds and consist of straight or branched chain compounds, for example:



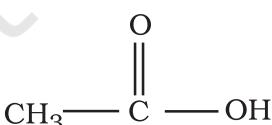
Ethane



Isobutane



Acetaldehyde



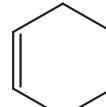
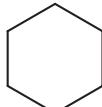
Acetic acid

### II Cyclic or closed chain or ring compounds

#### (a) Alicyclic compounds

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring

(homocyclic).



Cyclopropane    Cyclohexene    Cyclohexane

Sometimes atoms other than carbon are also present in the ring (heterocyclic). Tetrahydrofuran given below is an example of this type of compound:



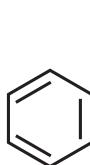
Tetrahydrofuran

These exhibit some of the properties similar to those of aliphatic compounds.

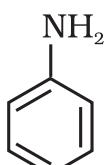
#### (b) Aromatic compounds

Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 9. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic compounds may also have hetero atom in the ring. Such compounds are called heterocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are:

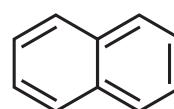
#### Benzenoid aromatic compounds



Benzene

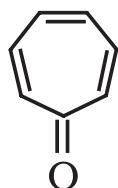


Aniline



Naphthalene

#### Non-benzenoid compound



Tropone

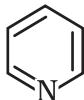
### Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

Organic compounds can also be classified on the basis of functional groups, into *families* or *homologous series*.

#### 8.4.1 Functional Group

The functional group is an atom or a group of atoms joined to the carbon chain 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.

#### 8.4.2 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<sub>2</sub> 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.

It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds.

### 8.5 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

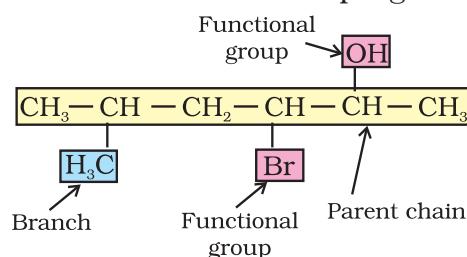
so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is *formica*. These names are traditional and are considered as *trivial* or *common names*. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C<sub>60</sub> 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 8.1.

**Table 8.1 Common or Trivial Names of Some Organic Compounds**

Compound	Common name
CH <sub>4</sub>	Methane
H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	n-Butane
(H <sub>3</sub> C) <sub>2</sub> CHCH <sub>3</sub>	Isobutane
(H <sub>3</sub> C) <sub>4</sub> C	Neopentane
H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> OH	n-Propyl alcohol
HCHO	Formaldehyde
(H <sub>3</sub> C) <sub>2</sub> CO	Acetone
CHCl <sub>3</sub>	Chloroform
CH <sub>3</sub> COOH	Acetic acid
C <sub>6</sub> H <sub>6</sub>	Benzene
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Anisole
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	Aniline
C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	Acetophenone
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>3</sub>	Ethyl methyl ether

#### 8.5.1 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.

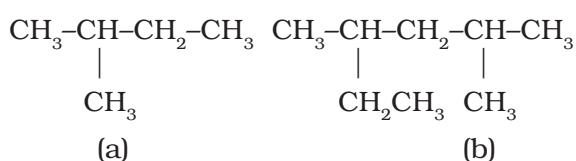
### 8.5.2 IUPAC Nomenclature of Alkanes

**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<sub>4</sub> to C<sub>4</sub>H<sub>10</sub>, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 8.2. The alkanes in Table 8.2 differ from each other by merely the number of -CH<sub>2</sub> groups in the chain. They are homologues of alkane series.

**Table 8.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons**

Name	Molecular formula	Name	Molecular formula
Methane	CH <sub>4</sub>	Heptane	C <sub>7</sub> H <sub>16</sub>
Ethane	C <sub>2</sub> H <sub>6</sub>	Octane	C <sub>8</sub> H <sub>18</sub>
Propane	C <sub>3</sub> H <sub>8</sub>	Nonane	C <sub>9</sub> H <sub>20</sub>
Butane	C <sub>4</sub> H <sub>10</sub>	Decane	C <sub>10</sub> H <sub>22</sub>
Pentane	C <sub>5</sub> H <sub>12</sub>	Icosane	C <sub>20</sub> H <sub>42</sub>
Hexane	C <sub>6</sub> H <sub>14</sub>	Triacontane	C <sub>30</sub> H <sub>62</sub>

**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:

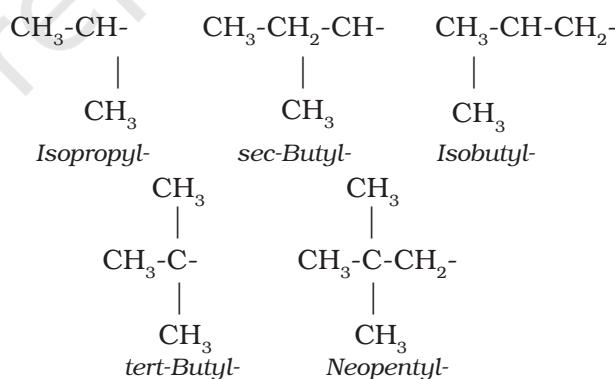


In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH<sub>4</sub> becomes -CH<sub>3</sub> and is called *methyl group*. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 8.3.

**Table 8.3 Some Alkyl Groups**

Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH <sub>4</sub>	Methane	-CH <sub>3</sub>	Methyl
C <sub>2</sub> H <sub>6</sub>	Ethane	-CH <sub>2</sub> CH <sub>3</sub>	Ethyl
C <sub>3</sub> H <sub>8</sub>	Propane	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Propyl
C <sub>4</sub> H <sub>10</sub>	Butane	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Butyl
C <sub>10</sub> H <sub>22</sub>	Decane	-CH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	Decyl

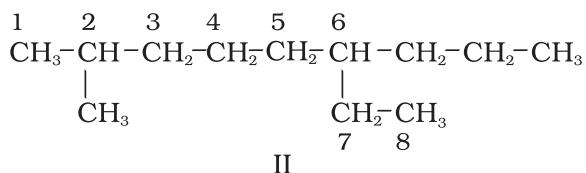
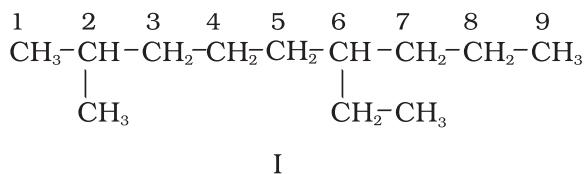
Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.



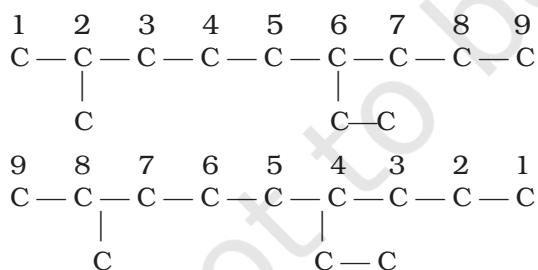
Common branched groups have specific trivial names. For example, the propyl groups can either be *n*-propyl group or isopropyl group. The branched butyl groups are called *sec*-butyl, isobutyl and *tert*-butyl group. We also encounter the structural unit, -CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, 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.

- 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.



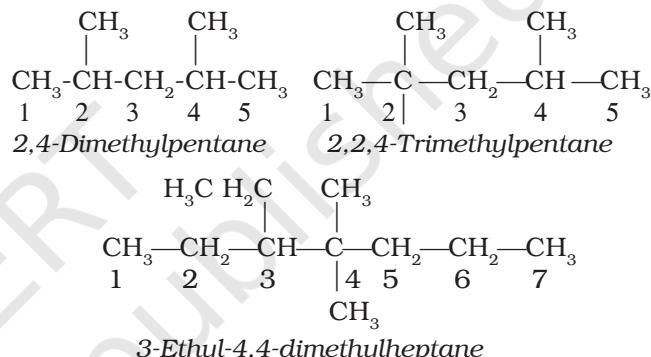
2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. **The numbering is done in such a way that the branched carbon atoms get 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).



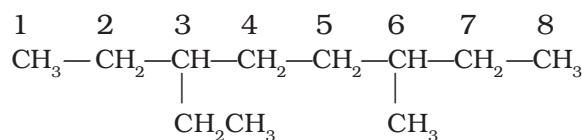
3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. [Note: the numbers are

separated from the groups by hyphens and there is no break between methyl and nonane.]

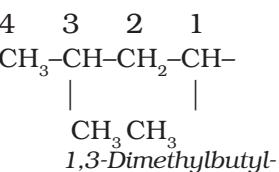
4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:



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.

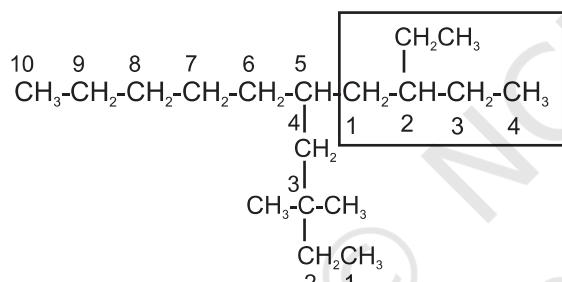


6. The branched alkyl groups can be named by following the above mentioned procedures. However, the **carbon atom of the branch that attaches to the root alkane** is numbered 1 as exemplified below.

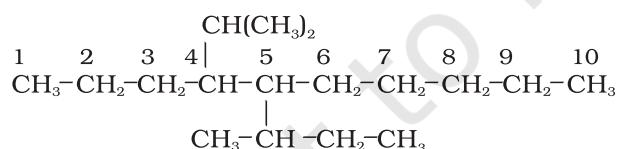


The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' **in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not** 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 also be remembered:

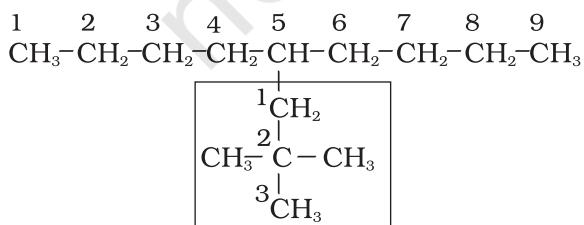
- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.



*5-(2-Ethylbutyl)-3,3-dimethyldecane  
(and not 5-(2,2-Dimethylbutyl)-3-ethyldecane)*

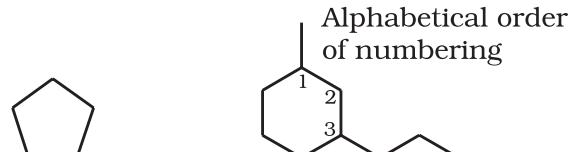


*5-sec-Butyl-4-isopropyldecane*

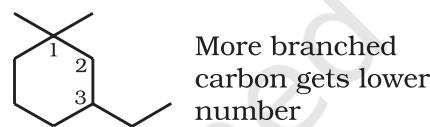


*5-(2,2-Dimethylpropyl)nonane*

**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.



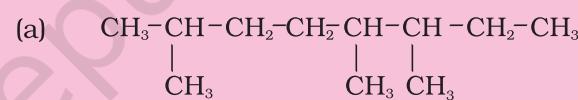
*Cyclopentane 1-Methyl-3-propylcyclohexane*



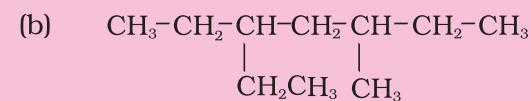
*3-Ethyl-1,1-dimethylcyclohexane  
(not 1-ethyl-3,3-dimethylcyclohexane)*

### Problem 8.7

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.



*2,5,6-Trimethyloctane  
(and not 3,4,7-Trimethyloctane)*



*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.

### 8.5.3 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,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , and  $(\text{CH}_3)_2\text{CHOH}$  — 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 8.4.

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 8.4, 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, - $\text{SO}_3\text{H}$ , -COOR (R=alkyl group), COCl, -CONH<sub>2</sub>, -CN, -HC=O, >C=O, -OH, -NH<sub>2</sub>, >C=C<, -C≡C- .

The -R,  $\text{C}_6\text{H}_5$ -, halogens (F, Cl, Br, I), -NO<sub>2</sub>, 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.

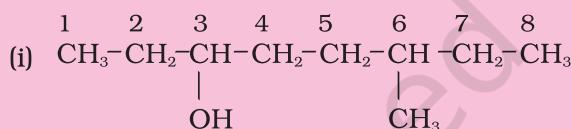
For example,  $\text{HOCH}_2(\text{CH}_2)_3\text{CH}_2\text{COCH}_3$  will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan-7-ol. Similarly,  $\text{BrCH}_2\text{CH}=\text{CH}_2$  is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

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  $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$  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,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  is named as buta-1,3-diene.

### Problem 8.8

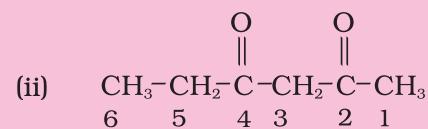
Write the IUPAC names of the compounds i-iv from their given structures.



### Solution

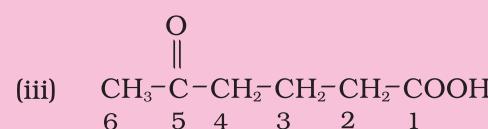
- The functional group present is an alcohol (OH). Hence the suffix is '-ol'.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at 6<sup>th</sup> carbon.

Hence, the systematic name of this compound is 6-Methyloctan-3-ol.



### 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.

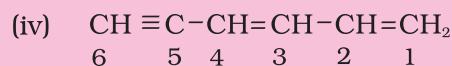


**Table 8.4 Some Functional Groups and Classes of Organic Compounds**

<b>Class of compounds</b>	<b>Functional group structure</b>	<b>IUPAC group prefix</b>	<b>IUPAC group suffix</b>	<b>Example</b>
Alkanes	-	-	-ane	Butane, $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Alkenes	$>\text{C}=\text{C}<$	-	-ene	But-1-ene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
Alkynes	$-\text{C}\equiv\text{C}-$	-	-yne	But-1-yne, $\text{CH}\equiv\text{CCH}_2\text{CH}_3$
Arenes	-	-	-	Benzene, 
Halides	$-\text{X}$ (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br}$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$
Aldehydes	-CHO	formyl, or oxo	-al	Butanal, $\text{CH}_3(\text{CH}_2)_2\text{CHO}$
Ketones	$>\text{C}=\text{O}$	oxo-	-one	Butan-2-one, $\text{CH}_3\text{CH}_2\text{COCH}_3$
Nitriles	$-\text{C}\equiv\text{N}$	cyano	nitrile	Pentanenitrile, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$
Ethers	$-\text{R-O-R-}$	alkoxy-	-	Ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$
Carboxylate ions	$-\text{COO}^-$	-	-oate	Sodium butanoate, $\text{CH}_3(\text{CH}_2)_2\text{CO}_2^- \text{Na}^+$
Esters	$-\text{COOR}$	alkoxycarbonyl	-oate	Methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$
Acyl halides	$-\text{COX}$ (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $\text{CH}_3(\text{CH}_2)_2\text{COCl}$
Amines	$-\text{NH}_2$ , $>\text{NH}$ , $>\text{N-}$	amino-	-amine	Butan-2-amine, $\text{CH}_3\text{CHNH}_2\text{CH}_2\text{CH}_3$
Amides	$-\text{CONH}_2$ , $-\text{CONHR}$ , $-\text{CONR}_2$	carbamoyl	-amide	Butanamide, $\text{CH}_3(\text{CH}_2)_2\text{CONH}_2$
Nitro compounds	$-\text{NO}_2$	nitro	-	1-Nitrobutane, $\text{CH}_3(\text{CH}_2)_3\text{NO}_2$
Sulphonic acids	$-\text{SO}_3\text{H}$	sulpho	sulphonic acid	Methylsulphonic acid $\text{CH}_3\text{SO}_3\text{H}$

### 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  $\text{--COOH}$  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.



### Solution

The two  $\text{C}=\text{C}$  functional groups are present at carbon atoms 1 and 3, while the  $\text{C}\equiv\text{C}$  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.

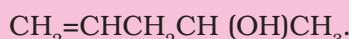
### Problem 8.9

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxyheptanal.

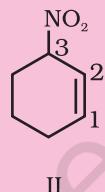
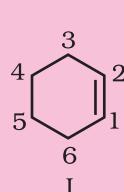
### Solution

(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  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ .

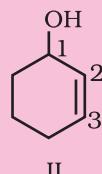
(ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups  $\text{C}=\text{C}$  and  $-\text{OH}$  at carbon atoms 4 and 2 respectively. Thus, the structure is



(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  $\text{NO}_2$  is prefixed functional group therefore double bond gets preference over  $-\text{NO}_2$  group:



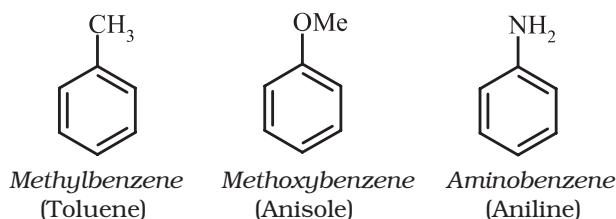
(iv) '1-ol' means that a  $-\text{OH}$  group is present at C-1. OH is suffixed functional group and gets preference over  $\text{C}=\text{C}$  bond. Thus the structure is as shown in (II):



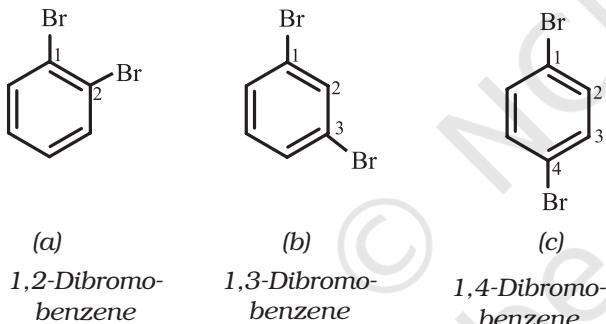
(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that  $-\text{OH}$  group is present at carbon 6. Thus, the structural formula of the compound is:  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$ . Carbon atom of  $-\text{CHO}$  group is included while numbering the carbon chain.

### 8.5.4 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.



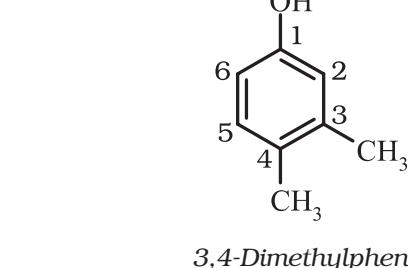
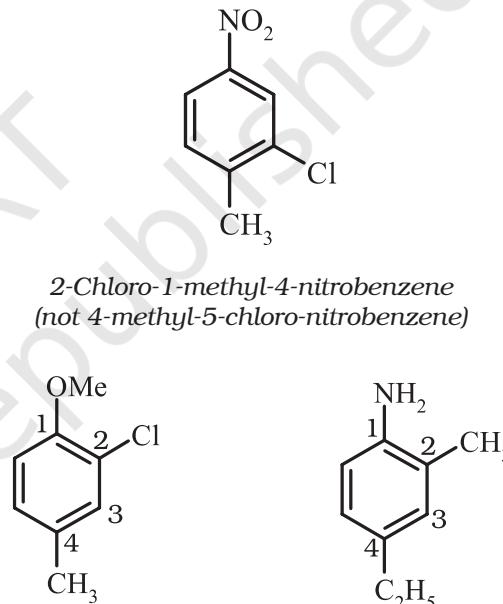
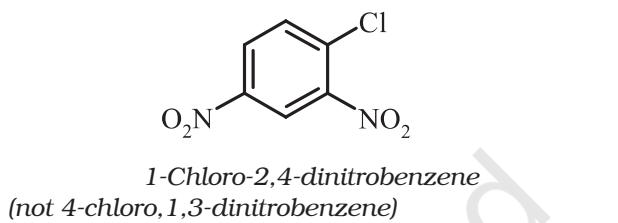
If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound (b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



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 number 1 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.

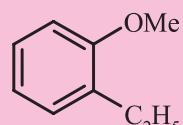


When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is *phenyl* ( $C_6H_5^-$ , also abbreviated as *Ph*).

**Problem 8.10**

Write the structural formula of:

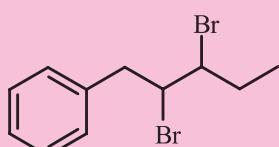
- o*-Ethylanisole,
- p*-Nitroaniline,
- 2,3-Dibromo-1-phenylpentane,
- 4-Ethyl-1-fluoro-2-nitrobenzene.

**Solution**

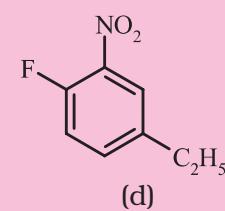
(a)



(b)



(c)



(d)

**8.6 ISOMERISM**

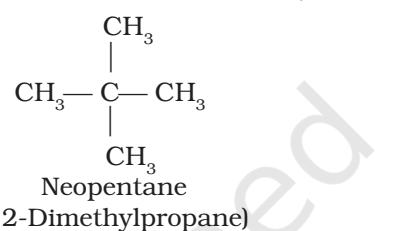
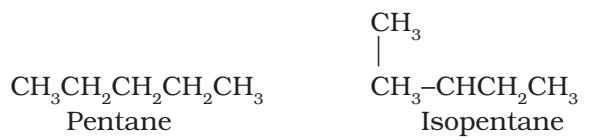
The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

**8.6.1 Structural Isomerism**

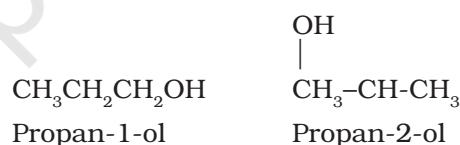
Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

**(i) Chain isomerism:** When two or more compounds have similar molecular formula but

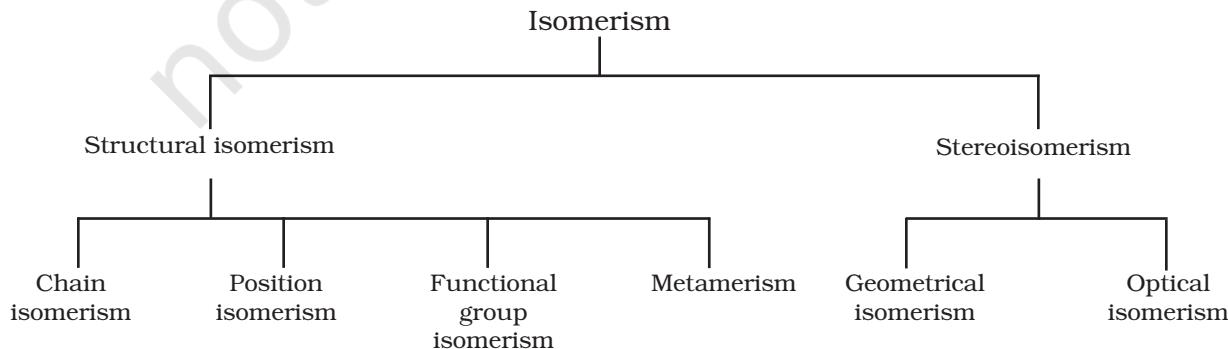
different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example,  $C_5H_{12}$  represents three compounds:

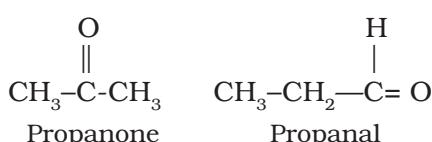


**(ii) Position isomerism:** When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula  $C_3H_8O$  represents two alcohols:



**(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:





**(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 ( $C_2H_5OC_2H_5$ ).

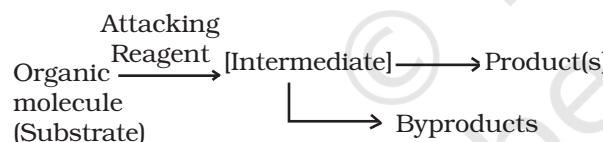
### 8.6.2 Stereoisomerism

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*.

## 8.7 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.

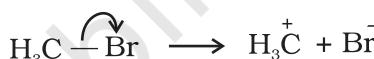
In the following sections, we shall learn some of the principles that explain how these reactions take place.

### 8.7.1 Fission of a Covalent Bond

A covalent bond can get cleaved either by : (i) ***heterolytic cleavage***, or by (ii) ***homolytic cleavage***.

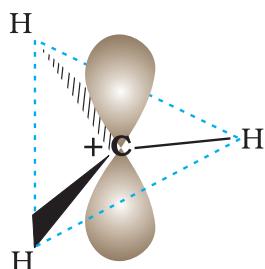
In **heterolytic cleavage**, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

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  $\text{CH}_3^+$  and  $\text{Br}^-$  as shown below.



A species having a carbon atom possessing sextet of electrons and a positive charge is called a *carbocation* (earlier called *carbonium ion*). The  $\overset{+}{\text{CH}_3}$  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:  $\text{CH}_3\overset{+}{\text{CH}_2}$  (ethyl cation, a primary carbocation),  $(\text{CH}_3)_2\overset{+}{\text{CH}}$  (isopropyl cation, a secondary carbocation), and  $(\text{CH}_3)_3\overset{+}{\text{C}}$  (*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 8.7.5 and 8.7.9. The observed order of carbocation stability is:  $\overset{+}{\text{CH}_3} < \text{CH}_3\overset{+}{\text{CH}_2} < (\text{CH}_3)_2\overset{+}{\text{CH}} < (\text{CH}_3)_3\overset{+}{\text{C}}$ . These carbocations have trigonal planar shape with positively charged carbon being  $sp^2$  hybridised. Thus, the shape of  $\overset{+}{\text{CH}_3}$  may be considered as being derived from the overlap of three equivalent  $\text{C}(sp^2)$  hybridised orbitals with 1s orbital of each of the three hydrogen

atoms. Each bond may be represented as C(sp<sup>2</sup>)-H(1s) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. [Fig. 8.3(a)].

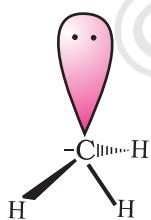


**Fig. 8.3(a)** Shape of methyl carbocation

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



electron pair, the methyl anion ( $\text{H}_3\text{C}^-$ ) is formed. Such a carbon species carrying a negative charge on carbon atom is called *carbanion*. Carbon in carbanion is generally sp<sup>3</sup> hybridised and its structure is distorted tetrahedron as shown in Fig. 8.3(b).

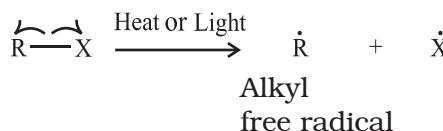


**Fig. 8.3(b)** Shape of methyl carbanion

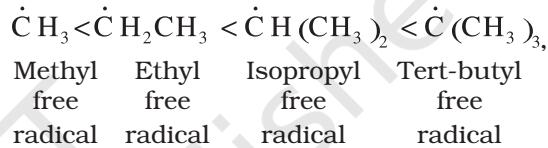
Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic or heteropolar** or just polar reactions.

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:



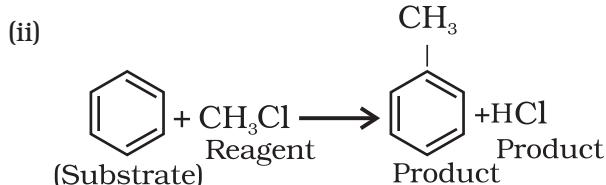
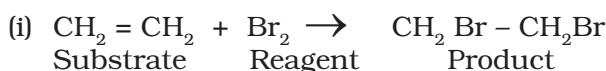
Alkyl radicals are classified as *primary*, *secondary*, or *tertiary*. Alkyl radical stability increases as we proceed from primary to tertiary:



Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar* reactions.

### 8.7.2 Substrate and Reagent

Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and other as reagent. In general, a molecule whose carbon is involved in new bond formation is called substrate and the other one is called reagent. When carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. Example:



### Nucleophiles and Electrophiles

Reagents attack the reactive site of the substrate. The reactive site may be electron

deficient portion of the molecule (a positive reactive site) e.g., an atom with incomplete electron shell or the positive end of the dipole in the molecule. If the attacking species is electron rich, it attacks these sites. If attacking species is electron deficient, the reactive site for it is that part of the substrate molecule which can supply electrons, e.g.,  $\pi$  electrons in a double bond.

A reagent that brings an electron pair to the reactive site is called a **nucleophile** ( $\text{Nu}^-$ ) i.e., nucleus seeking and the reaction is then called **nucleophilic**. A reagent that takes away an electron pair from reactive site is called **electrophile** ( $\text{E}^+$ ) i.e., electron seeking and the reaction is called **electrophilic**.

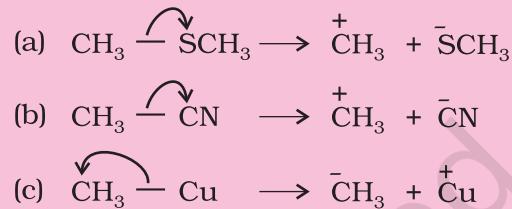
During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the substrate which is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate. Thus, the electrophiles receive electron pair from the substrate 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 ( $\text{HO}^-$ ), cyanide ( $\text{NC}^-$ ) ions and carbanions ( $\text{R}_3\text{C}^-$ ). Neutral molecules such as  $\text{H}_2\ddot{\text{O}}$ ,  $\text{R}_3\text{N}$ ,  $\text{R}_2\text{NH}$  etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ( $\dot{\text{C}}\text{H}_3$ ) and neutral molecules having functional groups like carbonyl group ( $>\text{C}=\text{O}$ ) or alkyl halides ( $\text{R}_3\text{C}-\text{X}$ , 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 8.11

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

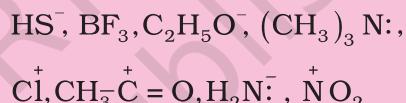
- (a)  $\text{CH}_3-\text{SCH}_3$ , (b)  $\text{CH}_3-\text{CN}$ , (c)  $\text{CH}_3-\text{Cu}$

#### Solution



### Problem 8.12

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:



#### Solution

**Nucleophiles:**  $\text{HS}^-$ ,  $\text{C}_2\text{H}_5\text{O}^-$ ,  $(\text{CH}_3)_3\text{N}^+$ :  $\text{H}_2\text{N}^-$ : These species have unshared pair of electrons, which can be donated and shared with an electrophile.

**Electrophiles:**  $\text{BF}_3$ ,  $\overset{+}{\text{C}}\text{H}_3-\overset{+}{\text{C}}=\text{O}$ ,  $\overset{+}{\text{NO}}_2$ . Reactive sites have only six valence electrons; can accept electron pair from a nucleophile.

### Problem 8.13

Identify electrophilic centre in the following:  $\text{CH}_3\text{CH}=\text{O}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{I}$ .

#### Solution

Among  $\overset{*}{\text{CH}_3}\overset{*}{\text{C}}=\text{O}$ ,  $\overset{*}{\text{H}_3\text{C}}\overset{*}{\text{C}}\equiv\text{N}$ , and  $\overset{*}{\text{H}_3\text{C}}-\text{I}$ , the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond.

### 8.7.3 Electron Movement in Organic Reactions

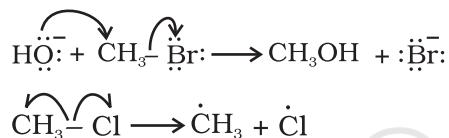
The movement of electrons in organic reactions can be shown by curved-arrow

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)  $\text{---}\gamma\downarrow\leftarrow\text{---}\gamma\text{---}$  from  $\pi$  bond to adjacent bond position
- (ii)  $\text{---}\dot{\gamma}\downarrow\leftarrow\text{---}\ddot{\gamma}\text{---}$  from  $\pi$  bond to adjacent atom
- (iii)  $\text{---}\ddot{\gamma}\downarrow\leftarrow\text{---}\gamma\text{---}$  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:



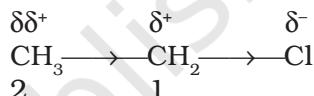
#### 8.7.4 Electron Displacement Effects in Covalent Bonds

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 polarisation 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.

#### 8.7.5 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 ( $\text{CH}_3\text{CH}_2\text{Cl}$ ) 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 ( $\delta^+$ ) and the chlorine some negative charge ( $\delta^-$ ). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol  $\delta$  (delta) and the shift of electron density is shown by an arrow that points from  $\delta^+$  to  $\delta^-$  end of the polar bond.



In turn carbon-1, which has developed partial positive charge ( $\delta^+$ ) 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  $\sigma$ -bond caused by the polarisation of adjacent  $\sigma$ -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 substituents can be classified as *electron-withdrawing* or *electron donating* groups relative to hydrogen. Halogens and many other groups such as nitro (-NO<sub>2</sub>), cyano (-CN), carboxy (-COOH), ester (COOR), aryloxy (-OAr, e.g. -OC<sub>6</sub>H<sub>5</sub>), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (-CH<sub>3</sub>) and ethyl (-CH<sub>2</sub>-CH<sub>3</sub>) are usually considered as electron donating groups.

**Problem 8.14**

Which bond is more polar in the following pairs of molecules: (a) H<sub>3</sub>C-H, H<sub>3</sub>C-Br  
 (b) H<sub>3</sub>C-NH<sub>2</sub>, H<sub>3</sub>C-OH (c) H<sub>3</sub>C-OH, H<sub>3</sub>C-SH

**Solution**

(a) C-Br, since Br is more electronegative than H, (b) C-O, (c) C-O

**Problem 8.15**

In which C-C bond of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 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.

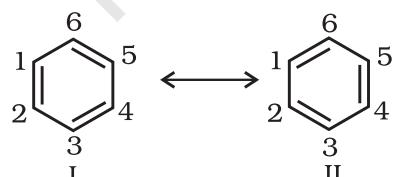
**8.7.6 Resonance Structure**

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

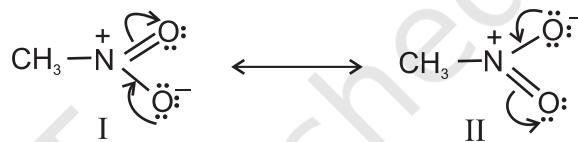
As per the above representation, benzene should exhibit two different bond lengths, due to C-C single and C=C double bonds. However, as determined experimentally benzene has a uniform C-C bond distances of 139 pm, a value intermediate between the C-C single(154 pm) and C=C double (134 pm) bonds. Thus, 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<sub>3</sub>NO<sub>2</sub>) 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:

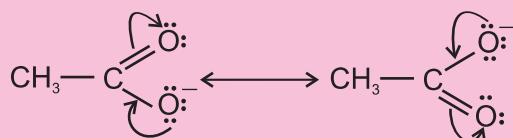
The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (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 8.16**

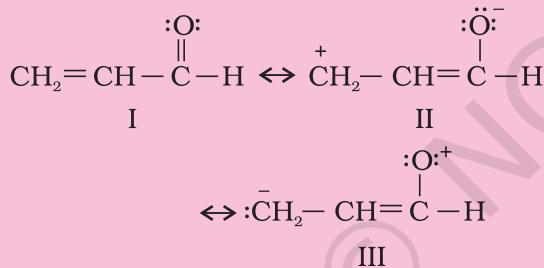
Write resonance structures of  $\text{CH}_3\text{COO}^-$  and show the movement of electrons by curved arrows.

**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 8.17**

Write resonance structures of  $\text{CH}_2=\text{CH}-\text{CHO}$ . Indicate relative stability of the contributing structures.

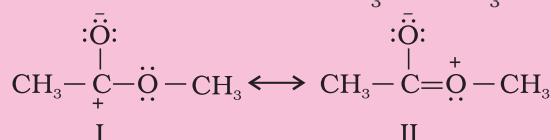
**Solution**

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 8.18**

Explain why the following two structures, I and II cannot be the major contributors to the real structure of  $\text{CH}_3\text{COOCH}_3$ .

**Solution**

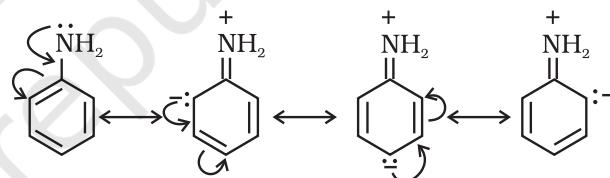
The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

**8.7.7 Resonance Effect**

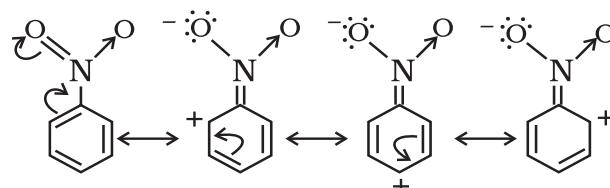
The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two  $\pi$ -bonds or between a  $\pi$ -bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated 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<sub>2</sub>, -NHR, -NR<sub>2</sub>, -NHCOR,

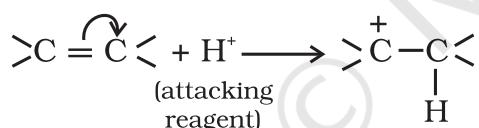
- R effect: - COOH, -CHO, >C=O, - CN, -NO<sub>2</sub>

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  $\pi$ -electrons are delocalised and the system develops polarity.

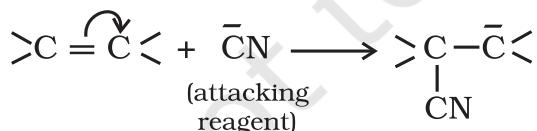
### 8.7.8 Electromeric Effect (E effect)

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  $\pi$ -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 ( $\curvearrowright$ ). There are two distinct types of electromeric effect.

(i) Positive Electromeric Effect (+E effect) In this effect the  $\pi$ -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  $\pi$  - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:



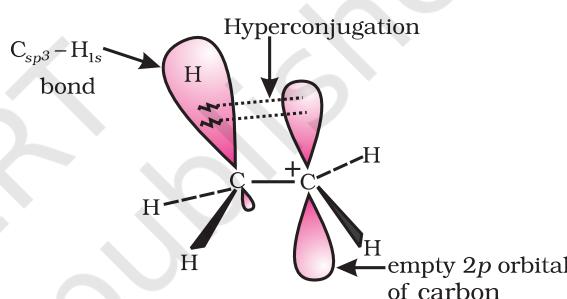
When inductive and electromeric effects operate in opposite directions, the electromeric effect predominates.

### 8.7.9 Hyperconjugation

Hyperconjugation is a general stabilising interaction. It involves delocalisation of  $\sigma$  electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated

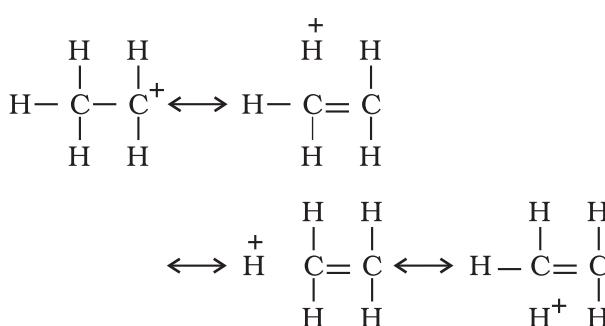
system or to an atom with an unshared  $p$  orbital. The  $\sigma$  electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared  $p$  orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of  $\text{CH}_3\dot{\text{C}}\text{H}_2$  (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. 8.4 (a).

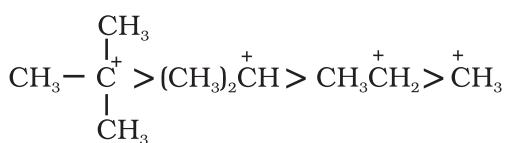


**Fig. 8.4(a)** Orbital diagram showing hyperconjugation in ethyl cation

This type of overlap stabilises the carbocation because electron density from the adjacent  $\sigma$  bond helps in dispersing the positive charge.

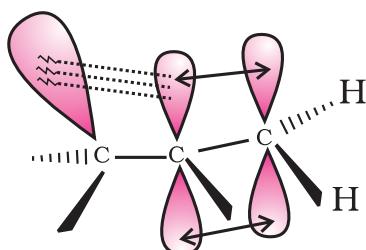


In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations :



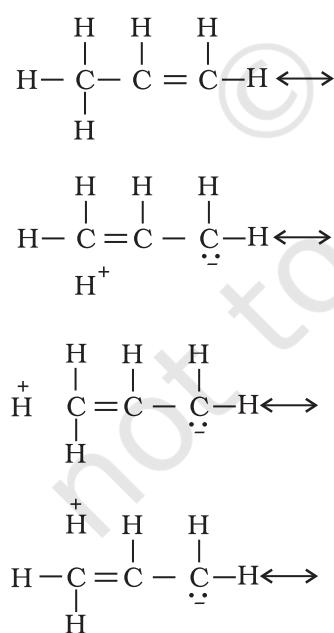
Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 8.4(b).



**Fig. 8.4(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 8.19

Explain why  $(\text{CH}_3)_3\dot{\text{C}}^+$  is more stable than  $\text{CH}_3\dot{\text{C}}^+\text{CH}_2$  and  $\dot{\text{C}}^+\text{H}_3$  is the least stable cation.

### Solution

Hyperconjugation interaction in  $(\text{CH}_3)_3\dot{\text{C}}^+$  is greater than in  $\text{CH}_3\dot{\text{C}}^+\text{CH}_2$  as the  $(\text{CH}_3)_3\dot{\text{C}}^+$  has nine C—H bonds. In  $\dot{\text{C}}^+\text{H}_3$ , vacant  $p$  orbital is perpendicular to the plane in which C—H bonds lie; hence cannot overlap with it. Thus,  $\dot{\text{C}}^+\text{H}_3$  lacks hyperconjugative stability.

### 8.7.10 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 9 and later in class XII.

### 8.8 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.

### 8.8.1 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.

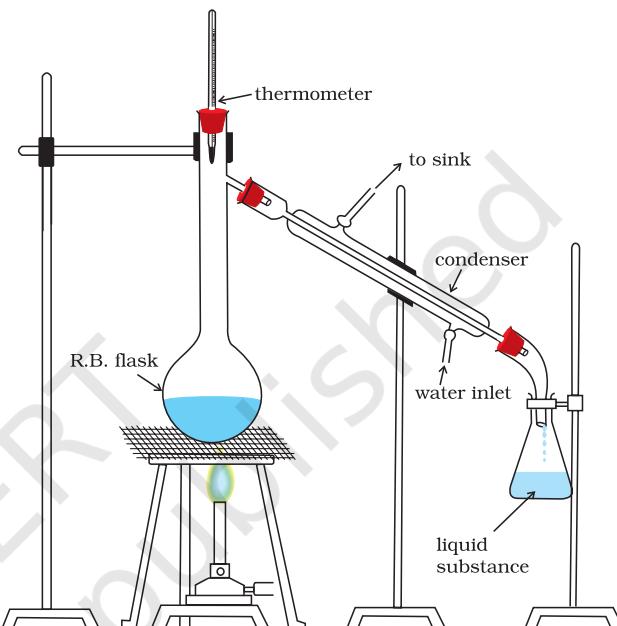
### 8.8.2 Crystallisation

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.

### 8.8.3 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 8.5). The liquid mixture is taken in a round bottom flask and heated

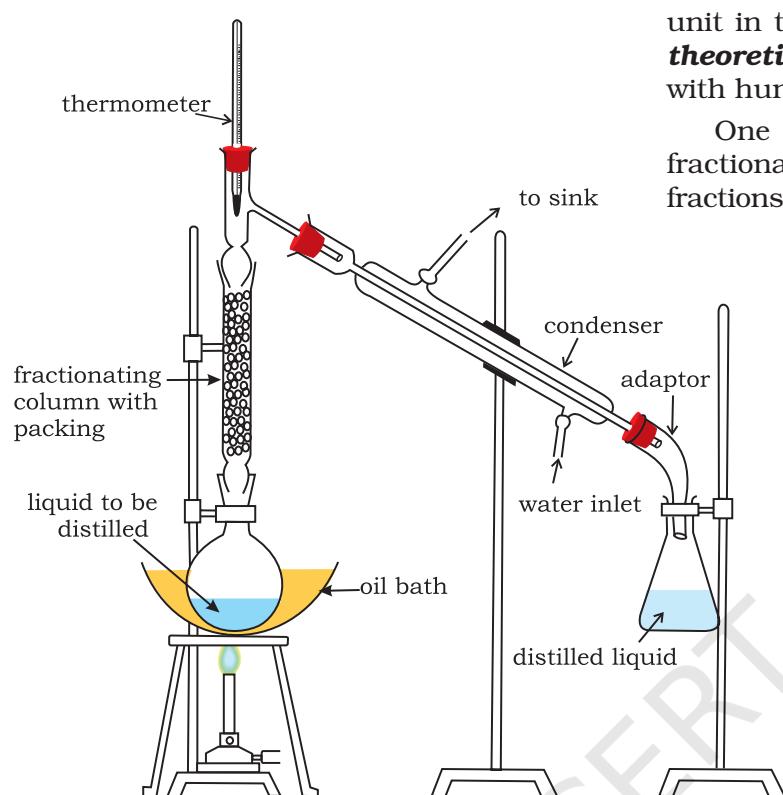
carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately.



**Fig.8.5** Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.

**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.8.6, page 280).

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



**Fig.8.6** Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

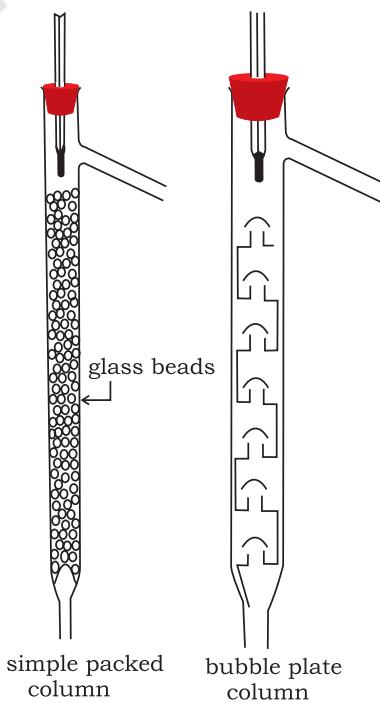
time the vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig.8.7. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revapourises. 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.

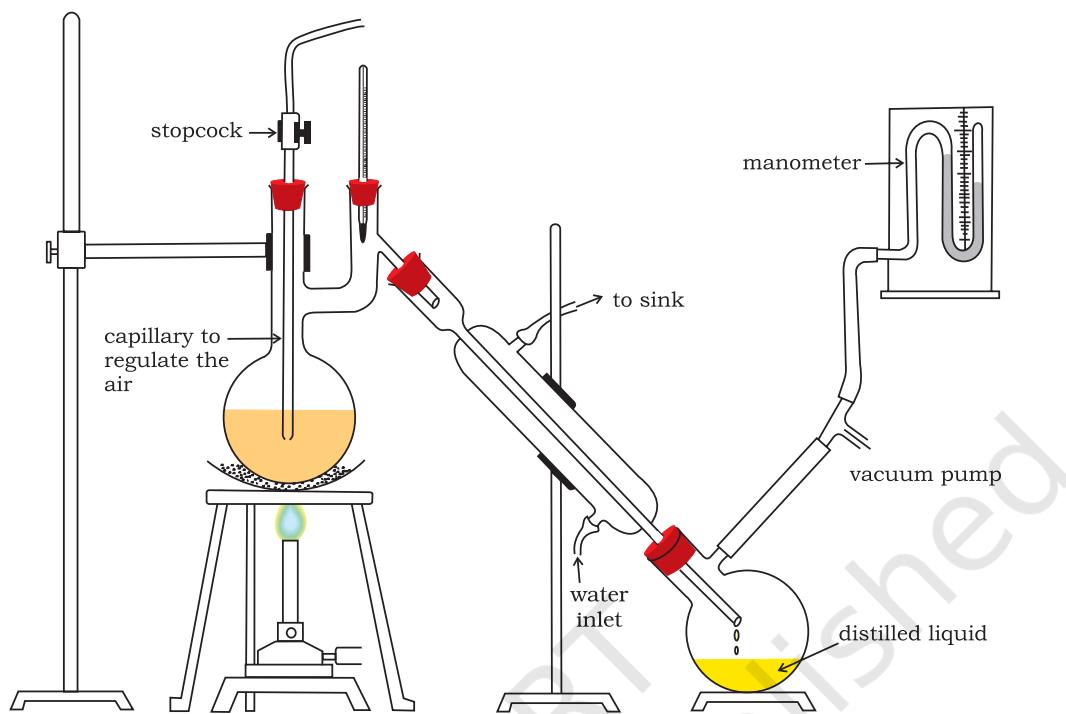
One of the technological applications of fractional distillation is to separate different fractions of **crude oil in petroleum industry**.

#### 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.8.8). Glycerol can be separated from **spent-lye in soap industry** by using this technique.



**Fig.8.7** Different types of fractionating columns.



**Fig. 8.8** Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.

**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.

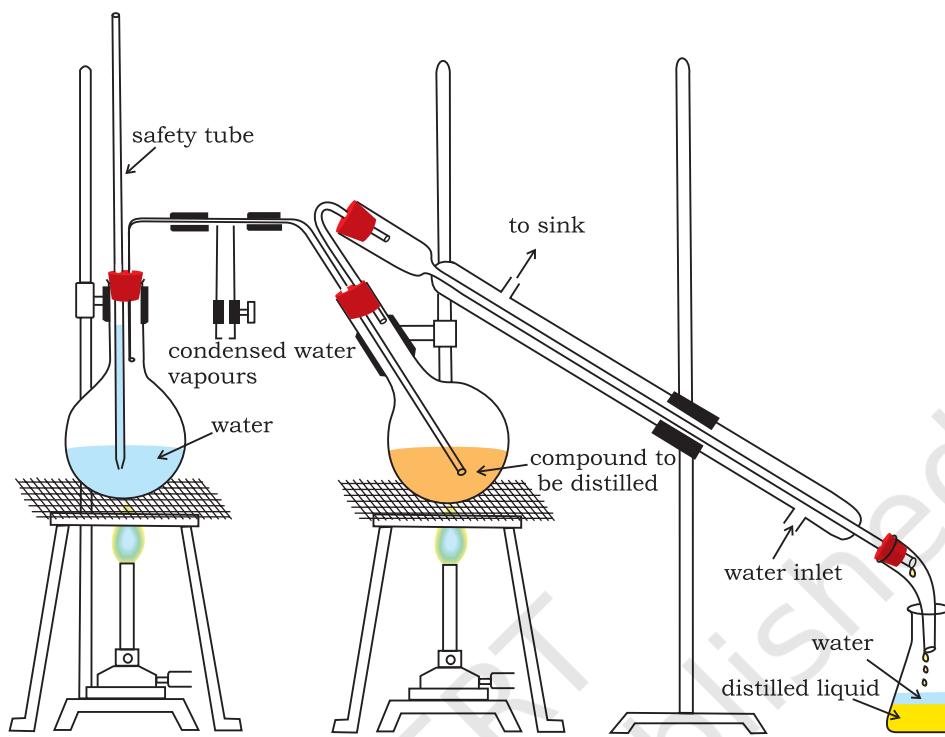
Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture (Fig. 8.9, Page 282).

#### 8.8.4 Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking 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. 8.10 (Page 282). If the organic compound is less 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.

#### 8.8.5 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



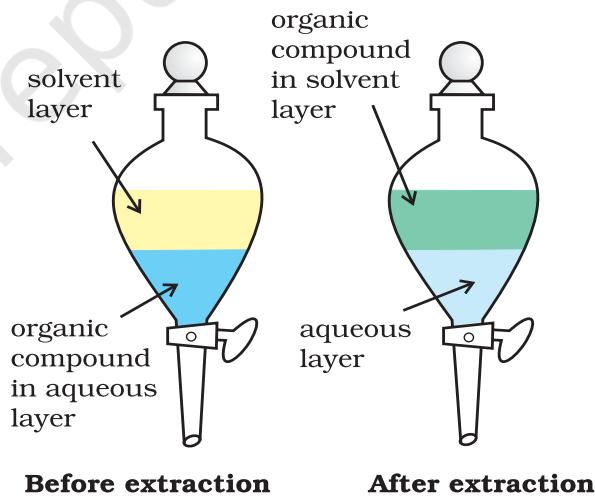
**Fig.8.9** Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.

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:

- Adsorption chromatography, and
- 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

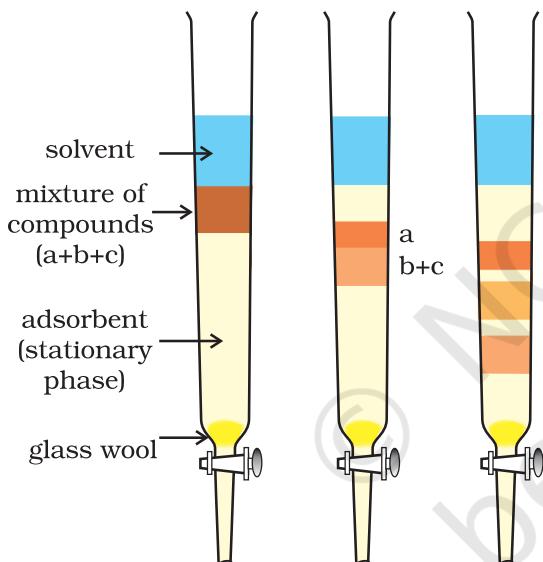


**Fig.8.10** Differential extraction. Extraction of compound takes place based on difference in solubility

distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

- Column chromatography, and
- 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. 8.11). The mixture adsorbed on 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. 8.11).

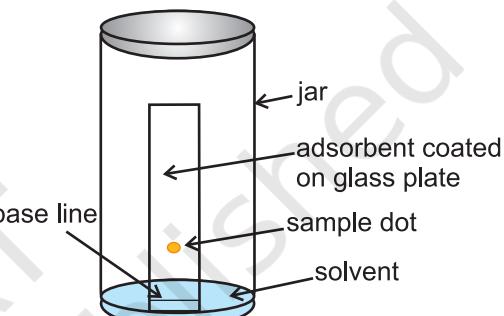


**Fig.8.11** Column chromatography. Different stages of separation of components of a mixture.

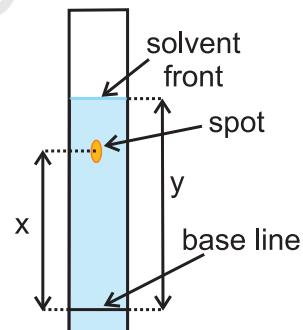
**Thin Layer Chromatography:** Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread 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. 8.12a). 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<sub>f</sub> value** (Fig.8.12 b).

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$



**Fig.8.12 (a)** Thin layer chromatography. Chromatogram being developed.



**Fig.8.12 (b)** Developed chromatogram.

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 in ultraviolet light, 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.8.12b).

**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. 8.13). 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

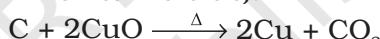
spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

### 8.9 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.

#### 8.9.1 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).



White                      Blue

#### 8.9.2 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:



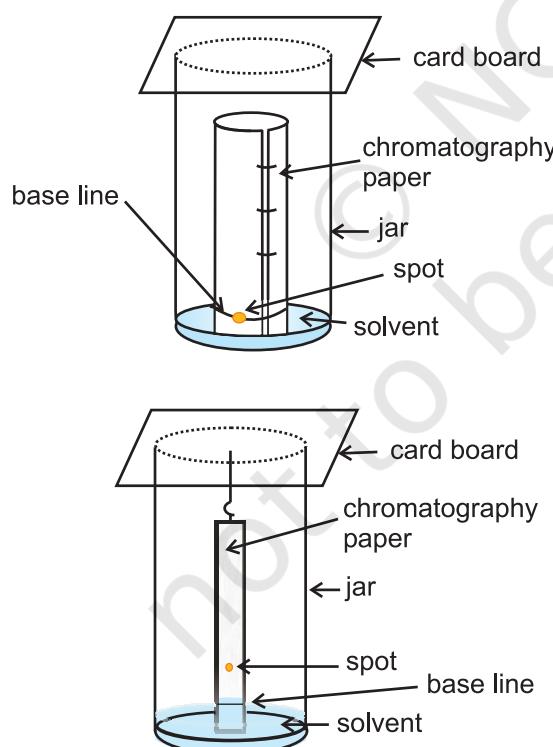
$(\text{X} = \text{Cl}, \text{Br} \text{ or } \text{I})$

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.

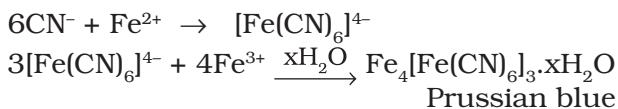
#### (A) Test for Nitrogen

The sodium fusion extract is boiled with iron(II) sulphate and then acidified with



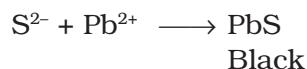
**Fig. 8.13** Paper chromatography.  
Chromatography paper in two different shapes.

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 hexacyanidoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanidoferrate(II) to produce iron(III) hexacyanidoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.



### (B) Test for Sulphur

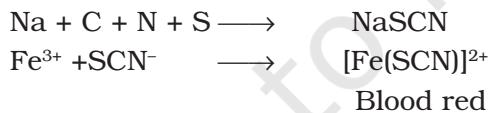
- (a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.



- (b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.



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.



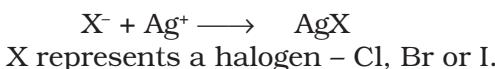
If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.



### (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

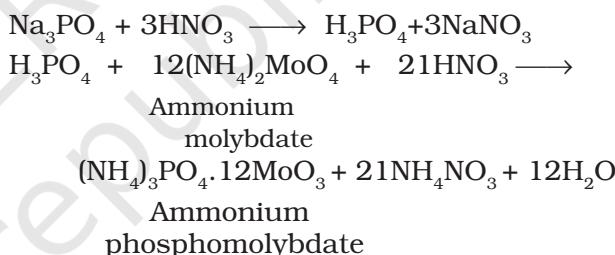
bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.



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.



## 8.10 QUANTITATIVE ANALYSIS

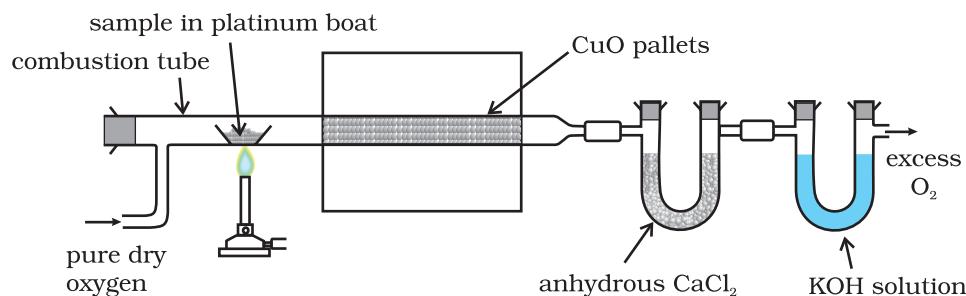
Quantitative analysis of compounds is very important in organic chemistry. It helps chemists in the determination of mass per cent of elements present in a compound. You have learnt in Unit-1 that mass per cent of elements is required for the determination of empirical and molecular formula.

The percentage composition of elements present in an organic compound is determined by the following methods:

### 8.10.1 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.





**Fig. 8.14** 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.

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. 8.14). The 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 8.20

On complete combustion, 0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water. Determine the percentage composition of carbon and hydrogen in the compound.

#### Solution

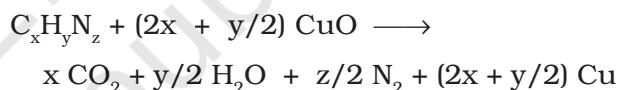
$$\begin{aligned}\text{Percentage of carbon} &= \frac{12 \times 0.198 \times 100}{44 \times 0.246} \\ &= 21.95\%\end{aligned}$$

$$\begin{aligned}\text{Percentage of hydrogen} &= \frac{2 \times 0.1014 \times 100}{18 \times 0.246} \\ &= 4.58\%\end{aligned}$$

### 8.10.2 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.



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. 8.15).

Let the mass of organic compound =  $m$  g

Volume of nitrogen collected =  $V_1$  mL

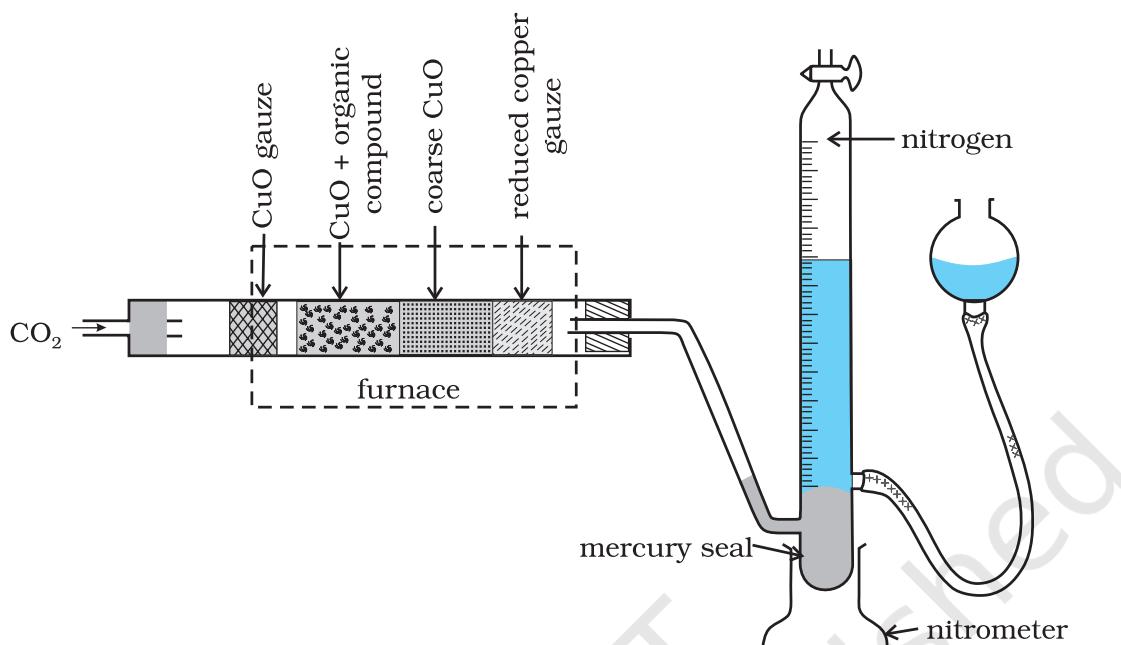
Room temperature =  $T_1$  K

$$\text{Volume of nitrogen at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1}$$

(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;

$p_1 = \text{Atmospheric pressure} - \text{Aqueous tension}$   
22400 mL  $\text{N}_2$  at STP weighs 28 g.



**Fig. 8.15** Dumas method. The organic compound yields nitrogen gas on heating it with copper(II) oxide in the presence of  $\text{CO}_2$  gas. The mixture of gases is collected over potassium hydroxide solution in which  $\text{CO}_2$  is absorbed and volume of nitrogen gas is determined.

$$V \text{ mL N}_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

### Problem 8.21

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

$$\text{Actual pressure} = 715 - 15 = 700 \text{ mm}$$

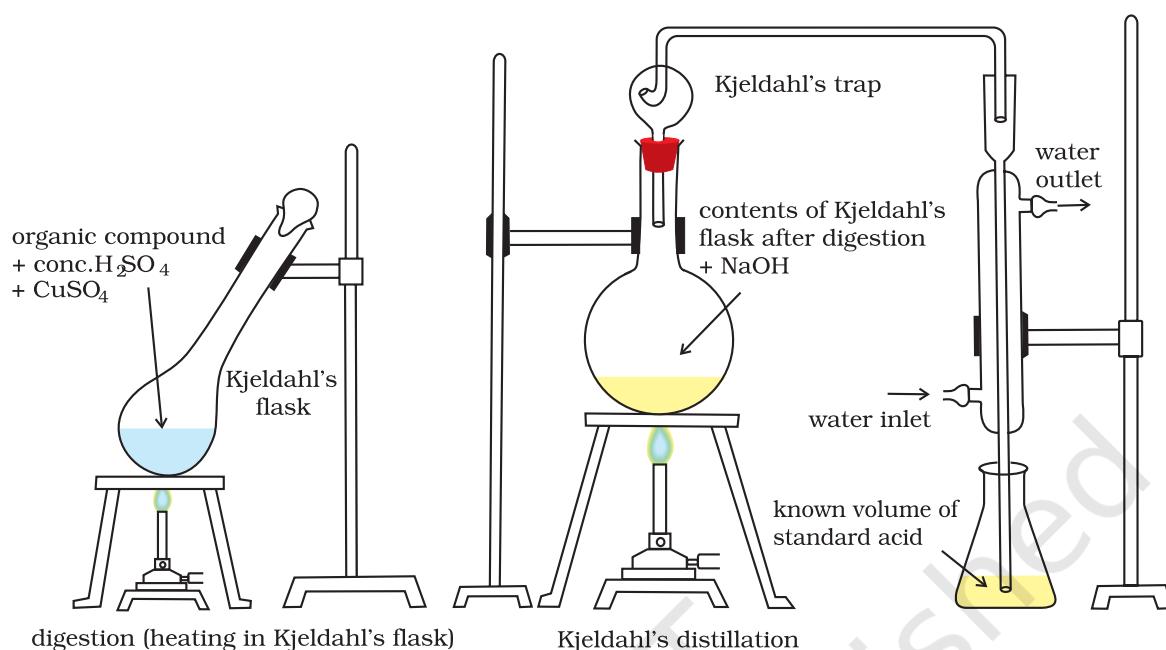
$$\text{Volume of nitrogen at STP} = \frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ mL}$$

$$22,400 \text{ mL of N}_2 \text{ at STP weighs} = 28 \text{ g}$$

$$41.9 \text{ mL of nitrogen weighs} = \frac{28 \times 41.9}{22400} \text{ g}$$

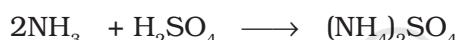
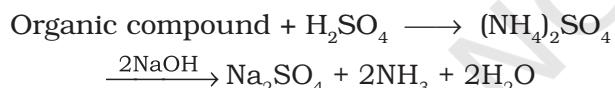
$$\text{Percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$$

**(ii) Kjeldahl's method:** The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate (Fig. 8.16). The resulting acid mixture is then heated with excess of sodium 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



**Fig.8.16** 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.

taken and that left after the reaction gives the amount of acid reacted with ammonia.



Let the mass of organic compound taken =  $m$  g  
 Volume of  $H_2SO_4$  of molarity,  $M$ , taken =  $V$  mL

Volume of  $NaOH$  of molarity,  $M$ , used for titration of excess of  $H_2SO_4$  =  $V_1$  mL

$V_1$  mL of  $NaOH$  of molarity  $M$

$$= V_1 / 2 \text{ mL of } H_2SO_4 \text{ of molarity } M$$

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 17 g  $NH_3$  or 14 g of N

$2(V - V_1/2)$  mL of  $NH_3$  solution of molarity  $M$  contains:

$$\frac{14 \times M \times 2(V - V_1/2)}{1000} \text{ g N}$$

$$\begin{aligned} \text{Percentage of N} &= \frac{14 \times M \times 2(V - V_1/2)}{1000} \times \frac{100}{m} \\ &= \frac{1.4 \times M \times 2(V - V_1/2)}{m} \end{aligned}$$

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 8.22

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  $H_2SO_4$  = 1 M of 20 mL  $NH_3$   
 1000 mL of 1 M ammonia contains 14 g nitrogen

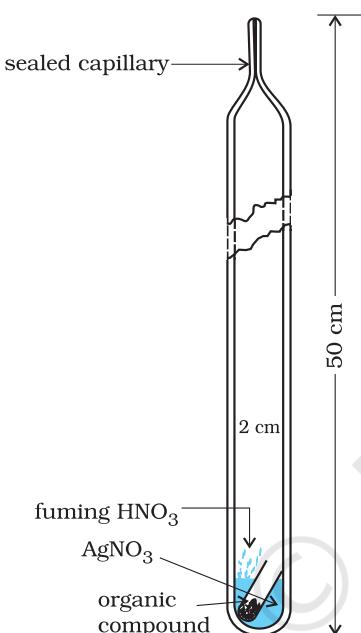
20 mL of 1 M ammonia contains

$$\frac{14 \times 20}{1000} \text{ g nitrogen}$$

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

### 8.10.3 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. 8.17)



**Fig. 8.17** Carius method. Halogen containing organic compound is heated with fuming nitric acid in the presence of silver nitrate.

in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide ( $\text{AgX}$ ). It is filtered, washed, dried and weighed.

Let the mass of organic

compound taken =  $m$  g

Mass of  $\text{AgX}$  formed =  $m_1$  g

1 mol of  $\text{AgX}$  contains 1 mol of  $X$

Mass of halogen in  $m_1$  g of  $\text{AgX}$

$$= \frac{\text{atomic mass of } X \times m_1 \text{ g}}{\text{molecular mass of } \text{AgX}}$$

Percentage of halogen

$$= \frac{\text{atomic mass of } X \times m_1 \text{ g}}{\text{molecular mass of } \text{AgX}}$$

### Problem 8.23

In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of  $\text{AgBr}$ . Find out the percentage of bromine in the compound.

**Solution**

$$\begin{aligned}\text{Molar mass of } \text{AgBr} &= 108 + 80 \\ &= 188 \text{ g mol}^{-1}\end{aligned}$$

188 g  $\text{AgBr}$  contains 80 g bromine

$$0.12 \text{ g } \text{AgBr} \text{ contains } \frac{80 \times 0.12}{188} \text{ g bromine}$$

$$\begin{aligned}\text{Percentage of bromine} &= \frac{80 \times 0.12 \times 100}{188 \times 0.15} \\ &= 34.04\%\end{aligned}$$

### 8.10.4 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 =  $m_1$  g

1 mol of  $\text{BaSO}_4$  = 233 g  $\text{BaSO}_4$  = 32 g sulphur

$$m_1 \text{ g } \text{BaSO}_4 \text{ contains } \frac{32 \times m_1}{233} \text{ g sulphur}$$

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

### Problem 8.24

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

$$\text{Molecular mass of BaSO}_4 = 137 + 32 + 64 \\ = 233 \text{ g}$$

233 g BaSO<sub>4</sub> contains 32 g sulphur

$$0.4813 \text{ g BaSO}_4 \text{ contains } \frac{32 \times 0.4813}{233} \text{ g sulphur}$$

$$\text{Percentage of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} \\ = 42.10\%$$

### 8.10.5 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<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as MgNH<sub>4</sub>PO<sub>4</sub> by adding magnesia mixture which on ignition yields Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

Let the mass of organic compound taken = m g and mass of ammonium phosphomolybdate = m<sub>1</sub>g

$$\text{Molar mass of (NH}_4)_3\text{PO}_4\cdot 12\text{MoO}_3 = 1877 \text{ g}$$

$$\text{Percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$

If phosphorus is estimated as Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>,

$$\text{Percentage of phosphorus} = \frac{62 \times m_1 \times 100}{222} \%$$

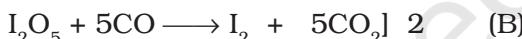
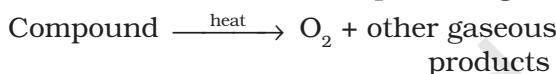
where, 222 u is the molar mass of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, m, the mass of organic compound taken, m<sub>1</sub>, the mass of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> formed and 62, the mass of two phosphorus atoms present in the compound Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

### 8.10.6 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<sub>2</sub>O<sub>5</sub>) when carbon monoxide is oxidised to carbon dioxide producing iodine.



On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbondioxide.

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be m g  
Mass of carbon dioxide produced be m<sub>1</sub> g

∴ m<sub>1</sub> g carbon dioxide is obtained from  
 $\frac{32 \times m_1}{88} \text{ g O}_2$

$$\therefore \text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{88 \times m} \%$$

The percentage of oxygen can be derived from the amount of iodine produced also.

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 1s orbital of hydrogen to give a carbon - hydrogen (C-H) single bond (sigma,  $\sigma$  bond). Overlap of a  $sp^2$  orbital of one carbon with  $sp^2$  orbital of another results in the formation of a carbon–carbon  $\sigma$  bond. The unhybridised  $p$  orbitals on two adjacent carbons can undergo lateral (side-by-side) overlap to give a pi ( $\pi$ ) 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.

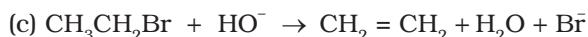
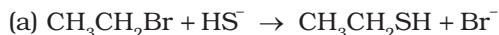
Purification, qualitative and quantitative analysis of organic compounds are carried out for determining their structures. The methods of purification namely : sublimation, distillation and differential extraction are based on the difference in one or more physical properties. **Chromatography** is a 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

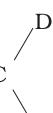
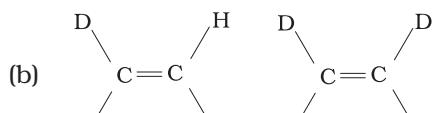
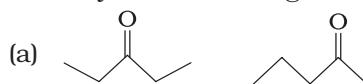
- 8.1 What are hybridisation states of each carbon atom in the following compounds ?  
 $\text{CH}_2=\text{C=O}$ ,  $\text{CH}_3\text{CH}=\text{CH}_2$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{CH}_2=\text{CHCN}$ ,  $\text{C}_6\text{H}_6$
- 8.2 Indicate the  $\sigma$  and  $\pi$  bonds in the following molecules :  
 $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{12}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2=\text{C=CH}_2$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{HCONHCH}_3$
- 8.3 Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one.
- 8.4 Give the IUPAC names of the following compounds :
- (a) (b) (c)
- (d) (e) (f)  $\text{Cl}_2\text{CHCH}_2\text{OH}$
- 8.5 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.
- 8.6 Draw formulas for the first five members of each homologous series beginning with the following compounds. (a)  $\text{H}-\text{COOH}$  (b)  $\text{CH}_3\text{COCH}_3$  (c)  $\text{H}-\text{CH}=\text{CH}_2$
- 8.7 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) Hexanodial
- 8.8 Identify the functional groups in the following compounds
- (a) (b) (c)
- 8.9 Which of the two:  $\text{O}_2\text{NCH}_2\text{CH}_2\text{O}^-$  or  $\text{CH}_3\text{CH}_2\text{O}^-$  is expected to be more stable and why?
- 8.10 Explain why alkyl groups act as electron donors when attached to a  $\pi$  system.
- 8.11 Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.  
(a)  $\text{C}_6\text{H}_5\text{OH}$  (b)  $\text{C}_6\text{H}_5\text{NO}_2$  (c)  $\text{CH}_3\text{CH}=\text{CHCHO}$  (d)  $\text{C}_6\text{H}_5-\text{CHO}$  (e)  $\text{C}_6\text{H}_5-\overset{+}{\text{CH}}_2$   
(f)  $\text{CH}_3\text{CH}=\text{CH}\overset{+}{\text{CH}}_2$
- 8.12 What are electrophiles and nucleophiles ? Explain with examples.
- 8.13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:  
(a)  $\text{CH}_3\text{COOH} + \text{HO}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$



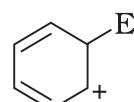
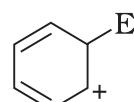
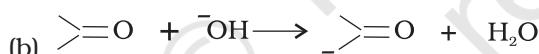
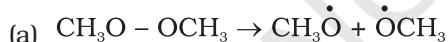
8.14 Classify the following reactions in one of the reaction type studied in this unit.



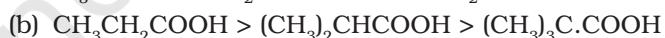
8.15 What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors ?



8.16 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.



8.17 Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?



8.18 Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation (b) Distillation (c) Chromatography

8.19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

8.20 What is the difference between distillation, distillation under reduced pressure and steam distillation ?

- 8.21 Discuss the chemistry of Lassaigne's test.
- 8.22 Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.
- 8.23 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.
- 8.24 Explain the principle of paper chromatography.
- 8.25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?
- 8.26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.
- 8.27 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.
- 8.28 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation ?
- 8.29 Will  $\text{CCl}_4$  give white precipitate of  $\text{AgCl}$  on heating it with silver nitrate? Give reason for your answer.
- 8.30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?
- 8.31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?
- 8.32 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.
- 8.33 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  $\text{H}_2\text{SO}_4$ . The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.
- 8.34 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.
- 8.35 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.
- 8.36 In the organic compound  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{C} \equiv \text{CH}$ , the pair of hybridised orbitals involved in the formation of:  $\text{C}_2 - \text{C}_3$  bond is:  
 (a)  $sp - sp^2$  (b)  $sp - sp^3$  (c)  $sp^2 - sp^3$  (d)  $sp^3 - sp^3$
- 8.37 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:  
 (a)  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  (b)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (c)  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$  (d)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$
- 8.38 Which of the following carbocation is most stable ?  
 (a)  $(\text{CH}_3)_3\text{C}^+$  (b)  $(\text{CH}_3)_3\overset{\cdot}{\text{C}}$  (c)  $\text{CH}_3\text{CH}_2\overset{\cdot}{\text{C}}\text{H}_2$  (d)  $\text{CH}_3\overset{\cdot}{\text{C}}\text{H}\text{CH}_2\text{CH}_3$
- 8.39 The best and latest technique for isolation, purification and separation of organic compounds is:  
 (a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography
- 8.40 The reaction:  

$$\text{CH}_3\text{CH}_2\text{I} + \text{KOH(aq)} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{KI}$$
  
 is classified as :  
 (a) electrophilic substitution (b) nucleophilic substitution  
 (c) elimination (d) addition



## UNIT 9

11083CH13

# 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 liquification 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.

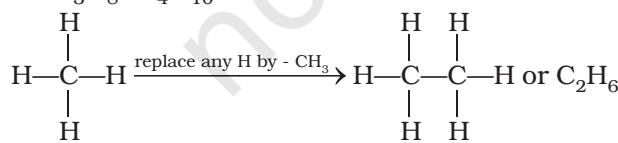
### 9.1 CLASSIFICATION

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 8. 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.

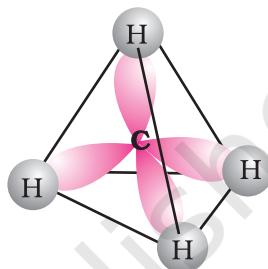
## 9.2 ALKANES

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane ( $\text{CH}_4$ ) 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 tetrivalence of the other carbon atom, what do you get? You get  $\text{C}_2\text{H}_6$ . This hydrocarbon with molecular formula  $\text{C}_2\text{H}_6$  is known as ethane. Thus you can consider  $\text{C}_2\text{H}_6$  as derived from  $\text{CH}_4$  by replacing one hydrogen atom by  $-\text{CH}_3$  group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by  $-\text{CH}_3$  group. The next molecules will be  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$  ...



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**? If we examine the formula of different alkanes we find that the general formula for alkanes is  $\text{C}_n\text{H}_{2n+2}$ . It represents any particular homologue when  $n$  is given appropriate value. Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 9.1), 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 .



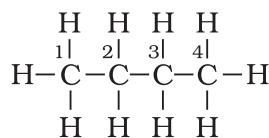
**Fig. 9.1** Structure of methane

In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 8). You have already read that C-C and C-H  $\sigma$  bonds are formed by head-on overlapping of  $sp^3$  hybrid orbitals of carbon and 1s orbitals of hydrogen atoms.

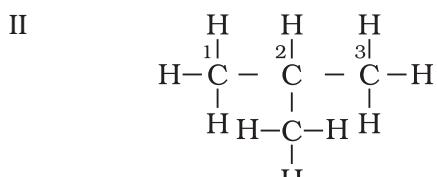
### 9.2.1 Nomenclature and Isomerism

You have already read about nomenclature of different classes of organic compounds in Unit 8. 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  $\text{C}_4\text{H}_{10}$ . Four carbon atoms of  $\text{C}_4\text{H}_{10}$  can be joined either in a continuous chain or with a branched chain in the following two ways :

I

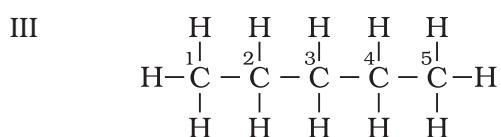


Butane (*n*-butane), (b.p. 273 K)

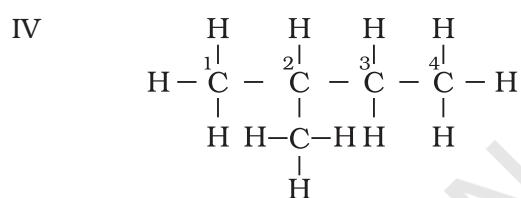


2-Methylpropane (isobutane)  
(b.p. 261 K)

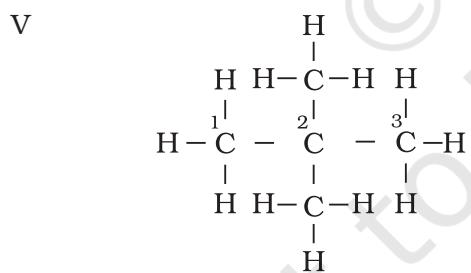
In how many ways, you can join five carbon atoms and twelve hydrogen atoms of  $\text{C}_5\text{H}_{12}$ ? They can be arranged in three ways as shown in structures III-V



Pentane (*n*-pentane)  
(b.p. 309 K)



2-Methylbutane (isopentane)  
(b.p. 301 K)



2,2-Dimethylpropane (neopentane)  
(b.p. 282.5 K)

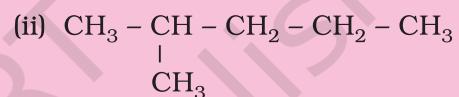
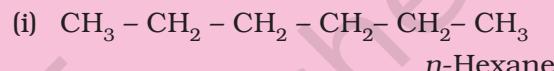
Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. 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  $\text{C}_4\text{H}_{10}$  and  $\text{C}_5\text{H}_{12}$  have two and three chain isomers respectively.

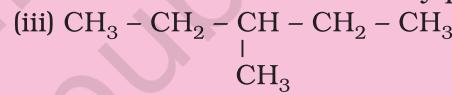
### Problem 9.1

Write structures of different chain isomers of alkanes corresponding to the molecular formula  $\text{C}_6\text{H}_{14}$ . Also write their IUPAC names.

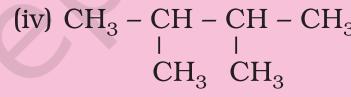
### Solution



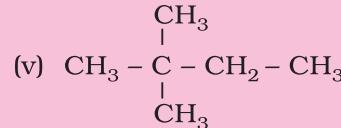
2-Methylpentane



3-Methylpentane



2,3-Dimethylbutane



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 8).

Let us recall the general rules for nomenclature already discussed in Unit 8. Nomenclature of substituted alkanes can further be understood by considering the following problem:

### Problem 9.2

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	Name of alcohol
(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) $CH_3 - \underset{ }{CH} - CH_2 - CH_2 - CH_3$	$CH_3 - \underset{OH}{ }CH - CH_2 - CH_2 - CH_3$	Pentan-2-ol
(iii) $CH_3 - CH_2 - \underset{ }{CH} - CH_2 - CH_3$	$CH_3 - CH_2 - \underset{OH}{ }CH - CH_2 - CH_3$	Pentan-3-ol
$CH_3$   (iv) $CH_3 - CH - CH_2 - CH_2 -$	$CH_3$   $CH_3 - CH - CH_2 - CH_2 - OH$	3-Methylbutan-1-ol
$CH_3$   (v) $CH_3 - CH_2 - CH - CH_2 -$	$CH_3$   $CH_3 - CH_2 - CH - CH_2 - OH$	2-Methylbutan-1-ol
$CH_3$   (vi) $CH_3 - C - CH_2 - CH_3$	$CH_3$   $CH_3 - C - CH_2 - CH_3$ OH	2-Methylbutan-2-ol
$CH_3$   (vii) $CH_3 - C - CH_2 -$ $CH_3$	$CH_3$   $CH_3 - C - CH_2 OH$ $CH_3$	2,2-Dimethylpropan-1-ol
$CH_3$   (viii) $CH_3 - CH - CH - CH_3$	$CH_3$ $OH$        $CH_3 - CH - CH - CH_3$	3-Methylbutan-2-ol

**Table 9.1 Nomenclature of a Few Organic Compounds**

<b>Structure and IUPAC Name</b>	<b>Remarks</b>
(a) $\begin{array}{ccccccc} & \text{CH}_3 & & \text{CH}_2 - \text{CH}_3 \\ &   & &   \\ \text{CH}_3 - & \text{CH} - & \text{CH}_2 - & \text{CH} - & \text{CH}_2 - & \text{CH}_3 \\   & & &   & & \\ \text{CH}_3 & & \text{CH}_2 & \text{CH}_3 & \text{CH}_2 & \text{CH}_3 \\ (4-\text{Ethyl}-2-\text{methylhexane}) \end{array}$	Lowest sum and alphabetical arrangement
(b) $\begin{array}{ccccccccc} & & \text{CH}_2 - \text{CH}_3 & & & & & & \\ & &   & & & & & & \\ & & \text{CH}_2 & - & \text{CH}_3 & - & \text{CH}_2 & - & \text{CH}_3 \\ & &   & &   & &   & & \\ & & \text{CH} & & \text{CH}_3 & & \text{CH}_2 - \text{CH}_3 & & \\ & & / \backslash & & & & & & \\ & & \text{CH}_3 & & \text{CH}_3 & & & & \\ (3,3\text{-Diethyl-5-isopropyl-4-methyloctane}) \end{array}$	Lowest sum and alphabetical arrangement
(c) $\begin{array}{cccccccccc} & & \text{CH}(\text{CH}_3)_2 & & & & & & & \\ & &   & & & & & & & \\ & & \text{CH}_3 - & \text{CH}_2 - & \text{CH}_2 - & \text{CH} - & \text{CH} - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_3 \\ & &   & & & & & & & \\ & & \text{H}_3\text{C} - & \text{CH} - & \text{CH}_2 - & \text{CH}_3 & & & & \\ 5\text{-sec- Butyl-4-isopropyldecane} \end{array}$	sec is not considered while arranging alphabetically; isopropyl is taken as one word
(d) $\begin{array}{cccccccccc} & & \text{CH}(\text{CH}_3)_2 & & & & & & & \\ & &   & & & & & & & \\ & & \text{CH}_3 - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_2 - & \text{CH} - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_3 \\ & &   & & & &   & & & \\ & & \text{CH}_2 & & & & \text{CH}_3 & & & \\ & &   & & & &   & & & \\ & & \text{CH}_3 - & \text{C} - & \text{CH}_3 & & & & & \\ & &   & & & & & & & \\ & & \text{CH}_3 & & & & & & & \\ 5\text{-}(2,2\text{- Dimethylpropyl)nonane} \end{array}$	Further numbering to the substituents of the side chain
(e) $\begin{array}{cccccccccc} & & \text{CH}(\text{CH}_3)_2 & & & & & & & \\ & &   & & & & & & & \\ & & \text{CH}_3 - & \text{CH}_2 - & \text{CH} - & \text{CH}_2 - & \text{CH} - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_3 \\ & &   & &   & &   & & & \\ & & \text{CH}_2 - & \text{CH}_3 & \text{CH}_3 & & & & & \\ 3\text{-Ethyl-5-methylheptane} \end{array}$	Alphabetical priority order

**Problem 9.3**

Write IUPAC names of the following compounds :

- (i)  $(\text{CH}_3)_3 \text{C CH}_2 \text{C}(\text{CH}_3)_3$
- (ii)  $(\text{CH}_3)_2 \text{C}(\text{C}_2\text{H}_5)_2$
- (iii) tetra - *tert*-butylmethane

**Solution**

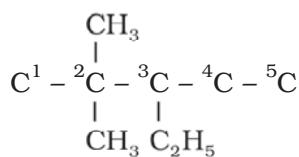
- (i) 2, 2, 4, 4-Tetramethylpentane
- (ii) 3, 3-Dimethylpentane
- (iii) 3,3-Di-*tert*-butyl -2, 2, 4, 4 - tetramethylpentane

If it is important to write the correct IUPAC name for a given structure, it is equally

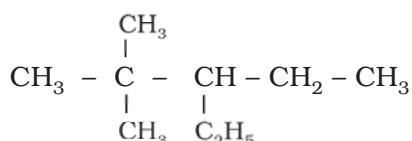
important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is 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:  
 $\text{C} - \text{C} - \text{C} - \text{C} - \text{C}$
- ii) Give number to carbon atoms:  
 $\text{C}^1 - \text{C}^2 - \text{C}^3 - \text{C}^4 - \text{C}^5$

- 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 :



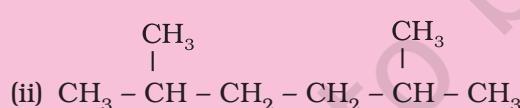
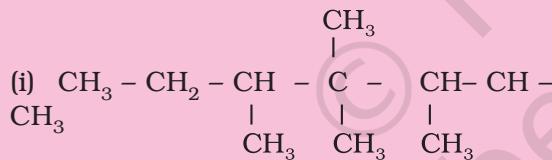
Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems.

### Problem 9.4

Write structural formulas of the following compounds :

- (i) 3, 4, 4, 5-Tetramethylheptane
  - (ii) 2,5-Dimethylhexane

### Solution

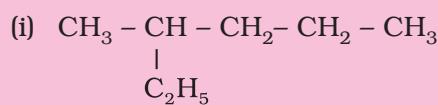


### Problem 9.5

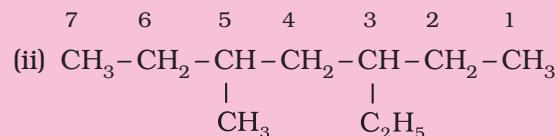
Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names.

- (i) 2-Ethylpentane
  - (ii) 5-Ethyl – 3-methylheptane

### Solution



Longest chain is of six carbon atoms and not that of five. Hence, correct name is 3-Methylhexane.



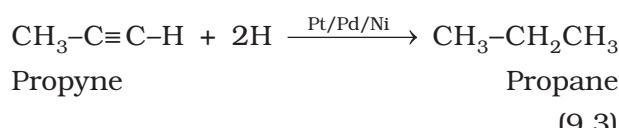
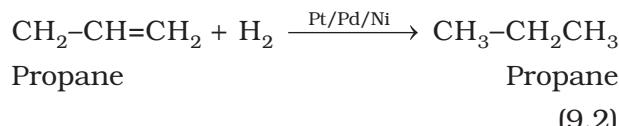
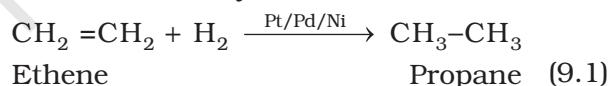
Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane.

## 9.2.2 Preparation

Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods :

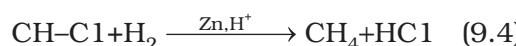
## **1. From unsaturated hydrocarbons**

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.

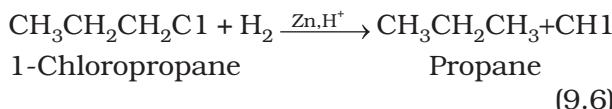
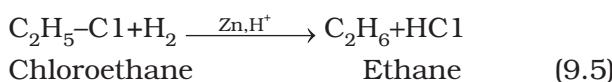


## 2. From alkyl halides

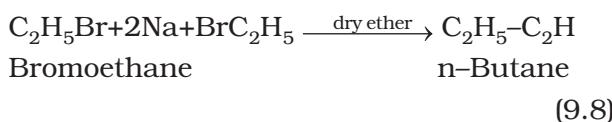
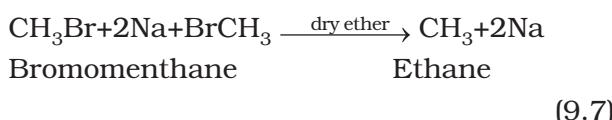
- i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.



## Chloromethane      Methane



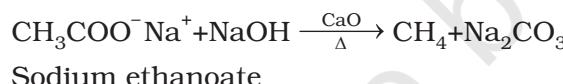
- ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction** and is used for the preparation of higher alkanes containing even number of carbon atoms.



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**.

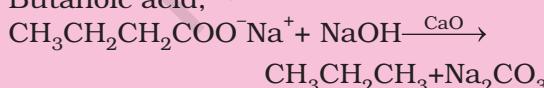


#### Problem 9.6

Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction.

#### Solution

Butanoic acid,



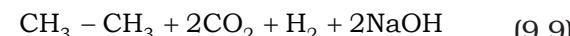
- ii) **Kolbe's electrolytic method:** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives

alkane containing even number of carbon atoms at the anode.

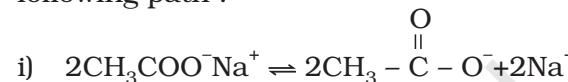


Sodium acetate

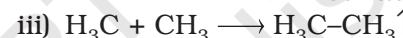
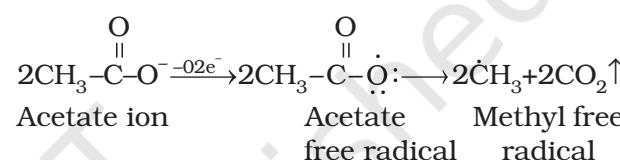
↓ Electrolysts



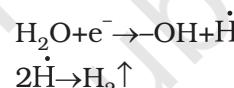
The reaction is supposed to follow the following path :



#### ii) At anode:



#### iv) At cathode :



Methane cannot be prepared by this method. Why?

#### 9.2.3 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<sub>1</sub> to C<sub>4</sub> are gases, C<sub>5</sub> to C<sub>17</sub> 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 9.2 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 9.2) 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

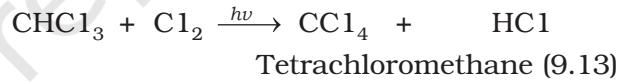
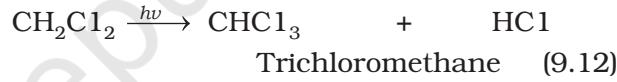
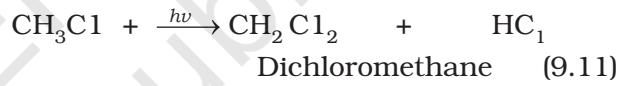
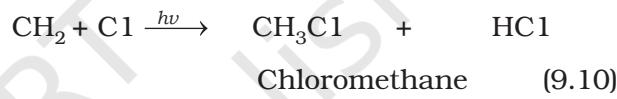
As already mentioned, alkanes are generally inert towards acids, bases, oxidising and

reducing agents. However, they undergo the following reactions under certain conditions.

### 1. Substitution reactions

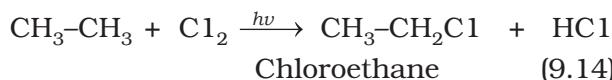
One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. **Halogenation** takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. 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



**Table 9.2 Variation of Melting Point and Boiling Point in Alkanes**

Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH <sub>4</sub>	Methane	16	111.0	90.5
C <sub>2</sub> H <sub>6</sub>	Ethane	30	184.4	101.0
C <sub>3</sub> H <sub>8</sub>	Propane	44	230.9	85.3
C <sub>4</sub> H <sub>10</sub>	Butane	58	272.4	134.6
C <sub>4</sub> H <sub>10</sub>	2-Methylpropane	58	261.0	114.7
C <sub>5</sub> H <sub>12</sub>	Pentane	72	309.1	143.3
C <sub>5</sub> H <sub>12</sub>	2-Methylbutane	72	300.9	113.1
C <sub>5</sub> H <sub>12</sub>	2,2-Dimethylpropane	72	282.5	256.4
C <sub>6</sub> H <sub>14</sub>	Hexane	86	341.9	178.5
C <sub>7</sub> H <sub>16</sub>	Heptane	100	371.4	182.4
C <sub>8</sub> H <sub>18</sub>	Octane	114	398.7	216.2
C <sub>9</sub> H <sub>20</sub>	Nonane	128	423.8	222.0
C <sub>10</sub> H <sub>22</sub>	Decane	142	447.1	243.3
C <sub>20</sub> H <sub>42</sub>	Eicosane	282	615.0	236.2



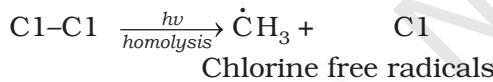
It is found that the rate of reaction of alkanes with halogens is  $F_2 > Cl_2 > Br_2 > I_2$ . Rate of replacement of hydrogens of alkanes is : 3 > 2 > 1 . Fluorination is too violent to be controlled. Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like  $HIO_3$  or  $HNO_3$ .



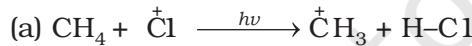
Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely initiation, propagation and termination as given below:

## **Mechanism**

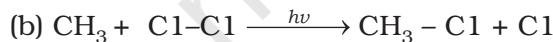
**(i) Initiation :** The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl-Cl bond is weaker than the C-C and C-H bond and hence, is easiest to break.



**(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.

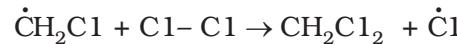


The methyl radical thus obtained attacks the second molecule of chlorine to form  $\text{CH}_3\text{-Cl}$  with the liberation of another chlorine free radical by homolysis of chlorine molecule.



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 halogenated products are formed.



**(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)  $\dot{\text{C}}\text{l} + \dot{\text{C}}\text{l} \rightarrow \text{C}\text{l}-\text{C}\text{l}$

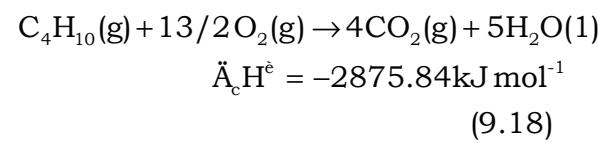
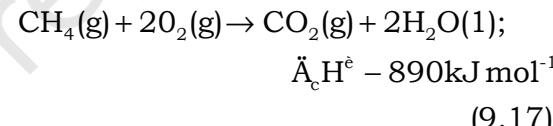
(b)  $\text{H}_3\dot{\text{C}} + \dot{\text{C}}\text{H}_3 \rightarrow \text{H}_3\text{C}-\text{CH}_3$

(c)  $\text{H}_3\dot{\text{C}}\text{l} + \dot{\text{C}}\text{l} \rightarrow \text{H}_3\text{C}-\text{C}\text{l}$

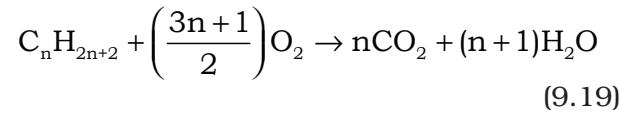
Though in (c),  $\text{CH}_3 - \text{Cl}$ , the one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane.

## 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.

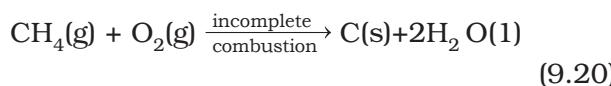


The general combustion equation for any alkane is :



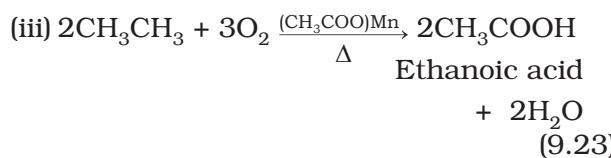
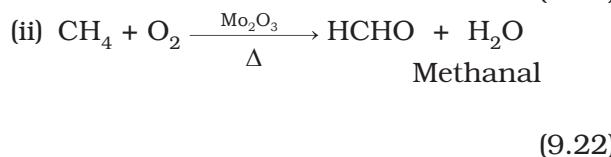
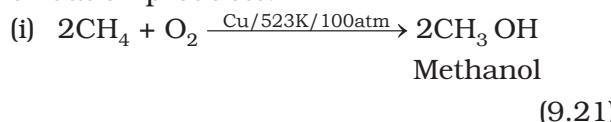
Due to the evolution of large amount of heat during combustion, alkanes are used as fuels.

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.

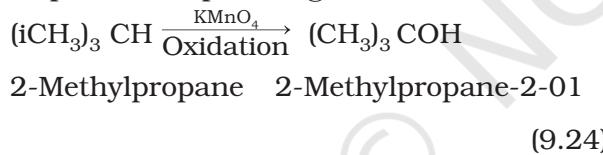


### **3. Controlled oxidation**

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.

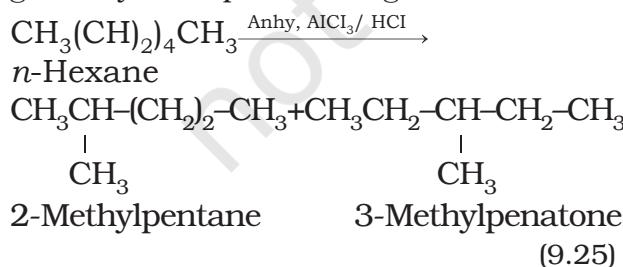


(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.



## **4. Isomerisation**

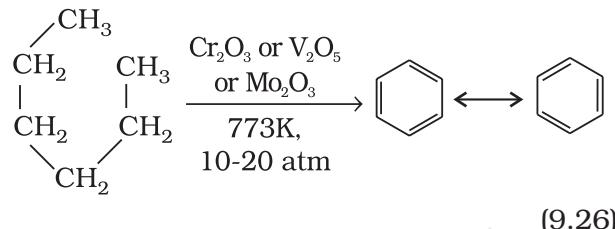
*n*-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions.



## 5. Aromatization

*n*-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric

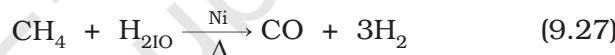
pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get **dehydrogenated** and cyclised to benzene and its homologues. This reaction is known as *aromatization* or *reforming*.



Toluene ( $C_7H_8$ ) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ?

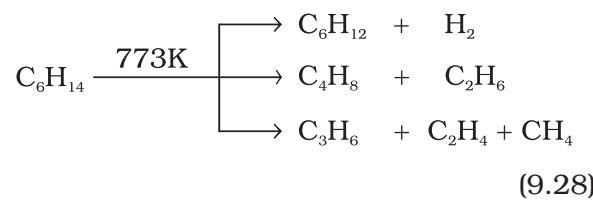
## **6. Reaction with steam**

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

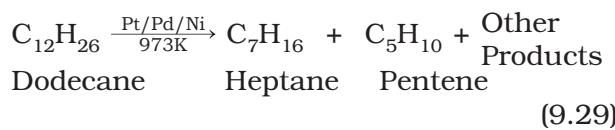


## 7. Pyrolysis

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*.



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.



### 9.2.4 Conformations

Alkanes contain carbon-carbon sigma ( $\sigma$ ) 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  $1\text{-}20 \text{ kJ mol}^{-1}$  due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

**Conformations of ethane :** Ethane molecule ( $\text{C}_2\text{H}_6$ ) 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  $120^\circ$  to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 9.2.

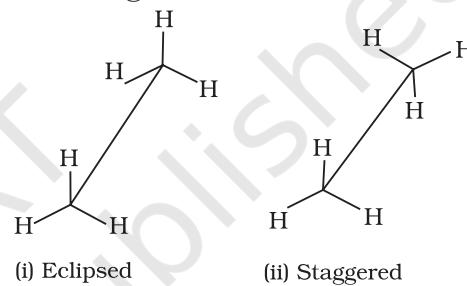


Fig. 9.2 Sawhorse projections of ethane

### 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  $120^\circ$  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  $120^\circ$  to each other. The Newman's projections are depicted in Fig. 9.3.

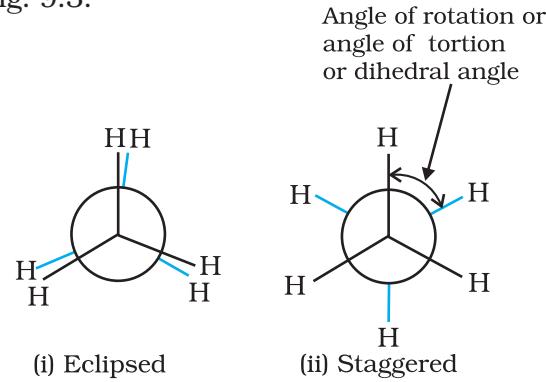


Fig. 9.3 Newman's projections of ethane

**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*. Therefore, staggered conformation is more stable than the eclipsed conformation. Hence, molecule largely remains in staggered conformation or we can say that it is preferred conformation. 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  $12.5 \text{ kJ mol}^{-1}$ , which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of  $12.5 \text{ kJ mol}^{-1}$  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.

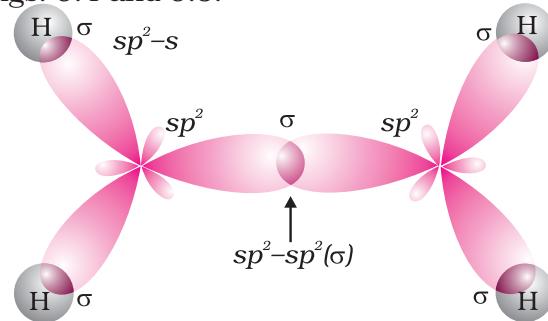
### 9.3 ALKENES

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  $\text{C}_n\text{H}_{2n}$ . Alkenes are also known as olefins (oil forming) since

the first member, ethylene or ethene ( $\text{C}_2\text{H}_4$ ) was found to form an oily liquid on reaction with chlorine.

#### 9.3.1 Structure of Double Bond

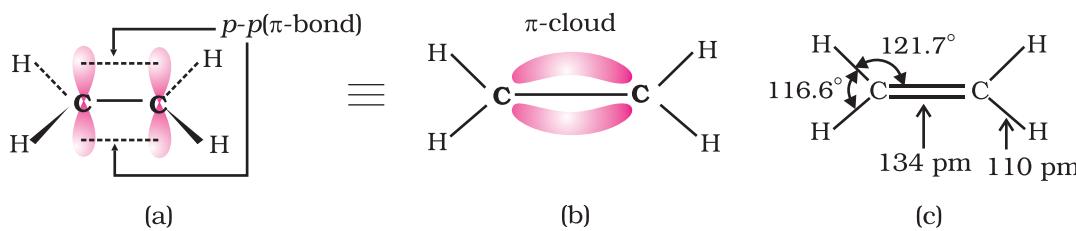
Carbon–carbon double bond in alkenes consists of one strong sigma ( $\sigma$ ) bond (bond enthalpy about  $397 \text{ kJ mol}^{-1}$ ) due to head-on overlapping of  $sp^2$  hybridised orbitals and one weak pi ( $\pi$ ) bond (bond enthalpy about  $284 \text{ kJ mol}^{-1}$ ) obtained by lateral or sideways overlapping of the two  $2p$  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 ( $\pi$ ) bond is a weaker bond due to poor sideways overlapping between the two  $2p$  orbitals. Thus, the presence of the pi ( $\pi$ ) 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  $\pi$ -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,  $681 \text{ kJ mol}^{-1}$ ) is greater than that of a carbon–carbon single bond in ethane (bond enthalpy,  $348 \text{ kJ mol}^{-1}$ ). Orbital diagrams of ethene molecule are shown in Figs. 9.4 and 9.5.



**Fig. 9.4** Orbital picture of ethene depicting  $\sigma$  bonds only

#### 9.3.2 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



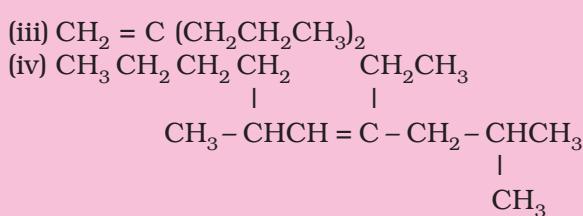
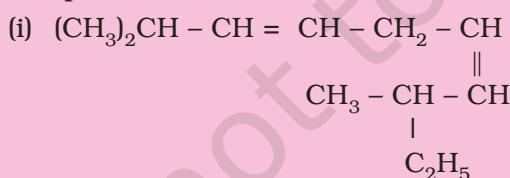
**Fig. 9.5** Orbital picture of ethene showing formation of (a)  $\pi$ -bond, (b)  $\pi$ -cloud and (c) bond angles and bond lengths

the double bond. The suffix ‘ene’ replaces ‘ane’ of alkanes. It may be remembered that first member of alkene series is:  $\text{CH}_2$  (replacing n by 1 in  $\text{C}_n\text{H}_{2n}$ ) known as methene but has a very short life. As already mentioned, first stable member of alkene series is  $\text{C}_2\text{H}_4$  known as ethylene (common) or ethene (IUPAC). IUPAC names of a few members of alkenes are given below :

<b>Structure</b>	<b>IUPAC name</b>
$\text{CH}_3 - \text{CH} = \text{CH}_2$	Propene
$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$	But - 1 - ene
$\text{CH}_3 - \text{CH} = \text{CH-CH}_3$	But-2-ene
$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$	Buta - 1,3 - diene
$\text{CH}_2 = \text{C} - \text{CH}_3$   $\text{CH}_3$	2-Methylprop-1-ene
$\text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_3$   $\text{CH}_3$	3-Methylbut-1-ene

### Problem 9.7

Write IUPAC names of the following compounds:



## 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 9.8

Calculate number of sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds in the above structures (i-iv).

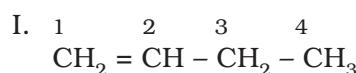
## Solution

- $\sigma$  bonds : 33,  $\pi$  bonds : 2  
 $\sigma$  bonds : 17,  $\pi$  bonds : 4  
 $\sigma$  bonds : 23,  $\pi$  bond : 1  
 $\sigma$  bonds : 41,  $\pi$  bond : 1

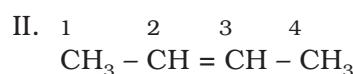
### 9.3.3 Isomerism

Alkenes show both structural isomerism and geometrical isomerism.

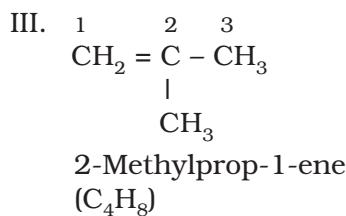
**Structural isomerism :** As in alkanes, ethene ( $C_2H_4$ ) and propene ( $C_3H_6$ ) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing  $C_4H_8$  as molecular formula can be written in the following three ways:



But-1-ene  
(C<sub>4</sub>H<sub>8</sub>)



But-2-ene  
(C<sub>4</sub>H<sub>8</sub>)



Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.

### Problem 9.9

Write structures and IUPAC names of different structural isomers of alkenes corresponding to  $C_5H_{10}$ .

### Solution

- (a)  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$   
Pent-1-ene

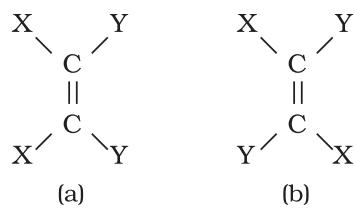
(b)  $\text{CH}_3 - \text{CH}=\text{CH} - \text{CH}_2 - \text{CH}_3$   
Pent-2-ene

(c)  $\begin{array}{c} \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$   
2-Methylbut-2-ene

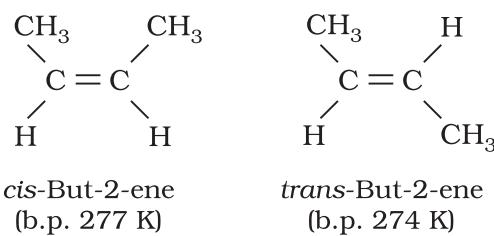
(d)  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH} = \text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$   
3-Methylbut-1-ene

(e)  $\begin{array}{c} \text{CH}_2 = \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$   
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  $\text{YX C} = \text{C XY}$  like structure.  $\text{YX C} = \text{C XY}$  can be represented in space in the following two ways :

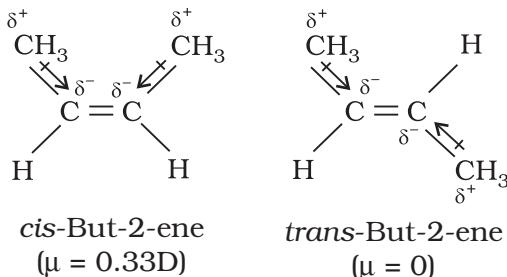


In (a), the two identical atoms i.e., both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) i.e. disposition of atoms or groups in space in 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* 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, therefore, dipole moments of C-CH<sub>3</sub> bonds cancel, thus making the *trans* form non-polar.



In the case of solids, it is observed that the *trans* isomer has higher melting point than the *cis* form.

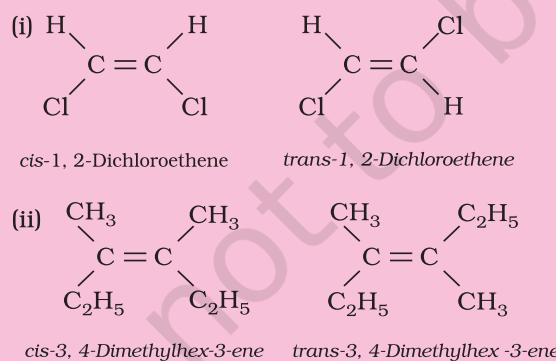
Geometrical or *cis-trans* isomerism is also shown by alkenes of the types  $\text{XYC}=\text{CXZ}$  and  $\text{XYC}=\text{CZW}$

### Problem 9.10

Draw *cis* and *trans* isomers of the following compounds. Also write their IUPAC names :

- (i)  $\text{CHCl} = \text{CHCl}$   
(ii)  $\text{C}_2\text{H}_5\text{CCH}_3 = \text{CCH}_3\text{C}_2\text{H}_5$

### Solution



### Problem 9.11

Which of the following compounds will show *cis-trans* isomerism?

- (i)  $(CH_3)_2C = CH - C_2H_5$

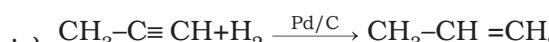
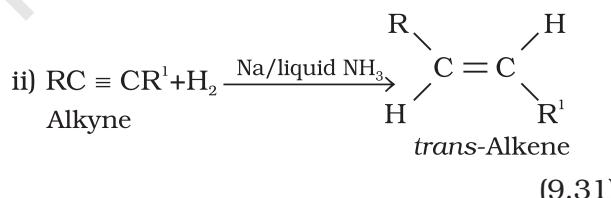
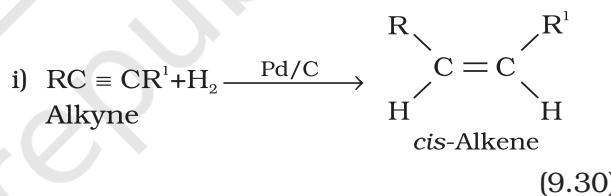
- (ii)  $\text{CH}_2 = \text{CBr}_2$
  - (iii)  $\text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{CH}_3$
  - (iv)  $\text{CH}_3\text{CH} = \text{CCl} \text{ CH}_3$

## Solution

(iii) and (iv). In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atom.

### 9.3.4 Preparation

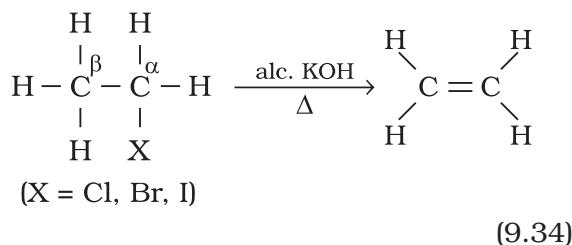
- 1. From alkynes:** Alkynes on partial reduction with calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as *Lindlar's catalyst*. Alkenes thus obtained are having *cis* geometry. However, alkynes on reduction with sodium in liquid ammonia form *trans* alkenes.



Will propene thus obtained show geometrical isomerism? Think for the reason in support of your answer.

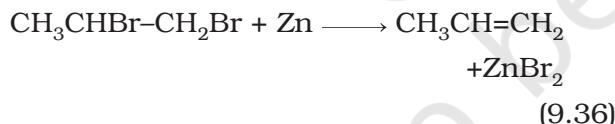
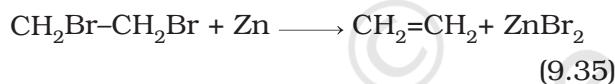
- 2. From alkyl halides:** Alkyl halides ( $R-X$ ) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, say,

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  **$\beta$ -elimination reaction**, since hydrogen atom is eliminated from the  $\beta$  carbon atom (carbon atom next to the carbon to which halogen is attached).



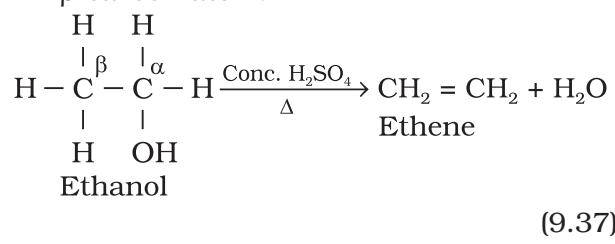
Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tertiary > secondary > primary.

- 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  $\text{ZnX}_2$  to form an alkene. This reaction is known as **dehalogenation**.



- 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  $\text{R}-\text{OH}$  where, R is  $\text{C}_n\text{H}_{2n+1}$ . 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  $\beta$ -elimination reaction since  $-\text{OH}$  group

takes out one hydrogen atom from the  $\beta$ -carbon atom.



(9.37)

### 9.3.5 Properties

#### Physical properties

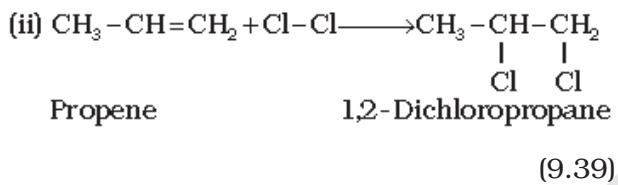
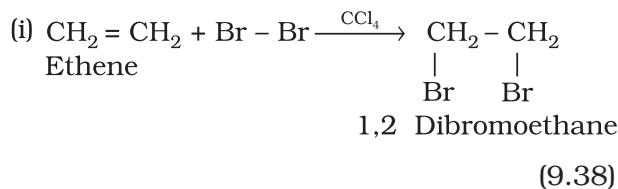
Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless 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  $-\text{CH}_2$  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  $\pi$  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:

- 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 9.2.2)
- Addition of halogens :** Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under

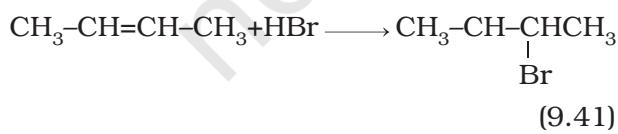
normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes.



**3. Addition of hydrogen halides:** Hydrogen halides ( $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is  $\text{HI} > \text{HBr} > \text{HCl}$ . 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  $\text{HBr}$  to symmetrical and unsymmetrical alkenes

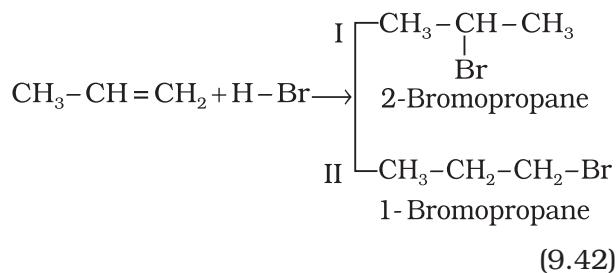
### Addition reaction of HBr to symmetrical alkenes

Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.



## Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

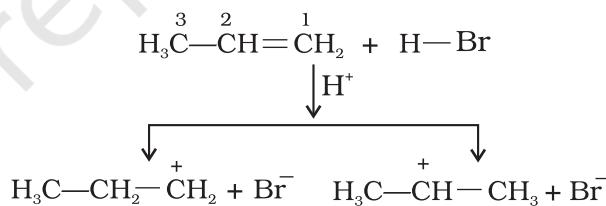
How will H – Br add to propene ? The two possible products are I and II.



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.

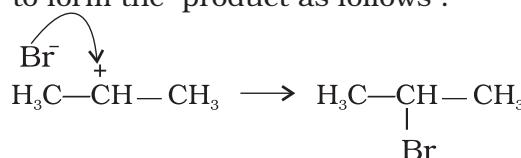
## Mechanism

Hydrogen bromide provides an electrophile,  $H^+$ , which attacks the double bond to form carbocation as shown below :



(a) less stable              (b) more stable  
 primary carbocation    secondary carbocation

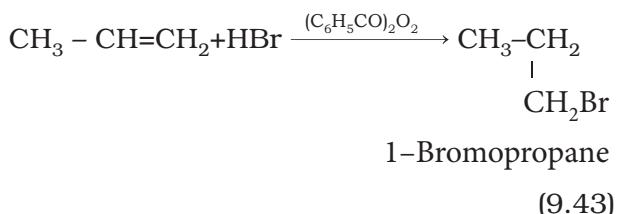
- (i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.
  - (ii) The carbocation (b) is attacked by  $\text{Br}^-$  ion to form the product as follows :



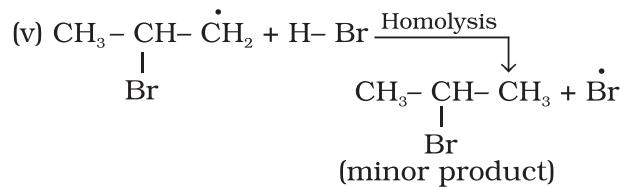
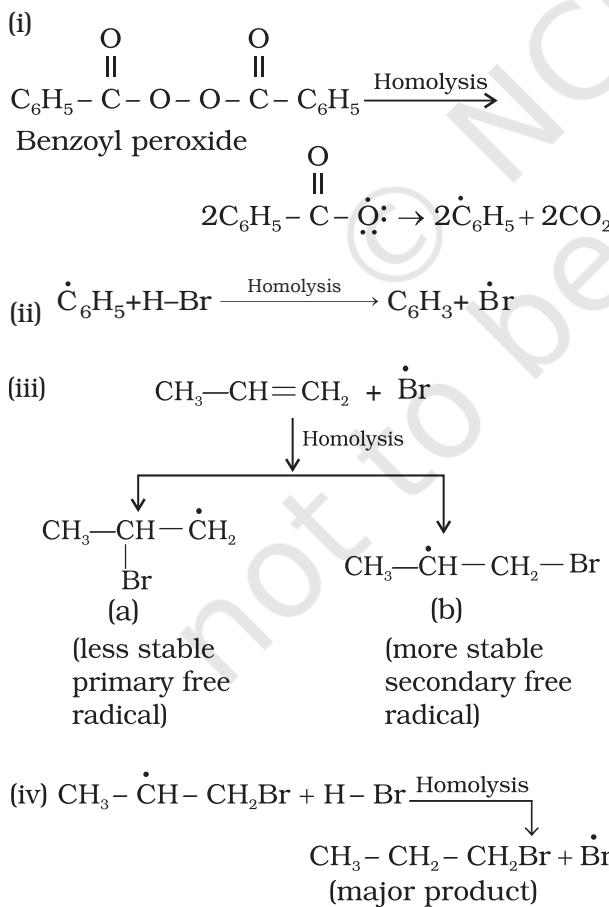
## 2-Bromopropane (major product)

### 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.



**Mechanism :** Peroxide effect proceeds via free radical chain mechanism as given below:



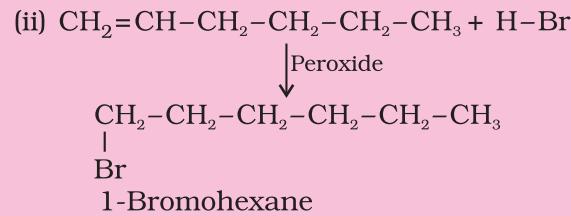
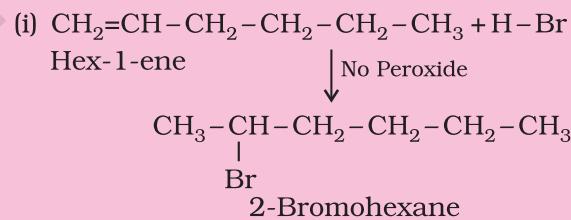
The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H-Cl bond being stronger ( $430.5 \text{ kJ mol}^{-1}$ ) than H-Br bond ( $363.7 \text{ kJ mol}^{-1}$ ), is not cleaved by the free radical, whereas the H-I bond is weaker ( $296.8 \text{ kJ mol}^{-1}$ ) and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

### Problem 9.12

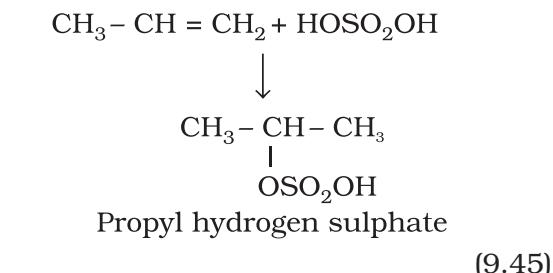
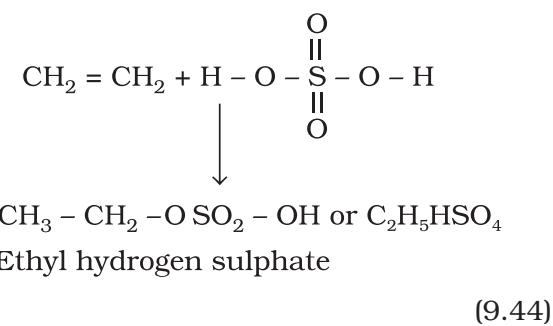
Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene

- (i) in the absence of peroxide and
- (ii) in the presence of peroxide.

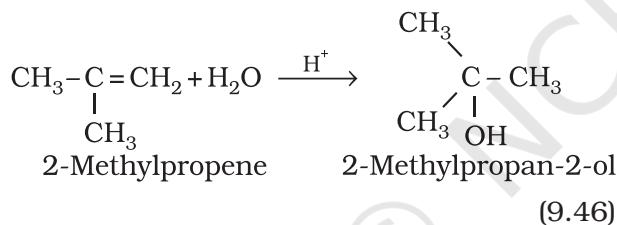
#### Solution



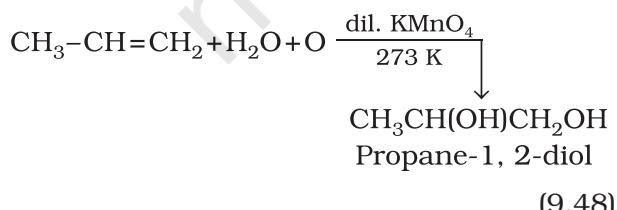
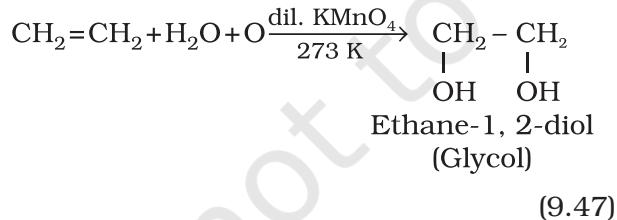
**4. Addition of sulphuric acid :** Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction.



**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.

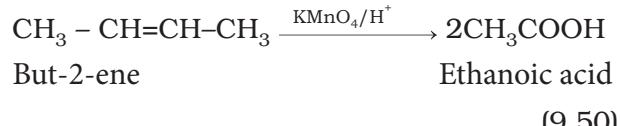
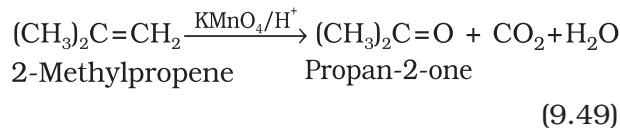


**6. Oxidation:** Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of  $\text{KMnO}_4$  solution is used as a test for unsaturation.

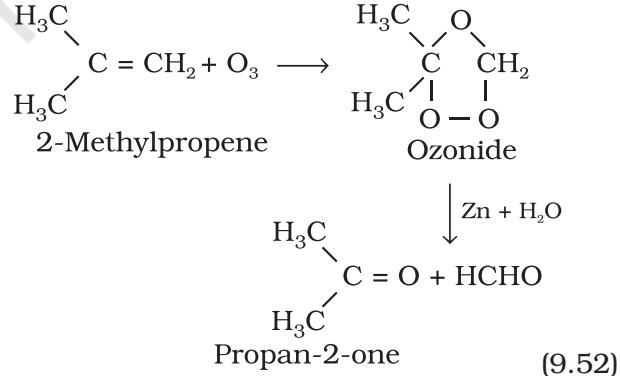
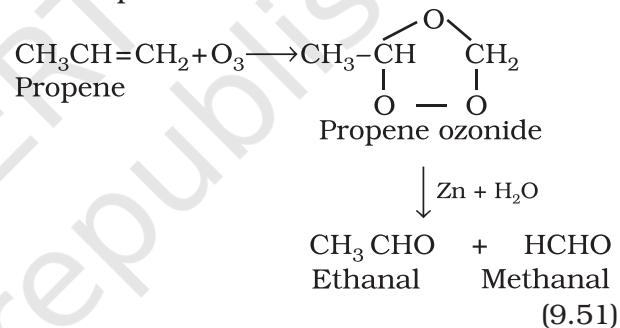


- b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to

ketones and/or acids depending upon the nature of the alkene and the experimental conditions

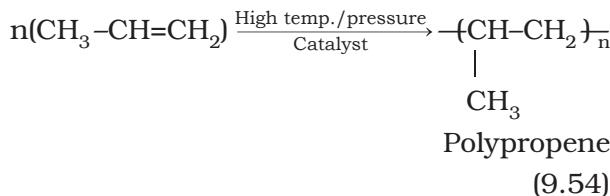
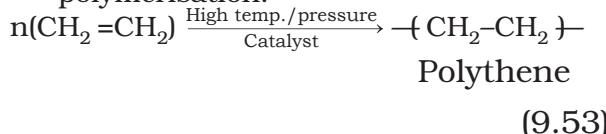


**7. Ozonolysis :** Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by  $\text{Zn}-\text{H}_2\text{O}$  to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



**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.



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.

#### 9.4 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  $\text{C}_n\text{H}_{2n-2}$ .

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.

##### 9.4.1 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 9.2.

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  $\text{C}_5\text{H}_8$ ? 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
$\begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \\   & & & &   \\ \text{HC} \equiv \text{C} - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_3 \\   & 2 & 3 & 4 & 5 \end{array}$	Pent-1-yne
$\begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \\   & & & &   \\ \text{H}_3\text{C} - \text{C} \equiv \text{C} - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_3 & \\   & 3 & 2 & 1 & \end{array}$	Pent-2-yne
$\begin{array}{ccccc} & & & & \\ & & & & \\ \text{III. H}_3\text{C} - \text{CH} - \text{C} \equiv \text{CH} & & & & 3\text{-Methylbut-1-yne} \\   & & & & \\ & & & & \text{CH}_3 \end{array}$	

Structures I and II are position isomers and structures I and III or II and III are chain isomers.

#### Problem 9.13

Write structures of different isomers corresponding to the 5<sup>th</sup> member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

#### Solution

5<sup>th</sup> member of alkyne has the molecular formula  $\text{C}_6\text{H}_{10}$ . The possible isomers are:

Table 9.2 Common and IUPAC Names of Alkynes ( $\text{C}_n\text{H}_{2n-2}$ )

Value of n	Formula	Structure	Common name	IUPAC name
2	$\text{C}_2\text{H}_2$	$\text{H}-\text{C} \equiv \text{CH}$	Acetylene	Ethyne
3	$\text{C}_3\text{H}_4$	$\text{CH}_3-\text{C} \equiv \text{CH}$	Methylacetylene	Propyne
4	$\text{C}_4\text{H}_6$	$\text{CH}_3\text{CH}_2-\text{C} \equiv \text{CH}$	Ethylacetylene	But-1-yne
4	$\text{C}_4\text{H}_6$	$\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_3$	Dimethylacetylene	But-2-yne

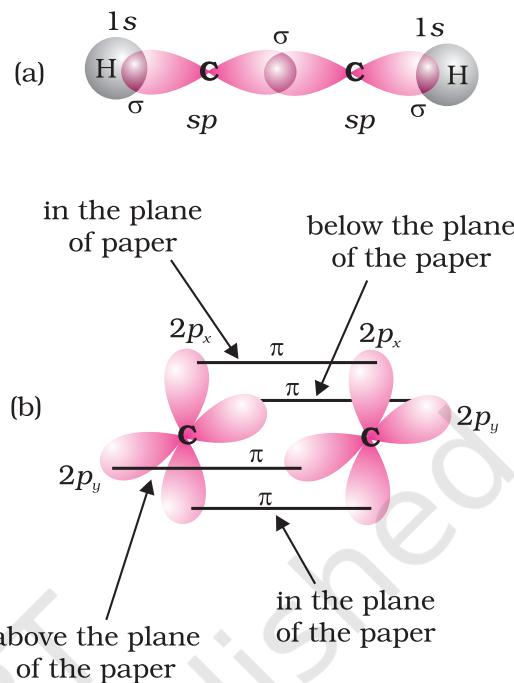
- (a)  $\text{HC} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$   
Hex-1-yne
- (b)  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$   
Hex-2-yne
- (c)  $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$   
Hex-3-yne
- (d)  $\text{HC} \equiv \text{C}-\text{CH}-\text{CH}_2-\text{CH}_3$   
 $\quad |$   
 $\quad \text{CH}_3$   
3-Methylpent-1-yne
- (e)  $\text{HC} \equiv \text{C}-\text{CH}_2-\text{CH}-\text{CH}_3$   
 $\quad |$   
 $\quad \text{CH}_3$   
4-Methylpent-1-yne
- (f)  $\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}-\text{CH}_3$   
 $\quad |$   
 $\quad \text{CH}_3$   
4-Methylpent-2-yne
- (g)  $\text{HC} \equiv \text{C}-\text{C}-\text{CH}_3$   
 $\quad |$   
 $\quad \text{CH}_3$   
3,3-Dimethylbut-1-yne

Position and chain isomerism shown by different pairs.

#### 9.4.2 Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 9.6.

Each carbon atom of ethyne has two  $sp$  hybridised orbitals. Carbon-carbon sigma ( $\sigma$ ) 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  $1s$  orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of  $180^\circ$ . 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  $2p$  orbitals of one carbon atom are parallel to the  $2p$



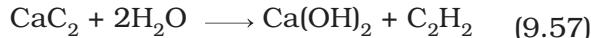
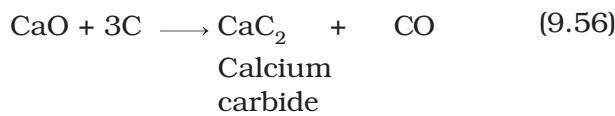
**Fig. 9.6** Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.

orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi ( $\pi$ ) bonds between two carbon atoms. Thus ethyne molecule consists of one C-C  $\sigma$  bond, two C-H  $\sigma$  bonds and two C-C  $\pi$  bonds. The strength of C≡C bond (bond enthalpy  $823 \text{ kJ mol}^{-1}$ ) is more than those of C=C bond (bond enthalpy  $681 \text{ kJ mol}^{-1}$ ) and C-C bond (bond enthalpy  $348 \text{ kJ mol}^{-1}$ ). 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.

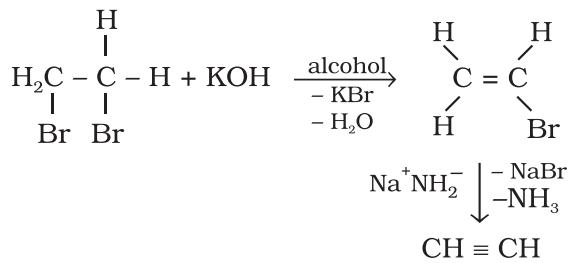
#### 9.4.3 Preparation

**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:





**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.



#### 9.4.4 Properties

##### Physical properties

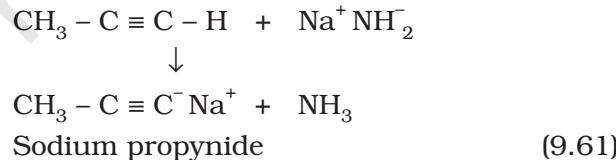
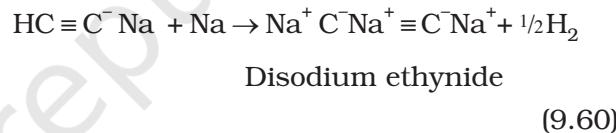
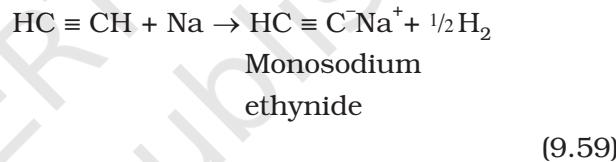
Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyne has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are 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 ( $\text{NaNH}_2$ ) are strong bases. They react with ethyne to form sodium acetylidyde 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

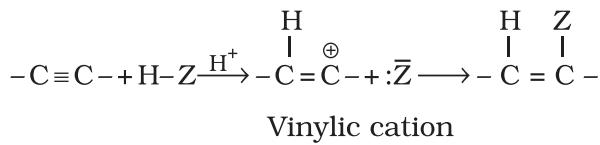
the  $sp$  hybridised carbon atoms whereas they are attached to  $sp^2$  hybridised carbon atoms in ethene and  $sp^3$  hybridised carbons in ethane. Due to the maximum percentage of s character (50%), the  $sp$  hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; 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.



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 :

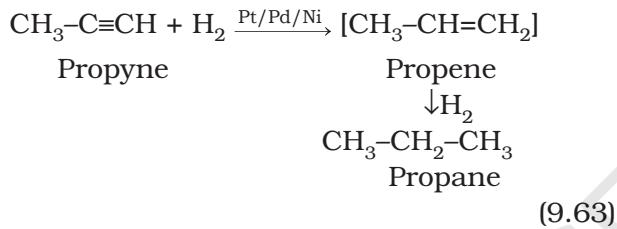
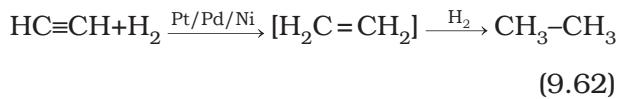
- i)  $\text{CH} \equiv \text{CH} > \text{H}_2\text{C}-\text{CH}_2 > \text{CH}_3-\text{CH}_3$
- ii)  $\text{HC} \equiv \text{CH} > \text{CH}_3-\text{C} \equiv \text{CH} >> \text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_3$

**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.

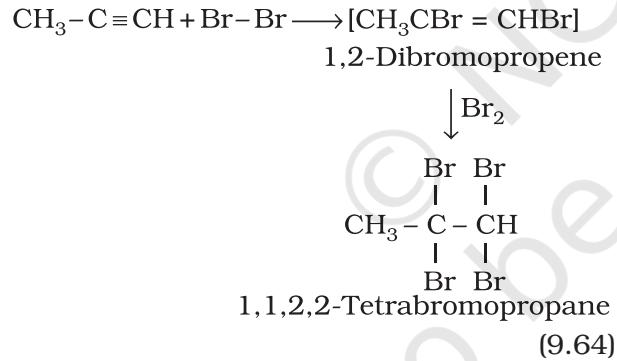


The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

### (i) Addition of dihydrogen



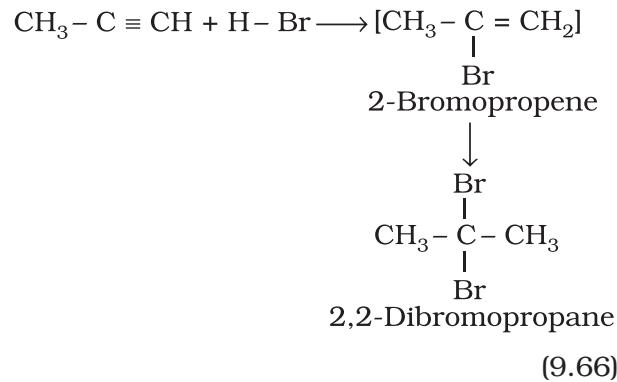
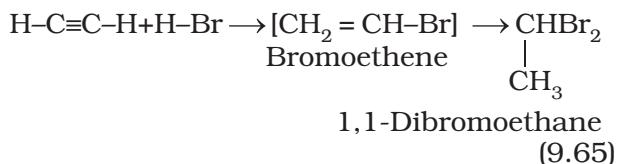
### (ii) Addition of halogens



Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

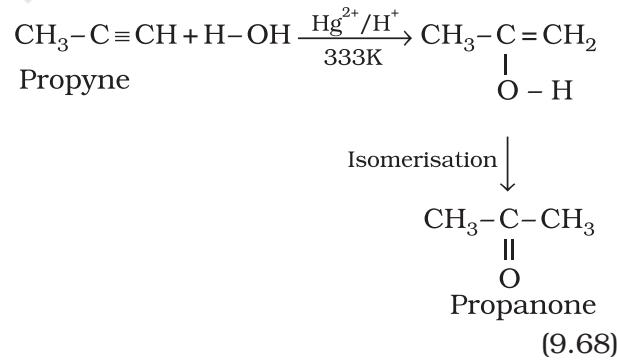
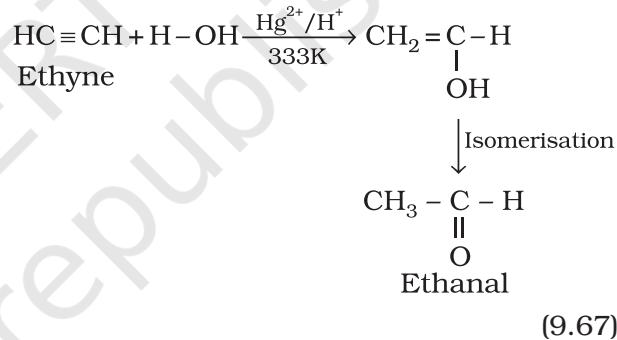
### (iii) Addition of hydrogen halides

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)



### (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.

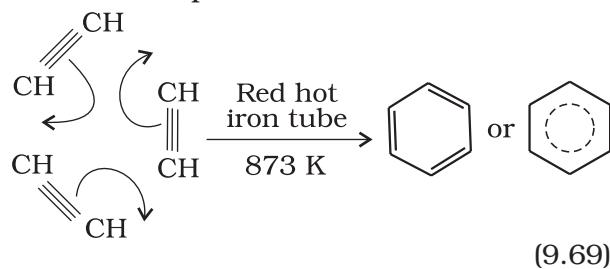


### (v) Polymerisation

**(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  $(\text{CH}=\text{CH}-\text{CH}=\text{CH})$  and can be represented as  $-(\text{CH}=\text{CH}-\text{CH}=\text{CH})_n-$ . 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.

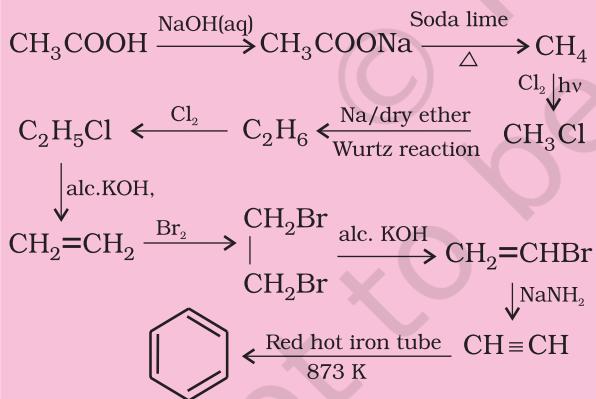
**(b) Cyclic polymerisation:** Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below:



### Problem 9.14

How will you convert ethanoic acid into benzene?

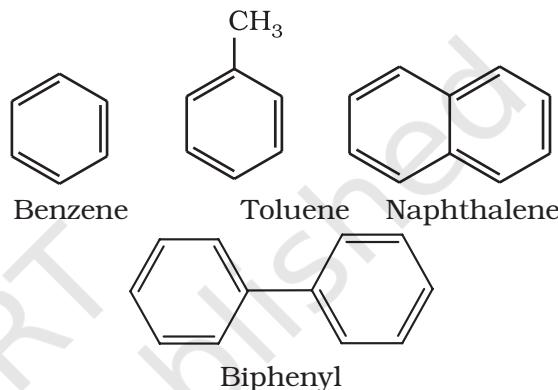
### Solution



## 9.5 AROMATIC HYDROCARBON

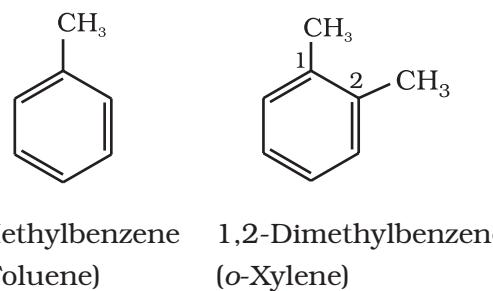
These hydrocarbons are also known as '**arenes**'. Since most of them possess pleasant odour (*Greek; aroma meaning pleasant smelling*), the class of compounds was named as '*aromatic compounds*'. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated

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:



### 9.5.1 Nomenclature and Isomerism

The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 8. 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:



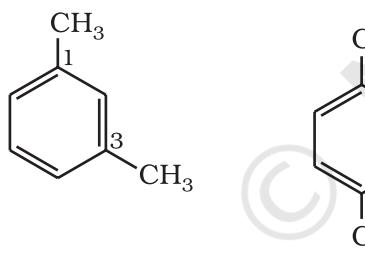
Friedrich August Kekulé, a German chemist was born in 1829 at Darmstadt in Germany. He became Professor in 1856 and Fellow of Royal Society in 1875. He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865, 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 textbook, 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).

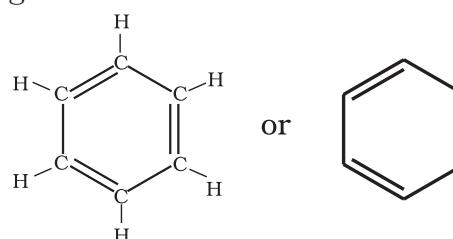
One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes.



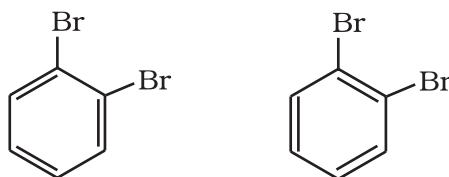
### 9.5.2 Structure of Benzene

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

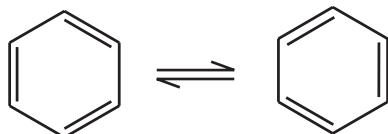
was further found to produce one and only one monosubstituted derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekulé in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.



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.



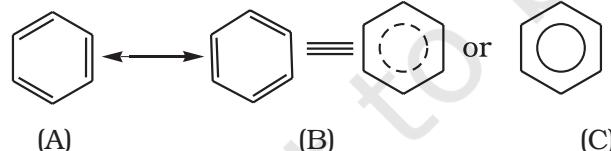
However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below.



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.

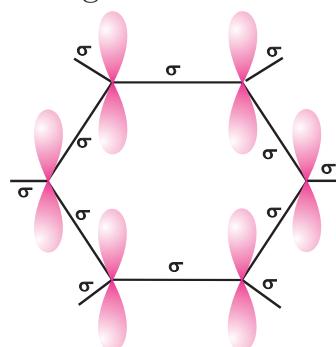
### Resonance and stability of benzene

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.

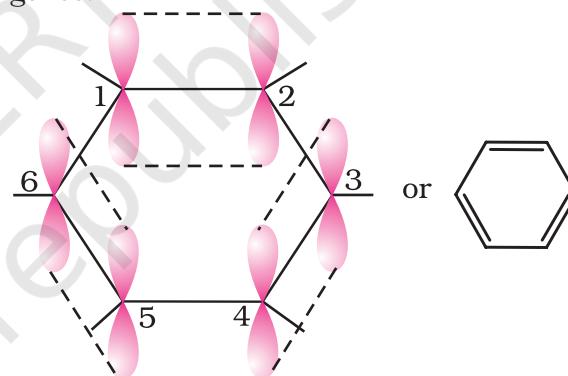


The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are  $sp^2$  hybridized. Two  $sp^2$  hybrid orbitals of each carbon atom overlap with  $sp^2$  hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal 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

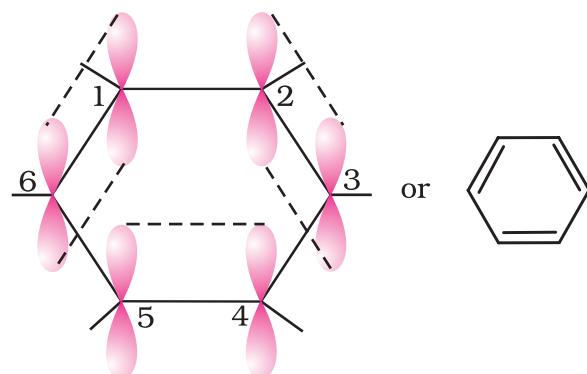
unhybridised  $p$  orbital perpendicular to the plane of the ring as shown below:



The unhybridised  $p$  orbital of carbon atoms are close enough to form a  $\pi$  bond by lateral overlap. There are two equal possibilities of forming three  $\pi$  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.



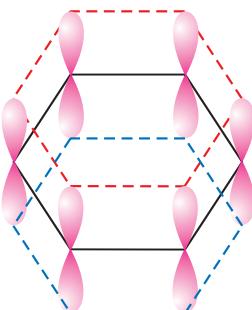
**Fig. 9.7 (a)**



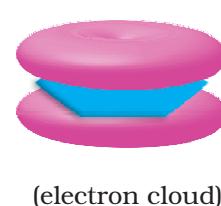
**Fig. 9.7 (b)**

Structures shown in Fig. 9.7(a) and (b) correspond to two Kekulé's structure with localised  $\pi$  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. 9.7 (c)]. This can be represented in the form of two doughnuts (rings) of electron clouds [Fig. 9.7 (d)], one above and one below the plane of the hexagonal ring as shown below:

**Fig. 9.7 (c)**

or



(electron cloud)

**Fig. 9.7 (d)**

The six  $\pi$  electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 9.6 (a) or (b). The delocalised  $\pi$  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  $\pi$  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.

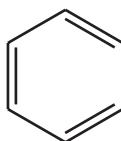
### 9.5.3 Aromaticity

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.

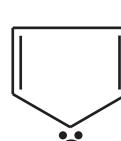
- Planarity
- Complete delocalisation of the  $\pi$  electrons in the ring
- Presence of  $(4n + 2)\pi$  electrons in the ring where  $n$  is an integer ( $n = 0, 1, 2, \dots$ ).

This is often referred to as **Hückel Rule**.

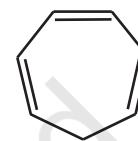
Some examples of aromatic compounds are given below:



Benzene

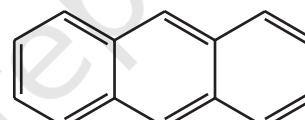


Cyclopentadienyl anion

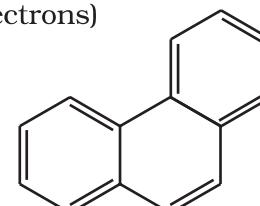


Cycloheptatrienyl cation

$(n=1, 6\pi \text{ electrons})$

Naphthalene  
 $(n = 2, 10\pi \text{ electrons})$ 

Anthracene



Phenanthrene

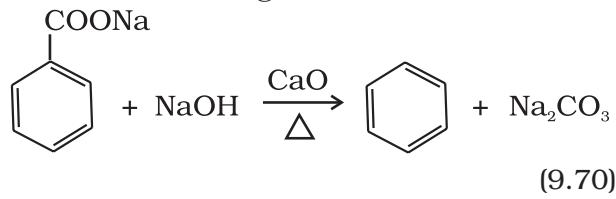
$(n = 3, 14\pi \text{ electrons})$

### 9.5.4 Preparation of Benzene

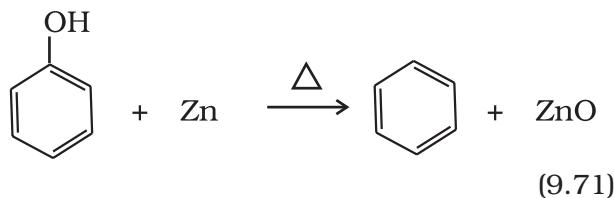
Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods.

- Cyclic polymerisation of ethyne:** (Section 9.4.4)

- Decarboxylation of aromatic acids:** Sodium salt of benzoic acid on heating with sodalime gives benzene.



- (iii) **Reduction of phenol:** Phenol is reduced to benzene by passing its vapours over heated zinc dust



### 9.5.5 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.

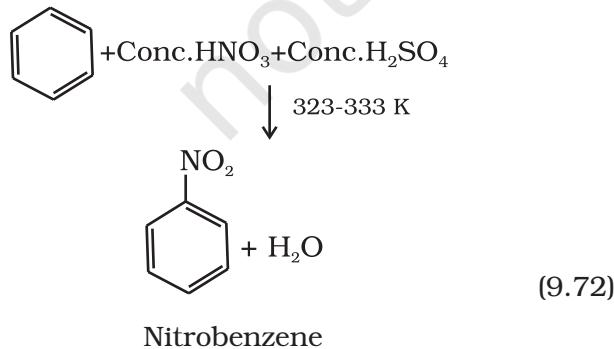
#### Chemical properties

Arenes are characterised by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

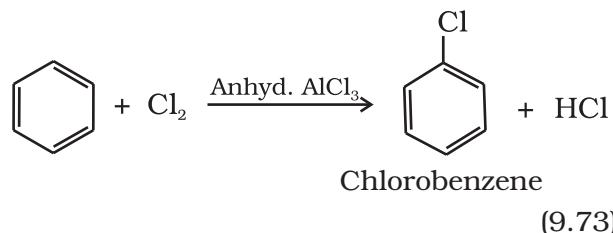
#### Electrophilic substitution reactions

The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel-Crafts alkylation and acylation reactions in which attacking reagent is an electrophile ( $\text{E}^+$ )

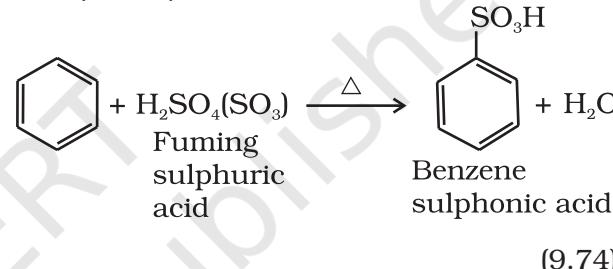
- (i) **Nitration:** A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture).



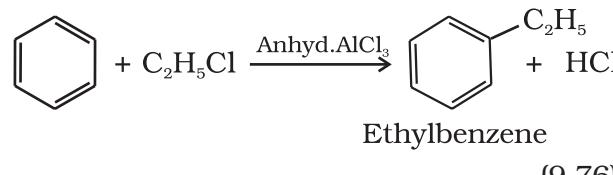
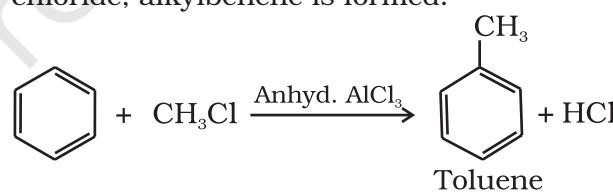
- (ii) **Halogenation:** Arenes react with halogens in the presence of a Lewis acid like anhydrous  $\text{FeCl}_3$ ,  $\text{FeBr}_3$  or  $\text{AlCl}_3$  to yield haloarenes.



- (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).

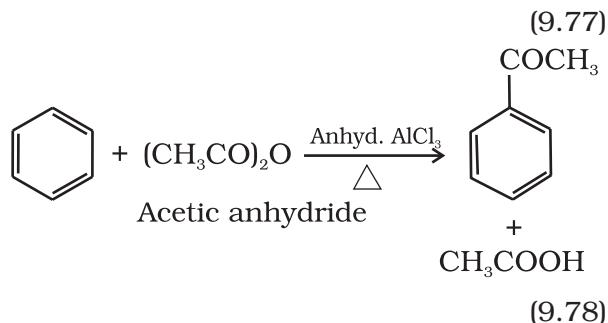
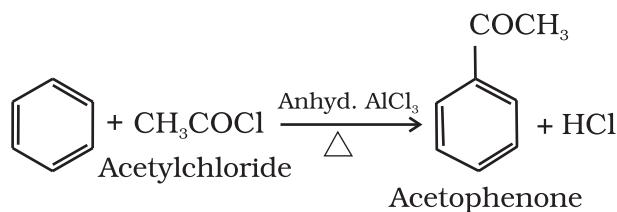


- (iv) **Friedel-Crafts alkylation reaction:** When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenzene is formed.

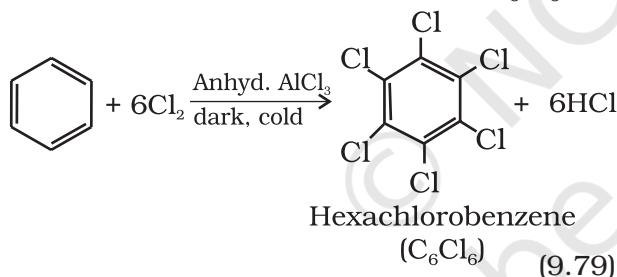


Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of *n*-propyl benzene?

- (v) **Friedel-Crafts acylation reaction:** The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ( $\text{AlCl}_3$ ) yields acyl benzene.



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  $\text{AlCl}_3$  can be chlorinated to hexachlorobenzene ( $\text{C}_6\text{Cl}_6$ )

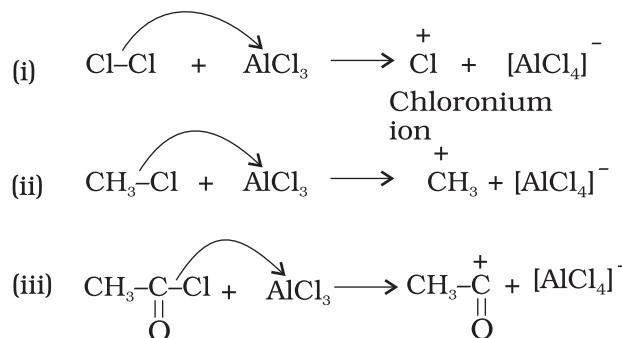


### **Mechanism of electrophilic substitution reactions:**

According to experimental evidences,  $S_E$  ( $S =$  substitution;  $E =$  electrophilic) reactions are supposed to proceed via the following three steps:

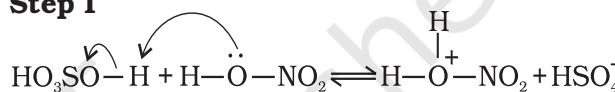
- (a) Generation of the electrophile
  - (b) Formation of carbocation intermediate
  - (c) Removal of proton from the carbocation intermediate

**(a) Generation of electrophile  $E^+$ :** During chlorination, alkylation and acylation of benzene, anhydrous  $\text{AlCl}_3$ , being a Lewis acid helps in generation of the electrophile  $\text{Cl}^+$ ,  $\text{R}^+$ ,  $\text{RC}^+\text{O}$  (acylium ion) respectively by combining with the attacking reagent.

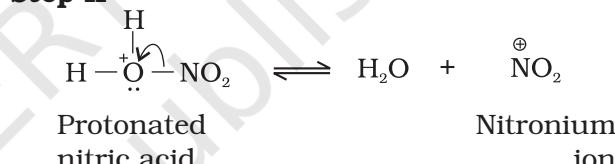


In the case of nitration, the electrophile, nitronium ion,  $\text{NO}_2^+$  is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

## Step I



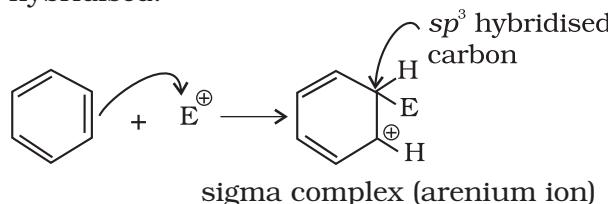
## Step II



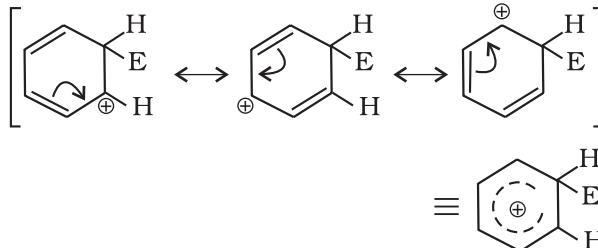
It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium.

### **(b) Formation of Carbocation**

**(arenium ion):** Attack of electrophile results in the formation of  $\sigma$ -complex or arenium ion in which one of the carbon is  $sp^3$  hybridised.

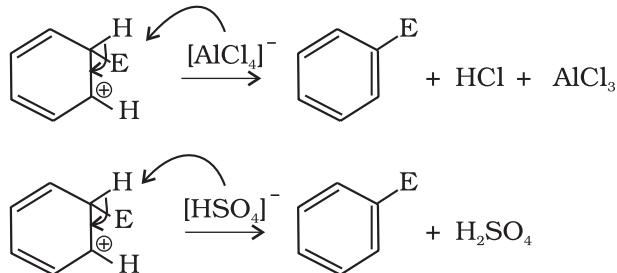


The arenium ion gets stabilised by resonance:



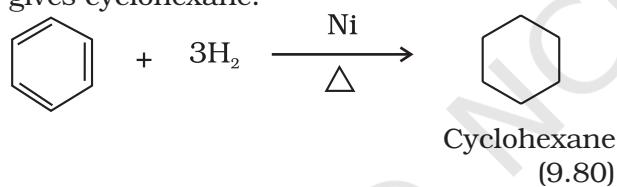
Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at  $sp^3$  hybridised carbon.

**(c) Removal of proton:** To restore the aromatic character,  $\sigma$ -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).

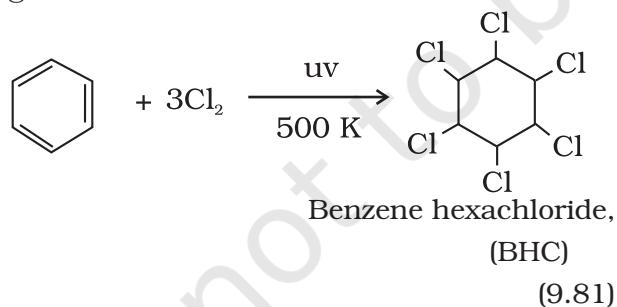


### Addition reactions

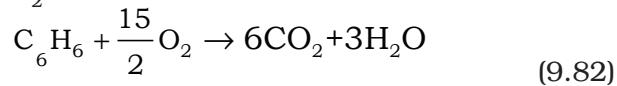
Under vigorous conditions, i.e., at high temperature and/or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.



Under ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride,  $C_6H_6Cl_6$  which is also called gammamaxane.

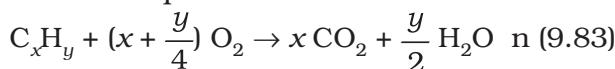


**Combustion:** When heated in air, benzene burns with sooty flame producing  $CO_2$  and  $H_2O$



General combustion reaction for any hydrocarbon may be given by the following

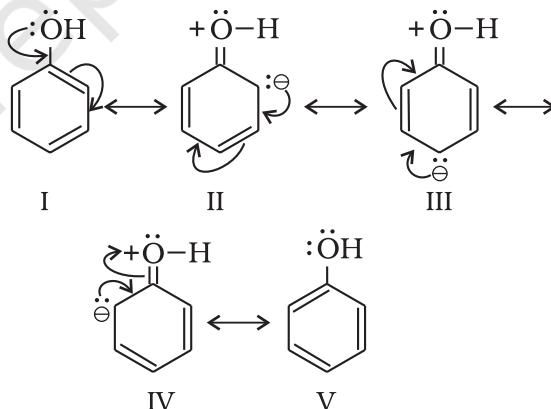
chemical equation:



### 9.5.6 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 is 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:

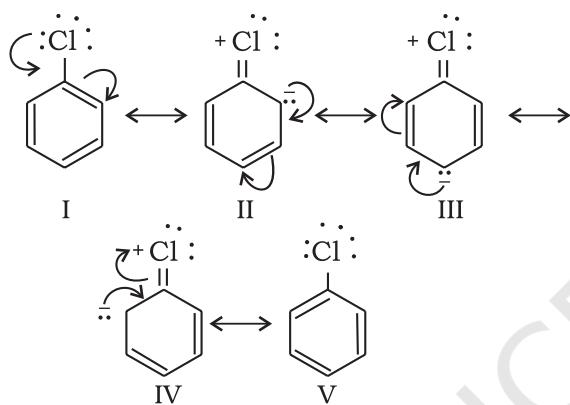
**Ortho and para directing groups:** The groups which direct the incoming group to *ortho* and *para* positions are called *ortho* and *para* directing groups. As an example, let us discuss the directive influence of phenolic ( $-OH$ ) group. Phenol is resonance hybrid of following structures:



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

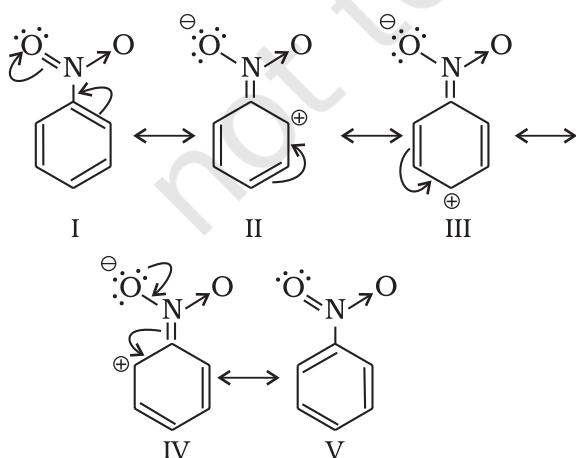
an electrophile. Other examples of **activating** groups are  $-NH_2$ ,  $-NHR$ ,  $-NHCOCH_3$ ,  $-OCH_3$ ,  $-CH_3$ ,  $-C_2H_5$ , etc.

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. Resonance structures of chlorobenzene are given below:



**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.

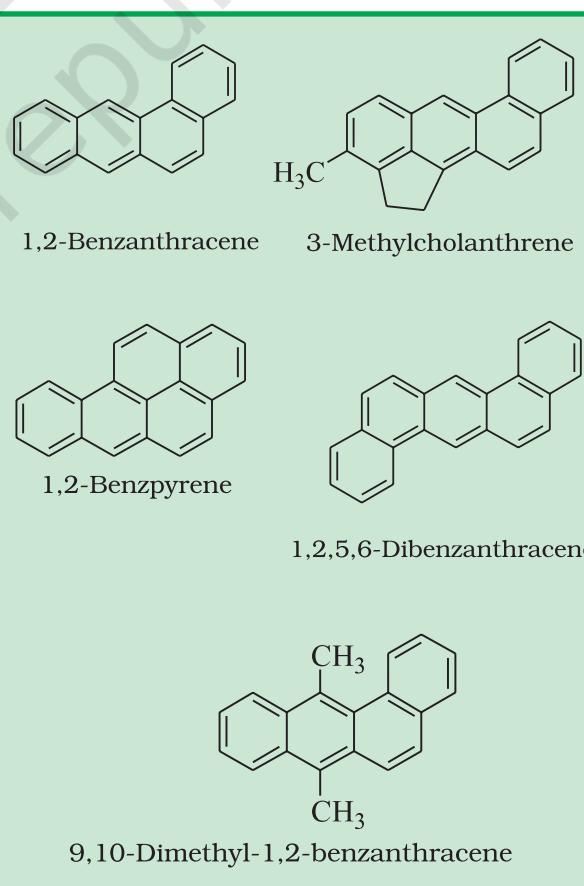
Let us take the example of nitro group. Nitro group reduces the electron density in the benzene ring due to its strong- $I$  effect. Nitrobenzene is a resonance hybrid of the following structures.



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.

## 9.6 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).



## 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** (acyclic) and **aromatic**, according to their structure.

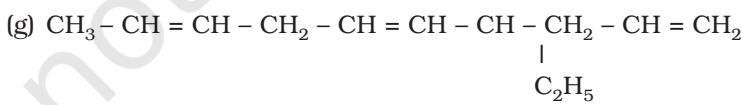
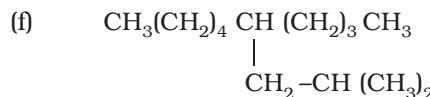
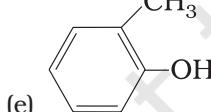
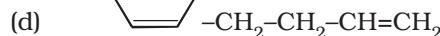
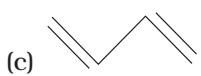
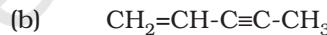
The important reactions of alkanes are **free radical substitution**, **combustion**, **oxidation** and **aromatization**. Alkenes and alkynes undergo addition reactions, which are mainly **electrophilic additions**. Aromatic hydrocarbons, despite having unsaturation, undergo mainly **electrophilic substitution** 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**

- 9.1 How do you account for the formation of ethane during chlorination of methane ?  
9.2 Write IUPAC names of the following compounds :



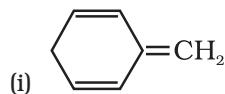
- 9.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated :



- 9.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds :



- 9.5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.
- 9.6 An alkene 'A' contains three C – C, eight C – H  $\sigma$  bonds and one C – C  $\pi$  bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.
- 9.7 Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene?
- 9.8 Write chemical equations for combustion reaction of the following hydrocarbons:
- (i) Butane
  - (ii) Pentene
  - (iii) Hexyne
  - (iv) Toluene
- 9.9 Draw the *cis* and *trans* structures of hex-2-ene. Which isomer will have higher b.p. and why?
- 9.10 Why is benzene extra ordinarily stable though it contains three double bonds?
- 9.11 What are the necessary conditions for any system to be aromatic?
- 9.12 Explain why the following systems are not aromatic?



(ii)



(iii)



- 9.13 How will you convert benzene into
- (i) *p*-nitrochlorobenzene
  - (ii) *m*-nitrochlorobenzene
  - (iii) *p*-nitrotoluene
  - (iv) acetophenone?
- 9.14 In the alkane  $\text{H}_3\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ , identify 1, 2, 3 carbon atoms and give the number of H atoms bonded to each one of these.
- 9.15 What effect does branching of an alkane chain has on its boiling point?
- 9.16 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.
- 9.17 Write down the products of ozonolysis of 1,2-dimethylbenzene (*o*-xylene). How does the result support Kekulé structure for benzene?
- 9.18 Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.
- 9.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?
- 9.20 How would you convert the following compounds into benzene?
- (i) Ethyne
  - (ii) Ethene
  - (iii) Hexane
- 9.21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.
- 9.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile,  $\text{E}^+$
- Chlorobenzene, 2,4-dinitrochlorobenzene, *p*-nitrochlorobenzene
  - Toluene,  $\text{p-H}_3\text{C}-\text{C}_6\text{H}_4-\text{NO}_2$ ,  $\text{p-O}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$ .
- 9.23 Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?
- 9.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.
- 9.25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.



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## 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.

Unit

1

## 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.

### 1.1 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 1.1.

**Table 1.1: 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

## 1.2 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

$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100 \quad (1.1)$$

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:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100 \quad (1.2)$$

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 =

$$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6 \quad (1.3)$$

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  $6 \times 10^{-3}$  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  $\mu\text{g mL}^{-1}$  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 =

$$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}} \quad (1.4)$$

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

$$x_A = \frac{n_A}{n_A + n_B} \quad (1.5)$$

For a solution containing  $i$  number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + \dots + n_i} = \frac{n_i}{\sum n_i} \quad (1.6)$$

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \dots + x_i = 1 \quad (1.7)$$

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 1.1** 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.

$$\text{Molar mass of } C_2H_6O_2 = 12 \times 2 + 1 \times 6 + 16 \times 2 = 62 \text{ g mol}^{-1}$$

$$\text{Moles of } C_2H_6O_2 = \frac{20 \text{ g}}{62 \text{ g mol}^{-1}} = 0.322 \text{ mol}$$

$$\text{Moles of water} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.444 \text{ mol}$$

$$x_{\text{glycol}} = \frac{\text{moles of } C_2H_6O_2}{\text{moles of } C_2H_6O_2 + \text{moles of } H_2O}$$

$$= \frac{0.322 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.068$$

$$\text{Similarly, } x_{\text{water}} = \frac{4.444 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.932$$

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,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}} \quad (1.8)$$

For example,  $0.25 \text{ mol L}^{-1}$  (or  $0.25 \text{ M}$ ) solution of NaOH means that  $0.25 \text{ mol}$  of NaOH has been dissolved in one litre (or one cubic decimetre).

**Example 1.2** Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution.

**Solution** Moles of NaOH =  $\frac{5 \text{ g}}{40 \text{ g mol}^{-1}} = 0.125 \text{ mol}$

Volume of the solution in litres =  $450 \text{ mL} / 1000 \text{ mL L}^{-1}$   
Using equation (2.8),

$$\text{Molarity} = \frac{0.125 \text{ mol} \times 1000 \text{ mL L}^{-1}}{450 \text{ mL}}$$

$$= 0.278 \text{ mol L}^{-1}$$

$$= 0.278 \text{ mol dm}^{-3}$$

- (vii) **Molality:** Molality ( $m$ ) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \quad (1.9)$$

For example,  $1.00 \text{ mol kg}^{-1}$  (or  $1.00 \text{ m}$ ) solution of KCl means that  $1 \text{ mol}$  (74.5 g) of KCl is dissolved in  $1 \text{ kg}$  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.

Calculate molality of 2.5 g of ethanoic acid ( $\text{CH}_3\text{COOH}$ ) in 75 g of benzene.

### Example 1.3

Molar mass of  $\text{C}_2\text{H}_4\text{O}_2$ :  $12 \times 2 + 1 \times 4 + 16 \times 2 = 60 \text{ g mol}^{-1}$

### Solution

$$\text{Moles of } \text{C}_2\text{H}_4\text{O}_2 = \frac{2.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0417 \text{ mol}$$

$$\text{Mass of benzene in kg} = 75 \text{ g}/1000 \text{ g kg}^{-1} = 75 \times 10^{-3} \text{ kg}$$

$$\begin{aligned} \text{Molality of } \text{C}_2\text{H}_4\text{O}_2 &= \frac{\text{Moles of } \text{C}_2\text{H}_4\text{O}_2}{\text{kg of benzene}} = \frac{0.0417 \text{ mol} \times 1000 \text{ g kg}^{-1}}{75 \text{ g}} \\ &= 0.556 \text{ mol kg}^{-1} \end{aligned}$$

### Intext Questions

- 1.1 Calculate the mass percentage of benzene ( $\text{C}_6\text{H}_6$ ) and carbon tetrachloride ( $\text{CCl}_4$ ) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.
- 1.2 Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.
- 1.3 Calculate the molarity of each of the following solutions: (a) 30 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 4.3 L of solution (b) 30 mL of 0.5 M  $\text{H}_2\text{SO}_4$  diluted to 500 mL.
- 1.4 Calculate the mass of urea ( $\text{NH}_2\text{CONH}_2$ ) required in making 2.5 kg of 0.25 molal aqueous solution.
- 1.5 Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is  $1.202 \text{ g mL}^{-1}$ .

### 1.3 Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. 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.

### 1.3.1 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.



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 1.10. This, being dynamic equilibrium, must follow **Le Chateliers Principle**. In general, if in a *nearly saturated solution*, the dissolution process is endothermic ( $\Delta_{\text{sol}} H > 0$ ), the solubility should increase with rise in temperature and if it is exothermic ( $\Delta_{\text{sol}} H < 0$ ) the solubility should decrease. These trends are also observed experimentally.

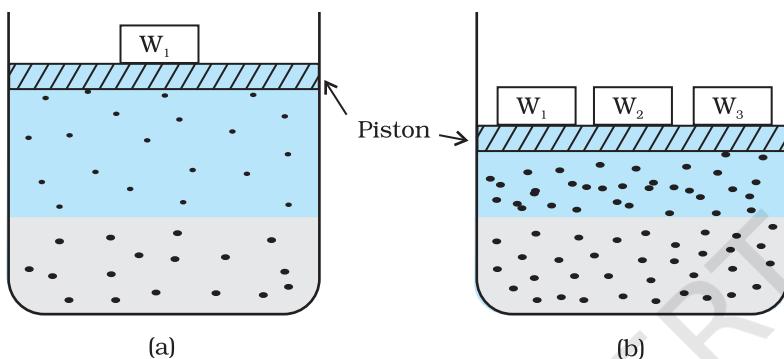
#### *Effect of pressure*

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.

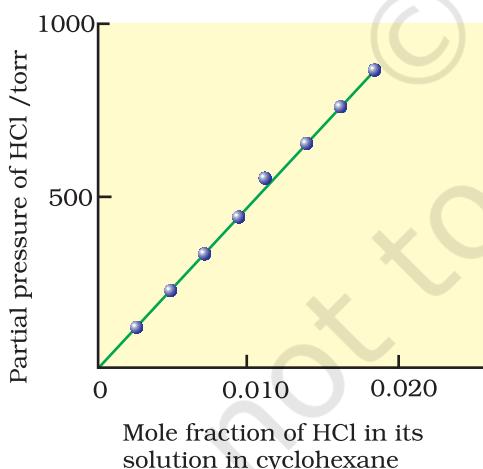
### 1.3.2 Solubility of a Gas in a Liquid

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. 1.1 (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. 1.1 (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. 1.1:** 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.



**Fig. 1.2:** Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant,  $K_H$ .

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 partial pressure of the gas present above the surface of liquid or solution**. 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:

$$p = K_H x \quad (1.11)$$

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. 1.2.

Different gases have different  $K_H$  values at the same temperature (Table 1.2). This suggests that  $K_H$  is a function of the nature of the gas.

It is obvious from equation (1.11) 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 1.2 that  $K_H$  values for both  $N_2$  and  $O_2$  increase with increase of temperature indicating that the solubility of gases

**Table 1.2: 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	$1.83 \times 10^{-5}$
$N_2$	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 1.4

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 kbar.

#### 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  $n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol}$

$$= \frac{7.16 \times 10^{-4} \text{ mol} \times 1000 \text{ mmol}}{1 \text{ mol}} = 0.716 \text{ mmol}$$

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**

- 1.6**  $\text{H}_2\text{S}$ , a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of  $\text{H}_2\text{S}$  in water at STP is 0.195 m, calculate Henry's law constant.
- 1.7** Henry's law constant for  $\text{CO}_2$  in water is  $1.67 \times 10^8$  Pa at 298 K. Calculate the quantity of  $\text{CO}_2$  in 500 mL of soda water when packed under 2.5 atm  $\text{CO}_2$  pressure at 298 K.

### **1.4 Vapour Pressure of Liquid Solutions**

#### **1.4.1 Vapour Pressure of Liquid-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 1.3.2. 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.

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  $p_{\text{total}}$  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 of the solution is directly proportional to its mole fraction present in solution.**

Thus, for component 1

$$p_1 \propto x_1$$

and  $p_1 = p_1^0 x_1$  (1.12)

where  $p_1^0$  is the vapour pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^0 x_2$$

where  $p_2^0$  represents the vapour pressure of the pure component 2. (1.13)

According to **Dalton's law of partial pressures**, the total pressure ( $p_{\text{total}}$ ) 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:

$$p_{\text{total}} = p_1 + p_2$$
 (1.14)

Substituting the values of  $p_1$  and  $p_2$ , we get

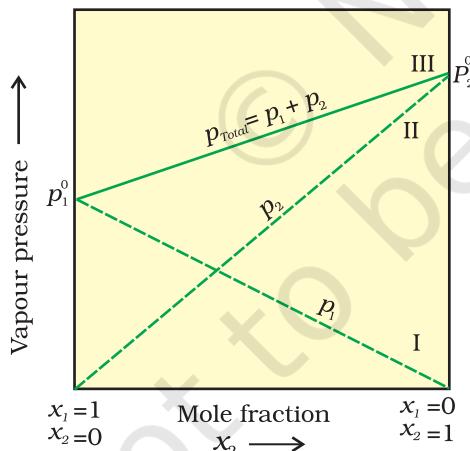
$$p_{\text{total}} = x_1 p_1^0 + x_2 p_2^0$$

$$= (1 - x_2) p_1^0 + x_2 p_2^0$$
 (1.15)

$$= p_1^0 + (p_2^0 - p_1^0) x_2$$
 (1.16)

Following conclusions can be drawn from equation (1.16).

- (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. 1.3:** 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. 1.3. These lines (I and II) pass through the points for which  $x_1$  and  $x_2$  are equal to unity. Similarly the plot (line III) of  $p_{\text{total}}$  versus  $x_2$  is also linear (Fig. 1.3). The minimum value of  $p_{\text{total}}$  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:

$$p_1 = y_1 p_{\text{total}} \quad (1.17)$$

$$p_2 = y_2 p_{\text{total}} \quad (1.18)$$

In general

$$p_i = y_i p_{\text{total}} \quad (1.19)$$

Vapour pressure of chloroform ( $\text{CHCl}_3$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) 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  $\text{CHCl}_3$  and 40 g of  $\text{CH}_2\text{Cl}_2$  at 298 K and, (ii) mole fractions of each component in vapour phase.

### Example 1.5

#### Solution

$$\text{(i) Molar mass of } \text{CH}_2\text{Cl}_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85 \text{ g mol}^{-1}$$

$$\text{Molar mass of } \text{CHCl}_3 = 12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5 \text{ g mol}^{-1}$$

$$\text{Moles of } \text{CH}_2\text{Cl}_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$$

$$\text{Moles of } \text{CHCl}_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

$$\text{Total number of moles} = 0.47 + 0.213 = 0.683 \text{ mol}$$

$$x_{\text{CH}_2\text{Cl}_2} = \frac{0.47 \text{ mol}}{0.683 \text{ mol}} = 0.688$$

$$x_{\text{CHCl}_3} = 1.00 - 0.688 = 0.312$$

Using equation (2.16),

$$\begin{aligned} p_{\text{total}} &= p_1^0 + (p_2^0 - p_1^0) x_2 = 200 + (415 - 200) \times 0.688 \\ &= 200 + 147.9 = 347.9 \text{ mm Hg} \end{aligned}$$

(ii) Using the relation (2.19),  $y_i = p_i/p_{\text{total}}$ , we can calculate the mole fraction of the components in gas phase ( $y_i$ ).

$$p_{\text{CH}_2\text{Cl}_2} = 0.688 \times 415 \text{ mm Hg} = 285.5 \text{ mm Hg}$$

$$p_{\text{CHCl}_3} = 0.312 \times 200 \text{ mm Hg} = 62.4 \text{ mm Hg}$$

$$y_{\text{CH}_2\text{Cl}_2} = 285.5 \text{ mm Hg}/347.9 \text{ mm Hg} = 0.82$$

$$y_{\text{CHCl}_3} = 62.4 \text{ mm Hg}/347.9 \text{ mm Hg} = 0.18$$

**Note:** Since,  $\text{CH}_2\text{Cl}_2$  is a more volatile component than  $\text{CHCl}_3$ , [ $p_{\text{CH}_2\text{Cl}_2}^0 = 415 \text{ mm Hg}$  and  $p_{\text{CHCl}_3}^0 = 200 \text{ mm Hg}$ ] and the vapour phase is also richer in  $\text{CH}_2\text{Cl}_2$  [ $y_{\text{CH}_2\text{Cl}_2} = 0.82$  and  $y_{\text{CHCl}_3} = 0.18$ ], it may thus be concluded that **at equilibrium, vapour phase will be always rich in the component which is more volatile.**

### 1.4.2 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

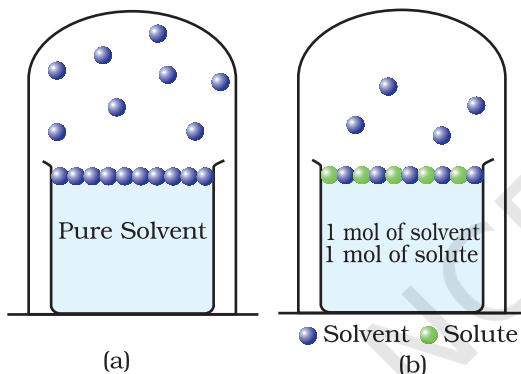
$$p = K_H x.$$

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  $p_i^0$ . Thus, Raoult's law becomes a special case of Henry's law in which  $K_H$  becomes equal to  $p_i^0$ .

### 1.4.3 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. 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. 1.4 (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. 1.4.(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.



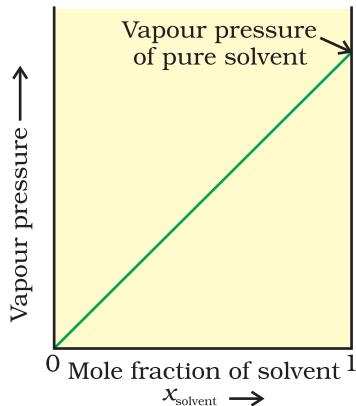
**Fig. 1.4:** Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.

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. 1.5**  
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

$$p_1 \propto x_1 \quad \text{and} \quad p_1 = x_1 p_1^0 \quad (1.20)$$

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. 1.5).

## 1.5 Ideal and Non-ideal Solutions

### 1.5.1 Ideal Solutions

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

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.,

$$\Delta_{\text{mix}} H = 0, \quad \Delta_{\text{mix}} V = 0 \quad (1.21)$$

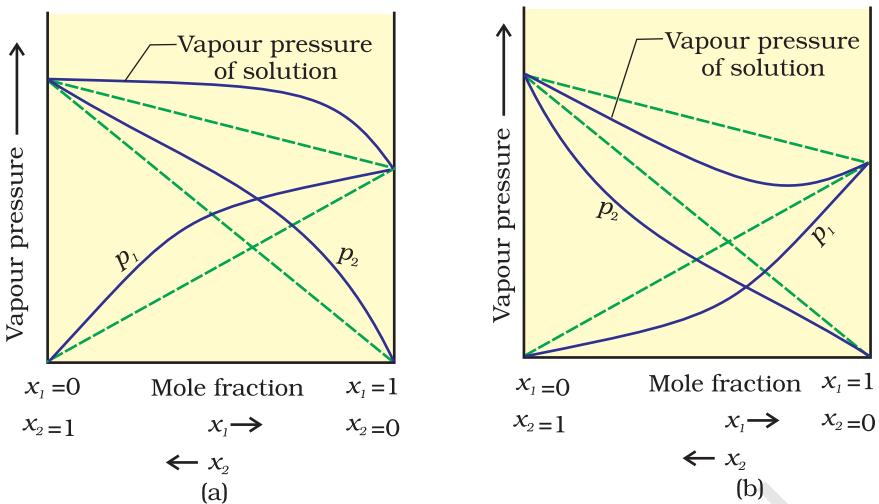
It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular 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.

### 1.5.2 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 1.16). 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. 1.6.

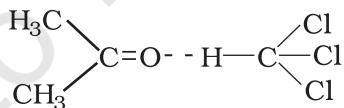
The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker 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. 1.6**  
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. 1.6 (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. 1.6. (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

- 1.8** 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.

## 1.6 Colligative Properties and Determination of Molar Mass

We have learnt in Section 1.4.3 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.

### 1.6.1 Relative Lowering of Vapour Pressure

We have learnt in Section 1.4.3 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 (1.20) given in Section 1.4.3 establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1 p_1^0 \quad (1.22)$$

The reduction in the vapour pressure of solvent ( $\Delta p_1$ ) is given as:

$$\begin{aligned} \Delta p_1 &= p_1^0 - p_1 = p_1^0 - p_1^0 x_1 \\ &= p_1^0 (1 - x_1) \end{aligned} \quad (1.23)$$

Knowing that  $x_2 = 1 - x_1$ , equation (1.23) reduces to

$$\Delta p_1 = x_2 p_1^0 \quad (1.24)$$

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 (1.24) can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \quad (1.25)$$

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:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \left( \text{since } x_2 = \frac{n_2}{n_1 + n_2} \right) \quad (1.26)$$

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

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \quad (1.27)$$

$$\text{or } \frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \quad (1.28)$$

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 (1.28), knowing all other quantities, the molar mass of solute ( $M_2$ ) can be calculated.

### Example 1.6

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  $78 \text{ g mol}^{-1}$ ). 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:

$$p_1^0 = 0.850 \text{ bar}; p = 0.845 \text{ bar}; M_1 = 78 \text{ g mol}^{-1}; w_2 = 0.5 \text{ g}; w_1 = 39 \text{ g}$$

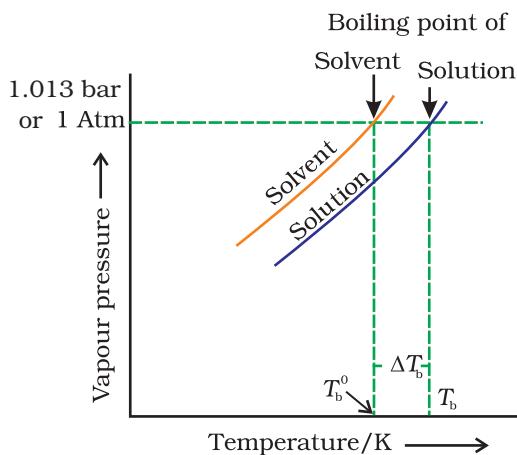
Substituting these values in equation (2.28), we get

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

$$\text{Therefore, } M_2 = 170 \text{ g mol}^{-1}$$

### 1.6.2 Elevation of Boiling Point

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 ( $100^\circ \text{C}$ ) 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. 1.7 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 point of a solution is



**Fig. 1.7:** The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that  $\Delta T_b$  denotes the elevation of boiling point of a solvent in solution.

always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 1.7. 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 ( $\Delta T_b$ ) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m \quad (1.29)$$

$$\text{or } \Delta T_b = K_b m \quad (1.30)$$

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  $\text{K kg mol}^{-1}$ . Values of  $K_b$  for some common solvents are given in Table 1.3. 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:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \quad (1.31)$$

Substituting the value of molality in equation (1.30) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \quad (1.32)$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \quad (1.33)$$

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  $\Delta T_b$  is determined experimentally for a known solvent whose  $K_b$  value is known.

18 g of glucose,  $C_6H_{12}O_6$ , is dissolved in 1 kg of water in a saucepan. **Example 1.7**  
At what temperature will water boil at 1.013 bar?  $K_b$  for water is 0.52  $\text{K kg mol}^{-1}$ .

Moles of glucose = 18 g / 180 g  $\text{mol}^{-1}$  = 0.1 mol

Number of kilograms of solvent = 1 kg

Thus molality of glucose solution = 0.1 mol  $\text{kg}^{-1}$

For water, change in boiling point

**Solution**

$$\Delta T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be  $373.15 + 0.052 = 373.202 \text{ K}$ .

### **Example 1.8**

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<sup>-1</sup>

### **Solution**

The elevation ( $\Delta T_b$ ) in the boiling point =  $354.11 \text{ K} - 353.23 \text{ K} = 0.88 \text{ K}$   
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,  $M_2 = 58 \text{ g mol}^{-1}$

### **1.6.3 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. 1.8). 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. 1.8. 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.

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.

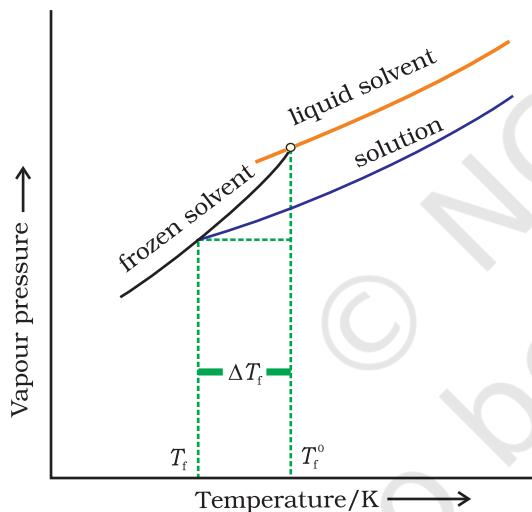
$\Delta T_f = T_f^0 - T_f$  is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point ( $\Delta T_f$ ) for **dilute solution** (ideal solution) is directly proportional to molality,  $m$  of the solution. Thus,

$$\Delta T_f \propto m$$

$$\text{or } \Delta T_f = K_f m \quad (1.34)$$

The proportionality constant,  $K_f$ , which depends on the nature of the solvent is known as **Freezing Point Depression Constant or Molal**



**Fig. 1.8:** Diagram showing  $\Delta T_f$ , depression of the freezing point of a solvent in a solution.

**Depression Constant or Cryoscopic Constant.** The unit of  $K_f$  is  $\text{K kg mol}^{-1}$ . Values of  $K_f$  for some common solvents are listed in Table 1.3.

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  $\Delta T_f$  of the solvent then molality of the solute is given by the equation (1.31).

$$m = \frac{w_2 / M_2}{w_1 / 1000} \quad (1.31)$$

Substituting this value of molality in equation (1.34) we get:

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000} \quad (1.35)$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \quad (1.35)$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \quad (1.36)$$

Thus for determining the molar mass of the solute we should know the quantities  $w_1$ ,  $w_2$ ,  $\Delta T_f$ , 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.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus}} H} \quad (1.37)$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap}} H} \quad (1.38)$$

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,  $\Delta_{\text{fus}} H$  and  $\Delta_{\text{vap}} H$  represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

**Table 1.3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents**

Solvent	b. p./K	$K_b/\text{K kg mol}^{-1}$	f. p./K	$K_f/\text{K kg mol}^{-1}$
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 1.9

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

$$\text{of the solution with respect to ethylene glycol} = \frac{\text{moles of ethylene glycol}}{\text{mass of water in kilogram}}$$

$$\text{Moles of ethylene glycol} = \frac{45 \text{ g}}{62 \text{ g mol}^{-1}} = 0.73 \text{ mol}$$

$$\text{Mass of water in kg} = \frac{600 \text{ g}}{1000 \text{ g kg}^{-1}} = 0.6 \text{ kg}$$

$$\text{Hence molality of ethylene glycol} = \frac{0.73 \text{ mol}}{0.60 \text{ kg}} = 1.2 \text{ mol kg}^{-1}$$

Therefore freezing point depression,

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$$

$$\text{Freezing point of the aqueous solution} = 273.15 \text{ K} - 2.2 \text{ K} = 270.95 \text{ K}$$

### Example 1.10

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  $5.12 \text{ K kg mol}^{-1}$ . Find the molar mass of the solute.

### Solution

Substituting the values of various terms involved in equation (1.36) we get,

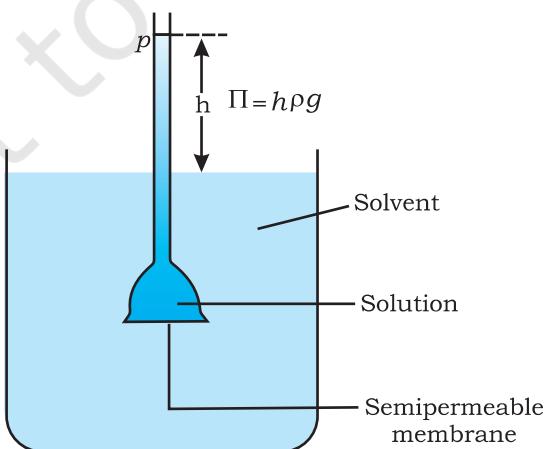
$$M_2 = \frac{5.12 \text{ K kg mol}^{-1} \times 1.00 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.40 \times 50 \text{ g}} = 256 \text{ g mol}^{-1}$$

Thus, molar mass of the solute =  $256 \text{ g mol}^{-1}$

#### 1.6.4 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

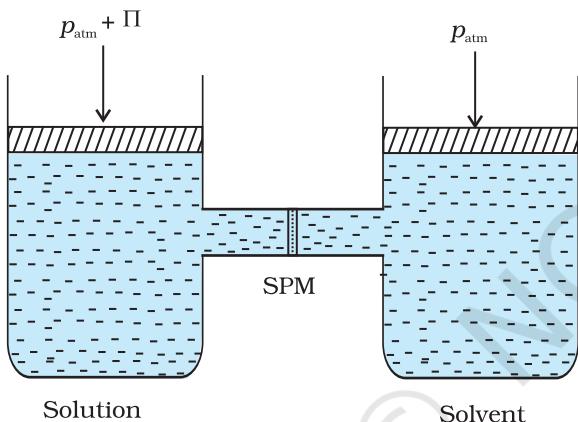


**Fig. 1.9**  
Level of solution rises in the thistle funnel due to osmosis of solvent.

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 semipermeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 1.9, 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. 1.10:** 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. 1.10. 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:

$$\Pi = C R T \quad (1.39)$$

Here  $\Pi$  is the osmotic pressure and  $R$  is the gas constant.

$$\Pi = (n_2 / V) R T \quad (1.40)$$

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,

$$\Pi V = \frac{w_2 R T}{M_2} \quad (1.41)$$

$$\text{or } M_2 = \frac{w_2 R T}{\Pi V} \quad (1.42)$$

Thus, knowing the quantities  $w_2$ ,  $T$ ,  $\Pi$  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 1.11** 200 cm<sup>3</sup> 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  $2.57 \times 10^{-3}$  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,

$$V = 200 \text{ cm}^3 = 0.200 \text{ litre}$$

$$T = 300 \text{ K}$$

$$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

Substituting these values in equation (2.42) we get

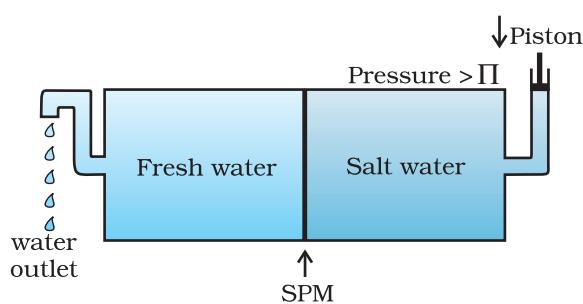
$$M_2 = \frac{1.26 \text{ g} \times 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ bar} \times 0.200 \text{ L}} = 61,022 \text{ g mol}^{-1}$$

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 its cells through osmosis. When placed in water containing less than 0.9% (mass/volume) salt, blood cells swell due to flow of water in them 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.

### 1.6.5 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. 1.11.



**Fig. 1.11:** Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

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.

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.

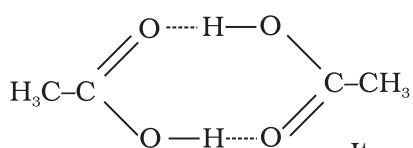
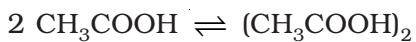
### Intext Questions

- 1.9 Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea ( $\text{NH}_2\text{CONH}_2$ ) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.
- 1.10 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.
- 1.11 Calculate the mass of ascorbic acid (Vitamin C,  $\text{C}_6\text{H}_8\text{O}_6$ ) to be dissolved in 75 g of acetic acid to lower its melting point by  $1.5^\circ\text{C}$ .  $K_f = 3.9 \text{ K kg mol}^{-1}$ .
- 1.12 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.

### 1.7 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  $\text{K}^+$  and  $\text{Cl}^-$  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  $2 \times 0.52 \text{ K} = 1.04 \text{ K}$ . 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.



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  $\Delta T_b$  or  $\Delta T_f$  for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this  $\Delta T_b$  or  $\Delta T_f$  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,

$$\frac{p_1^o - p_1}{p_1^o} = i \cdot \frac{n_2}{n_1}$$

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,  $\Pi = i n_2 R T / V$

Table 1.4 depicts values of the factor,  $i$  for several strong electrolytes. For KCl, NaCl and MgSO<sub>4</sub>,  $i$  values approach 2 as the solution becomes very dilute. As expected, the value of  $i$  gets close to 3 for K<sub>2</sub>SO<sub>4</sub>.

**Table 1.4: Values of van't Hoff factor,  $i$ , at Various Concentrations for NaCl, KCl, MgSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>.**

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 <sub>4</sub>	1.21	1.53	1.82	2.00
K <sub>2</sub> SO <sub>4</sub>	2.32	2.70	2.84	3.00

\* represent  $i$  values for incomplete dissociation.

2 g of benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) 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<sup>-1</sup>. What is the percentage association of acid if it forms dimer in solution?

The given quantities are: w<sub>2</sub> = 2 g; K<sub>f</sub> = 4.9 K kg mol<sup>-1</sup>; w<sub>1</sub> = 25 g,

$$\Delta T_f = 1.62 \text{ K}$$

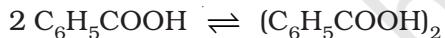
Substituting these values in equation (1.36) we get:

$$M_2 = \frac{4.9 \text{ K kg mol}^{-1} \times 2 \text{ g} \times 1000 \text{ g kg}^{-1}}{25 \text{ g} \times 1.62 \text{ K}} = 241.98 \text{ g mol}^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene is

$$= 241.98 \text{ g mol}^{-1}$$

Now consider the following equilibrium for the acid:



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  $i$ .

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

### Example 1.12

### Solution

$$= \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}}$$

$$\text{or } \frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$$

$$\text{or } x = 2 \times 0.496 = 0.992$$

Therefore, degree of association of benzoic acid in benzene is 99.2 %.

### Example 1.13

0.6 mL of acetic acid ( $\text{CH}_3\text{COOH}$ ), having density  $1.06 \text{ g mL}^{-1}$ , is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was  $0.0205^\circ\text{C}$ . Calculate the van't Hoff factor and the dissociation constant of acid.

$$\begin{aligned}\text{Solution} \quad \text{Number of moles of acetic acid} &= \frac{0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}^{-1}} \\ &= 0.0106 \text{ mol} = n\end{aligned}$$

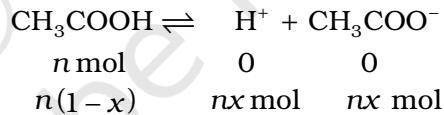
$$\text{Molality} = \frac{0.0106 \text{ mol}}{1000 \text{ mL} \times 1 \text{ g mL}^{-1}} = 0.0106 \text{ mol kg}^{-1}$$

Using equation (1.35)

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} = 0.0197 \text{ K}$$

$$\text{van't Hoff Factor (i)} = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

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  $\text{CH}_3\text{COO}^-$  and  $nx$  moles of  $\text{H}^+$  ions,



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  $[\text{CH}_3\text{COOH}] = n(1-x) = 0.0106 (1-0.041)$ ,

$[\text{CH}_3\text{COO}^-] = nx = 0.0106 \times 0.041$ ,  $[\text{H}^+] = nx = 0.0106 \times 0.041$ .

$$\begin{aligned}K_a &= \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106 (1.00 - 0.041)} \\ &= 1.86 \times 10^{-5}\end{aligned}$$

## 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

- 1.1** Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.
- 1.2** Give an example of a solid solution in which the solute is a gas.
- 1.3** Define the following terms:
  - (i) Mole fraction    (ii) Molality    (iii) Molarity    (iv) Mass percentage.
- 1.4** 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  $1.504 \text{ g mL}^{-1}$ ?

- 1.5** 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  $1.2 \text{ g mL}^{-1}$ , then what shall be the molarity of the solution?
- 1.6** How many mL of 0.1 M HCl are required to react completely with 1 g mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  containing equimolar amounts of both?
- 1.7** 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.
- 1.8** An antifreeze solution is prepared from 222.6 g of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) and 200 g of water. Calculate the molality of the solution. If the density of the solution is  $1.072 \text{ g mL}^{-1}$ , then what shall be the molarity of the solution?
- 1.9** A sample of drinking water was found to be severely contaminated with chloroform ( $\text{CHCl}_3$ ) 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.
- 1.10** What role does the molecular interaction play in a solution of alcohol and water?
- 1.11** Why do gases always tend to be less soluble in liquids as the temperature is raised?
- 1.12** State Henry's law and mention some important applications.
- 1.13** The partial pressure of ethane over a solution containing  $6.56 \times 10^{-3}$  g of ethane is 1 bar. If the solution contains  $5.00 \times 10^{-2}$  g of ethane, then what shall be the partial pressure of the gas?
- 1.14** What is meant by positive and negative deviations from Raoult's law and how is the sign of  $\Delta_{\text{mix}}H$  related to positive and negative deviations from Raoult's law?
- 1.15** 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?
- 1.16** 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?
- 1.17** 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.
- 1.18** Calculate the mass of a non-volatile solute (molar mass  $40 \text{ g mol}^{-1}$ ) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.
- 1.19** 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.
- 1.20** 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.
- 1.21** Two elements A and B form compounds having formula  $\text{AB}_2$  and  $\text{AB}_4$ . When dissolved in 20 g of benzene ( $\text{C}_6\text{H}_6$ ), 1 g of  $\text{AB}_2$  lowers the freezing point by 2.3 K whereas 1.0 g of  $\text{AB}_4$  lowers it by 1.3 K. The molar depression constant for benzene is  $5.1 \text{ K kg mol}^{-1}$ . Calculate atomic masses of A and B.

- 1.22** 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?
- 1.23** Suggest the most important type of intermolecular attractive interaction in the following pairs.
- n-hexane and n-octane
  - $I_2$  and  $CCl_4$
  - $NaClO_4$  and water
  - methanol and acetone
  - acetonitrile ( $CH_3CN$ ) and acetone ( $C_3H_6O$ ).
- 1.24** Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane,  $KCl$ ,  $CH_3OH$ ,  $CH_3CN$ .
- 1.25** Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?
- phenol
  - toluene
  - formic acid
  - ethylene glycol
  - chloroform
  - pentanol.
- 1.26** If the density of some lake water is  $1.25\text{ g mL}^{-1}$  and contains 92 g of  $Na^+$  ions per kg of water, calculate the molarity of  $Na^+$  ions in the lake.
- 1.27** If the solubility product of  $CuS$  is  $6 \times 10^{-16}$ , calculate the maximum molarity of  $CuS$  in aqueous solution.
- 1.28** 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  $CH_3CN$ .
- 1.29** 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  $1.5 \times 10^{-3}\text{ M}$  aqueous solution required for the above dose.
- 1.30** Calculate the amount of benzoic acid ( $C_6H_5COOH$ ) required for preparing 250 mL of 0.15 M solution in methanol.
- 1.31** 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.
- 1.32** Calculate the depression in the freezing point of water when 10 g of  $CH_3CH_2CHClCOOH$  is added to 250 g of water.  $K_a = 1.4 \times 10^{-3}$ ,  $K_f = 1.86\text{ K kg mol}^{-1}$ .
- 1.33** 19.5 g of  $CH_2FCOOH$  is dissolved in 500 g of water. The depression in the freezing point of water observed is  $1.0^\circ\text{C}$ . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.
- 1.34** 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.
- 1.35** Henry's law constant for the molality of methane in benzene at 298 K is  $4.27 \times 10^5\text{ mm Hg}$ . Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.
- 1.36** 100 g of liquid A (molar mass  $140\text{ g mol}^{-1}$ ) was dissolved in 1000 g of liquid B (molar mass  $180\text{ g mol}^{-1}$ ). 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.

- 1.37** 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  $p_{\text{total}}$ ,  $p_{\text{chloroform}}$ , and  $p_{\text{acetone}}$  as a function of  $x_{\text{acetone}}$ . The experimental data observed for different compositions of mixture is:

100 $x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{\text{acetone}}$ /mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}$ /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.

- 1.38** Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene 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 toluene.
- 1.39** 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  $3.30 \times 10^7$  mm and  $6.51 \times 10^7$  mm respectively, calculate the composition of these gases in water.
- 1.40** Determine the amount of  $\text{CaCl}_2$  ( $i = 2.47$ ) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C.
- 1.41** Determine the osmotic pressure of a solution prepared by dissolving 25 mg of  $\text{K}_2\text{SO}_4$  in 2 litre of water at 25° C, assuming that it is completely dissociated.

#### Answers to Some Intext Questions

- 1.1**  $\text{C}_6\text{H}_6 = 15.28\%$ ,  $\text{CCl}_4 = 84.72\%$
- 1.2** 0.459, 0.541
- 1.3** 0.024 M, 0.03 M
- 1.4** 36.946 g
- 1.5**  $1.5 \text{ mol kg}^{-1}$ ,  $1.45 \text{ mol L}^{-1}$  0.0263
- 1.9** 23.4 mm Hg
- 1.10** 121.67 g
- 1.11** 5.077 g
- 1.12** 30.96 Pa



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Unit

2

## Electrochemistry

### Objectives

After studying this Unit, you will be able to

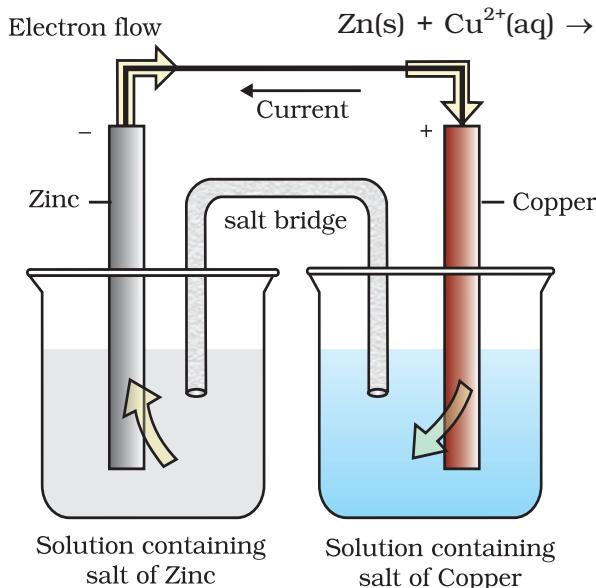
- describe an electrochemical cell and differentiate between galvanic and electrolytic cells;
- apply Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell;
- derive relation between standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant;
- define resistivity ( $\rho$ ), conductivity ( $\kappa$ ) and molar conductivity ( $\Lambda_m$ ) 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  $\Lambda_m^\circ$  (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.

## 2.1 Electrochemical Cells

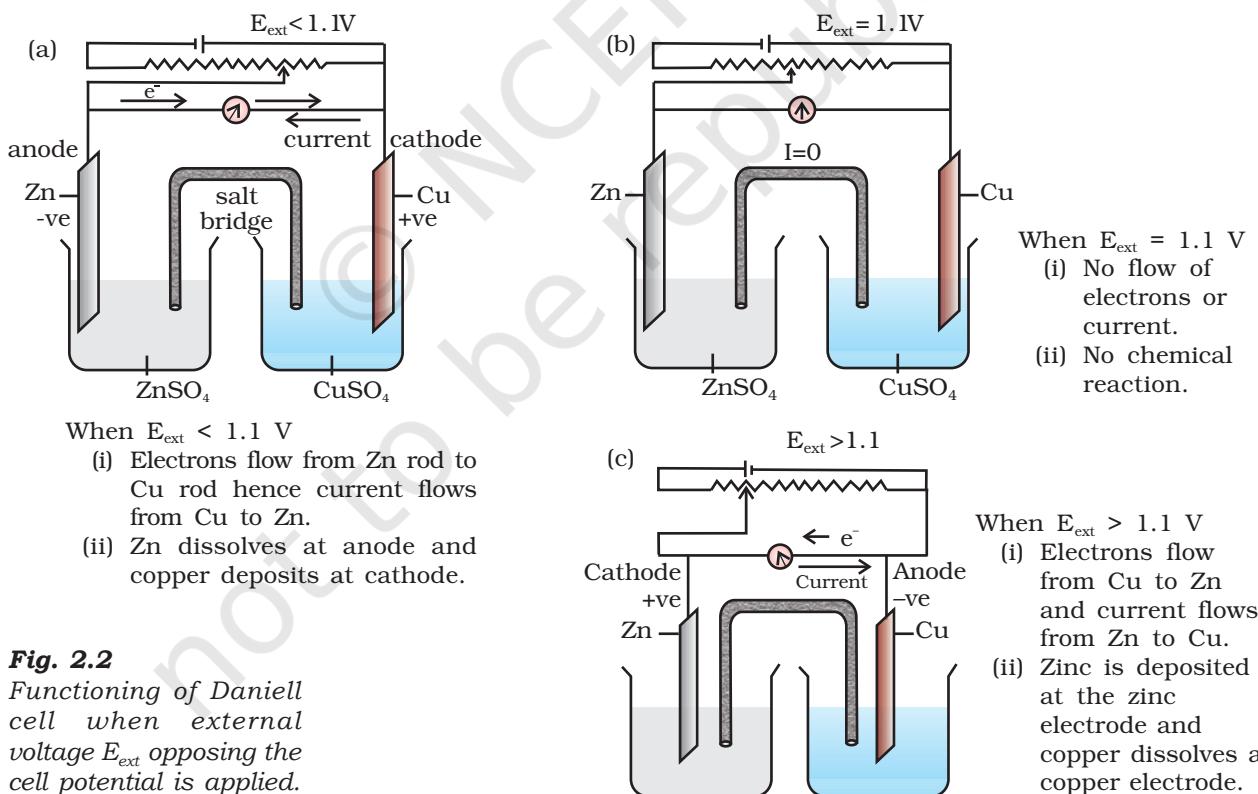
We had studied the construction and functioning of **Daniell cell** (Fig. 2.1). This cell converts the chemical energy liberated during the redox reaction



to electrical energy and has an electrical potential equal to 1.1 V when concentration of  $Zn^{2+}$  and  $Cu^{2+}$  ions is unity ( $1 \text{ mol dm}^{-3}$ )\*. Such a device is called a **galvanic** or a **voltaic** cell.

If an external opposite potential is applied in the galvanic cell [Fig. 2.2(a)] and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 2.2(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. 2.2(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.

**Fig. 2.1:** Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.



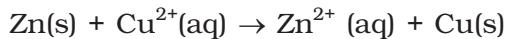
**Fig. 2.2**  
Functioning of Daniell cell when external voltage  $E_{ext}$  opposing the cell potential is applied.

\* 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.

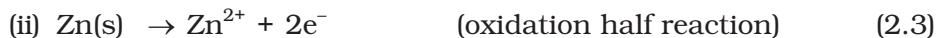
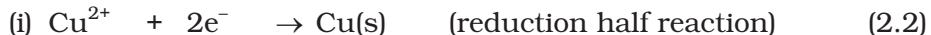
## 2.2 Galvanic Cells

As mentioned earlier 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.



This reaction is a combination of two half reactions whose addition gives the overall cell reaction:



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. 2.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.

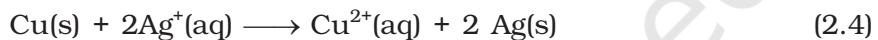
At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode 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.,

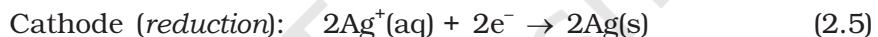
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

This is illustrated by the following example:

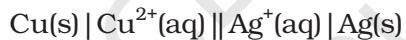
Cell reaction:



Half-cell reactions:

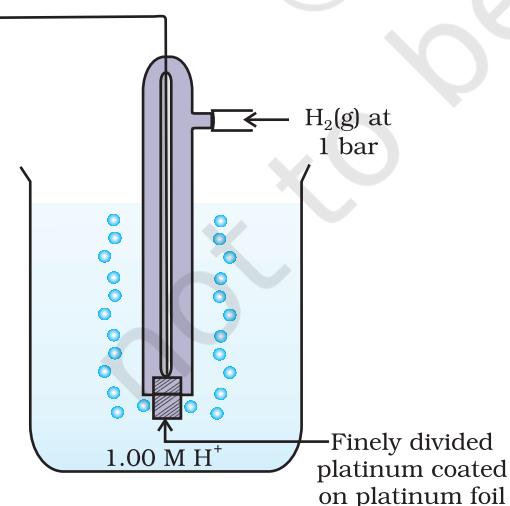


It can be seen that the sum of (2.5) and (2.6) leads to overall reaction (2.4) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:



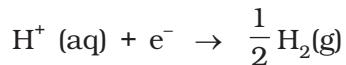
$$\text{and we have } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^+ | \text{Ag}} - E_{\text{Cu}^{2+} | \text{Cu}} \quad (2.7)$$

### 2.2.1 Measurement of Electrode Potential



**Fig. 2.3:** Standard Hydrogen Electrode (SHE).

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. 2.3) represented by  $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$ , is assigned a zero potential at all temperatures corresponding to the reaction



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. 2.3). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.

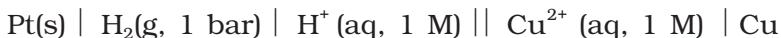
At 298 K the emf of the cell, standard hydrogen electrode || second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential,  $E^{\circ}_R$  of the given half-cell.

$$E^{\circ} = E^{\circ}_R - E^{\circ}_L$$

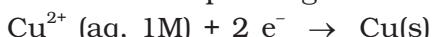
As  $E^{\circ}_L$  for standard hydrogen electrode is zero.

$$E^{\circ} = E^{\circ}_R - 0 = E^{\circ}_R$$

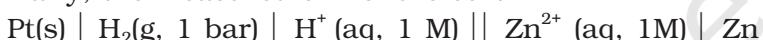
The measured emf of the cell:



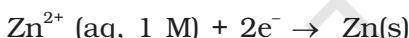
is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction:



Similarly, the measured emf of the cell:

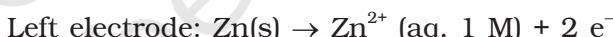


is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

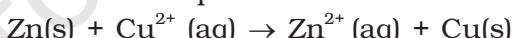


The positive value of the standard electrode potential in the first case indicates that  $\text{Cu}^{2+}$  ions get reduced more easily than  $\text{H}^+$  ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively we can say that hydrogen gas can reduce copper 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. 2.1 can be written as:

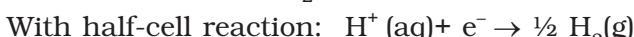
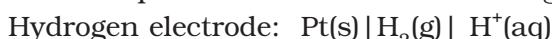


The overall reaction of the cell is the sum of above two reactions and we obtain the equation:



$$\begin{aligned}\text{emf of the cell} &= E^{\circ}_{\text{cell}} = E^{\circ}_R - E^{\circ}_L \\ &= 0.34\text{V} - (-0.76)\text{V} = 1.10 \text{ V}\end{aligned}$$

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:



With half-cell reaction:  $\frac{1}{2} \text{Br}_2(\text{aq}) + \text{e}^- \rightarrow \text{Br}^-(\text{aq})$

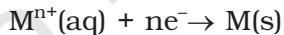
The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half-cell reduction reactions are given in Table 2.1. If the standard electrode potential of an electrode is greater than zero then 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 ( $\text{F}_2$ ) has the maximum tendency to get reduced to fluoride ions ( $\text{F}^-$ ) 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 2.1 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

- 2.1** How would you determine the standard electrode potential of the system  $\text{Mg}^{2+} | \text{Mg}$ ?
- 2.2** Can you store copper sulphate solutions in a zinc pot?
- 2.3** Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

## 2.3 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:



the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(\text{M}^{n+} / \text{M})} = E_{(\text{M}^{n+} / \text{M})}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{M}]}{[\text{M}^{n+}]}$$

but concentration of solid M is taken as unity and we have

$$E_{(\text{M}^{n+} / \text{M})} = E_{(\text{M}^{n+} / \text{M})}^{\circ} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]} \quad (2.8)$$

$E_{(\text{M}^{n+} / \text{M})}^{\circ}$  has already been defined, R is gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), F is Faraday constant ( $96487 \text{ C mol}^{-1}$ ), T is temperature in kelvin and  $[\text{M}^{n+}]$  is the concentration of the species,  $\text{M}^{n+}$ .

**Table 2.1: Standard Electrode Potentials at 298 K**

Ions are present as aqueous species and H<sub>2</sub>O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + ne <sup>-</sup> )	→ Reduced form)	E <sup>o</sup> /V
F <sub>2</sub> (g) + 2e <sup>-</sup>	→ 2F <sup>-</sup>	2.87
Co <sup>3+</sup> + e <sup>-</sup>	→ Co <sup>2+</sup>	1.81
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	→ 2H <sub>2</sub> O	1.78
MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup>	→ Mn <sup>2+</sup> + 4H <sub>2</sub> O	1.51
Au <sup>3+</sup> + 3e <sup>-</sup>	→ Au(s)	1.40
Cl <sub>2</sub> (g) + 2e <sup>-</sup>	→ 2Cl <sup>-</sup>	1.36
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup> + 6e <sup>-</sup>	→ 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	1.33
O <sub>2</sub> (g) + 4H <sup>+</sup> + 4e <sup>-</sup>	→ 2H <sub>2</sub> O	1.23
MnO <sub>2</sub> (s) + 4H <sup>+</sup> + 2e <sup>-</sup>	→ Mn <sup>2+</sup> + 2H <sub>2</sub> O	1.23
Br <sub>2</sub> + 2e <sup>-</sup>	→ 2Br <sup>-</sup>	1.09
NO <sub>3</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup>	→ NO(g) + 2H <sub>2</sub> O	0.97
2Hg <sup>2+</sup> + 2e <sup>-</sup>	→ Hg <sub>2</sub> <sup>2+</sup>	0.92
Ag <sup>+</sup> + e <sup>-</sup>	→ Ag(s)	0.80
Fe <sup>3+</sup> + e <sup>-</sup>	→ Fe <sup>2+</sup>	0.77
O <sub>2</sub> (g) + 2H <sup>+</sup> + 2e <sup>-</sup>	→ H <sub>2</sub> O <sub>2</sub>	0.68
I <sub>2</sub> + 2e <sup>-</sup>	→ 2I <sup>-</sup>	0.54
Cu <sup>+</sup> + e <sup>-</sup>	→ Cu(s)	0.52
Cu <sup>2+</sup> + 2e <sup>-</sup>	→ Cu(s)	0.34
AgCl(s) + e <sup>-</sup>	→ Ag(s) + Cl <sup>-</sup>	0.22
AgBr(s) + e <sup>-</sup>	→ Ag(s) + Br <sup>-</sup>	0.10
<b>2H<sup>+</sup> + 2e<sup>-</sup></b>	<b>→ H<sub>2</sub>(g)</b>	<b>0.00</b>
Pb <sup>2+</sup> + 2e <sup>-</sup>	→ Pb(s)	-0.13
Sn <sup>2+</sup> + 2e <sup>-</sup>	→ Sn(s)	-0.14
Ni <sup>2+</sup> + 2e <sup>-</sup>	→ Ni(s)	-0.25
Fe <sup>2+</sup> + 2e <sup>-</sup>	→ Fe(s)	-0.44
Cr <sup>3+</sup> + 3e <sup>-</sup>	→ Cr(s)	-0.74
Zn <sup>2+</sup> + 2e <sup>-</sup>	→ Zn(s)	-0.76
2H <sub>2</sub> O + 2e <sup>-</sup>	→ H <sub>2</sub> (g) + 2OH <sup>-</sup> (aq)	-0.83
Al <sup>3+</sup> + 3e <sup>-</sup>	→ Al(s)	-1.66
Mg <sup>2+</sup> + 2e <sup>-</sup>	→ Mg(s)	-2.36
Na <sup>+</sup> + e <sup>-</sup>	→ Na(s)	-2.71
Ca <sup>2+</sup> + 2e <sup>-</sup>	→ Ca(s)	-2.87
K <sup>+</sup> + e <sup>-</sup>	→ K(s)	-2.93
Li <sup>+</sup> + e <sup>-</sup>	→ Li(s)	-3.05

1. A negative E<sup>o</sup> means that the redox couple is a stronger reducing agent than the H<sup>+</sup>/H<sub>2</sub> couple.
2. A positive E<sup>o</sup> means that the redox couple is a weaker reducing agent than the H<sup>+</sup>/H<sub>2</sub> couple.

In Daniell cell, the electrode potential for any given concentration of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions, we write

For Cathode:

$$E_{(\text{Cu}^{2+}/\text{Cu})} = E_{(\text{Cu}^{2+}/\text{Cu})}^{\circ} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} \quad (2.9)$$

For Anode:

$$E_{(\text{Zn}^{2+}/\text{Zn})} = E_{(\text{Zn}^{2+}/\text{Zn})}^{\circ} - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]} \quad (2.10)$$

$$\text{The cell potential, } E_{(\text{cell})} = E_{(\text{Cu}^{2+}/\text{Cu})} - E_{(\text{Zn}^{2+}/\text{Zn})}$$

$$= E_{(\text{Cu}^{2+}/\text{Cu})}^{\circ} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} - E_{(\text{Zn}^{2+}/\text{Zn})}^{\circ} + \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]}$$

$$= E_{(\text{Cu}^{2+}/\text{Cu})}^{\circ} - E_{(\text{Zn}^{2+}/\text{Zn})}^{\circ} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}(\text{aq})]} - \ln \frac{1}{[\text{Zn}^{2+}(\text{aq})]}$$

$$E_{(\text{cell})} = E_{(\text{cell})}^{\circ} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (2.11)$$

It can be seen that  $E_{(\text{cell})}$  depends on the concentration of both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions. It increases with increase in the concentration of  $\text{Cu}^{2+}$  ions and decrease in the concentration of  $\text{Zn}^{2+}$  ions.

By converting the natural logarithm in Eq. (2.11) to the base 10 and substituting the values of  $R$ ,  $F$  and  $T = 298$  K, it reduces to

$$E_{(\text{cell})} = E_{(\text{cell})}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (2.12)$$

We should use the same number of electrons ( $n$ ) for both the electrodes and thus for the following cell

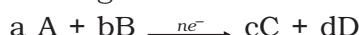


The cell reaction is  $\text{Ni(s)} + 2\text{Ag}^{+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{Ag(s)}$

The **Nernst equation** can be written as

$$E_{(\text{cell})} = E_{(\text{cell})}^{\circ} - \frac{RT}{2F} \ln \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

and for a general electrochemical reaction of the type:



Nernst equation can be written as:

$$\begin{aligned} E_{(\text{cell})} &= E_{(\text{cell})}^{\circ} - \frac{RT}{nF} \ln Q \\ &= E_{(\text{cell})}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \end{aligned} \quad (2.13)$$

Represent the cell in which the following reaction takes place  
 $Mg(s) + 2Ag^+(0.0001M) \rightarrow Mg^{2+}(0.130M) + 2Ag(s)$

### Example 2.1

Calculate its  $E_{(cell)}$  if  $E_{(cell)}^o = 3.17$  V.

The cell can be written as  $Mg | Mg^{2+}(0.130M) || Ag^+(0.0001M) | Ag$  **Solution**

$$E_{(cell)} = E_{(cell)}^o - \frac{RT}{2F} \ln \frac{Mg^{2+}}{Ag^+}$$

$$= 3.17 \text{ V} - \frac{0.059V}{2} \log \frac{0.130}{(0.0001)^2} = 3.17 \text{ V} - 0.21\text{V} = 2.96 \text{ V.}$$

### **2.3.1 Equilibrium Constant from Nernst Equation**

If the circuit in Daniell cell (Fig. 2.1) is closed then we note that the reaction



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:

$$E_{(cell)} = 0 = E_{(cell)}^o - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{or } E_{(cell)}^o = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c \text{ for the reaction 2.1}$$

and at  $T = 298K$  the above equation can be written as

$$E_{(cell)}^o = \frac{0.059 \text{ V}}{2} \log K_c = 1.1 \text{ V} \quad (E_{(cell)}^o = 1.1 \text{ V})$$

$$\log K_c = \frac{(1.1 \text{ V} \times 2)}{0.059 \text{ V}} = 37.288$$

$$K_c = 2 \times 10^{37} \text{ at } 298K.$$

In general,

$$E_{(cell)}^o = \frac{2.303RT}{nF} \log K_c \quad (2.14)$$

Thus, Eq. (2.14) 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  $E^o$  value of the cell.

**Example 2.2** Calculate the equilibrium constant of the reaction:



$$E_{(\text{cell})}^{\circ} = 0.46 \text{ V}$$

$$\text{Solution } E_{(\text{cell})}^{\circ} = \frac{0.059 \text{ V}}{2} \log K_C = 0.46 \text{ V or}$$

$$\log K_C = \frac{0.46 \text{ V} \times 2}{0.059 \text{ V}} = 15.6$$

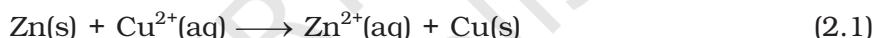
$$K_C = 3.92 \times 10^{15}$$

### 2.3.2 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

$$\Delta_r G = -nFE_{(\text{cell})} \quad (2.15)$$

It may be remembered that  $E_{(\text{cell})}$  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



$$\Delta_r G = -2FE_{(\text{cell})}$$

but when we write the reaction



$$\Delta_r G = -4FE_{(\text{cell})}$$

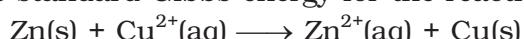
If the concentration of all the reacting species is unity, then  $E_{(\text{cell})} = E_{(\text{cell})}^{\circ}$  and we have

$$\Delta_r G^{\circ} = -nFE_{(\text{cell})}^{\circ} \quad (2.16)$$

Thus, from the measurement of  $E_{(\text{cell})}^{\circ}$  we can obtain an important thermodynamic quantity,  $\Delta_r G^{\circ}$ , standard Gibbs energy of the reaction. From the latter we can calculate equilibrium constant by the equation:

$$\Delta_r G^{\circ} = -RT \ln K.$$

**Example 2.3** The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:



**Solution**  $\Delta_r G^{\circ} = -nFE_{(\text{cell})}^{\circ}$

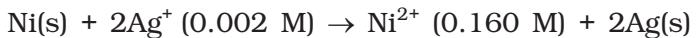
$n$  in the above equation is 2,  $F = 96487 \text{ C mol}^{-1}$  and  $E_{(\text{cell})}^{\circ} = 1.1 \text{ V}$

$$\begin{aligned} \text{Therefore, } \Delta_r G^{\circ} &= -2 \times 1.1 \text{ V} \times 96487 \text{ C mol}^{-1} \\ &= -21227 \text{ J mol}^{-1} \\ &= -212.27 \text{ kJ mol}^{-1} \end{aligned}$$

### Intext Questions

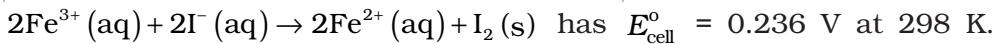
**2.4** Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

**2.5** Calculate the emf of the cell in which the following reaction takes place:



Given that  $E_{\text{cell}}^{\circ} = 1.05 \text{ V}$

**2.6** The cell in which the following reaction occurs:



Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

## **2.4 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 ( $\Omega$ ) which in terms of SI base units is equal to  $(\text{kg m}^2)/(\text{S}^3 \text{ A}^2)$ . 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,

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A} \quad (2.17)$$

The constant of proportionality,  $\rho$  (Greek, rho), is called **resistivity** (specific resistance). Its SI units are ohm metre ( $\Omega \text{ m}$ ) and quite often its submultiple, ohm centimetre ( $\Omega \text{ cm}$ ) 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  $\text{m}^2$ . It can be seen that:

$$1 \Omega \text{ m} = 100 \Omega \text{ cm} \text{ or } 1 \Omega \text{ cm} = 0.01 \Omega \text{ m}$$

The inverse of resistance,  $R$ , is called **conductance**,  $G$ , and we have the relation:

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l} \quad (2.18)$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to  $\text{ohm}^{-1}$  (also known as mho) or  $\Omega^{-1}$ . The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol,  $\kappa$  (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  $\text{S m}^{-1}$  but quite often,  $\kappa$  is expressed in  $\text{S cm}^{-1}$ . Conductivity of a material in  $\text{S m}^{-1}$  is its conductance when it is 1 m long and its area of cross section is 1  $\text{m}^2$ . It may be noted that  $1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$ .

**Table 2.2: The values of Conductivity of some Selected Materials at 298.15 K**

Material	Conductivity/ S m <sup>-1</sup>	Material	Conductivity/ S m <sup>-1</sup>
<b>Conductors</b>		<b>Aqueous Solutions</b>	
Sodium	$2.1 \times 10^3$	Pure water	$3.5 \times 10^{-5}$
Copper	$5.9 \times 10^3$	0.1 M HCl	3.91
Silver	$6.2 \times 10^3$	0.01M KCl	0.14
Gold	$4.5 \times 10^3$	0.01M NaCl	0.12
Iron	$1.0 \times 10^3$	0.1 M HAc	0.047
Graphite	$1.2 \times 10$	0.01M HAc	0.016
<b>Insulators</b>		<b>Semiconductors</b>	
Glass	$1.0 \times 10^{-16}$	CuO	$1 \times 10^{-7}$
Teflon	$1.0 \times 10^{-18}$	Si	$1.5 \times 10^{-2}$
		Ge	2.0

It can be seen from Table 2.2 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).

\* 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 polymers which have properties like 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.

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.

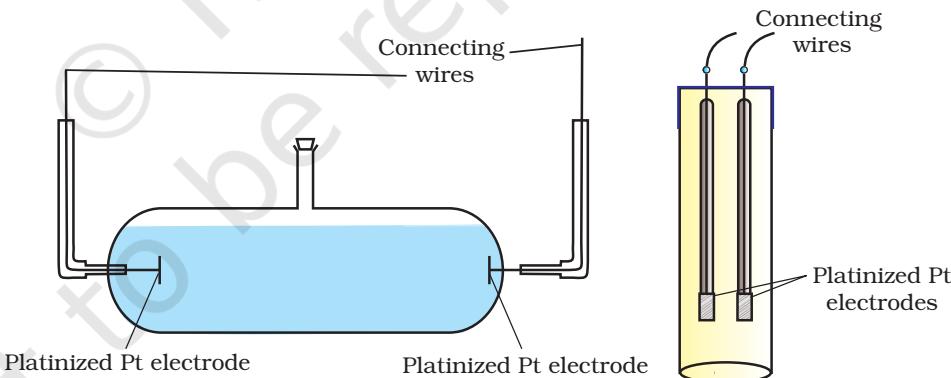
We already know that even very pure water has small amounts of hydrogen and hydroxyl ions ( $\sim 10^{-7} \text{ M}$ ) which lend it very low conductivity ( $3.5 \times 10^{-5} \text{ S m}^{-1}$ ). When electrolytes are dissolved in water, they furnish their own ions in the solution hence its conductivity 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 2.4.1).

#### 2.4.1 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. 2.4.



**Fig. 2.4**  
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:

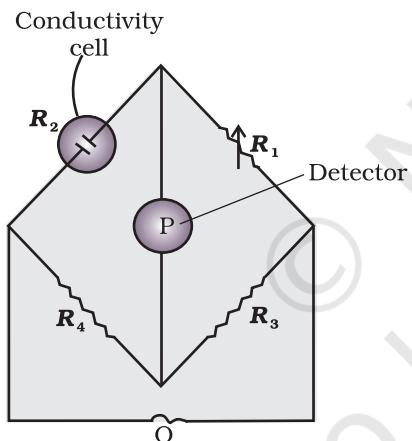
$$R = \rho \frac{l}{A} = \frac{l}{\kappa A} \quad (2.17)$$

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  $\text{length}^{-1}$  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 2.3) and at different temperatures. The cell constant,  $G^*$ , is then given by the equation:

$$G^* = \frac{l}{A} = R \kappa \quad (2.18)$$

**Table 2.3: Conductivity and Molar conductivity of KCl solutions at 298.15K**

Concentration/Molarity		Conductivity		Molar Conductivity	
mol L <sup>-1</sup>	mol m <sup>-3</sup>	S cm <sup>-1</sup>	S m <sup>-1</sup>	S cm <sup>2</sup> mol <sup>-1</sup>	S m <sup>2</sup> mol <sup>-1</sup>
1.000	1000	0.1113	11.13	111.3	111.3×10 <sup>-4</sup>
0.100	100.0	0.0129	1.29	129.0	129.0×10 <sup>-4</sup>
0.010	10.00	0.00141	0.141	141.0	141.0×10 <sup>-4</sup>



**Fig. 2.5:** Arrangement for measurement of resistance of a solution of an electrolyte.

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. 2.5.

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:

$$\text{Unknown resistance } R_2 = \frac{R_1 R_4}{R_3} \quad (2.19)$$

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:

$$\kappa = \frac{\text{cell constant}}{R} = \frac{G^*}{R} \quad (2.20)$$

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  $\Lambda_m$  (Greek, lambda). It is related to the conductivity of the solution by the equation:

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c} \quad (2.21)$$

In the above equation, if  $\kappa$  is expressed in  $\text{S m}^{-1}$  and the concentration,  $c$  in  $\text{mol m}^{-3}$  then the units of  $\Lambda_m$  are in  $\text{S m}^2 \text{mol}^{-1}$ . It may be noted that:

$$1 \text{ mol m}^{-3} = 1000(\text{L}/\text{m}^3) \times \text{molarity (mol/L)}, \text{ and hence}$$

$$\Lambda_m(\text{S cm}^2 \text{ mol}^{-1}) = \frac{\kappa (\text{S cm}^{-1})}{1000 \text{ L m}^{-3} \times \text{molarity (mol L}^{-1}\text{)}}$$

If we use  $\text{S cm}^{-1}$  as the units for  $\kappa$  and  $\text{mol cm}^{-3}$ , the units of concentration, then the units for  $\Lambda_m$  are  $\text{S cm}^2 \text{mol}^{-1}$ . It can be calculated by using the equation:

$$\Lambda_m(\text{S cm}^2 \text{ mol}^{-1}) = \frac{\kappa (\text{S cm}^{-1}) \times 1000 (\text{cm}^3 / \text{L})}{\text{molarity (mol/L)}}$$

Both type of units are used in literature and are related to each other by the equations:

$$1 \text{ S m}^2 \text{mol}^{-1} = 10^4 \text{ S cm}^2 \text{mol}^{-1} \quad \text{or}$$

$$1 \text{ S cm}^2 \text{mol}^{-1} = 10^{-4} \text{ S m}^2 \text{mol}^{-1}.$$

Resistance of a conductivity cell filled with  $0.1 \text{ mol L}^{-1}$  KCl solution is  $100 \Omega$ . If the resistance of the same cell when filled with  $0.02 \text{ mol L}^{-1}$  KCl solution is  $520 \Omega$ , calculate the conductivity and molar conductivity of  $0.02 \text{ mol L}^{-1}$  KCl solution. The conductivity of  $0.1 \text{ mol L}^{-1}$  KCl solution is  $1.29 \text{ S/m}$ .

#### Example 2.4

#### Solution

The cell constant is given by the equation:

$$\text{Cell constant} = G^* = \text{conductivity} \times \text{resistance}$$

$$= 1.29 \text{ S/m} \times 100 \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$$

$$\text{Conductivity of } 0.02 \text{ mol L}^{-1} \text{ KCl solution} = \text{cell constant} / \text{resistance}$$

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520 \Omega} = 0.248 \text{ S m}^{-1}$$

Concentration

$$= 0.02 \text{ mol L}^{-1}$$

$$= 1000 \times 0.02 \text{ mol m}^{-3} = 20 \text{ mol m}^{-3}$$

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}} = 124 \times 10^{-4} \text{ S m}^2 \text{mol}^{-1}$$

$$\text{Alternatively, } \kappa = \frac{1.29 \text{ cm}^{-1}}{520 \Omega} = 0.248 \times 10^{-2} \text{ S cm}^{-1}$$

and

$$\begin{aligned}\Lambda_m &= \kappa \times 1000 \text{ cm}^3 \text{ L}^{-1} \text{ molarity}^{-1} \\ &= \frac{0.248 \times 10^{-2} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.02 \text{ mol L}^{-1}} \\ &= 124 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

**Example 2.5** The electrical resistance of a column of  $0.05 \text{ mol L}^{-1}$  NaOH solution of diameter 1 cm and length 50 cm is  $5.55 \times 10^3$  ohm. Calculate its resistivity, conductivity and molar conductivity.

**Solution**  $A = \pi r^2 = 3.14 \times 0.5^2 \text{ cm}^2 = 0.785 \text{ cm}^2 = 0.785 \times 10^{-4} \text{ m}^2$

$$l = 50 \text{ cm} = 0.5 \text{ m}$$

$$R = \frac{\rho l}{A} \quad \text{or} \quad \rho = \frac{RA}{l} = \frac{5.55 \times 10^3 \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135 \Omega \text{ cm}$$

$$\begin{aligned}\text{Conductivity} &= \kappa = \frac{1}{\rho} = \left( \frac{1}{87.135} \right) \text{ S cm}^{-1} \\ &= 0.01148 \text{ S cm}^{-1}\end{aligned}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{c} \text{ cm}^3 \text{ L}^{-1}$$

$$\begin{aligned}&= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}} \\ &= 229.6 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

If we want to calculate the values of different quantities in terms of 'm' instead of 'cm',

$$\begin{aligned}\rho &= \frac{RA}{l} \\ &= \frac{5.55 \times 10^3 \Omega \times 0.785 \times 10^{-4} \text{ m}^2}{0.5 \text{ m}} = 87.135 \times 10^{-2} \Omega \text{ m}\end{aligned}$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135} \Omega \text{ m} = 1.148 \text{ S m}^{-1}$$

$$\text{and } \Lambda_m = \frac{\kappa}{c} = \frac{1.148 \text{ S m}^{-1}}{50 \text{ mol m}^{-3}} = 22.96 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}.$$

#### 2.4.2 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:

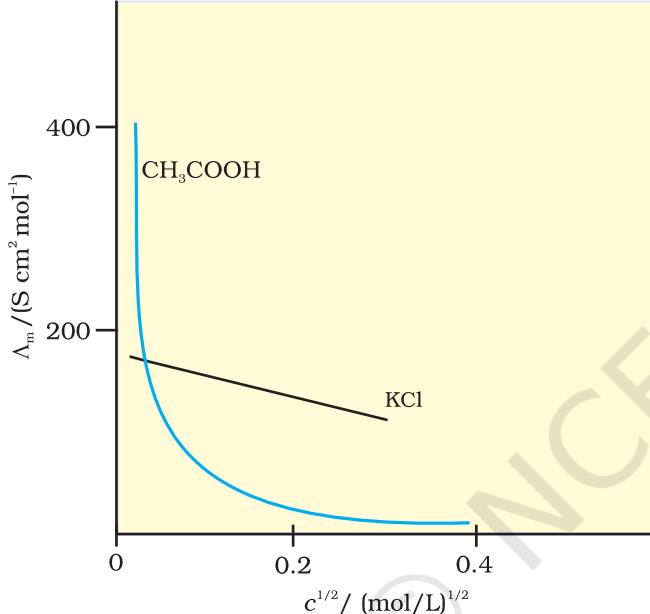
$$G = \frac{\kappa A}{l} = \kappa \text{ (both } A \text{ and } l \text{ are unity in their appropriate units in m or cm)}$$

**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)

$$\Lambda_m = \kappa V \quad (2.22)$$



**Fig. 2.6:** Molar conductivity versus  $c^{1/2}$  for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

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  $\kappa$  on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration,  $\Lambda_m$  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  $\Lambda_m^\circ$ . The variation in  $\Lambda_m$  with concentration is different (Fig. 2.6) for strong and weak electrolytes.

### Strong Electrolytes

For strong electrolytes,  $\Lambda_m$  increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \Lambda_m^\circ - A c^{1/2} \quad (2.23)$$

It can be seen that if we plot (Fig. 2.6)  $\Lambda_m$  against  $c^{1/2}$ , we obtain a straight line with intercept equal to  $\Lambda_m^\circ$  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 the solution. Thus, NaCl, CaCl<sub>2</sub>, MgSO<sub>4</sub> 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 2.6** The molar conductivity of KCl solutions at different concentrations at 298 K are given below:

$c/\text{mol L}^{-1}$	$\Lambda_m/\text{S cm}^2 \text{ mol}^{-1}$
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between  $\Lambda_m$  and  $c^{1/2}$  is a straight line. Determine the values of  $\Lambda_m^\circ$  and A for KCl.

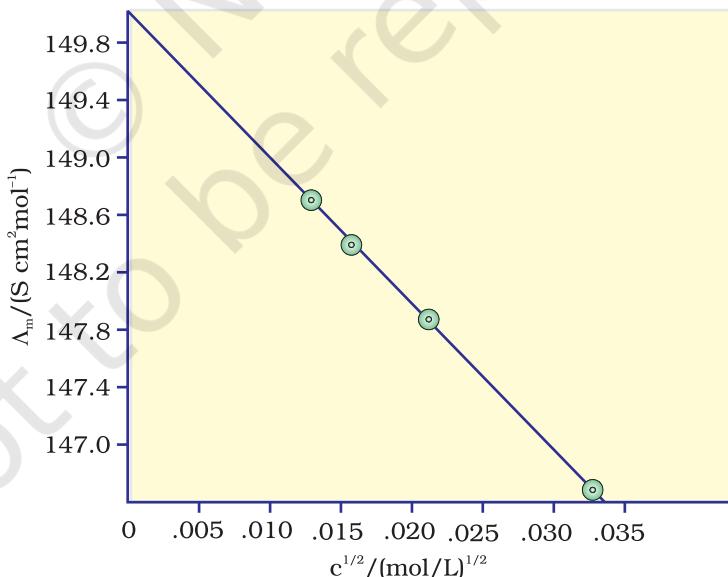
**Solution** Taking the square root of concentration we obtain:

$c^{1/2}/(\text{mol L}^{-1})^{1/2}$	$\Lambda_m/\text{S cm}^2 \text{ mol}^{-1}$
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

A plot of  $\Lambda_m$  (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

$$\Lambda_m^\circ = 150.0 \text{ S cm}^2 \text{ mol}^{-1} \text{ and}$$

$$A = -\text{slope} = 87.46 \text{ S cm}^2 \text{ mol}^{-1}/(\text{mol/L})^{1/2}.$$



**Fig. 2.7:** Variation of  $\Lambda_m$  against  $c^{1/2}$ .

Kohlrausch examined  $\Lambda_m^\circ$  values for a number of strong electrolytes and observed certain regularities. He noted that the difference in  $\Lambda_m^\circ$  of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:

$$\begin{aligned}\Lambda_m^\circ_{(\text{KCl})} - \Lambda_m^\circ_{(\text{NaCl})} &= \Lambda_m^\circ_{(\text{KBr})} - \Lambda_m^\circ_{(\text{NaBr})} \\ &= \Lambda_m^\circ_{(\text{KI})} - \Lambda_m^\circ_{(\text{NaI})} \approx 23.4 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

and similarly it was found that

$$\Lambda_m^\circ_{(\text{NaBr})} - \Lambda_m^\circ_{(\text{NaCl})} = \Lambda_m^\circ_{(\text{KBr})} - \Lambda_m^\circ_{(\text{KCl})} \approx 1.8 \text{ S cm}^2 \text{ mol}^{-1}$$

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  $\lambda_{\text{Na}^+}^\circ$  and  $\lambda_{\text{Cl}^-}^\circ$  are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:*

$$\Lambda_m^\circ_{(\text{NaCl})} = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad (2.24)$$

In general, if an electrolyte on dissociation gives  $v_+$  cations and  $v_-$  anions then its limiting molar conductivity is given by:

$$\Lambda_m^\circ = v_+ \lambda_+^\circ + v_- \lambda_-^\circ \quad (2.25)$$

Here,  $\lambda_+^\circ$  and  $\lambda_-^\circ$  are the limiting molar conductivities of the cation and anion respectively. The values of  $\lambda^\circ$  for some cations and anions at 298 K are given in Table 2.4.

**Table 2.4: Limiting Molar Conductivity for some Ions in Water at 298 K**

Ion	$\lambda^\circ / (\text{S cm}^2 \text{ mol}^{-1})$	Ion	$\lambda^\circ / (\text{S cm}^2 \text{ mol}^{-1})$
$\text{H}^+$	349.6	$\text{OH}^-$	199.1
$\text{Na}^+$	50.1	$\text{Cl}^-$	76.3
$\text{K}^+$	73.5	$\text{Br}^-$	78.1
$\text{Ca}^{2+}$	119.0	$\text{CH}_3\text{COO}^-$	40.9
$\text{Mg}^{2+}$	106.0	$\text{SO}_4^{2-}$	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  $\Lambda_m$  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  $\Lambda_m$  increases steeply (Fig. 2.6) on dilution, especially near lower concentrations. Therefore,  $\Lambda_m^\circ$  cannot be obtained by extrapolation of  $\Lambda_m$  to zero concentration. At infinite dilution (i.e., concentration  $c \rightarrow$  zero) electrolyte dissociates completely ( $\alpha = 1$ ), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately. Therefore,  $\Lambda_m^\circ$  for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions (Example 2.8). At any concentration  $c$ , if  $\alpha$  is the degree of dissociation

then it can be approximated to the ratio of molar conductivity  $\Lambda_m$  at the concentration  $c$  to limiting molar conductivity,  $\Lambda_m^0$ . Thus we have:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} \quad (2.26)$$

But we know that for a weak electrolyte like acetic acid (Class XI, Unit 7),

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{02} \left(1 - \frac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^0 (\Lambda_m^0 - \Lambda_m)} \quad (2.27)$$

#### **Applications of Kohlrausch law**

Using Kohlrausch law of independent migration of ions, it is possible to calculate  $\Lambda_m^0$  for any electrolyte from the  $\lambda^0$  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  $\Lambda_m^0$  and  $\Lambda_m$  at a given concentration  $c$ .

**Example 2.7** Calculate  $\Lambda_m^0$  for  $\text{CaCl}_2$  and  $\text{MgSO}_4$  from the data given in Table 3.4.

**Solution** We know from Kohlrausch law that

$$\begin{aligned} \Lambda_{m(\text{CaCl}_2)}^0 &= \lambda_{\text{Ca}^{2+}}^0 + 2\lambda_{\text{Cl}^-}^0 = 119.0 \text{ S cm}^2 \text{ mol}^{-1} + 2(76.3) \text{ S cm}^2 \text{ mol}^{-1} \\ &= (119.0 + 152.6) \text{ S cm}^2 \text{ mol}^{-1} \\ &= 271.6 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_{m(\text{MgSO}_4)}^0 &= \lambda_{\text{Mg}^{2+}}^0 + \lambda_{\text{SO}_4^{2-}}^0 = 106.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ S cm}^2 \text{ mol}^{-1} \\ &= 266 \text{ S cm}^2 \text{ mol}^{-1} . \end{aligned}$$

**Example 2.8**  $\Lambda_m^0$  for  $\text{NaCl}$ ,  $\text{HCl}$  and  $\text{NaAc}$  are 126.4, 425.9 and 91.0  $\text{S cm}^2 \text{ mol}^{-1}$  respectively. Calculate  $\Lambda_m^0$  for  $\text{HAc}$ .

**Solution** 
$$\begin{aligned} \Lambda_{m(\text{HAc})}^0 &= \lambda_{\text{H}^+}^0 + \lambda_{\text{Ac}^-}^0 = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 + \lambda_{\text{Ac}^-}^0 + \lambda_{\text{Na}^+}^0 - \lambda_{\text{Cl}^-}^0 - \lambda_{\text{Na}^+}^0 \\ &= \Lambda_{m(\text{HCl})}^0 + \Lambda_{m(\text{NaAc})}^0 - \Lambda_{m(\text{NaCl})}^0 \\ &= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1} \\ &= 390.5 \text{ S cm}^2 \text{ mol}^{-1} . \end{aligned}$$

**Example 2.9** The conductivity of  $0.001028 \text{ mol L}^{-1}$  acetic acid is  $4.95 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its dissociation constant if  $\Lambda_m^0$  for acetic acid is  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ .

**Solution** 
$$\begin{aligned} \Lambda_m &= \frac{\kappa}{c} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} = 48.15 \text{ S cm}^3 \text{ mol}^{-1} \\ \alpha &= \frac{\Lambda_m}{\Lambda_m^0} = \frac{48.15 \text{ S cm}^3 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1233 \\ k &= \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \text{ mol L}^{-1} \times (0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

### Intext Questions

**2.7** Why does the conductivity of a solution decrease with dilution?

**2.8** Suggest a way to determine the  $\Lambda_m^\circ$  value of water.

**2.9** The molar conductivity of  $0.025 \text{ mol L}^{-1}$  methanoic acid is  $46.1 \text{ S cm}^2 \text{ mol}^{-1}$ .

Calculate its degree of dissociation and dissociation constant. Given  $\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$ .

## 2.5 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  $\text{Cu}^{2+}$  ions discharge at the cathode (negatively charged) and the following reaction takes place:



Copper metal is deposited on the cathode. At the anode, copper is converted into  $\text{Cu}^{2+}$  ions by the reaction:



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 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:

- (i) *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).
- (ii) *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  $\div$  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:



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  $1.6021 \times 10^{-19}$  C.

Therefore, the charge on one mole of electrons is equal to:

$$N_A \times 1.6021 \times 10^{-19} \text{ C} = 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.6021 \times 10^{-19}$$

$$C = 96487 \text{ C mol}^{-1}$$

This quantity of electricity is called **Faraday** and is represented by the symbol **F**.

For approximate calculations we use  $1\text{F} \approx 96500 \text{ C mol}^{-1}$ .

For the electrode reactions:



It is obvious that one mole of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  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 2.10

A solution of  $\text{CuSO}_4$  is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

#### Solution

$t = 600 \text{ s}$  charge = current  $\times$  time =  $1.5 \text{ A} \times 600 \text{ s} = 900 \text{ C}$

According to the reaction:



We require 2F or  $2 \times 96487 \text{ C}$  to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited

$$= (63 \text{ g mol}^{-1} \times 900 \text{ C}) / (2 \times 96487 \text{ C mol}^{-1}) = 0.2938 \text{ g.}$$

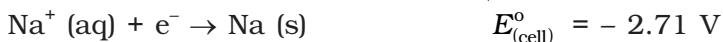
### 2.5.1 Products of Electrolysis

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 do not 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<sub>2</sub> gas. Here we have only one cation (Na<sup>+</sup>) which is reduced at the cathode (Na<sup>+</sup> + e<sup>-</sup> → Na) and one anion (Cl<sup>-</sup>) which is oxidised at the anode (Cl<sup>-</sup> → ½Cl<sub>2</sub> + e<sup>-</sup>). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl<sub>2</sub> and H<sub>2</sub>. In this case besides Na<sup>+</sup> and Cl<sup>-</sup> ions we also have H<sup>+</sup> and OH<sup>-</sup> ions along with the solvent molecules, H<sub>2</sub>O.

At the cathode there is competition between the following reduction reactions:



The reaction with higher value of  $E^\circ$  is preferred and therefore, the reaction at the cathode during electrolysis is:



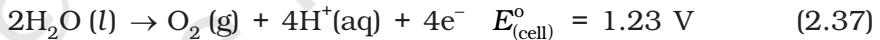
but H<sup>+</sup> (aq) is produced by the dissociation of H<sub>2</sub>O, i.e.,



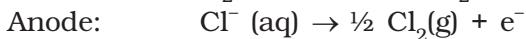
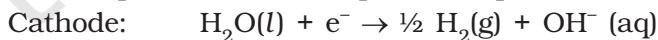
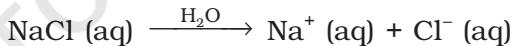
Therefore, the net reaction at the cathode may be written as the sum of (2.33) and (2.34) and we have



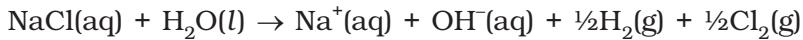
At the anode the following oxidation reactions are possible:



The reaction at anode with lower value of  $E^\circ$  is preferred and therefore, water should get oxidised in preference to Cl<sup>-</sup> (aq). However, on account of overpotential of oxygen, reaction (2.36) is preferred. Thus, the net reactions may be summarised as:

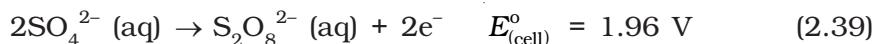


Net reaction:



The standard electrode potentials are replaced by electrode potentials given by Nernst equation (Eq. 2.8) to take into account the concentration effects. During the electrolysis of sulphuric acid, the following processes are possible at the anode:





For dilute sulphuric acid, reaction (2.38) is preferred but at higher concentrations of  $\text{H}_2\text{SO}_4$ , reaction (2.39) is preferred.

### Intext Questions

**2.10** If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

**2.11** Suggest a list of metals that are extracted electrolytically.

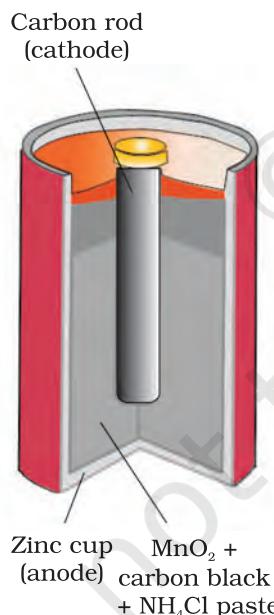
**2.12** Consider the reaction:  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

What is the quantity of electricity in coulombs needed to reduce 1 mol of  $\text{Cr}_2\text{O}_7^{2-}$ ?

## 2.6 Batteries

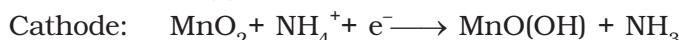
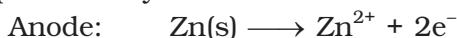
Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

### 2.6.1 Primary Batteries



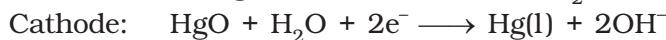
**Fig. 2.8:** A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.

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.2.8). The space between the electrodes is filled by a moist paste of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and zinc chloride ( $\text{ZnCl}_2$ ). The electrode reactions are complex, but they can be written approximately as follows :

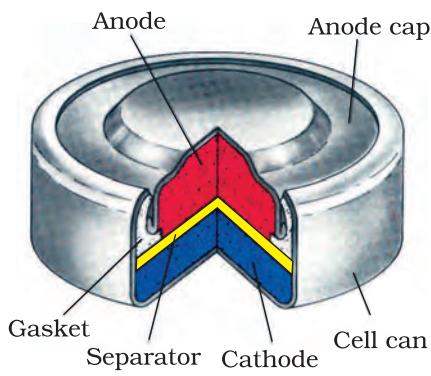


In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with  $\text{Zn}^{2+}$  to give  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ . The cell has a potential of nearly 1.5 V.

Mercury cell, (Fig. 2.9) suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of  $\text{HgO}$  and carbon as the cathode. The electrolyte is a paste of  $\text{KOH}$  and  $\text{ZnO}$ . The electrode reactions for the cell are given below:



**Fig. 2.9**  
Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.



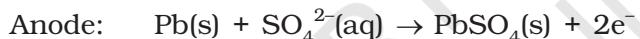
The overall reaction is represented by  
 $\text{Zn}(\text{Hg}) + \text{HgO}(\text{s}) \longrightarrow \text{ZnO}(\text{s}) + \text{Hg}(\text{l})$

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.

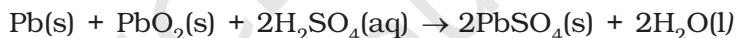
### 2.6.2 Secondary Batteries

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. 2.10) commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide ( $\text{PbO}_2$ ) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

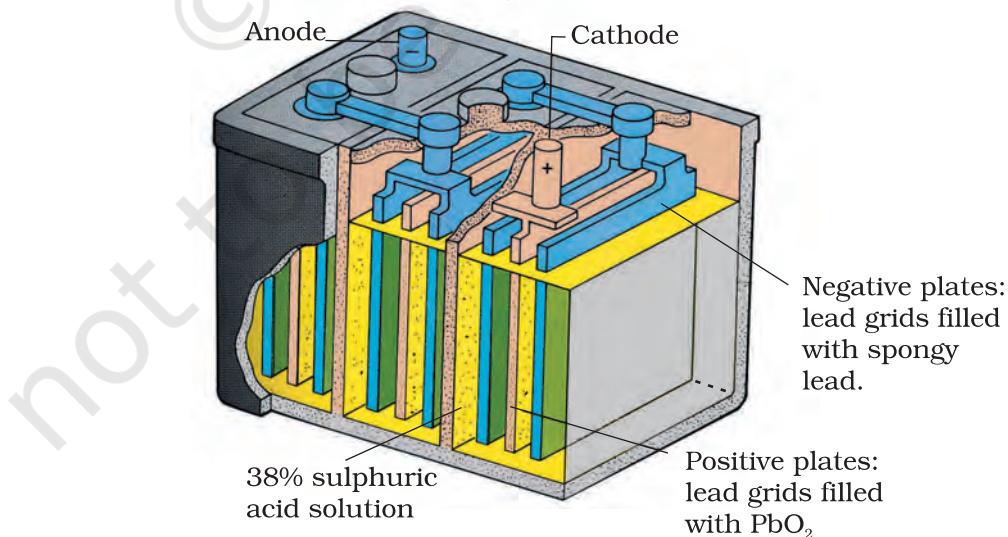
The cell reactions when the battery is in use are given below:



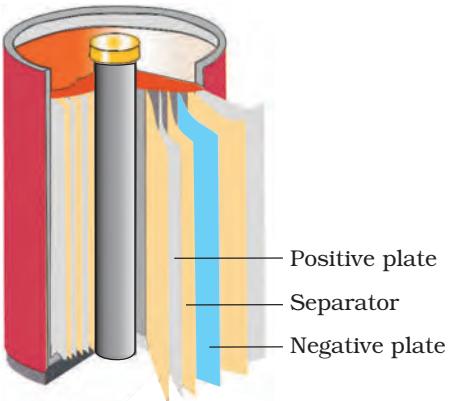
i.e., overall cell reaction consisting of cathode and anode reactions is:



On charging the battery the reaction is reversed and  $\text{PbSO}_4(\text{s})$  on anode and cathode is converted into Pb and  $\text{PbO}_2$ , respectively.



**Fig. 2.10:** The Lead storage battery.



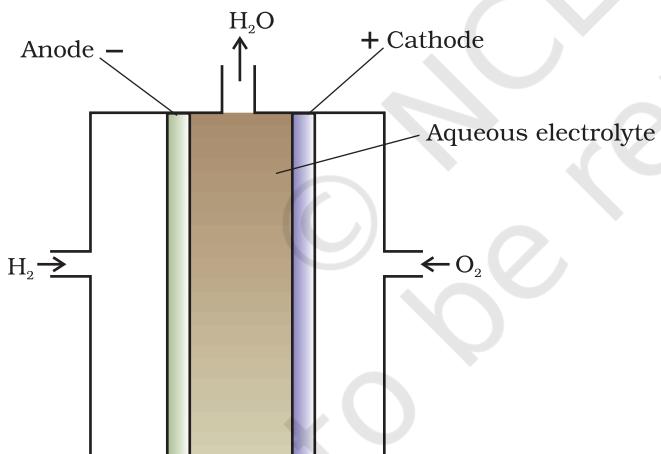
**Fig. 2.11**  
A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Another important secondary cell is the nickel-cadmium cell (Fig. 2.11) 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:



## 2.7 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**.

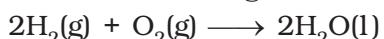


**Fig. 2.12:** Fuel cell using  $\text{H}_2$  and  $\text{O}_2$  produces electricity.

given below:



Overall reaction being:

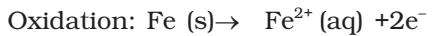
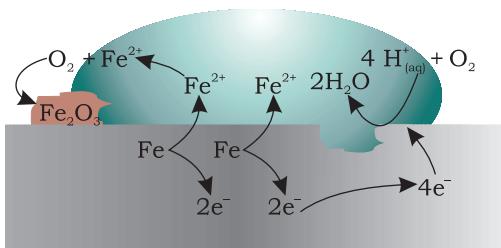


The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared

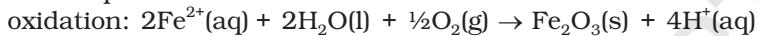
to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

## 2.8 Corrosion

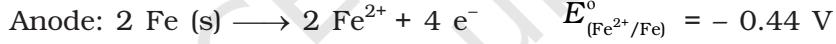
Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion.



Atmospheric



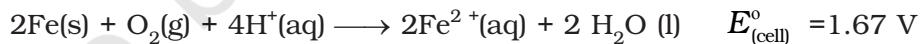
In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot (Fig. 2.13) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction



Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of  $\text{H}^+$  (which is believed to be available from  $\text{H}_2\text{CO}_3$  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



The overall reaction being:



The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ ) 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**

- 2.13** Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.
- 2.14** Suggest two materials other than hydrogen that can be used as fuels in fuel cells.
- 2.15** 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 catastrophe, 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 ( $E_{\text{cell}}^{\circ} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ ). The standard potential of the cells are related to standard Gibbs energy ( $\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$ ) and **equilibrium constant** ( $\Delta_r G^{\circ} = -RT \ln K$ ) 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**,  $\kappa$ , of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature. **Molar conductivity**,  $\Lambda_m$ , 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

- 2.1** 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.
- 2.2** 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.
- 2.3** 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.
- 2.4** 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  $\Delta_rG^\circ$  and equilibrium constant of the reactions.
- 2.5** 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)  $Pt(s) | Br^-(0.010 M) | Br_2(l) || H^+(0.030 M) | H_2(g) (1 bar) | Pt(s)$ .
- 2.6** 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  $\Delta_rG^\circ$  and  $E^\circ$  for the reaction.
- 2.7** Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.
- 2.8** The conductivity of 0.20 M solution of KCl at 298 K is  $0.0248 \text{ S cm}^{-1}$ . Calculate its molar conductivity.
- 2.9** The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is  $1500 \Omega$ . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is  $0.146 \times 10^{-3} \text{ S cm}^{-1}$ .

- 2.10** 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  |
|--|-------|-------|-------|-------|--------|
| $10^2 \times \kappa / \text{S m}^{-1}$ | 1.237 | 11.85 | 23.15 | 55.53 | 106.74 |
- Calculate  $\Lambda_m$  for all concentrations and draw a plot between  $\Lambda_m$  and  $c^{\frac{1}{2}}$ . Find the value of  $\Lambda_m^0$ .
- 2.11** Conductivity of 0.00241 M acetic acid is  $7.896 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its molar conductivity. If  $\Lambda_m^0$  for acetic acid is  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ , what is its dissociation constant?
- 2.12** How much charge is required for the following reductions:
- 1 mol of  $\text{Al}^{3+}$  to  $\text{Al}$ ?
  - 1 mol of  $\text{Cu}^{2+}$  to  $\text{Cu}$ ?
  - 1 mol of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ ?
- 2.13** How much electricity in terms of Faraday is required to produce
- 20.0 g of Ca from molten  $\text{CaCl}_2$ ?
  - 40.0 g of Al from molten  $\text{Al}_2\text{O}_3$ ?
- 2.14** How much electricity is required in coulomb for the oxidation of
- 1 mol of  $\text{H}_2\text{O}$  to  $\text{O}_2$ ?
  - 1 mol of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$ ?
- 2.15** A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?
- 2.16** Three electrolytic cells A,B,C containing solutions of  $\text{ZnSO}_4$ ,  $\text{AgNO}_3$  and  $\text{CuSO}_4$ , 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?
- 2.17** Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:
- $\text{Fe}^{3+}(\text{aq})$  and  $\text{I}^-(\text{aq})$
  - $\text{Ag}^+(\text{aq})$  and  $\text{Cu}(\text{s})$
  - $\text{Fe}^{3+}(\text{aq})$  and  $\text{Br}^-(\text{aq})$
  - $\text{Ag}(\text{s})$  and  $\text{Fe}^{3+}(\text{aq})$
  - $\text{Br}_2(\text{aq})$  and  $\text{Fe}^{2+}(\text{aq})$ .
- 2.18** Predict the products of electrolysis in each of the following:
- An aqueous solution of  $\text{AgNO}_3$  with silver electrodes.
  - An aqueous solution of  $\text{AgNO}_3$  with platinum electrodes.
  - A dilute solution of  $\text{H}_2\text{SO}_4$  with platinum electrodes.
  - An aqueous solution of  $\text{CuCl}_2$  with platinum electrodes.

#### Answers to Some Intext Questions

**2.5**  $E_{(\text{cell})} = 0.91 \text{ V}$

**2.6**  $\Delta_r G^\circ = -45.54 \text{ kJ mol}^{-1}$ ,  $K_c = 9.62 \times 10^7$

**2.9**  $0.114$ ,  $3.67 \times 10^{-4} \text{ mol L}^{-1}$



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Unit

3

## 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.

### 3.1 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:

- the rate of decrease in concentration of any one of the reactants, or
- 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.



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

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta [R]}{\Delta t} \quad (3.1)$$

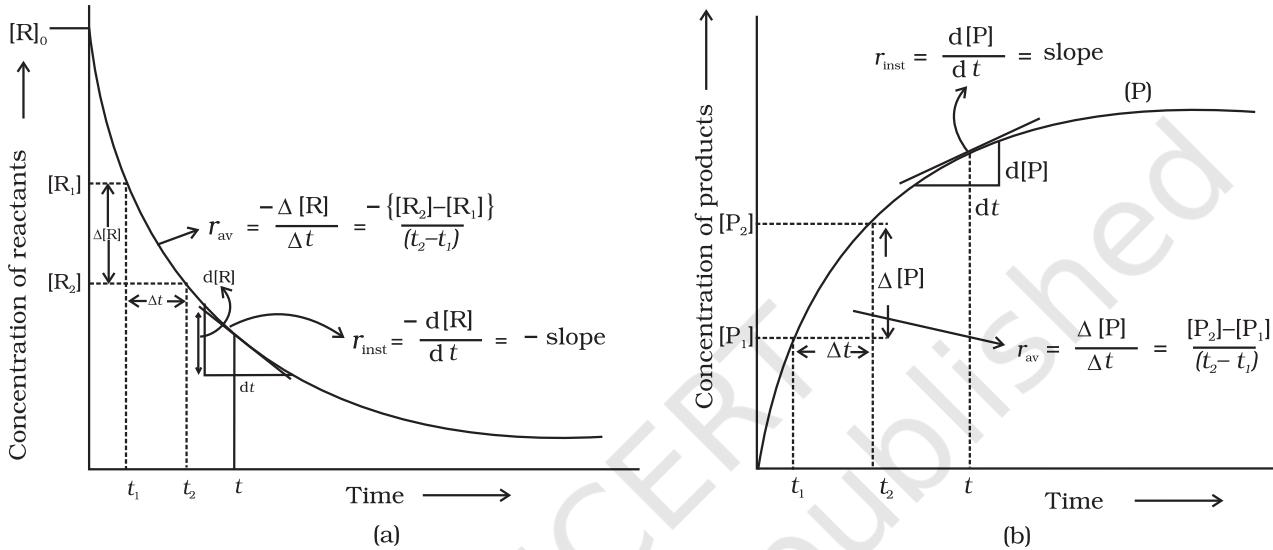
### Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = + \frac{\Delta [P]}{\Delta t} \quad (3.2)$$

Since,  $\Delta[R]$  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 (3.1) and (3.2) 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. 3.1).



**Fig. 3.1:** Instantaneous and average rate of a reaction

### Units of rate of a reaction

From equations (3.1) and (3.2), it is clear that units of rate are concentration time<sup>-1</sup>. For example, if concentration is in mol L<sup>-1</sup> and time is in seconds then the units will be mol L<sup>-1</sup>s<sup>-1</sup>. 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<sup>-1</sup>.

From the concentrations of C<sub>4</sub>H<sub>9</sub>Cl (butyl chloride) at different times given [Example 3.1](#) below, calculate the average rate of the reaction:



during different intervals of time.

t/s	0	50	100	150	200	300	400	700	800
[C <sub>4</sub> H <sub>9</sub> Cl]/mol L <sup>-1</sup>	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

We can determine the difference in concentration over different intervals of time and thus determine the average rate by dividing  $\Delta[R]$  by  $\Delta t$  (Table 3.1).

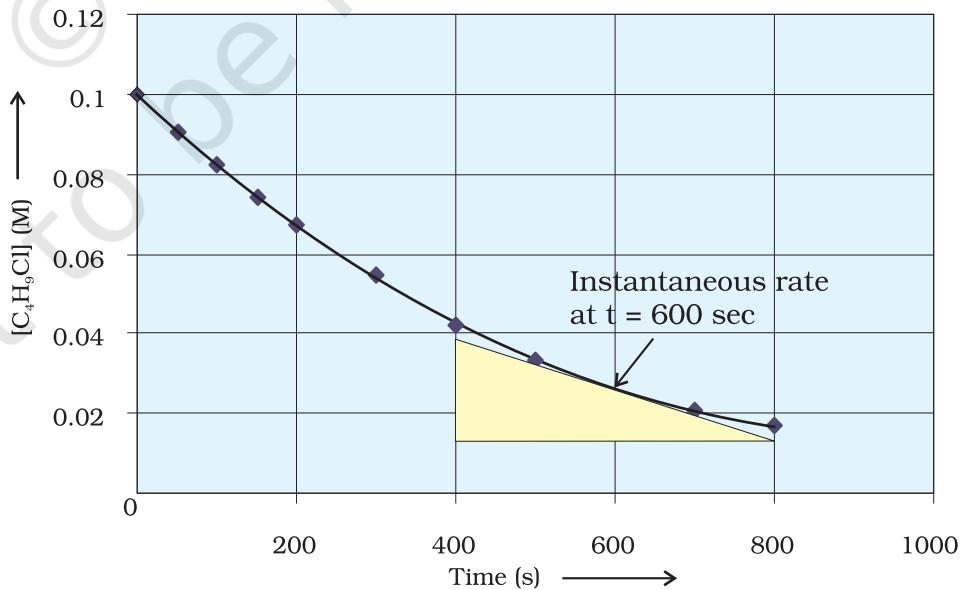
**Table 3.1: Average rates of hydrolysis of butyl chloride**

$[C_4H_9Cl]_{t_1} / mol L^{-1}$	$[C_4H_9Cl]_{t_2} / mol L^{-1}$	$t_1/s$	$t_2/s$	$r_{av} \times 10^4 / mol L^{-1}s^{-1}$ $= - \left[ [C_4H_9Cl]_{t_2} - [C_4H_9Cl]_{t_1} \right] / (t_2 - t_1) \times 10^4$
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 3.1) that the average rate falls from  $1.90 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$  to  $0.4 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$ . 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  $\Delta t$  approaches zero). Hence, mathematically for an infinitesimally small  $dt$  instantaneous rate is given by

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \quad (3.3)$$

$$\text{As } \Delta t \rightarrow 0 \quad \text{or} \quad r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$



**Fig 3.2**

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. 3.1). So in problem 3.1,  $r_{\text{inst}}$  at 600 s 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. 3.2).

The slope of this tangent gives the instantaneous rate.

$$\text{So, } r_{\text{inst}} \text{ at } 600 \text{ s} = - \left( \frac{0.0165 - 0.037}{(800 - 400) \text{ s}} \right) \text{ mol L}^{-1} = 5.12 \times 10^{-5} \text{ mol L}^{-1} \text{s}^{-1}$$

$$\text{At } t = 250 \text{ s } r_{\text{inst}} = 1.22 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$$

$$t = 350 \text{ s } r_{\text{inst}} = 1.0 \times 10^{-4} \text{ mol L}^{-1} \text{s}^{-1}$$

$$t = 450 \text{ s } r_{\text{inst}} = 6.4 \times 10^{-5} \text{ mol L}^{-1} \text{s}^{-1}$$

Now consider a reaction



Where stoichiometric coefficients of the reactants and products are same, then rate of the reaction is given as

$$\text{Rate of reaction} = - \frac{\Delta[\text{Hg}]}{\Delta t} = - \frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

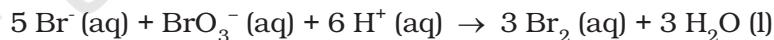
i.e., rate of disappearance of any of the reactants is same as the rate of appearance of the products. But in the following reaction, two moles of HI decompose to produce one mole each of H<sub>2</sub> and I<sub>2</sub>,



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<sub>2</sub> or I<sub>2</sub>, to make them equal, the term  $\Delta[\text{HI}]$  is divided by 2. The rate of this reaction is given by

$$\text{Rate of reaction} = - \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

Similarly, for the reaction



$$\text{Rate} = - \frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = - \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = - \frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

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 3.2** The decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  at 318K has been studied by monitoring the concentration of  $\text{N}_2\text{O}_5$  in the solution. Initially the concentration of  $\text{N}_2\text{O}_5$  is  $2.33 \text{ mol L}^{-1}$  and after 184 minutes, it is reduced to  $2.08 \text{ mol L}^{-1}$ . The reaction takes place according to the equation



Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of  $\text{NO}_2$  during this period?

**Solution**

$$\begin{aligned}\text{Average Rate} &= \frac{1}{2} \left\{ -\frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t} \right\} = -\frac{1}{2} \left[ \frac{(2.08 - 2.33) \text{ mol L}^{-1}}{184 \text{ min}} \right] \\ &= 6.79 \times 10^{-4} \text{ mol L}^{-1}/\text{min} = (6.79 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}) \times (60 \text{ min}/1\text{h}) \\ &= 4.07 \times 10^{-2} \text{ mol L}^{-1}/\text{h} \\ &= 6.79 \times 10^{-4} \text{ mol L}^{-1} \times 1\text{min}/60\text{s} \\ &= 1.13 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}\end{aligned}$$

It may be remembered that

$$\text{Rate} = \frac{1}{4} \left\{ \frac{\Delta [\text{NO}_2]}{\Delta t} \right\}$$

$$\frac{\Delta [\text{NO}_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4 \text{ mol L}^{-1} \text{ min}^{-1} = 2.72 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

### Intext Questions

- 3.1** For the reaction  $\text{R} \rightarrow \text{P}$ , the concentration of a reactant changes from  $0.03\text{M}$  to  $0.02\text{M}$  in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
- 3.2** In a reaction,  $2\text{A} \rightarrow \text{Products}$ , the concentration of A decreases from  $0.5 \text{ mol L}^{-1}$  to  $0.4 \text{ mol L}^{-1}$  in 10 minutes. Calculate the rate during this interval?

## 3.2 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.

### **3.2.1 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.

### **3.2.2 Rate Expression and Rate Constant**

The results in Table 3.1 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



where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

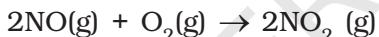
$$\text{Rate} \propto [A]^x [B]^y \quad (3.4)$$

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

$$\text{Rate} = k [A]^x [B]^y \quad (3.4a)$$

$$-\frac{d[R]}{dt} = k[A]^x [B]^y \quad (3.4b)$$

This form of equation (3.4 b) is known as differential rate equation, where  $k$  is a proportionality constant called **rate constant**. The equation like (3.4), 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:



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 3.2).

**Table 3.2: Initial rate of formation of NO<sub>2</sub>**

Experiment	Initial [NO]/ mol L <sup>-1</sup>	Initial [O <sub>2</sub> ]/ mol L <sup>-1</sup>	Initial rate of formation of NO <sub>2</sub> / mol L <sup>-1</sup> s <sup>-1</sup>
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<sub>2</sub> is kept constant then the initial rate increases by a factor of four from 0.096 to 0.384 mol L<sup>-1</sup>s<sup>-1</sup>. 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<sub>2</sub> is doubled the rate also gets doubled indicating that rate depends on concentration of O<sub>2</sub> to the first power. Hence, the rate equation for this reaction will be

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

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. $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$	Rate = $k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$
2. $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	Rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5]^1 [\text{H}_2\text{O}]^0$

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.*

### 3.2.3 Order of a Reaction

In the rate equation (3.4)

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

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 (3.4) 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 3.3

Calculate the overall order of a reaction which has the rate expression

(a) Rate =  $k[A]^{1/2}[B]^{3/2}$

(b) Rate =  $k[A]^{3/2}[B]^{-1}$

(a) Rate =  $k[A]^x[B]^y$

$$\text{order} = x + y$$

$$\text{So order} = 1/2 + 3/2 = 2, \text{ i.e., second order}$$

(b) order =  $3/2 + (-1) = 1/2$ , i.e., half order.

#### Solution

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<sub>2</sub> and H<sub>2</sub>O 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



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

Where x + y = n = order of the reaction

$$\begin{aligned} k &= \frac{\text{Rate}}{[A]^x [B]^y} \\ &= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n} \quad (\text{where } [A]=[B]) \end{aligned}$$

Taking SI units of concentration, mol L<sup>-1</sup> and time, s, the units of k for different reaction order are listed in Table 3.3

**Table 3.3: 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	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1}$

Identify the reaction order from each of the following rate constants. [Example 3.4](#)

(i)  $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$

(ii)  $k = 3 \times 10^{-4} \text{ s}^{-1}$

(i) The unit of second order rate constant is L mol<sup>-1</sup> s<sup>-1</sup>, therefore

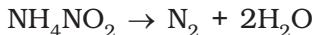
$k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$  represents a second order reaction.

(ii) The unit of a first order rate constant is s<sup>-1</sup> therefore

$k = 3 \times 10^{-4} \text{ s}^{-1}$  represents a first order reaction.

#### **3.2.4 Molecularity of a Reaction**

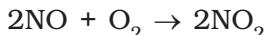
Another property of a reaction called molecularity helps in understanding its mechanism. **The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.** The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.



Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

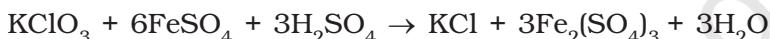


Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,



The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.

It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.



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.



The rate equation for this reaction is found to be

$$\text{Rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

This reaction is first order with respect to both  $\text{H}_2\text{O}_2$  and  $\text{I}^-$ . Evidences suggest that this reaction takes place in two steps

- (1)  $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$
- (2)  $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$

Both the steps are bimolecular elementary reactions. Species  $\text{IO}^-$  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 molecularity of the slowest step is same as the order of the overall reaction.

### Intext Questions

- 3.3** For a reaction,  $A + B \rightarrow \text{Product}$ ; the rate law is given by,  $r = k [A]^{1/2} [B]^2$ . What is the order of the reaction?
- 3.4** 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 ?

### **3.3 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. 3.1). 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.

#### **3.3.1 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,



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

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

$$[R] = -k t + I \quad (3.5)$$

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.

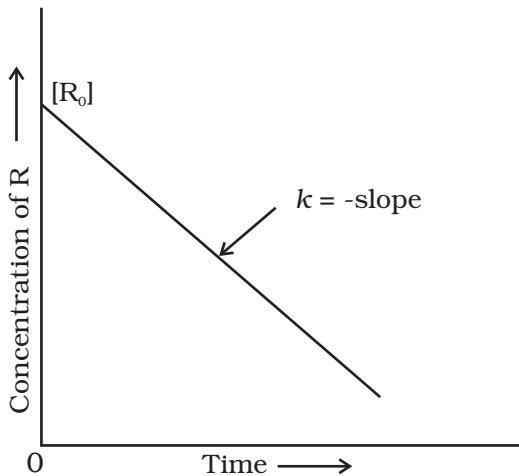
Substituting in equation (3.5)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (3.5)

$$[R] = -kt + [R]_0 \quad (3.6)$$



**Fig. 3.3:** Variation in the concentration vs time plot for a zero order reaction

Comparing (3.6) with equation of a straight line,  $y = mx + c$ , if we plot  $[R]$  against  $t$ , we get a straight line (Fig. 3.3) with slope  $= -k$  and intercept equal to  $[R]_0$ .

Further simplifying equation (3.6), we get the rate constant,  $k$  as

$$k = \frac{[R]_0 - [R]}{t} \quad (3.7)$$

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.

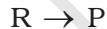


$$\text{Rate} = k [\text{NH}_3]^0 = k$$

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.

### 3.3.2 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,



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

$$\text{or } \frac{d[R]}{[R]} = -kdt$$

Integrating this equation, we get

$$\ln [R] = -kt + I \quad (3.8)$$

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 (3.8) can be written as

$$\begin{aligned} \ln [R]_0 &= -k \times 0 + I \\ \ln [R]_0 &= I \end{aligned}$$

Substituting the value of  $I$  in equation (3.8)

$$\ln [R] = -kt + \ln [R]_0 \quad (3.9)$$

Rearranging this equation

$$\ln \frac{[R]}{[R]_0} = -kt$$
$$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad (3.10)$$

At time  $t_1$  from equation (3.8)

$$*\ln[R]_1 = - kt_1 + *ln[R]_0 \quad (3.11)$$

At time  $t_2$

$$\ln[R]_2 = - kt_2 + \ln[R]_0 \quad (3.12)$$

where,  $[R]_1$  and  $[R]_2$  are the concentrations of the reactants at time  $t_1$  and  $t_2$  respectively.

Subtracting (3.12) from (3.11)

$$\ln[R]_1 - \ln[R]_2 = - kt_1 - (-kt_2)$$
$$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$
$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \quad (3.13)$$

Equation (3.9) can also be written as

$$\ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$[R] = [R]_0 e^{-kt} \quad (3.14)$$

Comparing equation (3.9) with  $y = mx + c$ , if we plot  $\ln [R]$  against  $t$  (Fig. 3.4) we get a straight line with slope  $= -k$  and intercept equal to  $\ln [R]_0$

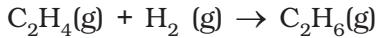
The first order rate equation (3.10) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad (3.15)$$

$$*\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between  $\log [R]_0/[R]$  vs  $t$ , (Fig. 3.5), the slope  $= k/2.303$

Hydrogenation of ethene is an example of first order reaction.



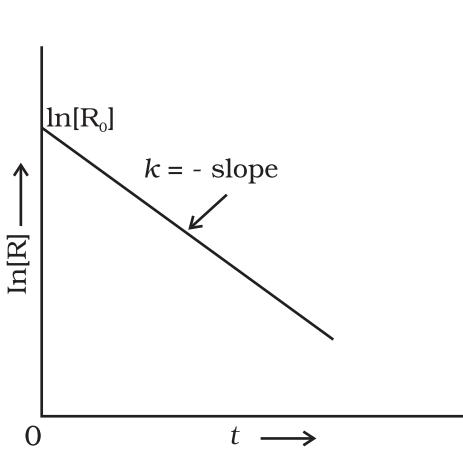
$$\text{Rate} = k [\text{C}_2\text{H}_4]$$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

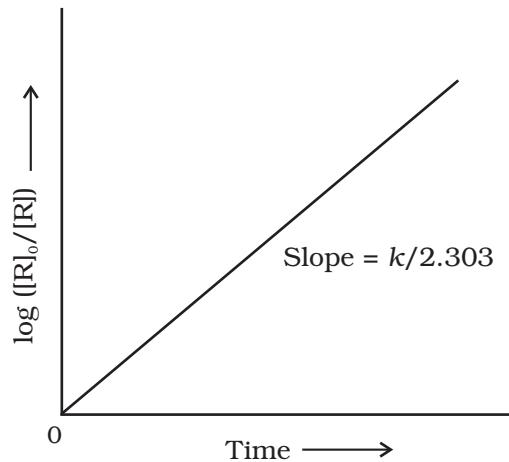
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\* Refer to Appendix-IV for  $\ln$  and  $\log$  (logarithms).

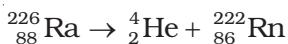
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**Fig. 3.4:** A plot between  $\ln[R]$  and  $t$  for a first order reaction



**Fig. 3.5:** Plot of  $\log [R]_0/[R]$  vs time for a first order reaction



$$\text{Rate} = k [\text{Ra}]$$

Decomposition of  $\text{N}_2\text{O}_5$  and  $\text{N}_2\text{O}$  are some more examples of first order reactions.

**Example 3.5** The initial concentration of  $\text{N}_2\text{O}_5$  in the following first order reaction  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$  was  $1.24 \times 10^{-2} \text{ mol L}^{-1}$  at 318 K. The concentration of  $\text{N}_2\text{O}_5$  after 60 minutes was  $0.20 \times 10^{-2} \text{ mol L}^{-1}$ . Calculate the rate constant of the reaction at 318 K.

**Solution** For a first order reaction

$$\begin{aligned} \log \frac{[\text{R}]_1}{[\text{R}]_2} &= \frac{k(t_2 - t_1)}{2.303} \\ k &= \frac{2.303}{(t_2 - t_1)} \log \frac{[\text{R}]_1}{[\text{R}]_2} \\ &= \frac{2.303}{(60 \text{ min} - 0 \text{ min})} \log \frac{1.24 \times 10^{-2} \text{ mol L}^{-1}}{0.20 \times 10^{-2} \text{ mol L}^{-1}} \\ &= \frac{2.303}{60} \log 6.2 \text{ min}^{-1} \\ k &= 0.0304 \text{ min}^{-1} \end{aligned}$$

Let us consider a typical first order gas phase reaction



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

$$\text{Total pressure } p_t = p_A + p_B + p_C \text{ (pressure units)}$$

$p_A$ ,  $p_B$  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  $t = 0$ .

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

$$\begin{aligned} \text{where, } p_A &= p_i - x = p_i - (p_t - p_i) \\ &= 2p_i - p_t \end{aligned}$$

$$k = \left( \frac{2.303}{t} \right) \left( \log \frac{p_i}{p_A} \right) \quad (3.16)$$

$$= \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

The following data were obtained during the first order thermal decomposition of  $N_2O_5(g)$  at constant volume: Example 3.6



S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

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. Solution

$2N_2O_5(g)$	→	$2N_2O_4(g)$	+	$O_2(g)$
Start $t = 0$	0.5 atm		0 atm	0 atm
At time $t$	$(0.5 - 2x)$ atm		$2x$ atm	$x$ atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

$$\text{At } t = 100 \text{ s; } p_t = 0.512 \text{ atm}$$

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Using equation (3.16)

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{p_i}{p_A} = \frac{2.303}{100 \text{ s}} \log \frac{0.5 \text{ atm}}{0.476 \text{ atm}} \\ &= \frac{2.303}{100 \text{ s}} \times 0.0216 = 4.98 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

### 3.3.3 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 3.7.

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, [R] = \frac{1}{2} [R]_0$$

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,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad (3.15)$$

$$\text{at } t_{1/2} [R] = \frac{[R]_0}{2} \quad (3.16)$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \quad (3.17)$$

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  $[R]_0$ .**

A first order reaction is found to have a rate constant,  $k = 5.5 \times 10^{-14} \text{ s}^{-1}$ . [Example 3.7](#)  
Find the half-life of the reaction.

Half-life for a first order reaction is

[Solution](#)

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} \text{ s}^{-1}} = 1.26 \times 10^{13} \text{ s}$$

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.

When reaction is completed 99.9%,  $[R]_n = [R]_0 - 0.999[R]_0$

[Example 3.8](#)

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

For half-life of the reaction

[Solution](#)

$$t_{1/2} = 0.693/k$$

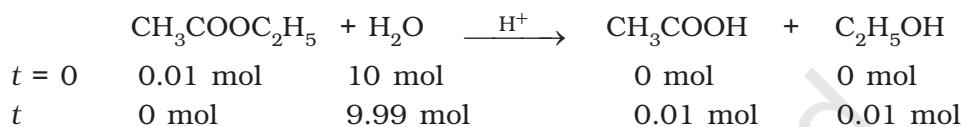
$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table 3.4 summarises the mathematical features of integrated laws of zero and first order reactions.

**Table 3.4: Integrated Rate Laws for the Reactions of Zero and First Order**

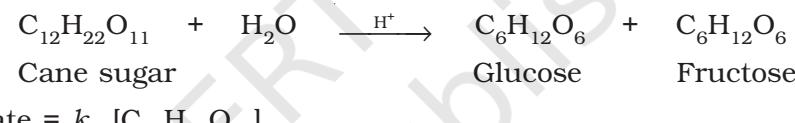
Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of $k$
0	$R \rightarrow P$	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs $t$	$[R]_0/2k$	conc time <sup>-1</sup> or mol L <sup>-1</sup> s <sup>-1</sup>
1	$R \rightarrow P$	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln([R]_0/[R])$	$\ln[R]$ vs $t$	$\ln 2/k$	time <sup>-1</sup> or s <sup>-1</sup>

The order of a reaction is sometimes altered by conditions. There are many reactions which obey first order rate law although they are higher order reactions. Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water. In reality, it is a second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction. But water is taken in large excess for hydrolysis, therefore, concentration of water is not altered much during the reaction. Thus, the rate of reaction is affected by concentration of ethyl acetate only. For example, during the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the reactants and products at the beginning ( $t = 0$ ) and completion ( $t$ ) of the reaction are given as under.



The concentration of water does not get altered much during the course of the reaction. So, 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.



$$\text{Rate} = k \cdot [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

## Intext Questions

- 3.5** A first order reaction has a rate constant  $1.15 \times 10^{-3} \text{ s}^{-1}$ . How long will 5 g of this reactant take to reduce to 3 g?

**3.6** Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

## 3.4 Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature. For example, in decomposition of  $\text{N}_2\text{O}_5$ , the time taken for half of the original amount of material to decompose is 12 min at  $50^\circ\text{C}$ , 5 h at  $25^\circ\text{C}$  and 10 days at  $0^\circ\text{C}$ . You also know that in a mixture of potassium permanganate ( $\text{KMnO}_4$ ) and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature.

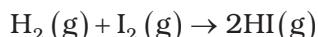
It has been found that **for a chemical reaction with rise in temperature by  $10^\circ$ , the rate constant is nearly doubled.**

The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius equation** (3.18). It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation.

$$k = A e^{-E_a/RT} \quad (3.18)$$

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 ( $J \text{ mol}^{-1}$ ).

It can be understood clearly using the following simple reaction



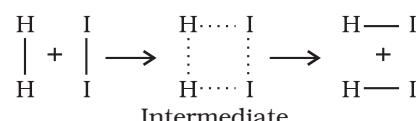
According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate (Fig. 3.6). It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

The energy required to form this intermediate, called **activated complex** ( $C$ ), is known as **activation energy** ( $E_a$ ). Fig. 3.7 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy change when reactants change into products.

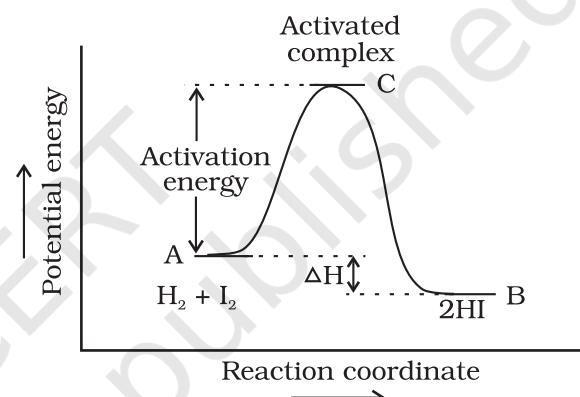
Some energy is released when the complex decomposes to form products. So, the final enthalpy of the reaction depends upon the nature of reactants and products.

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. 3.8). Here,  $N_E$  is the number of molecules with energy  $E$  and  $N_T$  is total number of molecules.

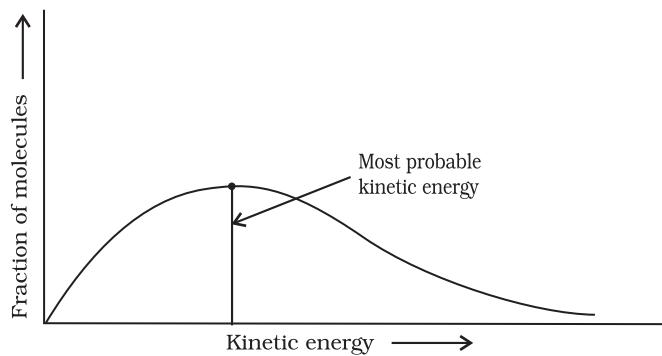
The peak of the curve corresponds to the **most probable kinetic energy**, i.e., kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the



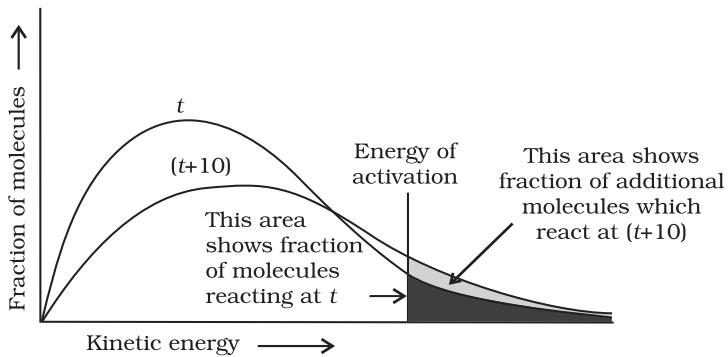
**Fig. 3.6:** Formation of  $\text{HI}$  through the intermediate



**Fig. 3.7:** Diagram showing plot of potential energy vs reaction coordinate



**Fig. 3.8:** Distribution curve showing energies among gaseous molecules



**Fig. 3.9:** Distribution curve showing temperature dependence of rate of a reaction

temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 3.9) 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. 3.9).

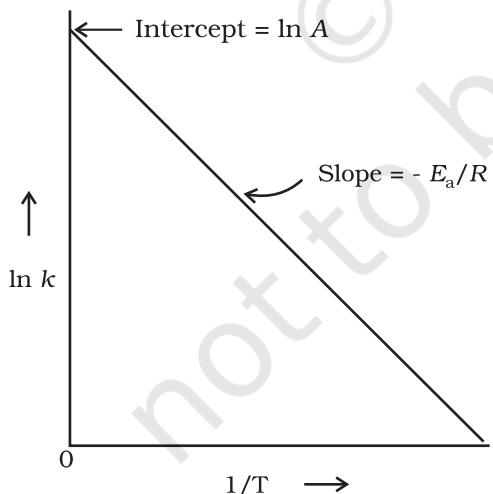
Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than  $E_a$ . It is clear from the diagram that in the curve at  $(t + 10)$ , the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (3.18) the factor  $e^{-E_a/RT}$  corresponds to the fraction of molecules that have kinetic energy greater than  $E_a$ . Taking natural logarithm of both sides of equation (3.18)

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (3.19)$$

The plot of  $\ln k$  vs  $1/T$  gives a straight line according to the equation (3.19) as shown in Fig. 3.10.

Thus, it has been found from Arrhenius equation (3.18) 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. 3.10, 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 (3.19) is

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad (3.20)$$

At temperature  $T_2$ , equation (3.19) is

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad (3.21)$$

(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.

**Fig. 3.10:** A plot between  $\ln k$  and  $1/T$

Subtracting equation (3.20) from (3.21), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (3.22)$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

**Example 3.9** The rate constants of a reaction at 500K and 700K are  $0.02\text{s}^{-1}$  and  $0.07\text{s}^{-1}$  respectively. Calculate the values of  $E_a$  and  $A$ .

**Solution**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{0.07}{0.02} = \left( \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1}} \right) \left[ \frac{700 - 500}{700 \times 500} \right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4} / 19.15$$

$$E_a = 0.544 \times 19.15 / 5.714 \times 10^{-4} = 18230.8 \text{ J}$$

Since  $k = Ae^{-E_a/RT}$

$$0.02 = Ae^{-18230.8 / 8.314 \times 500}$$

$$A = 0.02 / 0.012 = 1.61$$

**Example 3.10** The first order rate constant for the decomposition of ethyl iodide by the reaction



at 600K is  $1.60 \times 10^{-5} \text{ s}^{-1}$ . Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700K.

**Solution**

We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

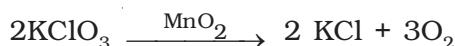
$$= \log(1.60 \times 10^{-5}) + \frac{209000 \text{ J mol L}^{-1}}{2.303 \times 8.314 \text{ J mol L}^{-1} \text{ K}^{-1}} \left[ \frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}} \right]$$

$$\log k_2 = -4.796 + 2.599 = -2.197$$

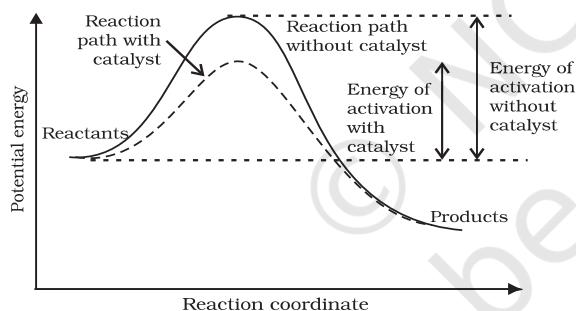
$$k_2 = 6.36 \times 10^{-3} \text{ s}^{-1}$$

### 3.4.1 Effect of Catalyst

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. For example,  $\text{MnO}_2$  catalyses the following reaction so as to increase its rate considerably.



The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibitor. 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. 3.11:** 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. 3.11.

It is clear from Arrhenius equation (3.18) 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**,  $\Delta G$  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.

## 3.5 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



rate of reaction can be expressed as

$$\text{Rate} = Z_{AB} e^{-E_a / RT} \quad (3.23)$$

where  $Z_{AB}$  represents the collision frequency of reactants, A and B and  $e^{-E_a/RT}$  represents the fraction of molecules with energies equal to or greater than  $E_a$ . Comparing (3.23) with Arrhenius equation, we can say that  $A$  is related to collision frequency.

Equation (3.23) 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**.

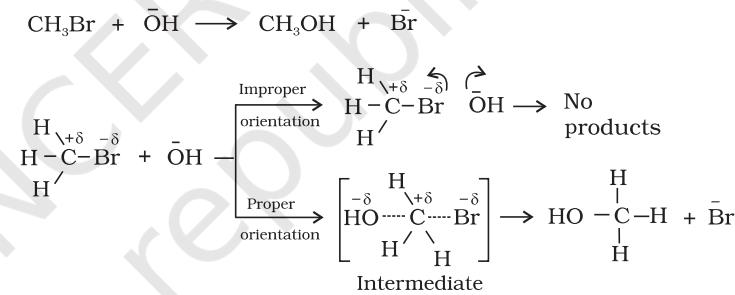
For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 3.12. The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

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.

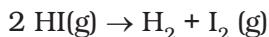


**Fig. 3.12:** Diagram showing molecules having proper and improper orientation

\* Threshold energy = Activation Energy + energy possessed by reacting species.

### **Intext Questions**

- 3.7** What will be the effect of temperature on rate constant ?
- 3.8** The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate  $E_a$ .
- 3.9** The activation energy for the reaction



is 209.5 kJ mol<sup>-1</sup> at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

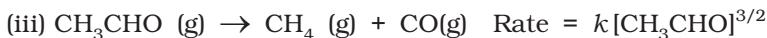
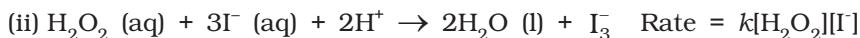
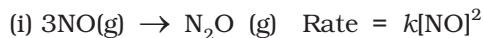
### **Summary**

**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.

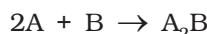
Temperature dependence of rate constants is described by Arrhenius equation ( $k = Ae^{-E_a/RT}$ ).  $E_a$  corresponds to the **activation energy** and is given by the energy difference between activated complex and the reactant molecules, and  $A$  (Arrhenius factor or pre-exponential factor) corresponds 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

- 3.1** From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.



- ### 3.2 For the reaction:



the rate =  $k[A][B]^2$  with  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ . Calculate the initial rate of the reaction when  $[A] = 0.1 \text{ mol L}^{-1}$ ,  $[B] = 0.2 \text{ mol L}^{-1}$ . Calculate the rate of reaction after  $[A]$  is reduced to  $0.06 \text{ mol L}^{-1}$ .

- 3.3** The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$ , if  $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ ?

- 3.4** The decomposition of dimethyl ether leads to the formation of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  and the reaction rate is given by

$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$$

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.,

$$\text{Rate} = k(p_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?



t/s	0	30	60	90
[A]/ mol L <sup>-1</sup>	0.55	0.31	0.17	0.085

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

- 3.9** 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?

- 3.10** 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 <sup>-1</sup>	0.20	0.20	0.40
B/ mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0/\text{mol L}^{-1}\text{s}^{-1}$	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

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

- 3.11** The following results have been obtained during the kinetic studies of the reaction:



Experiment	[A]/mol L <sup>-1</sup>	[B]/mol L <sup>-1</sup>	Initial rate of formation of D/mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Determine the rate law and the rate constant for the reaction.

- 3.12** 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 <sup>-1</sup>	[B]/ mol L <sup>-1</sup>	Initial rate/ mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$2.0 \times 10^{-2}$
II	—	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	—
IV	—	0.2	$2.0 \times 10^{-2}$

- 3.13** Calculate the half-life of a first order reaction from their rate constants given below:

(i)  $200 \text{ s}^{-1}$       (ii)  $2 \text{ min}^{-1}$       (iii)  $4 \text{ years}^{-1}$

- 3.14** The half-life for radioactive decay of  $^{14}\text{C}$  is 5730 years. An archaeological artifact containing wood had only 80% of the  $^{14}\text{C}$  found in a living tree. Estimate the age of the sample.

- 3.15** The experimental data for decomposition of  $\text{N}_2\text{O}_5$



in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

- (i) Plot  $[\text{N}_2\text{O}_5]$  against  $t$ .  
(ii) Find the half-life period for the reaction.  
(iii) Draw a graph between  $\log[\text{N}_2\text{O}_5]$  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).
- 3.16** The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value?
- 3.17** During nuclear explosion, one of the products is  $^{90}\text{Sr}$  with half-life of 28.1 years. If  $1\mu\text{g}$  of  $^{90}\text{Sr}$  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.
- 3.18** For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
- 3.19** A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{1/2}$ .
- 3.20** 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.

- 3.21** The following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume.



Experiment	Time/ $\text{s}^{-1}$	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

- 3.22** The rate constant for the decomposition of  $\text{N}_2\text{O}_5$  at various temperatures is given below:

$T/\text{ }^{\circ}\text{C}$	0	20	40	60	80
$10^5 \times k/\text{s}^{-1}$	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  $30^{\circ}$  and  $50^{\circ}\text{C}$ .

- 3.23** The rate constant for the decomposition of hydrocarbons is  $2.418 \times 10^{-5}\text{s}^{-1}$  at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.
- 3.24** Consider a certain reaction  $\text{A} \rightarrow \text{Products}$  with  $k = 2.0 \times 10^{-2}\text{s}^{-1}$ . Calculate the concentration of  $\text{A}$  remaining after 100 s if the initial concentration of  $\text{A}$  is  $1.0 \text{ mol L}^{-1}$ .
- 3.25** 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 ?
- 3.26** The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11}\text{s}^{-1}) e^{-28000K/T}$$

Calculate  $E_a$ .

- 3.27** The rate constant for the first order decomposition of  $\text{H}_2\text{O}_2$  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?
- 3.28** The decomposition of A into product has value of  $k$  as  $4.5 \times 10^3 \text{ s}^{-1}$  at  $10^\circ\text{C}$  and energy of activation  $60 \text{ kJ mol}^{-1}$ . At what temperature would  $k$  be  $1.5 \times 10^4 \text{ s}^{-1}$ ?
- 3.29** The time required for 10% completion of a first order reaction at  $298\text{K}$  is equal to that required for its 25% completion at  $308\text{K}$ . If the value of A is  $4 \times 10^{10} \text{ s}^{-1}$ . Calculate  $k$  at  $318\text{K}$  and  $E_a$ .
- 3.30** The rate of a reaction quadruples when the temperature changes from  $293 \text{ K}$  to  $313 \text{ K}$ . Calculate the energy of activation of the reaction assuming that it does not change with temperature.

#### Answers to Some Intext Questions

- 3.1**  $r_{av} = 6.66 \times 10^{-6} \text{ Ms}^{-1}$
- 3.2** Rate of reaction = rate of disappearance of A  
=  $0.005 \text{ mol litre}^{-1}\text{min}^{-1}$
- 3.3** Order of the reaction is 2.5
- 3.4**  $X \rightarrow Y$   
Rate =  $k[X]^2$   
The rate will increase 9 times
- 3.5**  $t = 444 \text{ s}$
- 3.6**  $1.925 \times 10^{-4} \text{ s}^{-1}$
- 3.8**  $E_a = 52.897 \text{ kJ mol}^{-1}$
- 3.9**  $1.471 \times 10^{-19}$



Unit

4

## 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 *f*-block consists of elements in which 4 *f* and 5 *f* orbitals are progressively filled. They are placed in a separate panel at the bottom 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 four series of the transition metals, 3*d* series (Sc to Zn), 4*d* series (Y to Cd), 5*d* series (La and Hf to Hg) and 6*d* series which has Ac and elements from Rf to Cn. The two series of the inner transition metals; 4*f* (Ce to Lu) and 5*f* (Th to Lr) are known as *lanthanoids* and *actinoids* respectively.

Originally the name transition metals was derived from the fact that their chemical properties were transitional between those of *s* and *p*-block elements. Now according to IUPAC, transition metals are defined as metals which have incomplete *d* subshell either in neutral atom or in their ions. 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 3*d*, 4*d* and 5*d* transition series, respectively, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled *d* or *f* orbitals in their atoms makes transition elements different from that of

the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non-transition elements can be applied successfully to the transition elements also.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series.

In this Unit, we shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row ( $3d$ ) transition metals along with 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)

#### **4.1 Position in the Periodic Table**

The  $d$ -block occupies the large middle section of the periodic table flanked between  $s$ - and  $p$ -blocks in the periodic table. The  $d$ -orbitals of the penultimate energy level of atoms receive electrons giving rise to four rows of the transition metals, i.e.,  $3d$ ,  $4d$ ,  $5d$  and  $6d$ . All these series of transition elements are shown in Table 4.1.

#### **4.2 Electronic Configurations of the $d$ -Block Elements**

In general the electronic configuration of outer orbitals of these elements is  $(n-1)d^{1-10}ns^{1-2}$  except for Pd where its electronic configuration is  $4d^{10}5s^0$ . The  $(n-1)$  stands for the inner  $d$  orbitals which may have one to ten electrons and the outermost  $ns$  orbital may have one or two electrons. However, this generalisation has several exceptions because of very little energy difference between  $(n-1)d$  and  $ns$  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  $3d$  series. For example, consider the case of Cr, which has  $3d^5 4s^1$  configuration instead of  $3d^4 4s^2$ ; the energy gap between the two sets ( $3d$  and  $4s$ ) of orbitals is small enough to prevent electron entering the  $3d$  orbitals. Similarly in case of Cu, the configuration is  $3d^{10} 4s^1$  and not  $3d^9 4s^2$ . The ground state electronic configurations of the outer orbitals of transition elements are given in Table 4.1.

**Table 4.1: Electronic Configurations of outer orbitals of the Transition Elements (ground state)**

1st Series											
Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
4s	2	2	2	1	2	2	2	2	1	2	
3d	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
5s	2	2	1	1	1	1	1	0	1	2
4d	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
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn 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 protrude 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 affect 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 similarities in the properties of the transition elements of a horizontal row in contrast to the non-transition elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3d row) and then consider some group similarities.

On what ground can you say that scandium ( $Z = 21$ ) is a transition element but zinc ( $Z = 30$ ) is not?

On the basis of incompletely filled 3d 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.

### Solution

### Intext Question

- 4.1 Silver atom has completely filled *d* orbitals ( $4d^{10}$ ) in its ground state. How can you say that it is a transition element?

We will discuss the properties of elements of first transition series only in the following sections.

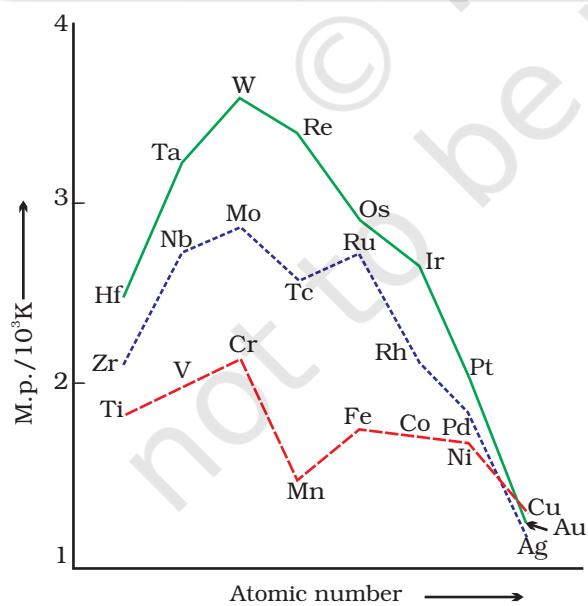
## 4.3 General Properties of the Transition Elements (*d*-Block)

### 4.3.1 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	X (bcc, ccp)	bcc (hcp)	ccp (hcp)	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



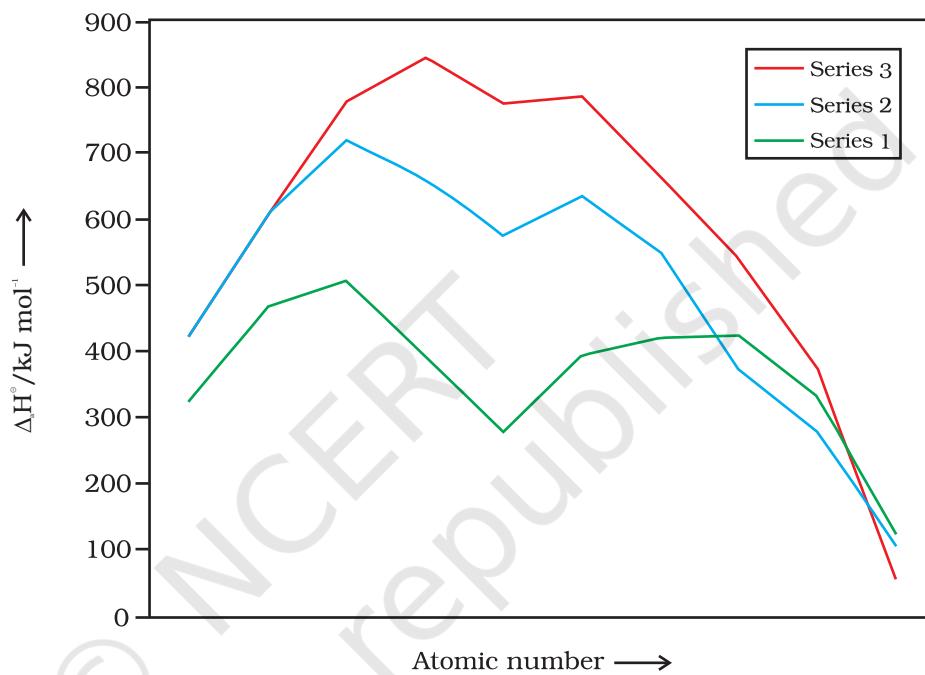
(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure).

The transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. Their melting and boiling points are high. Fig. 4.1 depicts the melting points of transition metals belonging to 3d, 4d and 5d series. 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 ns 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. 4.2. The maxima at about the middle of each series indicate that one unpaired electron per *d* orbital is particularly

Fig. 4.1: Trends in melting points of transition elements

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. 4.2 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.

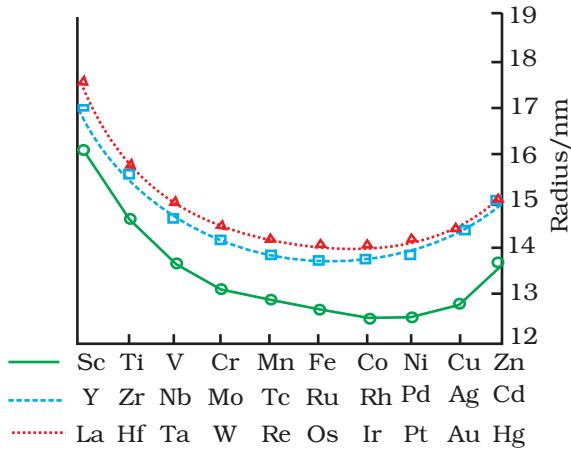


**Fig. 4.2**  
Trends in enthalpies of atomisation of transition elements

#### 4.3.2 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. 4.3 show an increase from the first ( $3d$ ) to the second ( $4d$ ) series of the elements but the radii of the third ( $5d$ ) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the  $4f$  orbitals which must be filled before the  $5d$  series of elements begin. The filling of  $4f$  before  $5d$  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. 4.3:** 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 *4f* 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 4.2).

**Table 4.2: Electronic Configurations and some other Properties of the First Series of Transition Elements**

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
<b>Atomic number</b>	21	22	23	24	25	26	27	28	29	30
<b>Electronic configuration</b>										
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]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
<b>Enthalpy of atomisation, <math>\Delta_a H^\circ/\text{kJ mol}^{-1}</math></b>										
	326	473	515	397	281	416	425	430	339	126
<b>Ionisation enthalpy/<math>\Delta_i H^\circ/\text{kJ mol}^{-1}</math></b>										
$\Delta_i H^\circ$ I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\circ$ II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\circ$ III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3837
<b>Metallic/ionic radii/pm</b>										
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	–	–
<b>Standard electrode potential <math>E^\circ/\text{V}</math></b>										
$M^{2+}/M$	–	-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	–	–	–
<b>Density/g cm<sup>-3</sup></b>										
	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

Why do the transition elements exhibit higher enthalpies of atomisation?

Example 4.2

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.

Solution

Intext Question

- 4.2** In the series Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ), the enthalpy of atomisation of zinc is the lowest, i.e.,  $126 \text{ kJ mol}^{-1}$ . Why?

**4.3.3 Ionisation Enthalpies**

There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner  $d$  orbitals. Table 4.2 gives the values of the first three ionisation enthalpies of the first series of transition elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the case of non-transition elements. The variation in ionisation enthalpy along a series of transition elements is much less in comparison to the variation along a period of non-transition elements. The first ionisation enthalpy, in general, increases, but the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, is much higher along a series.

The irregular trend in the first ionisation enthalpy of the metals of  $3d$  series, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of  $4s$  and  $3d$  orbitals. You have learnt that when  $d$ -block elements form ions,  $ns$  electrons are lost before  $(n - 1)d$  electrons. As we move along the period in  $3d$  series, we see that nuclear charge increases from scandium to zinc but electrons are added to the orbital of inner subshell, i.e.,  $3d$  orbitals. These  $3d$  electrons shield the  $4s$  electrons from the increasing nuclear charge somewhat more effectively than the outer shell electrons can shield one another. Therefore, the atomic radii decrease less rapidly. Thus, ionization energies increase only slightly along the  $3d$  series. The doubly or more highly charged ions have  $d^n$  configurations with no  $4s$  electrons. A general trend of increasing values of second ionisation enthalpy is expected as the effective nuclear charge increases because one  $d$  electron does not shield another electron from the influence of nuclear charge because  $d$ -orbitals differ in direction. However, the trend of steady increase in second and third ionisation enthalpy breaks for the formation of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  respectively. In both the cases, ions have  $d^5$  configuration. Similar breaks occur at corresponding elements in the later transition series.

The interpretation of variation in ionisation enthalpy for an electronic configuration  $d^n$  is as follows:

The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the

electrons and the exchange energy. Exchange energy is responsible for the stabilisation of energy state. Exchange energy is approximately proportional to the total number of possible pairs of parallel spins in the degenerate orbitals. When several electrons occupy a set of degenerate orbitals, the lowest energy state corresponds to the maximum possible extent of single occupation of orbital and parallel spins (Hunds rule). The loss of exchange energy increases the stability. As the stability increases, the ionisation becomes more difficult. There is no loss of exchange energy at  $d^6$  configuration.  $Mn^+$  has  $3d^54s^1$  configuration and configuration of  $Cr^+$  is  $d^5$ , therefore, ionisation enthalpy of  $Mn^+$  is lower than  $Cr^+$ . In the same way,  $Fe^{2+}$  has  $d^6$  configuration and  $Mn^{2+}$  has  $3d^5$  configuration. Hence, ionisation enthalpy of  $Fe^{2+}$  is lower than the  $Mn^{2+}$ . In other words, we can say that the third ionisation enthalpy of Fe is lower than that of Mn.

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 enthalpy is required in addition to the enthalpy of atomisation. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where  $M^+$  ions have the  $d^5$  and  $d^{10}$  configurations respectively. The value for Zn is correspondingly low as the ionisation causes the removal of one 4s electron which results in the formation of stable  $d^{10}$  configuration. The trend in the third ionisation enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the  $d^5$  ( $Mn^{2+}$ ) and  $d^{10}$  ( $Zn^{2+}$ ) ions. In general, the third ionisation enthalpies are quite high. Also the high values for third ionisation enthalpies of 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 amenable to ready generalisation.

#### 4.3.4 Oxidation States

One of the notable features of a transition elements is the great variety of oxidation states these may show in their compounds. Table 4.3 lists the common oxidation states of the first row transition elements.

**Table 4.3: Oxidation States of the first row Transition Metal (the most common ones are in bold types)**

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2	+2	+2	<b>+2</b>	<b>+2</b>	<b>+2</b>	<b>+2</b>	+1	+2
	+3	+3	<b>+3</b>	+3	<b>+3</b>	<b>+3</b>	+3	<b>+2</b>	
	<b>+4</b>	+4	+4	+4	+4	+4	+4		
			<b>+5</b>	+5	+5				
				<b>+6</b>	+6	+6			
					<b>+7</b>				

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 ( $\text{Ti}^{\text{IV}}\text{O}_2$ ,  $\text{V}^{\text{V}}\text{O}_2^+$ ,  $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ ,  $\text{Mn}^{\text{VII}}\text{O}_4^-$ ) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are  $\text{Fe}^{\text{II,III}}$ ,  $\text{Co}^{\text{II,III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{I,II}}$ ,  $\text{Zn}^{\text{II}}$ .

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.,  $\text{V}^{\text{II}}$ ,  $\text{V}^{\text{III}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{V}^{\text{V}}$ . 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  $\text{MoO}_3$  and  $\text{WO}_3$  are not.

Low oxidation states are found when a complex compound has ligands capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. For example, in  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , the oxidation state of nickel and iron is zero.

Name a transition element which does not exhibit variable [Example 4.3](#)

Scandium ( $Z = 21$ ) does not exhibit variable oxidation states.

[Solution](#)

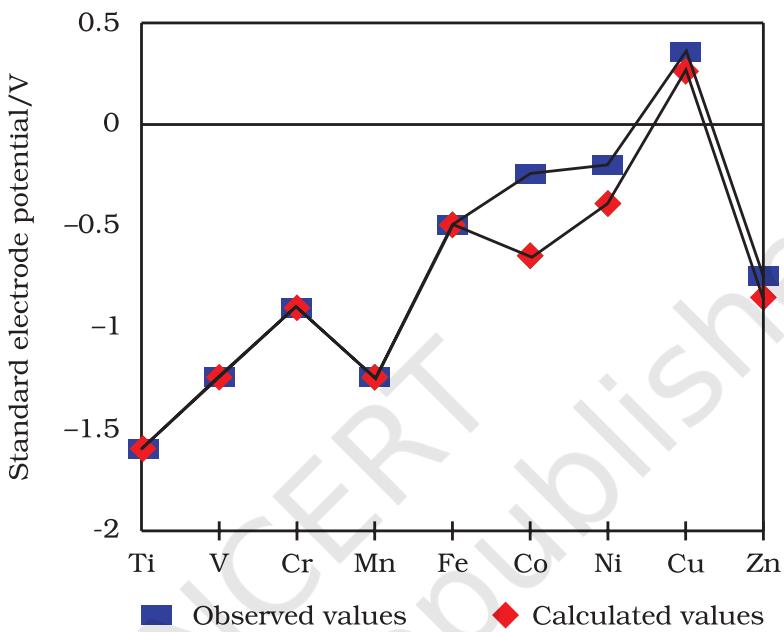
### Intext Question

- 4.3** Which of the  $3d$  series of the transition metals exhibits the largest number of oxidation states and why?

#### 4.3.5 Trends in the $M^{2+}/M$ Standard Electrode Potentials

Table 4.4 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 4.4 are compared in Fig. 4.4.

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



**Fig. 4.4:** Observed and calculated values for the standard electrode potentials ( $M^{2+} \rightarrow M^\circ$ ) of the elements Ti to Zn

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 4.4](#)

$Cr^{2+}$  is reducing as its configuration changes from  $d^4$  to  $d^3$ , the latter having a half-filled  $t_{2g}$  level (see Unit 5). On the other hand, the change from  $Mn^{3+}$  to  $Mn^{2+}$  results in the half-filled ( $d^5$ ) configuration which has extra stability.

#### Intext Question

**4.4** The  $E^\ominus(M^{2+}/M)$  value for copper is positive (+0.34V). What is possible reason for this? (Hint: consider its high  $\Delta_a H^\circ$  and low  $\Delta_{hyd} H^\circ$ )

**Table 4.4: Thermochemical data ( $\text{kJ mol}^{-1}$ ) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of  $\text{M}^{II}$  to  $\text{M}$ .**

Element (M)	$\Delta_a H^\circ (\text{M})$	$\Delta_1 H_1^\circ$	$\Delta_1 H_2^\circ$	$\Delta_{\text{hyd}} H^\circ (\text{M}^{2+})$	$E^\circ / \text{V}$
Ti	469	656	1309	-1866	-1.63
V	515	650	1414	-1895	-1.18
Cr	398	653	1592	-1925	-0.90
Mn	279	717	1509	-1862	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121	-0.25
Cu	339	745	1958	-2121	0.34
Zn	130	906	1734	-2059	-0.76

The stability of the half-filled  $d$  sub-shell in  $\text{Mn}^{2+}$  and the completely filled  $d^{10}$  configuration in  $\text{Zn}^{2+}$  are related to their  $E^\circ$  values, whereas  $E^\circ$  for Ni is related to the highest negative  $\Delta_{\text{hyd}} H^\circ$ .

#### 4.3.6 Trends in the $\text{M}^{3+}/\text{M}^{2+}$ Standard Electrode Potentials

An examination of the  $E^\circ(\text{M}^{3+}/\text{M}^{2+})$  values (Table 4.2) shows the varying trends. The low value for Sc reflects the stability of  $\text{Sc}^{3+}$  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  $\text{Zn}^{2+}$ . The comparatively high value for Mn shows that  $\text{Mn}^{2+}(d^5)$  is particularly stable, whereas comparatively low value for Fe shows the extra stability of  $\text{Fe}^{3+}(d^5)$ . The comparatively low value for V is related to the stability of  $\text{V}^{2+}$  (half-filled  $t_{2g}$  level, Unit 5).

#### 4.3.7 Trends in Stability of Higher Oxidation States

Table 4.5 shows the stable halides of the 3d series of transition metals. The highest oxidation numbers are achieved in  $\text{TiX}_4$  (tetrahalides),  $\text{VF}_5$  and  $\text{CrF}_6$ . The +7 state for Mn is not represented in simple halides but  $\text{MnO}_3\text{F}$  is known, and beyond Mn no metal has a trihalide except  $\text{FeX}_3$  and  $\text{CoF}_3$ . The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of  $\text{CoF}_3$ , or higher bond enthalpy terms for the higher covalent compounds, e.g.,  $\text{VF}_5$  and  $\text{CrF}_6$ .

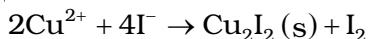
Although  $\text{V}^{+5}$  is represented only by  $\text{VF}_5$ , the other halides, however, undergo hydrolysis to give oxohalides,  $\text{VOX}_3$ . Another feature of fluorides is their instability in the low oxidation states e.g.,  $\text{VX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ )

**Table 4.5: Formulas of Halides of 3d Metals**

Oxidation Number								
+ 6				$\text{CrF}_6$				
+ 5		$\text{VF}_5$		$\text{CrF}_5$				
+ 4	$\text{TiX}_4$	$\text{VX}_4$	$\text{CrX}_4$	$\text{MnF}_4$				
+ 3	$\text{TiX}_{3\text{III}}$	$\text{VX}_3$	$\text{CrX}_3$	$\text{MnF}_3$	$\text{FeX}_3^{\text{I}}$	$\text{CoF}_3$		
+ 2	$\text{TiX}_2^{\text{III}}$	$\text{VX}_2$	$\text{CrX}_2$	$\text{MnX}_2$	$\text{FeX}_2$	$\text{CoX}_2$	$\text{NiX}_2$	$\text{CuX}_2^{\text{II}}$
+ 1								$\text{ZnX}_2$
								$\text{CuX}^{\text{III}}$

Key:  $\text{X} = \text{F} \rightarrow \text{I}$ ;  $\text{X}^{\text{I}}$  = F → Br;  $\text{X}^{\text{II}}$  = F, Cl;  $\text{X}^{\text{III}}$  = Cl → I

and the same applies to CuX. On the other hand, all Cu<sup>II</sup> halides are known except the iodide. In this case, Cu<sup>2+</sup> oxidises I<sup>-</sup> to I<sub>2</sub>:



However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



The stability of Cu<sup>2+</sup> (aq) rather than Cu<sup>+</sup>(aq) is due to the much more negative  $\Delta_{\text{hyd}}H^\circ$  of Cu<sup>2+</sup> (aq) than Cu<sup>+</sup>, 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 4.6) coincides with the group number and is attained in Sc<sub>2</sub>O<sub>3</sub> to Mn<sub>2</sub>O<sub>7</sub>. Beyond Group 7, no higher oxides of Fe above Fe<sub>2</sub>O<sub>3</sub>, are known, although ferrates (VI)(FeO<sub>4</sub>)<sup>2-</sup>, are formed in alkaline media but they readily decompose to Fe<sub>2</sub>O<sub>3</sub> and O<sub>2</sub>. Besides the oxides, oxocations stabilise V<sup>v</sup> as VO<sub>2</sub><sup>+</sup>, V<sup>IV</sup> as VO<sup>2+</sup> and Ti<sup>IV</sup> as TiO<sup>2+</sup>. The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF<sub>4</sub> whereas the highest oxide is Mn<sub>2</sub>O<sub>7</sub>. The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide Mn<sub>2</sub>O<sub>7</sub>, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The tetrahedral [MO<sub>4</sub>]<sup>4-</sup> ions are known for V<sup>v</sup>, Cr<sup>VI</sup>, Mn<sup>v</sup>, Mn<sup>VI</sup> and Mn<sup>VII</sup>.

Table 4.6: Oxides of 3d Metals

Oxidation Number	Groups									
	3	4	5	6	7	8	9	10	11	12
+ 7					Mn <sub>2</sub> O <sub>7</sub>					
+ 6				CrO <sub>3</sub>						
+ 5			V <sub>2</sub> O <sub>5</sub>							
+ 4		TiO <sub>2</sub>	V <sub>2</sub> O <sub>4</sub>	CrO <sub>2</sub>	MnO <sub>2</sub>					
+ 3	Sc <sub>2</sub> O <sub>3</sub>	Ti <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>				
					Mn <sub>3</sub> O <sub>4</sub> <sup>*</sup>	Fe <sub>3</sub> O <sub>4</sub> <sup>*</sup>	Co <sub>3</sub> O <sub>4</sub> <sup>*</sup>			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1										Cu <sub>2</sub> O

\* mixed oxides

How would you account for the increasing oxidising power in the [Example 4.5](#) series VO<sub>2</sub><sup>+</sup> < Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> < MnO<sub>4</sub><sup>-</sup>?

This is due to the increasing stability of the lower species to which they [Solution](#) are reduced.

### Intext Question

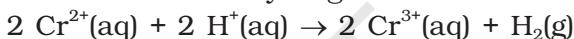
**4.5** How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements?

### 4.3.8 Chemical Reactivity and $E^\circ$ 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 single 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  $E^\circ$  values for  $M^{2+}/M$  (Table 4.2) indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative  $E^\circ$  values is related to the increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the  $E^\circ$  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  $E^\circ$  values; for nickel,  $E^\circ$  value is related to the highest negative enthalpy of hydration.

An examination of the  $E^\circ$  values for the redox couple  $M^{3+}/M^{2+}$  (Table 4.2) 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.,



#### Example 4.6

For the first row transition metals the  $E^\circ$  values are:

$E^\circ$ ( $M^{2+}/M$ )	V	Cr	Mn	Fe	Co	Ni	Cu
-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	

Explain the irregularity in the above values.

#### Solution

The  $E^\circ$  ( $M^{2+}/M$ ) 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 4.7

Why is the  $E^\circ$  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

4.6 Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

4.7 Which is a stronger reducing agent  $Cr^{2+}$  or  $Fe^{2+}$  and why ?

### 4.3.9 Magnetic Properties

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism* and *paramagnetism*. 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  $\mu$  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 4.7. The experimental data are mainly for hydrated ions in solution or in the solid state.

**Table 4.7: Calculated and Observed Magnetic Moments (BM)**

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc <sup>3+</sup>	3d <sup>0</sup>	0	0	0
Ti <sup>3+</sup>	3d <sup>1</sup>	1	1.73	1.75
Tl <sup>2+</sup>	3d <sup>2</sup>	2	2.84	2.76
V <sup>2+</sup>	3d <sup>3</sup>	3	3.87	3.86
Cr <sup>2+</sup>	3d <sup>4</sup>	4	4.90	4.80
Mn <sup>2+</sup>	3d <sup>5</sup>	5	5.92	5.96
Fe <sup>2+</sup>	3d <sup>6</sup>	4	4.90	5.3 – 5.5
Co <sup>2+</sup>	3d <sup>7</sup>	3	3.87	4.4 – 5.2
Ni <sup>2+</sup>	3d <sup>8</sup>	2	2.84	2.9 – 3, 4
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73	1.8 – 2.2
Zn <sup>2+</sup>	3d <sup>10</sup>	0	0	

Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

#### Example 4.8

With atomic number 25, the divalent ion in aqueous solution will have  $d^5$  configuration (five unpaired electrons). The magnetic moment,  $\mu$  is

#### Solution

$$\mu = \sqrt{5(5+2)} = 5.92 \text{ BM}$$

### **Intext Question**

**4.8** Calculate the ‘spin only’ magnetic moment of  $M^{2+}_{(aq)}$  ion ( $Z = 27$ ).

#### **4.3.10 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 5). 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 4.8. A few coloured solutions of  $d$ -block elements are illustrated in Fig. 4.5.



**Fig. 4.5:** 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 4.8: 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
$3d^63d^7$	$Co^{3+}Co^{2+}$	bluepink
$3d^8$	$Ni^{2+}$	green
$3d^9$	$Cu^{2+}$	blue
$3d^{10}$	$Zn^{2+}$	colourless

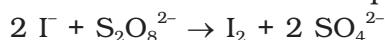
#### **4.3.11 Formation of Complex Compounds**

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

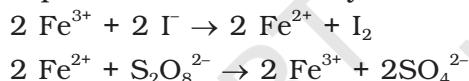
dealt with in detail in Unit 5). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

#### 4.3.12 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.



An explanation of this catalytic action can be given as:



#### 4.3.13 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<sub>4</sub>N, Fe<sub>3</sub>H, VH<sub>0.56</sub> and TiH<sub>1.7</sub>, 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.

#### 4.3.14 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 4.Q** 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.



### Intext Question

**4.9** Explain why  $\text{Cu}^+$  ion is not stable in aqueous solutions?

## 4.4 Some Important Compounds of Transition Elements

### 4.4.1 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  $\text{Sc}_2\text{O}_3$  to  $\text{Mn}_2\text{O}_7$ . Beyond group 7, no higher oxides of iron above  $\text{Fe}_2\text{O}_3$  are known. Besides the oxides, the oxocations stabilise V<sup>V</sup> as  $\text{VO}_2^+$ , V<sup>IV</sup> as  $\text{VO}^{2+}$  and Ti<sup>IV</sup> as  $\text{TiO}^{2+}$ .

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn,  $\text{Mn}_2\text{O}_7$  is a covalent green oil. Even  $\text{CrO}_3$  and  $\text{V}_2\text{O}_5$  have low melting points. In these higher oxides, the acidic character is predominant.

Thus,  $\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$  and  $\text{CrO}_3$  gives  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ .  $\text{V}_2\text{O}_5$  is, however, amphoteric though mainly acidic and it gives  $\text{VO}_4^{3-}$  as well as  $\text{VO}_2^+$  salts. In vanadium there is gradual change from the basic  $\text{V}_2\text{O}_3$  to less basic  $\text{V}_2\text{O}_4$  and to amphoteric  $\text{V}_2\text{O}_5$ .  $\text{V}_2\text{O}_4$  dissolves in acids to give  $\text{VO}^{2+}$  salts. Similarly,  $\text{V}_2\text{O}_5$  reacts with alkalies as well as acids to give  $\text{VO}_4^{3-}$  and  $\text{VO}_4^+$  respectively. The well characterised  $\text{CrO}$  is basic but  $\text{Cr}_2\text{O}_3$  is amphoteric.

#### **Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$**

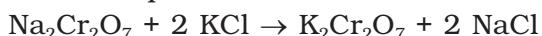
Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ( $\text{FeCr}_2\text{O}_4$ ) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:



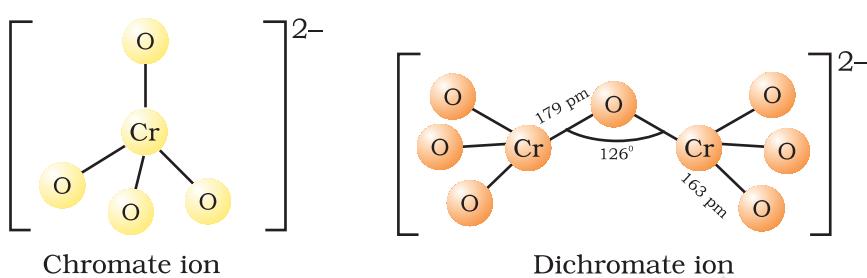
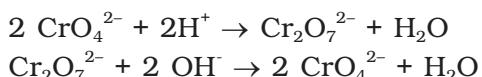
The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  can be crystallised.



Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.



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.



The structures of chromate ion,  $\text{CrO}_4^{2-}$  and the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$  are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with  $\text{Cr}-\text{O}-\text{Cr}$  bond angle of  $126^\circ$ .

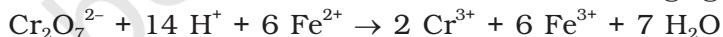
Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:



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:

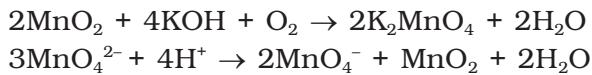


The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

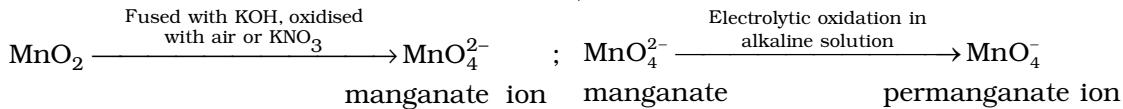


#### Potassium permanganate $\text{KMnO}_4$

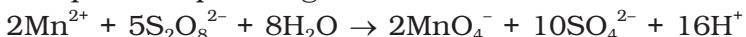
Potassium permanganate is prepared by fusion of  $\text{MnO}_2$  with an alkali metal hydroxide and an oxidising agent like  $\text{KNO}_3$ . This produces the dark green  $\text{K}_2\text{MnO}_4$  which disproportionates in a neutral or acidic solution to give permanganate.



Commercially it is prepared by the alkaline oxidative fusion of  $\text{MnO}_2$  followed by the electrolytic oxidation of manganate (VI).



In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.



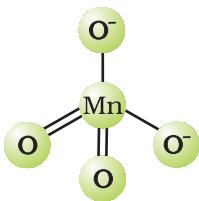
Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of  $\text{KClO}_4$ . The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.



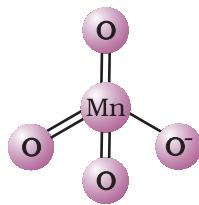
It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.

The manganate and permanganate ions are tetrahedral; the  $\pi$ -bonding takes place by overlap of  $p$  orbitals of oxygen with  $d$  orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.

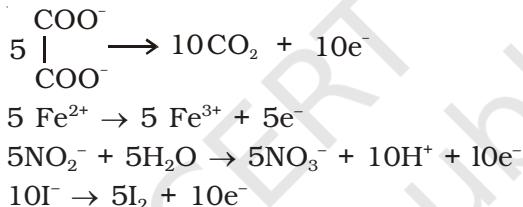
Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:



Tetrahedral manganate ion (green)

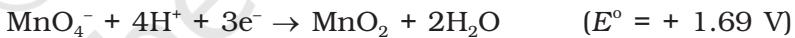


Tetrahedral permanganate ion (purple)



The full reaction can be written by adding the half-reaction for  $\text{KMnO}_4$  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,

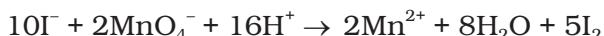


We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at  $[\text{H}^+] = 1$  should oxidise water but in practice the reaction is extremely slow unless either manganese(II) ions are present or the temperature is raised.

A few important oxidising reactions of  $\text{KMnO}_4$  are given below:

#### 1. In acid solutions:

(a) Iodine is liberated from potassium iodide :



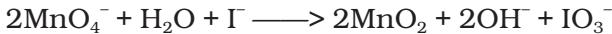
(b)  $\text{Fe}^{2+}$  ion (green) is converted to  $\text{Fe}^{3+}$  (yellow):



- (c) Oxalate ion or oxalic acid is oxidised at 333 K:
- $$5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$$
- (d) Hydrogen sulphide is oxidised, sulphur being precipitated:
- $$\text{H}_2\text{S} \longrightarrow 2\text{H}^+ + \text{S}^{2-}$$
- $$5\text{S}^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$$
- (e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:
- $$5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$$
- (f) Nitrite is oxidised to nitrate:
- $$5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$$

## 2. In neutral or faintly alkaline solutions:

- (a) A notable reaction is the oxidation of iodide to iodate:



- (b) Thiosulphate is oxidised almost quantitatively to sulphate:



- (c) Manganese salt is oxidised to  $\text{MnO}_2$ ; the presence of zinc sulphate or zinc oxide catalyses the oxidation:



**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.

## 4.5 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 4.9.

#### 4.5.1 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 4.9). 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).

#### 4.5.2 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.

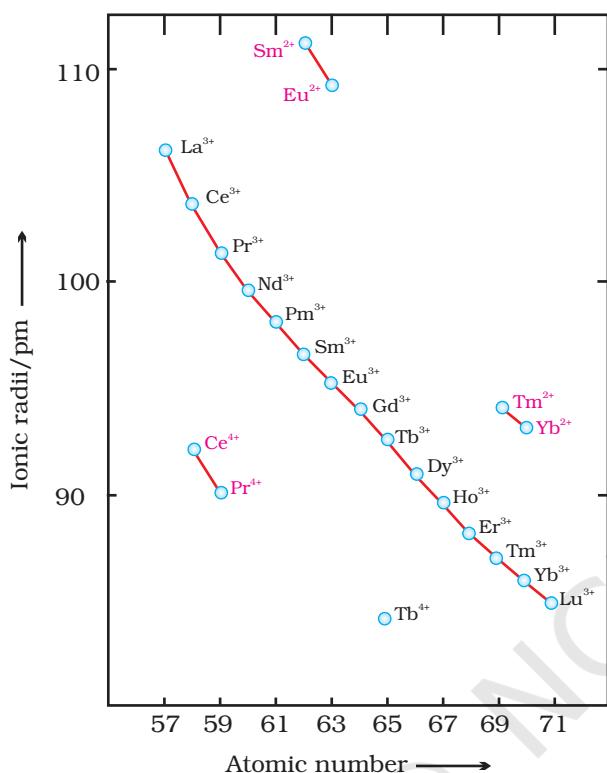
The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in  $M^{3+}$  ions (Fig. 4.6). This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron 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.

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.

Fig. 4.6: Trends in ionic radii of lanthanoids

#### 4.5.3 Oxidation States

In the lanthanoids, La(II) 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  $E^\circ$  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 4.9: Electronic Configurations and Radii of Lanthanum and Lanthanoids**

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm		
			Ln	Ln <sup>2+</sup>	Ln <sup>3+</sup>	Ln <sup>4+</sup>	Ln	Ln <sup>3+</sup>
57	Lanthanum	La	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>1</sup>	4f <sup>0</sup>		187	106
58	Cerium	Ce	4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>2</sup>	4f <sup>1</sup>	4f <sup>0</sup>	183	103
59	Praseodymium	Pr	4f <sup>3</sup> 6s <sup>2</sup>	4f <sup>3</sup>	4f <sup>2</sup>	4f <sup>1</sup>	182	101
60	Neodymium	Nd	4f <sup>4</sup> 6s <sup>2</sup>	4f <sup>4</sup>	4f <sup>3</sup>	4f <sup>2</sup>	181	99
61	Promethium	Pm	4f <sup>5</sup> 6s <sup>2</sup>	4f <sup>5</sup>	4f <sup>4</sup>		181	98
62	Samarium	Sm	4f <sup>6</sup> 6s <sup>2</sup>	4f <sup>6</sup>	4f <sup>5</sup>		180	96
63	Europium	Eu	4f <sup>7</sup> 6s <sup>2</sup>	4f <sup>7</sup>	4f <sup>6</sup>		199	95
64	Gadolinium	Gd	4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>7</sup>		180	94
65	Terbium	Tb	4f <sup>9</sup> 6s <sup>2</sup>	4f <sup>9</sup>	4f <sup>8</sup>	4f <sup>7</sup>	178	92
66	Dysprosium	Dy	4f <sup>10</sup> 6s <sup>2</sup>	4f <sup>10</sup>	4f <sup>9</sup>	4f <sup>8</sup>	177	91
67	Holmium	Ho	4f <sup>11</sup> 6s <sup>2</sup>	4f <sup>11</sup>	4f <sup>10</sup>		176	89
68	Erbium	Er	4f <sup>12</sup> 6s <sup>2</sup>	4f <sup>12</sup>	4f <sup>11</sup>		175	88
69	Thulium	Tm	4f <sup>13</sup> 6s <sup>2</sup>	4f <sup>13</sup>	4f <sup>12</sup>		174	87
70	Ytterbium	Yb	4f <sup>14</sup> 6s <sup>2</sup>	4f <sup>14</sup>	4f <sup>13</sup>		173	86
71	Lutetium	Lu	4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>14</sup> 5d <sup>1</sup>	4f <sup>14</sup>	—	—	—

\* Only electrons outside [Xe] core are indicated

#### 4.5.4 General Characteristics

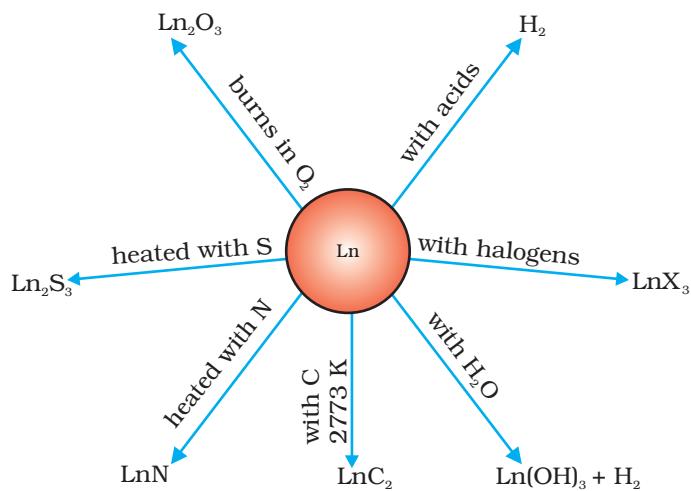
All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of 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<sup>3+</sup> nor Lu<sup>3+</sup> 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<sup>0</sup> type (La<sup>3+</sup> and Ce<sup>4+</sup>) and the f<sup>14</sup> type (Yb<sup>2+</sup> and Lu<sup>3+</sup>) are all paramagnetic.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol<sup>-1</sup>, the second about 1200 kJ mol<sup>-1</sup> comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3d 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° for the half-reaction:





**Fig 4.7:** 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,  $\text{Ln}_3\text{C}$ ,  $\text{Ln}_2\text{C}_3$  and  $\text{LnC}_2$  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  $\text{M}_2\text{O}_3$  and hydroxides  $\text{M}(\text{OH})_3$ . 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. 4.7.

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.

## 4.6 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 4.10.

**Table 4.10: Some Properties of Actinium and Actinoids**

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm	
			M	$\text{M}^{3+}$	$\text{M}^{4+}$	$\text{M}^{3+}$	$\text{M}^{4+}$
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	$5f^76d^17s^2$	$5f^7$	$5f^6$	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.

#### 4.6.1 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  $5f$ , though not in thorium ( $Z = 90$ ) but from Pa onwards the  $5f$  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  $[Rn] 5f^6 6d^1 7s^2$ . Although the  $5f$  orbitals resemble the  $4f$  orbitals in their angular part of the wave-function, they are not as buried as  $4f$  orbitals and hence  $5f$  electrons can participate in bonding to a far greater extent.

#### 4.6.2 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  $5f$  electrons.

#### 4.6.3 Oxidation States

There is a greater range of oxidation states, which is in part attributed to the fact that the  $5f$ ,  $6d$  and  $7s$  levels are of comparable energies. The known oxidation states of actinoids are listed in Table 4.11.

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 4.11). 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 former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

Table 4.11: Oxidation States of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	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										

#### 4.6.4 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  $5f$  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  $5f$  orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The  $5f$  electrons, will therefore, be more effectively shielded from the nuclear charge than the  $4f$  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 4.10** Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

**Solution** Cerium ( $Z = 58$ )

#### **Intext Question**

- 4.10** Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

## **4.7 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  $TiO_2$  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, *4f* and *5f* orbitals are progressively filled.

Corresponding to the filling of *3d*, *4d* and *5d* 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, *4f*, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (**lanthanoid contraction**). This has far reaching 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

- 4.16** Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii)  $\text{SO}_2$  and (iii) oxalic acid? Write the ionic equations for the reactions.
- 4.17** For  $M^{2+}/M$  and  $M^{3+}/M^{2+}$  systems the  $E^\circ$  values for some metals are as follows:
- |                            |       |                                 |        |
|----------------------------|-------|---------------------------------|--------|
| $\text{Cr}^{2+}/\text{Cr}$ | -0.9V | $\text{Cr}^3/\text{Cr}^{2+}$    | -0.4 V |
| $\text{Mn}^{2+}/\text{Mn}$ | -1.2V | $\text{Mn}^{3+}/\text{Mn}^{2+}$ | +1.5 V |
| $\text{Fe}^{2+}/\text{Fe}$ | -0.4V | $\text{Fe}^3/\text{Fe}^{2+}$    | +0.8 V |
- Use this data to comment upon:
- the stability of  $\text{Fe}^{3+}$  in acid solution as compared to that of  $\text{Cr}^{3+}$  or  $\text{Mn}^{3+}$  and
  - the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.
- 4.18** Predict which of the following will be coloured in aqueous solution?  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Sc}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$ . Give reasons for each.
- 4.19** Compare the stability of +2 oxidation state for the elements of the first transition series.
- 4.20** Compare the chemistry of actinoids with that of the lanthanoids with special reference to:
- electronic configuration
  - atomic and ionic sizes and
  - oxidation state
  - chemical reactivity.
- 4.21** How would you account for the following:
- Of the  $d^4$  species,  $\text{Cr}^{2+}$  is strongly reducing while manganese(III) is strongly oxidising.
  - Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
  - The  $d^1$  configuration is very unstable in ions.
- 4.22** What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.
- 4.23** Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
- 4.24** Calculate the number of unpaired electrons in the following gaseous ions:  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$  and  $\text{Ti}^{3+}$ . Which one of these is the most stable in aqueous solution?
- 4.25** Give examples and suggest reasons for the following features of the transition metal chemistry:
- The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
  - A transition metal exhibits highest oxidation state in oxides and fluorides.
  - The highest oxidation state is exhibited in oxoanions of a metal.
- 4.26** Indicate the steps in the preparation of:
- $\text{K}_2\text{Cr}_2\text{O}_7$  from chromite ore.
  - $\text{KMnO}_4$  from pyrolusite ore.
- 4.27** What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.
- 4.28** 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.
- 4.29** 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.
- 4.30** 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.

- 4.31** Use Hund's rule to derive the electronic configuration of  $\text{Ce}^{3+}$  ion, and calculate its magnetic moment on the basis of 'spin-only' formula.
- 4.32** 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.
- 4.33** Compare the chemistry of the actinoids with that of lanthanoids with reference to:  
(i) electronic configuration (ii) oxidation states and (iii) chemical reactivity.
- 4.34** Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.
- 4.35** 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.
- 4.36** Write down the number of 3d electrons in each of the following ions:  $\text{Ti}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).
- 4.37** Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.
- 4.38** What can be inferred from the magnetic moment values of the following complex species ?

Example	Magnetic Moment (BM)
$\text{K}_4[\text{Mn}(\text{CN})_6]$	2.2
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	5.3
$\text{K}_2[\text{MnCl}_4]$	5.9

#### Answers to Some Intext Questions

- 4.1** Silver ( $Z = 47$ ) can exhibit +2 oxidation state wherein it will have incompletely filled  $d$ -orbitals ( $4d$ ), hence a transition element.
- 4.2** In the formation of metallic bonds, no electrons from  $3d$ -orbitals are involved in case of zinc, while in all other metals of the  $3d$  series, electrons from the  $d$ -orbitals are always involved in the formation of metallic bonds.
- 4.3** Manganese ( $Z = 25$ ), as its atom has the maximum number of unpaired electrons.
- 4.5** Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different  $3d$ -configurations (e.g.,  $d^0$ ,  $d^5$ ,  $d^{10}$  are exceptionally stable).
- 4.6** Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.
- 4.7**  $\text{Cr}^{2+}$  is stronger reducing agent than  $\text{Fe}^{2+}$   
Reason:  $d^4 \rightarrow d^3$  occurs in case of  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$   
But  $d^6 \rightarrow d^5$  occurs in case of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
In a medium (like water)  $d^3$  is more stable as compared to  $d^5$  (see CFSE)
- 4.9**  $\text{Cu}^+$  in aqueous solution undergoes disproportionation, i.e.,  
 $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$   
The  $E^\circ$  value for this is favourable.
- 4.10** The  $5f$  electrons are more effectively shielded from nuclear charge. In other words the  $5f$  electrons themselves provide poor shielding from element to element in the series.



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## 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;
- appreciate the importance and applications of coordination compounds in our day to day life.

# Unit 5

## Coordination Compounds

*Coordination Compounds are the backbone of modern inorganic and bio-inorganic chemistry and chemical industry.*

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 by sharing of electrons. 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 these compounds as vital components of biological systems. Chlorophyll, haemoglobin and vitamin B<sub>12</sub> 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.

### 5.1 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<sub>3</sub>, CoCl<sub>2</sub> or PdCl<sub>2</sub> 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	$\text{CoCl}_3 \cdot 6\text{NH}_3$ (Yellow)	gave	3 mol $\text{AgCl}$
1 mol	$\text{CoCl}_3 \cdot 5\text{NH}_3$ (Purple)	gave	2 mol $\text{AgCl}$
1 mol	$\text{CoCl}_3 \cdot 4\text{NH}_3$ (Green)	gave	1 mol $\text{AgCl}$
1 mol	$\text{CoCl}_3 \cdot 4\text{NH}_3$ (Violet)	gave	1 mol $\text{AgCl}$

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 5.1, 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 5.1: Formulation of Cobalt(III) Chloride-Ammonia Complexes**

Colour	Formula	Solution conductivity corresponds to
Yellow	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	1:3 electrolyte
Purple	$[\text{CoCl}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	1:2 electrolyte
Green	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1 electrolyte
Violet	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1 electrolyte

Note that the last two compounds in Table 5.1 have identical empirical formula,  $\text{CoCl}_3 \cdot 4\text{NH}_3$ , 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,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  and  $[\text{CoCl}_2(\text{NH}_3)_4]^+$  are octahedral entities, while  $[\text{Ni}(\text{CO})_4]$  and  $[\text{PtCl}_4]^{2-}$  are tetrahedral and square planar, respectively.

On the basis of the following observations made with aqueous solutions, Example 5.1 assign secondary valences to metals in the following compounds:

Formula	Moles of AgCl precipitated per mole of the compounds with excess AgNO <sub>3</sub>
(i) PdCl <sub>2</sub> .4NH <sub>3</sub>	2
(ii) NiCl <sub>2</sub> .6H <sub>2</sub> O	2
(iii) PtCl <sub>4</sub> .2HCl	0
(iv) CoCl <sub>3</sub> .4NH <sub>3</sub>	1
(v) PtCl <sub>2</sub> .2NH <sub>3</sub>	0

(i) Secondary 4  
(iii) Secondary 6

(ii) Secondary 6  
(iv) Secondary 6

Solution  
(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<sub>2</sub>.6H<sub>2</sub>O, Mohr's salt, FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O, potash alum, KAl(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as [Fe(CN)<sub>6</sub>]<sup>4-</sup> of K<sub>4</sub>[Fe(CN)<sub>6</sub>] do not dissociate into Fe<sup>2+</sup> and CN<sup>-</sup> 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 van't 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.

## 5.2 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,  $[\text{CoCl}_3(\text{NH}_3)_3]$  is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{PtCl}_2(\text{NH}_3)_2]$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

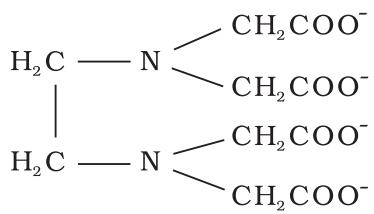
**(b) Central atom/ion**

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:  $[\text{NiCl}_2(\text{H}_2\text{O})_4]$ ,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{Fe}^{3+}$ , respectively. These central atoms/ions are also referred to as **Lewis acids**.

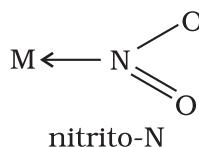
### (c) Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as  $\text{Cl}^-$ , small molecules such as  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , larger molecules such as  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  or  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$  or even macromolecules, such as proteins.

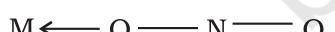
When a ligand is bound to a metal ion through a single donor atom, as with  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the ligand is said to be **unidentate**.



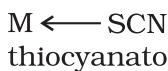
When a ligand can bind through two donor atoms as in  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethane-1,2-diamine) or  $\text{C}_2\text{O}_4^{2-}$  (oxalate), the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ , the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ( $\text{EDTA}^{4-}$ ) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.



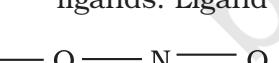
### **nitrito-N**



## **nitrito-O**



M ← SCN  
thiocyanato



When a di- or polydentate ligand uses its two or more donor atoms simultaneously 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. Ligand which has two different donor atoms and either of

the two ligates in the complex is called **ambidentate ligand**. Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}_2^-$  ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.

Similarly,  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom.

#### **(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,  $[\text{PtCl}_6]^{2-}$  and  $[\text{Ni}(\text{NH}_3)_4]^{2+}$ , the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Co}(\text{en})_3]^{3+}$ , the coordination number of both, Fe and Co, is 6 because  $\text{C}_2\text{O}_4^{2-}$  and en (ethane-1,2-diamine) are didentate ligands.

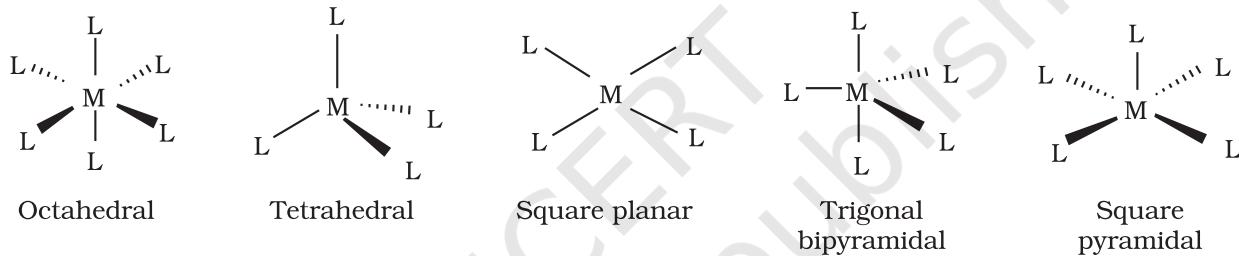
It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

#### (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  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , the coordination sphere is  $[\text{Fe}(\text{CN})_6]^{4-}$  and the counter ion is  $\text{K}^+$ .

#### (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,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is octahedral,  $[\text{Ni}(\text{CO})_4]$  is tetrahedral and  $[\text{PtCl}_4]^{2-}$  is square planar. Fig. 5.1 shows the shapes of different coordination polyhedra.



**Fig. 5.1:** 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  $[\text{Cu}(\text{CN})_4]^{3-}$  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.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g.,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ , are known as heteroleptic.

### 5.3 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).

### 5.3.1 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,  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , 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.

### 5.3.2 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  $\text{H}_2\text{O}$ , ammine for  $\text{NH}_3$ , carbonyl for  $\text{CO}$  and nitrosyl for  $\text{NO}$ . While writing the formula of coordination entity, these are enclosed in brackets ( ).
- (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,  $[\text{NiCl}_2(\text{PPh}_3)_2]$  is named as dichloridobis(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,  $[\text{Co}(\text{SCN})_4]^{2-}$  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.  $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  is named as:  
triaminetriaquachromium(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.  $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]_2(\text{SO}_4)_3$  is named as:  
tris(ethane-1,2-diamine)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.

3.  $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$  is named as:  
diamminesilver(I) dicyanidoargentate(I)

Notice how the name of the metal differs in cation and anion even though they contain the same metal ions.

**Example 5.2** Write the formulas for the following coordination compounds:

- Tetraammineaquachloridocobalt(III) chloride
- Potassium tetrahydroxidozincate(II)
- Potassium trioxalatoaluminate(III)
- Dichloridobis(ethane-1,2-diamine)cobalt(III)
- Tetracarbonylnickel(0)

**Solution** (a)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$       (b)  $\text{K}_2[\text{Zn}(\text{OH})_4]$       (c)  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$   
(d)  $[\text{CoCl}_2(\text{en})_2]^+$       (e)  $[\text{Ni}(\text{CO})_4]$

**Example 5.3** Write the IUPAC names of the following coordination compounds:

- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
- $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
- $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
- $\text{Hg}[\text{Co}(\text{SCN})_4]$

**Solution** (a) Diamminechloridonitrito-N-platinum(II)  
(b) Potassium trioxalatochromate(III)  
(c) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride  
(d) Pentaamminecarbonatocobalt(III) chloride  
(e) Mercury (I) tetrathiocyanato-S-cobaltate(III)

## Intext Questions

**5.1** Write the formulas for the following coordination compounds:

- (i) Tetraamminediaquacobalt(III) chloride
- (ii) Potassium tetracyanidonickelate(II)
- (iii) Tris(ethane-1,2-diamine) chromium(III) chloride
- (iv) Amminebromidochloridonitrito-N-platinato(II)
- (v) Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate
- (vi) Iron(III) hexacyanidoferate(II)

**5.2** Write the IUPAC names of the following coordination compounds:

- |  |   |   |
|--|---|---|
| (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$          | (ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ | (iii) $\text{K}_3[\text{Fe}(\text{CN})_6]$                                  |
| (iv) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ | (v) $\text{K}_2[\text{PdCl}_4]$                       | (vi) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$ |

## 5.4 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**

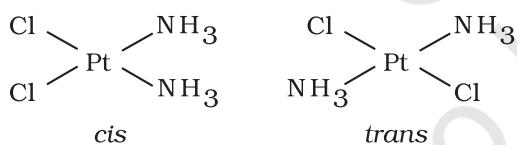
- (i) Geometrical isomerism      (ii) Optical isomerism

### **(b) Structural isomerism**

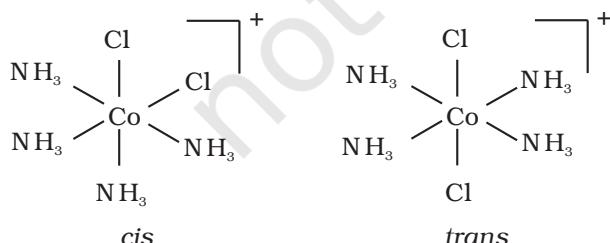
- |                            |                             |
|----------------------------|-----------------------------|
| (i) Linkage isomerism      | (ii) Coordination isomerism |
| (iii) Ionisation isomerism | (iv) Solvate isomerism      |

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.

### **5.4.1 Geometric Isomerism**



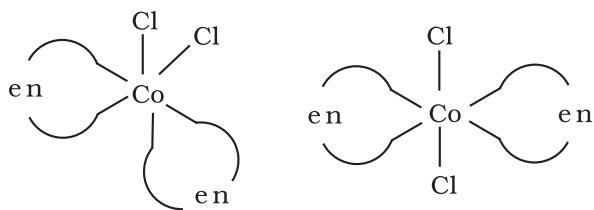
**Fig. 5.2:** Geometrical isomers (*cis* and *trans*) of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



**Fig. 5.3:** Geometrical isomers (*cis* and *trans*) of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

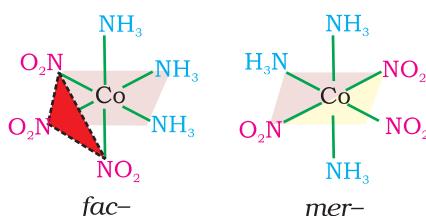
This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula  $[\text{MX}_2\text{L}_2]$  (X and L are unidentates), the two 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. 5.2.

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  $[\text{MX}_2\text{L}_4]$  in which the two ligands X may be oriented *cis* or *trans* to each other (Fig. 5.3).



**Fig. 5.4:** Geometrical isomers (cis and trans) of  $[CoCl_2(en)_2]$

**Fig. 5.5**  
The facial (fac) and  
meridional (mer)  
isomers of  
 $[Co(NH_3)_3(NO_2)_3]$



This type of isomerism also arises when didentate ligands L–L [e.g.,  $NH_2CH_2CH_2NH_2$  (en)] are present in complexes of formula  $[MX_2(L-L)_2]$  (Fig. 5.4).

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. 5.5).

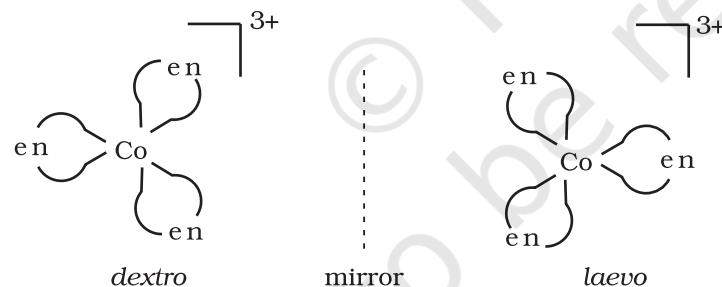
Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion?

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.

#### Example 5.4

#### Solution

#### 5.4.2 Optical Isomerism

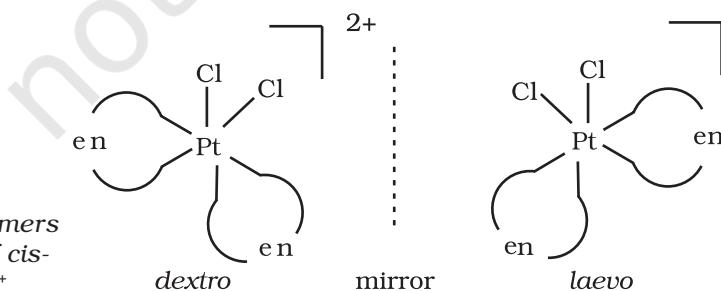


**Fig.5.6:** Optical isomers (d and l) of  $[Co(en)_3]^{3+}$

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. 5.6).

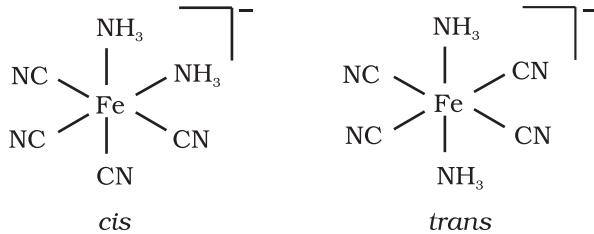
In a coordination entity of the type  $[PtCl_2(en)_2]^{2+}$ , only the *cis*-isomer shows optical activity (Fig. 5.7).

**Fig.5.7**  
Optical isomers  
(*d* and *l*) of *cis*-  
 $[PtCl_2(en)_2]^{2+}$



**Example 5.5** Draw structures of geometrical isomers of  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]$

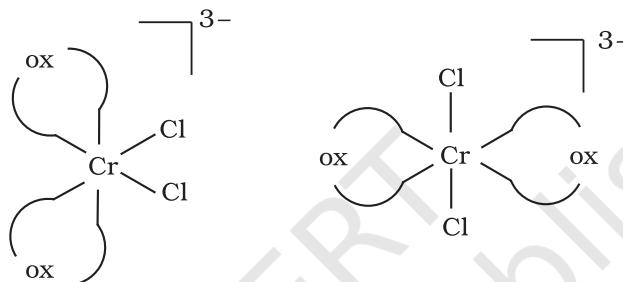
### Solution



**Example 5.6** Out of the following two coordination entities which is chiral (optically active)?

- (a)  $cis\text{-}[\text{CrCl}_2(\text{ox})_2]^{3-}$       (b)  $trans\text{-}[\text{CrCl}_2(\text{ox})_2]^{3-}$

**Solution** The two entities are represented as



Out of the two, (a) *cis* -  $[\text{CrCl}_2(\text{ox})_2]^{3-}$  is chiral (optically active).

### 5.4.3 Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand,  $\text{NCS}^-$ , which may bind through the nitrogen to give  $\text{M}-\text{NCS}$  or through sulphur to give  $\text{M}-\text{SCN}$ . Jørgensen discovered such behaviour in the complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ , which is obtained as the red form, in which the nitrite ligand is bound through oxygen ( $-\text{ONO}$ ), and as the yellow form, in which the nitrite ligand is bound through nitrogen ( $-\text{NO}_2$ ).

#### 5.4.4 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  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ , in which the  $\text{NH}_3$  ligands are bound to  $\text{Co}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Cr}^{3+}$ . In its coordination isomer  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ , the  $\text{NH}_3$  ligands are bound to  $\text{Cr}^{3+}$  and the  $\text{CN}^-$  ligands to  $\text{Co}^{3+}$ .

## 5.4.5 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  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .

## 5.4.6 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  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and its solvate isomer  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (grey-green).

## Intext Questions

- 5.3** Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

  - (i)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$
  - (ii)  $[\text{Co}(\text{en})_3]\text{Cl}_3$
  - (iii)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$
  - (iv)  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$

**5.4** Give evidence that  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$  are ionisation isomers.

## 5.5 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.

### 5.5.1 Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands can use its  $(n-1)d$ ,  $ns$ ,  $np$  or  $ns$ ,  $np$ ,  $nd$  orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 5.2). 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 5.2: Number of Orbitals and Types of Hybridisations**

<b>Coordination number</b>	<b>Type of hybridisation</b>	<b>Distribution of hybrid orbitals in space</b>
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.

Orbitals of $\text{Co}^{3+}$ ion	3d	4s	4p
$d^2sp^3$ hybridised orbitals of $\text{Co}^{3+}$	$d^2sp^3$ hybrid		
$[\text{Co}(\text{NH}_3)_6]^{3+}$ (inner orbital or low spin complex)	Six pairs of electrons from six $\text{NH}_3$ molecules		

In the diamagnetic octahedral complex,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , 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  $\text{NH}_3$  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 ( $3d$ ) is used in hybridisation, the complex,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is called an **inner orbital or low spin or spin paired complex**. The paramagnetic octahedral complex,  $[\text{CoF}_6]^{3-}$  uses outer orbital ( $4d$ ) in hybridisation ( $sp^3d^2$ ). It is thus called **outer orbital or high spin or spin free complex**. Thus:

Orbitals of $\text{Co}^{3+}$ ion	3d	4s	4p	4d
$sp^3d^2$ hybridised orbitals of $\text{Co}^{3+}$	$sp^3d^2$ hybrid			4d
$[\text{CoF}_6]^{3-}$ (outer orbital or high spin complex)	Six pairs of electrons from six $\text{F}^-$ ions			4d

Orbitals of $\text{Ni}^{2+}$ ion	3d	4s	4p
$sp^3$ hybridised orbitals of $\text{Ni}^{2+}$	$sp^3$ hybrid		
$[\text{NiCl}_4]^{2-}$ (high spin complex)	Four pairs of electrons from 4 $\text{Cl}^-$		

In tetrahedral complexes one  $s$  and three  $p$  orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for  $[\text{NiCl}_4]^{2-}$ . 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  $\text{Cl}^-$  ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly,  $[\text{Ni}(\text{CO})_4]$  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  $[\text{Ni}(\text{CN})_4]^{2-}$ . Here nickel is in +2 oxidation state and has the electronic configuration  $3d^8$ . The hybridisation scheme is as shown in diagram:

Orbitals of $\text{Ni}^{2+}$ ion	<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td></tr><tr><td colspan="5">3d</td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	3d					<table border="1"><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td>4s</td></tr></table>						4s	<table border="1"><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td>4p</td></tr></table>						4p
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$[\text{Ni}(\text{CN})_4]^{2-}$ (low spin complex)	<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td></tr><tr><td colspan="4">3d</td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	3d				<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	Four pairs of electrons from 4 $\text{CN}^-$ groups	<table border="1"><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td></td></tr><tr><td>4p</td></tr></table>						4p			
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3d																									
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$																						
4p																									

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.

### 5.5.2 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 number of unpaired electrons and hence 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  $\text{Ti}^{3+}$  ( $d^1$ );  $\text{V}^{3+}$  ( $d^2$ );  $\text{Cr}^{3+}$  ( $d^3$ ); two vacant  $d$  orbitals are available for octahedral hybridisation with 4s and 4p orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three  $3d$  electrons are present, the required pair of  $3d$  orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for  $d^4$  ( $\text{Cr}^{2+}$ ,  $\text{Mn}^{3+}$ ),  $d^5$  ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ),  $d^6$  ( $\text{Fe}^{2+}$ ,  $\text{Co}^{3+}$ ) cases, a vacant pair of  $d$  orbitals results only by pairing of  $3d$  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.  $[\text{Mn}(\text{CN})_6]^{3-}$  has magnetic moment of two unpaired electrons while  $[\text{MnCl}_6]^{3-}$  has a paramagnetic moment of four unpaired electrons.  $[\text{Fe}(\text{CN})_6]^{3-}$  has magnetic moment of a single unpaired electron while  $[\text{FeF}_6]^{3-}$  has a paramagnetic moment of five unpaired electrons.  $[\text{CoF}_6]^{3-}$  is paramagnetic with four unpaired electrons while  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities.  $[\text{Mn}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  are inner orbital complexes involving  $d^2sp^3$  hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand,  $[\text{MnCl}_6]^{3-}$ ,  $[\text{FeF}_6]^{3-}$  and  $[\text{CoF}_6]^{3-}$  are outer orbital complexes involving  $sp^3d^2$  hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

### Example 5.7

The spin only magnetic moment of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. Predict the geometry of the complex ion ?

### Solution

Since the coordination number of  $\text{Mn}^{2+}$  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.

### **5.5.3 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:

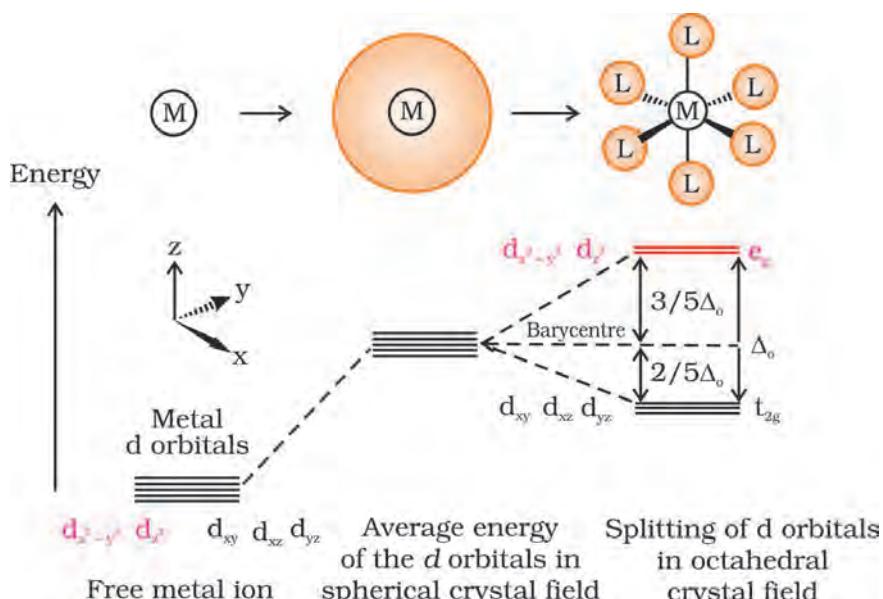
- (i) It involves a number of assumptions.
- (ii) It does not give quantitative interpretation of magnetic data.
- (iii) It does not explain the colour exhibited by coordination compounds.
- (iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination 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.

### **5.5.4 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 point 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  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) 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.

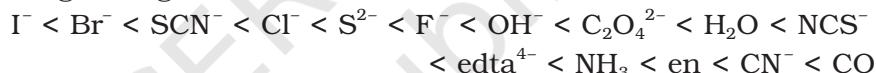
#### **(a) Crystal field splitting in octahedral coordination entities**

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  $d_{zx}$  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.5.8:** *d* orbital splitting in an octahedral crystal field

In general, ligands can be arranged in a series in the order of increasing field strength as given below:



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*<sub>2g</sub> orbitals. In *d*<sup>2</sup> and *d*<sup>3</sup> coordination entities, the *d* electrons occupy the *t*<sub>2g</sub> orbitals singly in accordance with the Hund's rule. For *d*<sup>4</sup> ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the *t*<sub>2g</sub> level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the *e*<sub>g</sub> level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta_o$  and the pairing energy, *P* (*P* represents the energy required for electron pairing in a single orbital). The two options are:

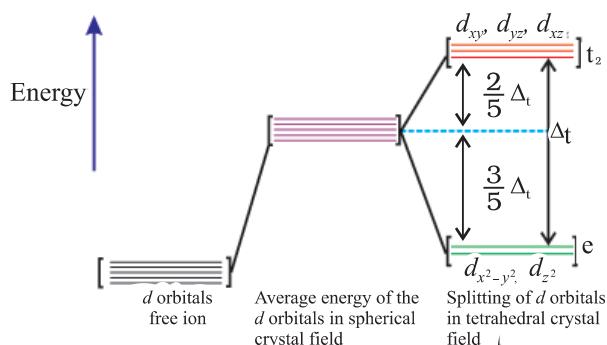
- (i) If  $\Delta_o < P$ , the fourth electron enters one of the *e*<sub>g</sub> orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_o < P$  are known as *weak field ligands* and form high spin complexes.
- (ii) If  $\Delta_o > P$ , it becomes more energetically favourable for the fourth electron to occupy a *t*<sub>2g</sub> 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*<sup>4</sup> to *d*<sup>7</sup> coordination entities are more stable for strong field as compared to weak field cases.

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  $\Delta_o$  (the subscript *o* is for octahedral) (Fig.5.8). Thus, the energy of the two *e*<sub>g</sub> orbitals will increase by (3/5)  $\Delta_o$  and that of the three *t*<sub>2g</sub> will decrease by (2/5)  $\Delta_o$ .

The crystal field splitting,  $\Delta_o$ , 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.

**(b) Crystal field splitting in tetrahedral coordination entities**



**Fig.5.9:** *d* orbital splitting in a tetrahedral crystal field.

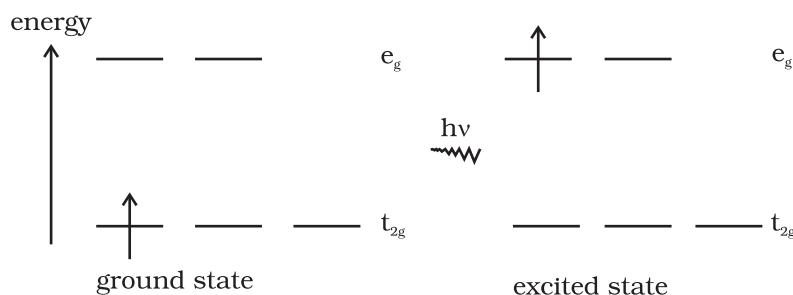
### 5.5.5 Colour in Coordination Compounds

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 5.3 gives the relationship of the different wavelength absorbed and the colour observed.

**Table 5.3: Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities**

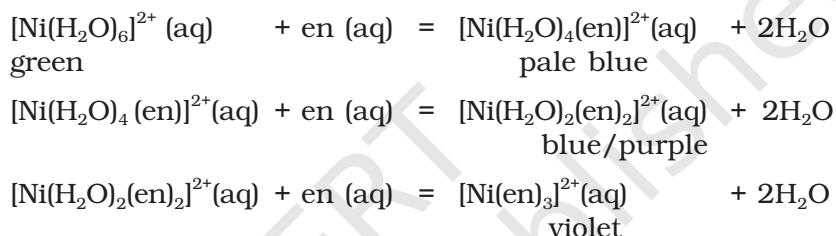
Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Violet

The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , which is violet in colour. This is an octahedral complex where the single electron ( $\text{Ti}^{3+}$  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 blue-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. 5.10). The crystal field theory attributes the colour of the coordination compounds to *d-d* transition of the electron.

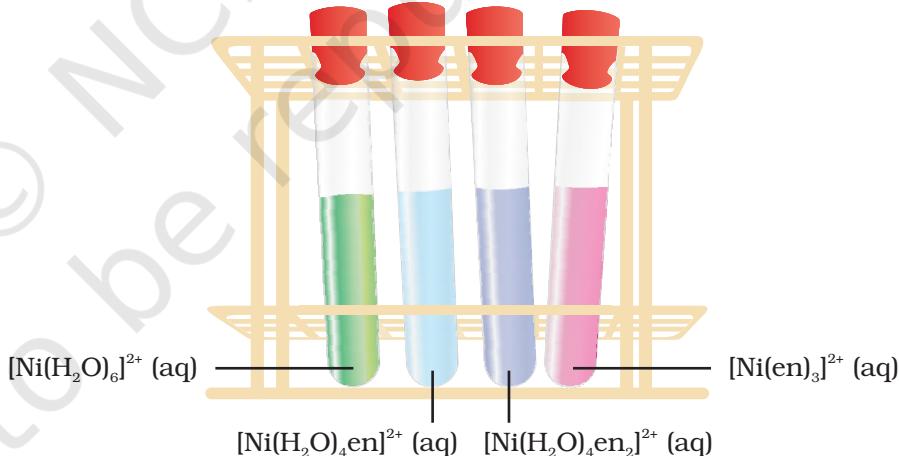


**Fig.5.10:** Transition of an electron in

of a complex may be illustrated by considering the  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  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:



This sequence is shown in Fig. 5.11.



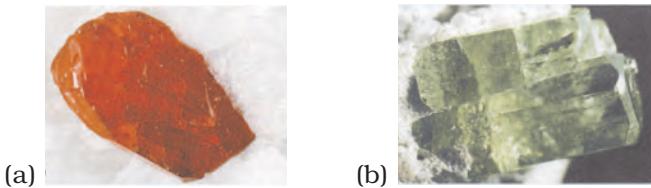
**Fig.5.11**  
Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands.

#### 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.5.12(a)] is aluminium oxide ( $\text{Al}_2\text{O}_3$ ) containing about 0.5-1%  $\text{Cr}^{3+}$  ions ( $d^3$ ), which are randomly distributed in positions normally occupied by  $\text{Al}^{3+}$ . 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.

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  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  on heating renders it colourless. Similarly, anhydrous  $\text{CuSO}_4$  is white, but  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour. The influence of the ligand on the colour

In emerald [Fig.5.12(b)], Cr<sup>3+</sup> ions occupy octahedral sites in the mineral beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ). 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.



**Fig.5.12:** (a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.

#### 5.5.6 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.

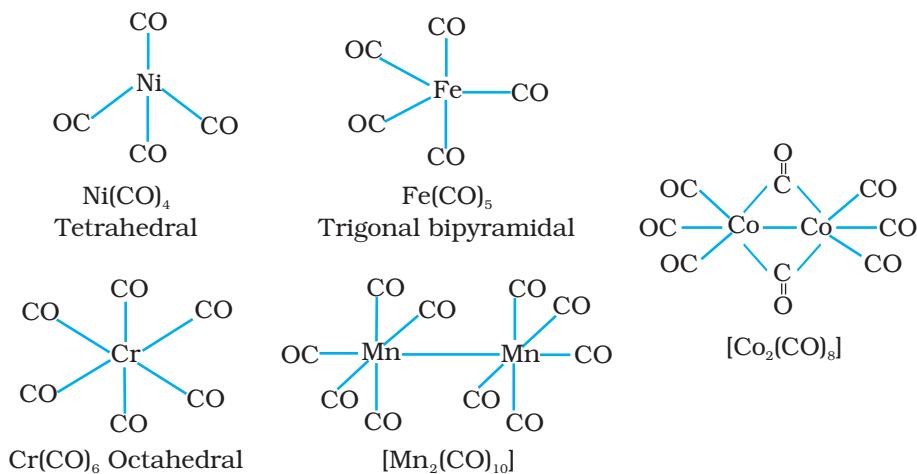
#### Intext Questions

- 5.5 Explain on the basis of valence bond theory that  $[\text{Ni}(\text{CN})_4]^{2-}$  ion with square planar structure is diamagnetic and the  $[\text{NiCl}_4]^{2-}$  ion with tetrahedral geometry is paramagnetic.
- 5.6  $[\text{NiCl}_4]^{2-}$  is paramagnetic while  $[\text{Ni}(\text{CO})_4]$  is diamagnetic though both are tetrahedral. Why?
- 5.7  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic. Explain.
- 5.8 Explain  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inner orbital complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is an outer orbital complex.
- 5.9 Predict the number of unpaired electrons in the square planar  $[\text{Pt}(\text{CN})_4]^{2-}$  ion.
- 5.10 The hexaquo manganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

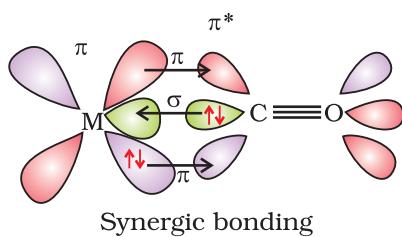
#### 5.6 Bonding in Metal Carbonyls

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  $\text{Mn}(\text{CO})_5$  units joined by a Mn – Mn bond. Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups (Fig.5.13).



**Fig. 5.13**  
Structures of some representative homoleptic metal carbonyls.



**Fig. 5.14:** Example of synergic bonding interactions in a carbonyl complex.

## 5.7 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),  $\alpha$ -nitroso- $\beta$ -naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with  $\text{Na}_2\text{EDTA}$ . The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  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  $[\text{Au}(\text{CN})_2]^-$  in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

For example, impure nickel is converted to  $[\text{Ni}(\text{CO})_4]$ , 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  $\text{B}_{12}$ , cyanocobalamin, 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,  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ , 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,  $[\text{Ag}(\text{CN})_2]^-$  and  $[\text{Au}(\text{CN})_2]^-$  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  $\text{AgBr}$  to form a complex ion,  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ .
- 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 constitute point charges creates many theoretical difficulties.

The metal–carbon bond in **metal carbonyls** possesses both  $\sigma$  and  $\pi$  character. The ligand to metal is  $\sigma$  bond and metal to ligand is  $\pi$  bond. This unique synergic bonding provides stability to metal carbonyls.

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

- 5.1 Explain the bonding in coordination compounds in terms of Werner's postulates.
- 5.2  $\text{FeSO}_4$  solution mixed with  $(\text{NH}_4)_2\text{SO}_4$  solution in 1:1 molar ratio gives the test of  $\text{Fe}^{2+}$  ion but  $\text{CuSO}_4$  solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of  $\text{Cu}^{2+}$  ion. Explain why?
- 5.3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.
- 5.4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.
- 5.5 Specify the oxidation numbers of the metals in the following coordination entities:  
(i)  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$       (iii)  $[\text{PtCl}_4]^{2-}$       (v)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$   
(ii)  $[\text{CoBr}_2(\text{en})_2]^+$       (iv)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- 5.6 Using IUPAC norms write the formulas for the following:  
(i) Tetrahydroxidozincate(II)      (vi) Hexaamminecobalt(III) sulphate  
(ii) Potassium tetrachloridopalladate(II)      (vii) Potassium tri(oxalato)chromate(III)  
(iii) Diamminedichloridoplatinum(II)      (viii) Hexaammineplatinum(IV)  
(iv) Potassium tetracyanidonickelate(II)      (ix) Tetrabromidocuprate(II)  
(v) Pentaamminenitrito-O-cobalt(III)      (x) Pentaamminenitrito-N-cobalt(III)
- 5.7 Using IUPAC norms write the systematic names of the following:  
(i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$       (iv)  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$       (vii)  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$   
(ii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$       (v)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$       (viii)  $[\text{Co}(\text{en})_3]^{3+}$   
(iii)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$       (vi)  $[\text{NiCl}_4]^{2-}$       (ix)  $[\text{Ni}(\text{CO})_4]$
- 5.8 List various types of isomerism possible for coordination compounds, giving an example of each.
- 5.9 How many geometrical isomers are possible in the following coordination entities?  
(i)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$       (ii)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
- 5.10 Draw the structures of optical isomers of:  
(i)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$       (ii)  $[\text{PtCl}_2(\text{en})_2]^{2+}$       (iii)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$

- 5.11** Draw all the isomers (geometrical and optical) of:  
 (i)  $[\text{CoCl}_2(\text{en})_2]^+$       (ii)  $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$       (iii)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$
- 5.12** Write all the geometrical isomers of  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{py})]$  and how many of these will exhibit optical isomers?
- 5.13** 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.
- 5.14** What is the coordination entity formed when excess of aqueous  $\text{KCN}$  is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when  $\text{H}_2\text{S(g)}$  is passed through this solution?
- 5.15** Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:  
 (i)  $[\text{Fe}(\text{CN})_6]^{4-}$       (ii)  $[\text{FeF}_6]^{3-}$       (iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$       (iv)  $[\text{CoF}_6]^{3-}$
- 5.16** Draw figure to show the splitting of  $d$  orbitals in an octahedral crystal field.
- 5.17** What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.
- 5.18** What is crystal field splitting energy? How does the magnitude of  $\Delta_o$  decide the actual configuration of  $d$  orbitals in a coordination entity?
- 5.19**  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain why?
- 5.20** A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green but a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless. Explain.
- 5.21**  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. Why?
- 5.22** Discuss the nature of bonding in metal carbonyls.
- 5.23** Give the oxidation state,  $d$  orbital occupation and coordination number of the central metal ion in the following complexes:  
 (i)  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$       (iii)  $(\text{NH}_4)_2[\text{CoF}_4]$   
 (ii) cis- $[\text{CrCl}_2(\text{en})_2]\text{Cl}$       (iv)  $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$
- 5.24** 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)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2].3\text{H}_2\text{O}$       (iii)  $[\text{CrCl}_3(\text{py})_3]$       (v)  $\text{K}_4[\text{Mn}(\text{CN})_6]$   
 (ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}_1]\text{Cl}_2$       (iv)  $\text{Cs}[\text{FeCl}_4]$
- 5.25** Explain the violet colour of the complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  on the basis of crystal field theory.
- 5.26** What is meant by the *chelate effect*? Give an example.
- 5.27** 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.
- 5.28** How many ions are produced from the complex  $\text{Co}(\text{NH}_3)_6\text{Cl}_2$  in solution?  
 (i) 6      (ii) 4      (iii) 3      (iv) 2

- 5.29** Amongst the following ions which one has the highest magnetic moment value?  
 (i)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$       (ii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$       (iii)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- 5.30** Amongst the following, the most stable complex is  
 (i)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$       (ii)  $[\text{Fe}(\text{NH}_3)_6]^{3+}$       (iii)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$       (iv)  $[\text{FeCl}_6]^{3-}$
- 5.31** What will be the correct order for the wavelengths of absorption in the visible region for the following:  
 $[\text{Ni}(\text{NO}_2)_6]^{4-}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ?

### Answers to Some Intext Questions

- 5.1** (i)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$       (iv)  $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^-$   
 (ii)  $\text{K}_2[\text{Ni}(\text{CN})_4]$       (v)  $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$   
 (iii)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$       (vi)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]\text{I}_3$
- 5.2** (i) Hexaamminecobalt(III) chloride  
 (ii) Pentaamminechloridocobalt(III) chloride  
 (iii) Potassium hexacyanidoferate(III)  
 (iv) Potassium trioxalatoferate(III)  
 (v) Potassium tetrachloridopalladate(II)  
 (vi) Diamminechlorido(methanamine)platinum(II) chloride
- 5.3** (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.
- 5.4** The ionisation isomers dissolve in water to yield different ions and thus react differently to various reagents:  
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4 + \text{Ba}^{2+} \rightarrow \text{BaSO}_4 (\text{s})$   
 $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} + \text{Ba}^{2+} \rightarrow \text{No reaction}$   
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4 + \text{Ag}^+ \rightarrow \text{No reaction}$   
 $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} + \text{Ag}^+ \rightarrow \text{AgBr} (\text{s})$
- 5.6** In  $\text{Ni}(\text{CO})_4$ , Ni is in zero oxidation state whereas in  $\text{NiCl}_4^{2-}$ , it is in +2 oxidation state. In the presence of CO ligand, the unpaired *d* electrons of Ni pair up but  $\text{Cl}^-$  being a weak ligand is unable to pair up the unpaired electrons.
- 5.7** In presence of  $\text{CN}^-$ , (a strong ligand) the *3d* electrons pair up leaving only one unpaired electron. The hybridisation is  $d^2sp^3$  forming inner orbital complex. In the presence of  $\text{H}_2\text{O}$ , (a weak ligand), *3d* electrons do not pair up. The hybridisation is  $sp^3d^2$  forming an outer orbital complex containing five unpaired electrons, it is strongly paramagnetic.
- 5.8** In the presence of  $\text{NH}_3$ , the *3d* electrons pair up leaving two *d* orbitals empty to be involved in  $d^2sp^3$  hybridisation forming inner orbital complex in case of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . In  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , Ni is in +2 oxidation state and has  $d^8$  configuration, the hybridisation involved is  $sp^3d^2$  forming outer orbital complex.
- 5.9** For square planar shape, the hybridisation is  $dsp^2$ . Hence the unpaired electrons in *5d* orbital pair up to make one *d* orbital empty for  $dsp^2$  hybridisation. Thus there is no unpaired electron.



Unit

6

## 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 an aliphatic or aromatic hydrocarbon 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 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.

## 6.1 Classification

### 6.1.1 On the Basis of Number of Halogen Atoms

Haloalkanes and haloarenes may be classified as follows:

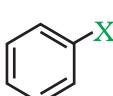
These may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,



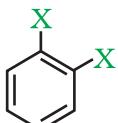
Monohaloalkane

Dihaloalkane

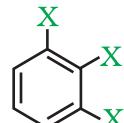
Trihaloalkane



Monohaloarene



Dihaloarene



Trihaloarene

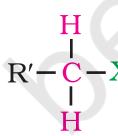
Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

### 6.1.2 Compounds Containing $\text{sp}^3\text{C}-\text{X}$ Bond ( $\text{X}=\text{F, Cl, Br, I}$ )

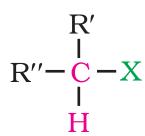
This class includes

#### (a) Alkyl halides or haloalkanes ( $\text{R}-\text{X}$ )

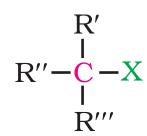
In alkyl halides, the halogen atom is bonded to an alkyl group (R). They form a homologous series represented by  $\text{C}_n\text{H}_{2n+1}\text{X}$ . They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached. If halogen is attached to a primary carbon atom in an alkyl halide, the alkyl halide is called primary alkyl halide or  $1^\circ$  alkyl halide. Similarly, if halogen is attached to secondary or tertiary carbon atom, the alkyl halide is called secondary alkyl halide ( $2^\circ$ ) and tertiary ( $3^\circ$ ) alkyl halide, respectively.



Primary ( $1^\circ$ )



Secondary ( $2^\circ$ )



Tertiary ( $3^\circ$ )

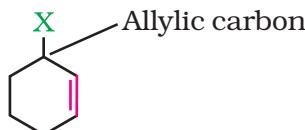
#### (b) Allylic halides

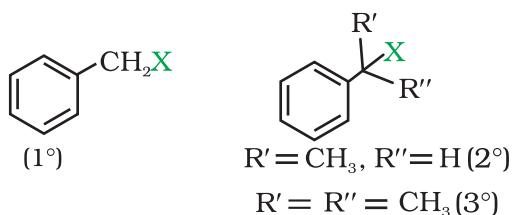
These are the compounds in which the halogen atom is bonded to an  $\text{sp}^3$ -hybridised carbon atom adjacent to carbon-carbon double bond ( $\text{C}=\text{C}$ ) i.e. to an allylic carbon.



#### (c) Benzylic halides

These are the compounds in which the halogen atom is bonded to an  $\text{sp}^3$ -hybridised carbon atom attached to an aromatic ring.



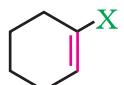


### 6.1.3 Compounds Containing $sp^2\text{C}-\text{X}$ Bond

This class includes:

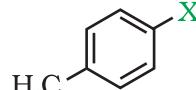
#### (a) Vinylic halides

These are the compounds in which the halogen atom is bonded to a  $sp^2$ -hybridised carbon atom of a carbon-carbon double bond ( $\text{C}=\text{C}$ ).



#### (b) Aryl halides

These are the compounds in which the halogen atom is directly bonded to the  $sp^2$ -hybridised carbon atom of an aromatic ring.



## 6.2 Nomenclature

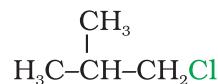
Having learnt the classification of halogenated compounds, let us now learn how these are named. The common names of alkyl halides are derived by naming the alkyl group followed by the name of halide. In the IUPAC system of nomenclature, alkyl halides are named as halosubstituted hydrocarbons. For mono halogen substituted derivatives of benzene, common and IUPAC names are the same. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, as you have learnt in Class XI, the numerals 1,2; 1,3 and 1,4 are used.



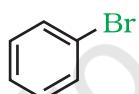
Common name: n-Propyl bromide  
IUPAC name: 1-Bromopropane



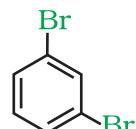
Isopropyl chloride  
2-Chloropropane



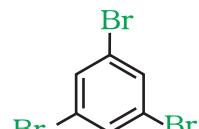
Isobutyl chloride  
1-Chloro-2-methylpropane



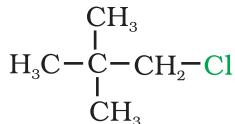
Common name: Bromobenzene  
IUPAC name: Bromobenzene



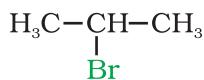
*m*-Dibromobenzene  
1,3-Dibromobenzene



*sym*-Tribromobenzene  
1,3,5-Tribromobenzene



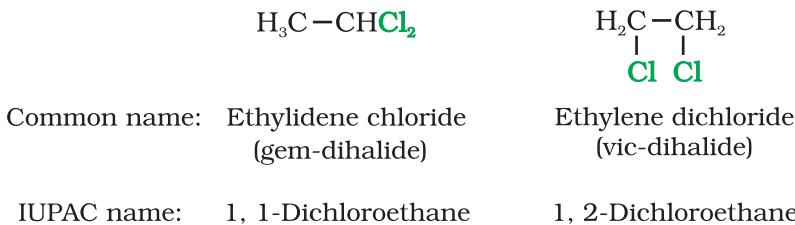
IUPAC name: 1-Chloro-2,2-dimethylpropane



2-Bromopropane

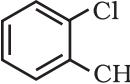
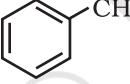
The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo-compounds having both the halogen atoms are further classified as geminal halides or gem-dihalides when both the halogen atoms are present on the same carbon atom of the

chain and vicinal halides or vic-dihalides when halogen atoms are present on 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.



Some common examples of halocompounds are mentioned in Table 6.1.

**Table 6.1: Common and IUPAC Names of some Halides**

Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	sec-Butyl chloride	2-Chlorobutane
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane
$\text{CH}_2 = \text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_2 = \text{CHCH}_2\text{Br}$	Allyl bromide	3-Bromopropene
	$\text{o}$ -Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
$\text{CH}_2\text{Cl}_2$	Methylene chloride	Dichloromethane
$\text{CHCl}_3$	Chloroform	Trichloromethane
$\text{CHBr}_3$	Bromoform	Tribromomethane
$\text{CCl}_4$	Carbon tetrachloride	Tetrachloromethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	n-Propyl fluoride	1-Fluoropropane

### Example 6.1

Draw the structures of all the eight structural isomers that have the molecular formula  $\text{C}_5\text{H}_{11}\text{Br}$ . Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

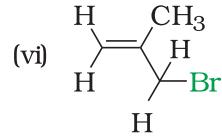
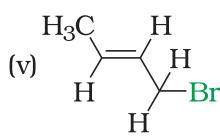
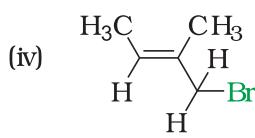
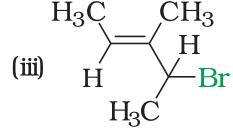
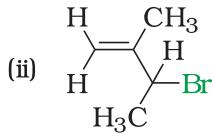
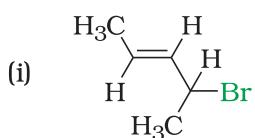
### Solution

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  1-Bromopentane ( $1^\circ$ )
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$  2-Bromopentane ( $2^\circ$ )
- $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$  3-Bromopentane ( $2^\circ$ )
- $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$  1-Bromo-3-methylbutane ( $1^\circ$ )

$(CH_3)_2CHCHBrCH_3$	2-Bromo-3-methylbutane( $2^\circ$ )
$(CH_3)_2CBrCH_2CH_3$	2-Bromo-2-methylbutane ( $3^\circ$ )
$CH_3CH_2CH(CH_3)CH_2Br$	1-Bromo-2-methylbutane( $1^\circ$ )
$(CH_3)_3CCH_2Br$	1-Bromo-2,2-dimethylpropane ( $1^\circ$ )

Write IUPAC names of the following:

### Example 6.2



(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

### Solution

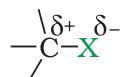
### Intext Question

**6.1** 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.

### 6.3 Nature of C-X Bond

Halogen atoms are more electronegative than carbon, therefore, 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.



As we go down the group in the periodic table, the size of halogen atom increases. Fluorine atom is the smallest and iodine atom is 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 6.2.

Alkyl halides are best prepared from alcohols, which are easily accessible.

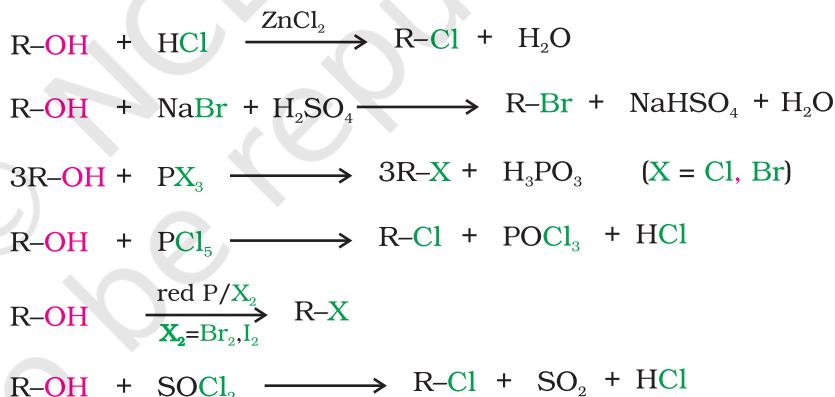
**Table 6.2: Carbon-Halogen (C—X) Bond Lengths, Bond Enthalpies and Dipole Moments**

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol <sup>-1</sup>	Dipole moment/Debye
CH <sub>3</sub> —F	139	452	1.847
CH <sub>3</sub> —Cl	178	351	1.860
CH <sub>3</sub> —Br	193	293	1.830
CH <sub>3</sub> —I	214	234	1.636

## 6.4 Methods of Preparation of Haloalkanes

### 6.4.1 From Alcohols

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 in this reaction alkyl halide is formed along with gases SO<sub>2</sub> and HCl. The two gaseous products are escapable, hence, the reaction gives pure alkyl halides. The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, ZnCl<sub>2</sub>. With tertiary alcohols, the reaction is conducted by simply shaking the alcohol 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% orthophosphoric acid. The order of reactivity of alcohols with a given haloacid is 3° > 2° > 1°. 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 mixture of alcohol and concentrated aqueous halogen acid.

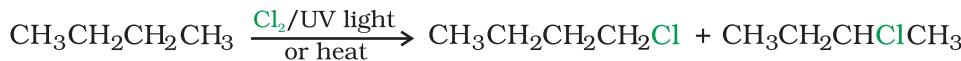
The above methods are not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.

### (I) From alkanes by free radical halogenation

Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to

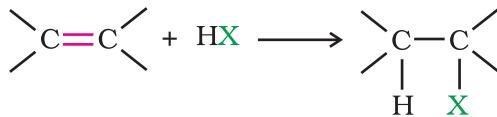
### 6.4.2 From Hydrocarbons

separate as pure compounds. Consequently, the yield of any single compound is low.

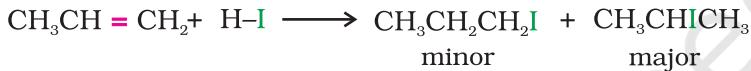


### (II) From alkenes

- (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)



- (ii) *Addition of halogens:* In the laboratory, addition of bromine in  $\text{CCl}_4$  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 9, Class XI).



Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ .

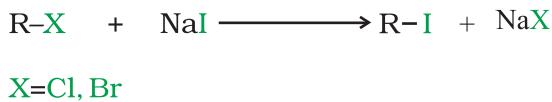
### Example 6.3

In the given molecule, there are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following



### 6.4.3 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**.



NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

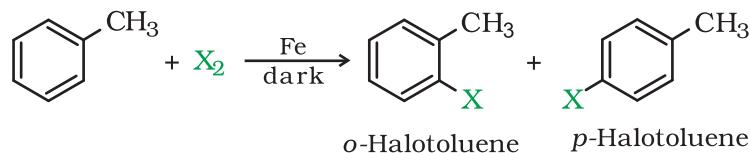
The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as

$\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ ,  $\text{CoF}_2$  or  $\text{SbF}_3$ . The reaction is termed as **Swarts reaction**.



## 6.5 Preparation of (i) From hydrocarbons by electrophilic substitution Haloarenes

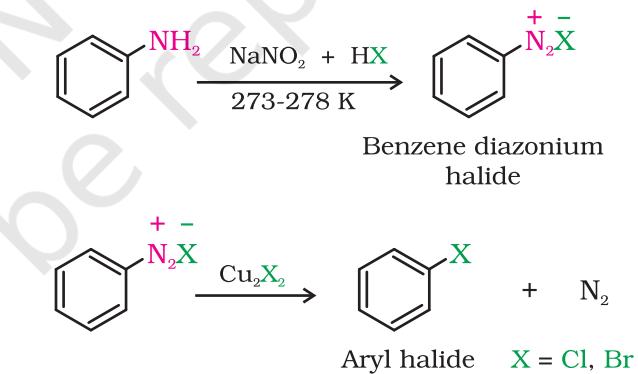
Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride.



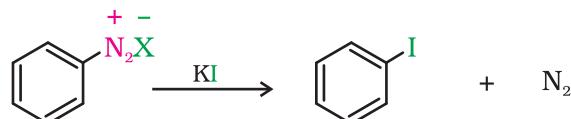
The *ortho* and *para* isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent ( $\text{HNO}_3$ ,  $\text{HIO}_4$ ) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

### (ii) From amines by Sandmeyer's reaction

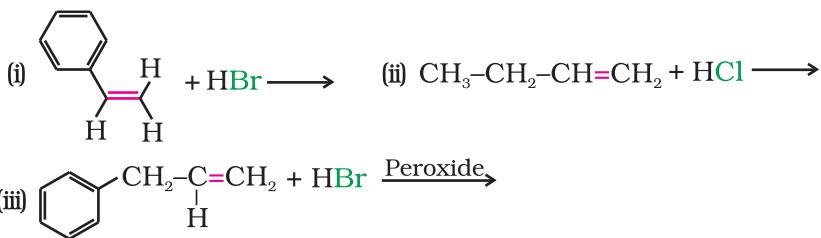
When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by  $-\text{Cl}$  or  $-\text{Br}$ .



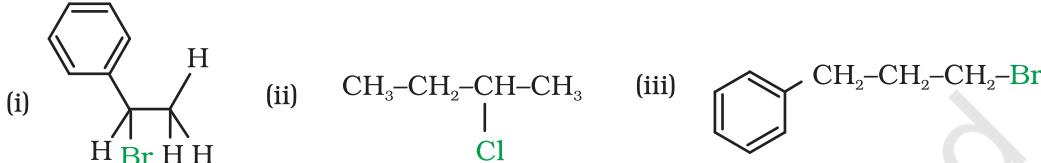
Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.



**Example 6.4** Write the products of the following reactions:

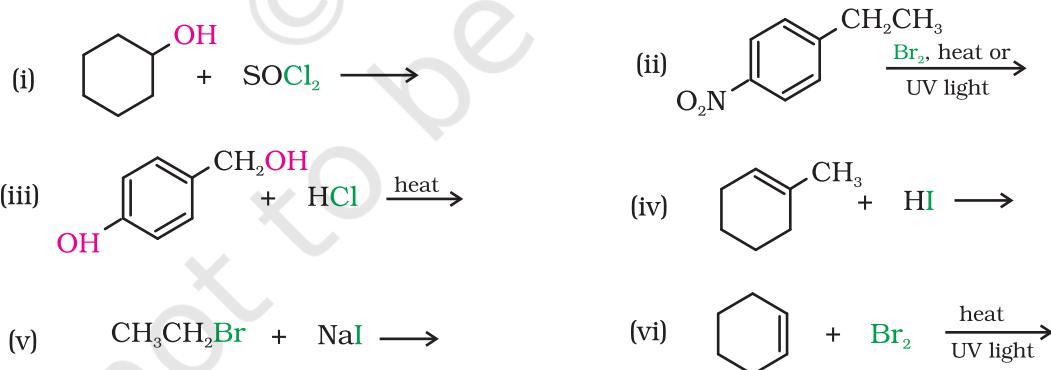


**Solution**



### Intext Questions

- 6.2 Why is sulphuric acid not used during the reaction of alcohols with KI?
- 6.3 Write structures of different dihalogen derivatives of propane.
- 6.4 Among the isomeric alkanes of molecular formula  $\text{C}_5\text{H}_{12}$ , identify the one that on photochemical chlorination yields
- A single monochloride.
  - Three isomeric monochlorides.
  - Four isomeric monochlorides.
- 6.5 Draw the structures of major monohalo products in each of the following reactions:



### 6.6 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.

### 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. 6.1. 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.

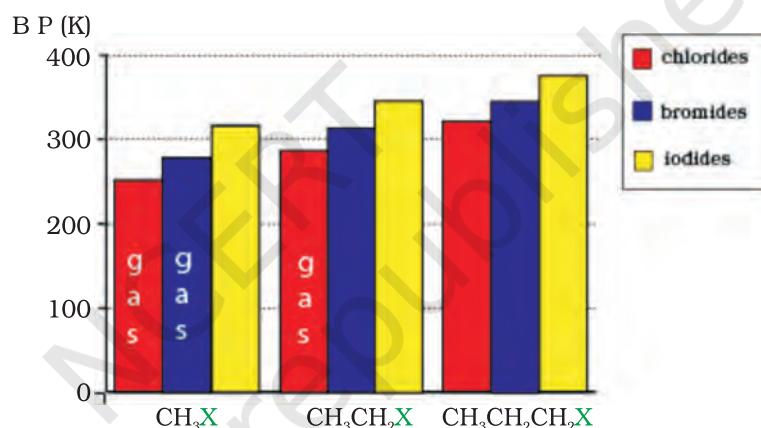


Fig. 6.1: Comparison of boiling points of some alkyl halides

The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.

CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> Br
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
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 6.3).

**Table 6.3: Density of Some Haloalkanes**

Compound	Density (g/mL)	Compound	Density (g/mL)
n-C <sub>3</sub> H <sub>7</sub> Cl	0.89	CH <sub>2</sub> Cl <sub>2</sub>	1.336
n-C <sub>3</sub> H <sub>7</sub> Br	1.335	CHCl <sub>3</sub>	1.489
n-C <sub>3</sub> H <sub>7</sub> I	1.747	CCl <sub>4</sub>	1.595

### Solubility

The haloalkanes are very slightly soluble in water. In order to dissolve haloalkane 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

**6.6** Arrange each set of compounds in order of increasing boiling points.

- (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
- (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

## 6.7 Chemical Reactions

### 6.7.1 Reactions of Haloalkanes

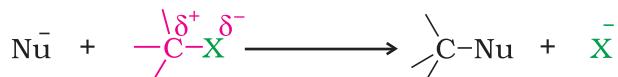
The reactions of haloalkanes may be divided into the following categories:

1. Nucleophilic substitution
2. Elimination reactions
3. Reaction with metals.

#### (1) Nucleophilic substitution reactions

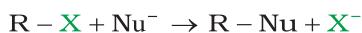
You have learnt in Class XI that nucleophiles are electron rich species. Therefore, they attack at that part of the substrate molecule which is electron deficient. The reaction in which a nucleophile replaces

already existing nucleophile in a molecule is called nucleophilic substitution reaction. Haloalkanes are substrate in these 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 6.4.

**Table 6.4: Nucleophilic Substitution of Alkyl Halides ( $\text{R}-\text{X}$ )**



Reagent	Nucleophile ( $\text{Nu}^-$ )	Substitution product $\text{R-Nu}$	Class of main product
$\text{NaOH}$ ( $\text{KOH}$ )	$\text{HO}^-$	$\text{ROH}$	Alcohol
$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	$\text{ROH}$	Alcohol
$\text{NaOR}'$	$\text{R}'\text{O}^-$	$\text{ROR}'$	Ether
$\text{NaI}$	$\text{I}^-$	$\text{R-I}$	Alkyl iodide
$\text{NH}_3$	$\text{NH}_3$	$\text{RNH}_2$	Primary amine
$\text{R}'\text{NH}_2$	$\text{R}'\text{NH}_2$	$\text{RNHR}'$	Sec. amine
$\text{R}'\text{R}''\text{NH}$	$\text{R}'\text{R}''\text{NH}$	$\text{RNR}'\text{R}''$	Tert. amine
$\text{KCN}$	$\bar{\text{C}}\equiv\text{N}: \quad \text{C}\equiv\text{N}$	$\text{RCN}$	Nitrile (cyanide)
$\text{AgCN}$	$\text{Ag-CN}: \quad \text{Ag}\text{---C}\equiv\text{N}$	$\text{RNC}$ (isocyanide)	Isonitrile
$\text{KNO}_2$	$\text{O}=\text{N}=\text{O}$	$\text{R-O-N=O}$	Alkyl nitrite
$\text{AgNO}_2$	$\text{Ag---}\ddot{\text{O}}=\text{N=O}$	$\text{R-NO}_2$	Nitroalkane
$\text{R'COOAg}$	$\text{R'COO}^-$	$\text{R'COOR}$	Ester
$\text{LiAlH}_4$	$\text{H}$	$\text{RH}$	Hydrocarbon
$\text{R}'-\text{M}^+$	$\text{R}'^-$	$\text{RR}'$	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 [ $^{\circ}\text{C}\equiv\text{N} \leftrightarrow :\text{C}=\text{N}^\ominus$ ], i.e., linking through

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

### Example 6.5

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.

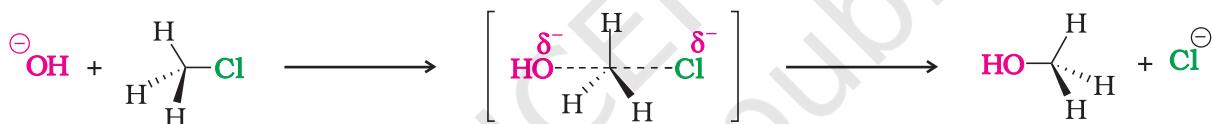
### Solution

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 [ $\text{O}=\text{O}$ ]. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

**Mechanism:** This reaction has been found to proceed by two different mechanisms which are described below:

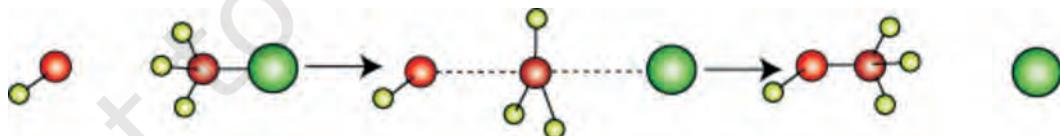
#### (a) Substitution nucleophilic bimolecular ( $S_N2$ )

The reaction between  $\text{CH}_3\text{Cl}$  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.



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.

The above reaction can be represented diagrammatically as shown in Fig. 6.2.



**Fig. 6.2:** Red ball represents the incoming hydroxide ion and green ball represents the outgoing halide ion

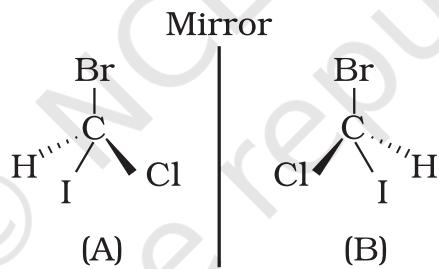
In the year 1937, Edward Davies Hughes and Sir Christopher Ingold proposed a mechanism for an  $S_N2$  reaction.

It depicts a bimolecular nucleophilic substitution ( $S_N2$ ) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break and a new bond is formed between carbon and attacking nucleophile. Here it is C—O bond formed between C and -OH. These two processes take place simultaneously in a

single step and no intermediate is formed. As the reaction progresses and the bond between the incoming nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the three carbon-hydrogen bonds of the substrate start moving away from the attacking nucleophile. In transition state all the three C-H bonds are in the same plane and the attacking and leaving nucleophiles are partially attached to the carbon. As the attacking nucleophile approaches closer to the carbon, C-H bonds still keep on moving in the same direction till the attacking nucleophile attaches to carbon and leaving group leaves the carbon. As a result configuration is inverted, the configuration (See box) of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind. 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. Such structures are unstable and cannot be isolated. Thus, in the transition state, carbon is simultaneously bonded to five atoms.

### Configuration

Spacial arrangement of functional groups around carbon is called its configuration. See the structures (A) and (B) given below carefully.

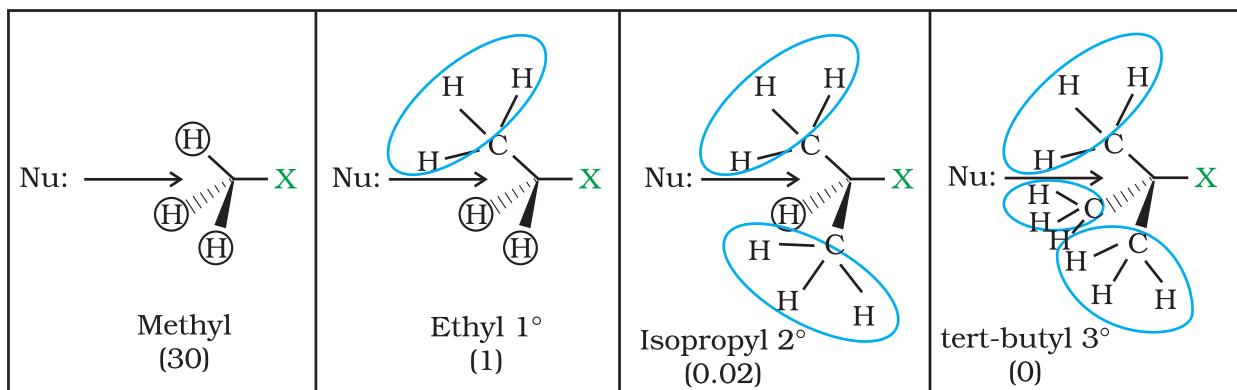


These are the two structures of the same compound. They differ in spacial arrangement of functional groups attached to carbon. Structure (A) is mirror image of Structure (B). We say configuration of carbon in structure (A) is mirror image of the configuration of carbon in structure (B).

*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.



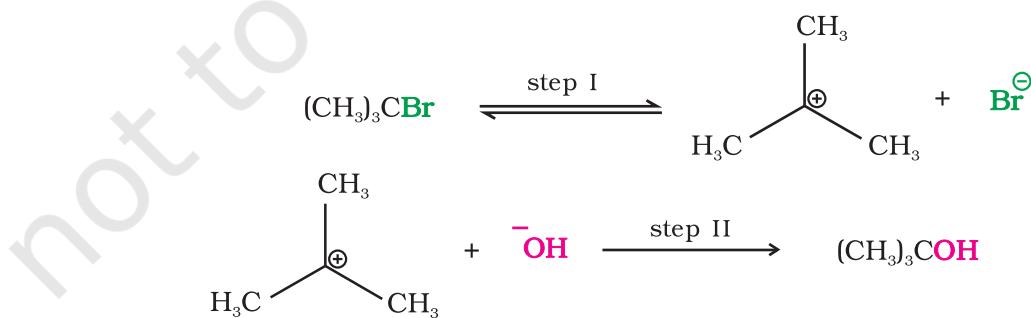
**Fig.6.3:** Steric effects in  $S_N2$  reaction. The relative rate of  $S_N2$  reaction is given in parenthesis.

**(b) Substitution nucleophilic unimolecular ( $S_N1$ )**

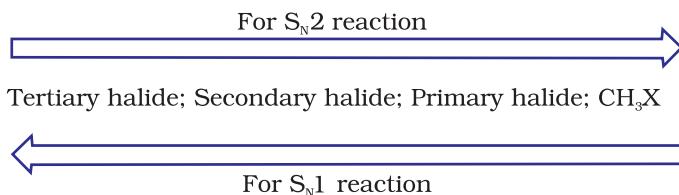
$S_N1$  reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between *tert*-butyl bromide and hydroxide ion yields *tert*-butyl alcohol and follows the first order kinetics, *i.e.*, the rate of reaction depends upon the concentration of only one reactant, which is *tert*-butyl bromide.



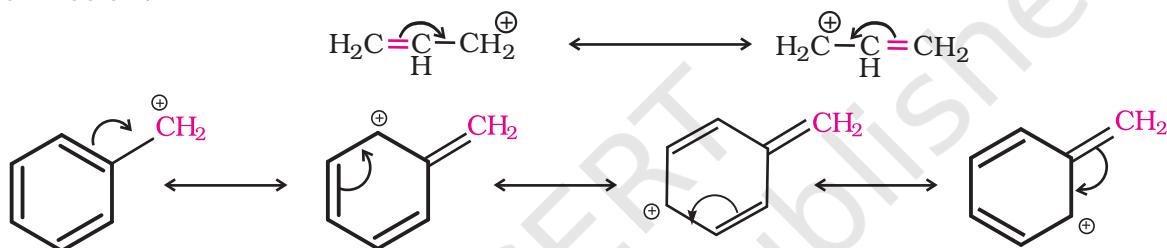
It occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction.



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,  $3^{\circ}$  alkyl halides undergo  $S_N1$  reaction very fast because of the high stability of  $3^{\circ}$  carbocations. We can sum up the order of reactivity of alkyl halides towards  $S_N1$  and  $S_N2$  reactions as follows:



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 8, Class XI) as shown below:



For a given alkyl group, the reactivity of the halide,  $\text{R}-\text{X}$ , follows the same order in both the mechanisms  $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$ .

In the following pairs of halogen compounds, which would undergo [Example 6.6](#)  $S_N2$  reaction faster?



It is primary halide and therefore undergoes  $S_N2$  reaction faster. [Solution](#)

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.

Predict the order of reactivity of the following compounds in  $S_N1$  and  $S_N2$  reactions:

[Example 6.7](#)

- (i) The four isomeric bromobutanes
- (ii)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ ,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ ,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ ,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$

**Solution** (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} < (\text{CH}_3)_2\text{CHCH}_2\text{Br} < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3 < (\text{CH}_3)_3\text{CBr}$  ( $\text{S}_{\text{N}}1$ )  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHCH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3 > (\text{CH}_3)_3\text{CBr}$  ( $\text{S}_{\text{N}}2$ )

Of the two primary bromides, the carbocation intermediate derived from  $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$  is more stable than derived from  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  because of greater electron donating inductive effect of  $(\text{CH}_3)_2\text{CH}-$  group. Therefore,  $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$  is more reactive than  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  in  $\text{S}_{\text{N}}1$  reactions.  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$  is a secondary bromide and  $(\text{CH}_3)_3\text{CBr}$  is a tertiary bromide. Hence the above order is followed in  $\text{S}_{\text{N}}1$ . The reactivity in  $\text{S}_{\text{N}}2$  reactions follows the reverse order as the steric hinderance around the electrophilic carbon increases in that order.

(ii)  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br} > \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br} > \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br} > \text{C}_6\text{H}_5\text{CH}_2\text{Br}$  ( $\text{S}_{\text{N}}1$ )

$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br} < \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br} < \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br} < \text{C}_6\text{H}_5\text{CH}_2\text{Br}$  ( $\text{S}_{\text{N}}2$ )

Of the two secondary bromides, the carbocation intermediate obtained from  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$  is more stable than obtained from  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$  because it is stabilised by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in  $\text{S}_{\text{N}}1$  reactions. A phenyl group is bulkier than a methyl group. Therefore,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$  is less reactive than  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$  in  $\text{S}_{\text{N}}2$  reactions.

**(c) Stereochemical aspects of nucleophilic substitution reactions**

In order to understand the stereochemical aspects of substitution reactions, we need to learn some basic stereochemical principles and notations (**optical activity**, **chirality**, **retention**, **inversion**, **racemisation**, etc.).

(i) **Optical activity:** Plane of plane polarised light produced by passing ordinary light through Nicol prism is rotated when it is passed through the solutions of certain compounds. 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 of 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 optical activity was associated with the three dimensional arrangements of atoms in the molecules (**configurations**) of

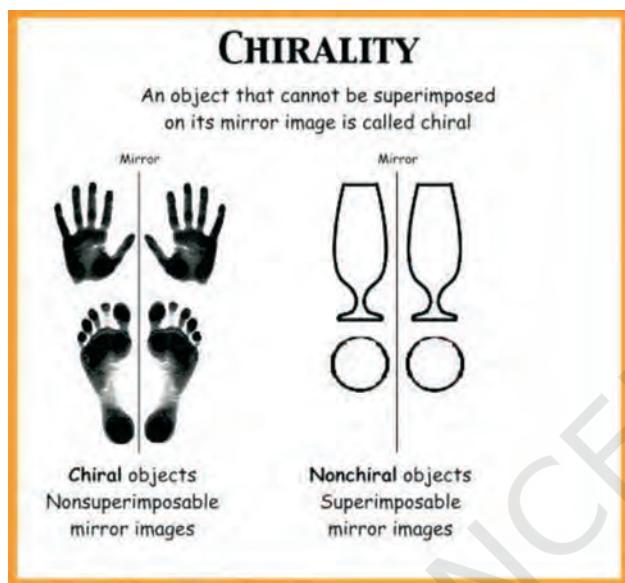
William Nicol (1768-1851) developed the first prism that produced plane polarised light.

*Jacobus Hendricus Van't Hoff (1852-1911) received the first Nobel Prize in Chemistry in 1901 for his work on solutions.*

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, the mirror image of the molecule is not superimposed (overlapped) on the molecule; 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 along with non superimposability of mirror images is responsible for the optical activity in such organic compounds.

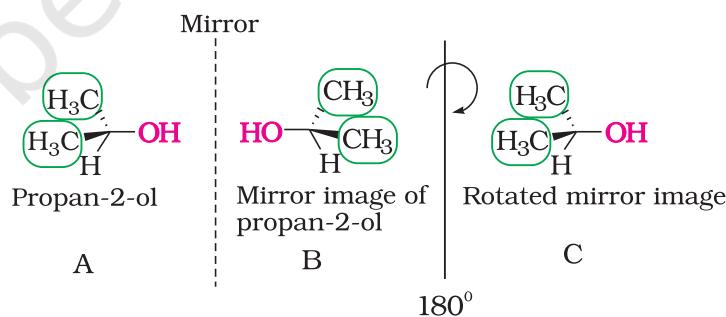
The symmetry and asymmetry are also observed in many day to day objects: a sphere, a cube, a cone, are all identical to their mirror images and can be superimposed. However, many objects are non superimposable on their mirror images. For example, your left and right hand look similar but if you put your left hand on your right hand by moving them in the same plane, 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**. Chiral molecules are optically active, while the objects, which are, superimposable on their mirror images are called **achiral**. These molecules are optically inactive.

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



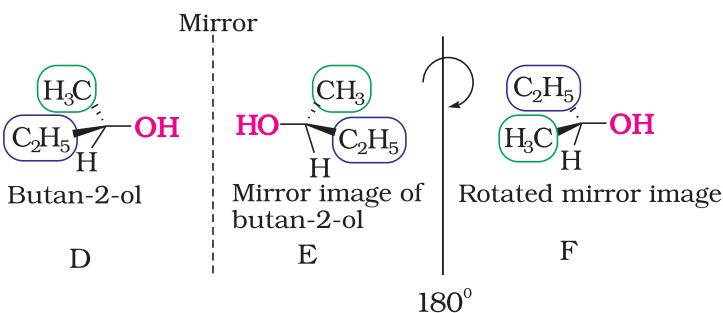
**Fig 6.4:** Some common examples of chiral and achiral objects

two simple molecules propan-2-ol (Fig.6.5) and butan-2-ol (Fig.6.6) and their mirror images.



**Fig 6.5:** B is mirror image of A; B is rotated by  $180^\circ$  and C is obtained; C is superimposable on A.

As you can see very clearly, propan-2-ol (A) does not contain an asymmetric carbon, as all the four groups attached to the tetrahedral carbon are not different. We rotate the mirror image (B) of the molecule by  $180^\circ$  (structure C) and try to overlap the structure (C) with the structure (A), these structures completely overlap. Thus propan-2-ol is an **achiral** molecule.



**Fig 6.6:** E is mirror image of D; E is rotated by 180° to get F and F is non superimposable on its mirror image D.

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-dihydroxypropanal, (OHC-CHOH-CH<sub>2</sub>OH), bromochloro-iodomethane (BrClCHI), 2-bromopropanoic acid (H<sub>3</sub>C-CHBr-COOH), etc.

The stereoisomers related to each other as non-superimposable mirror images are called **enantiomers** (Fig. 6.7). A and B in Fig. 6.5 and D and E in Fig. 6.6 are enantiomers.

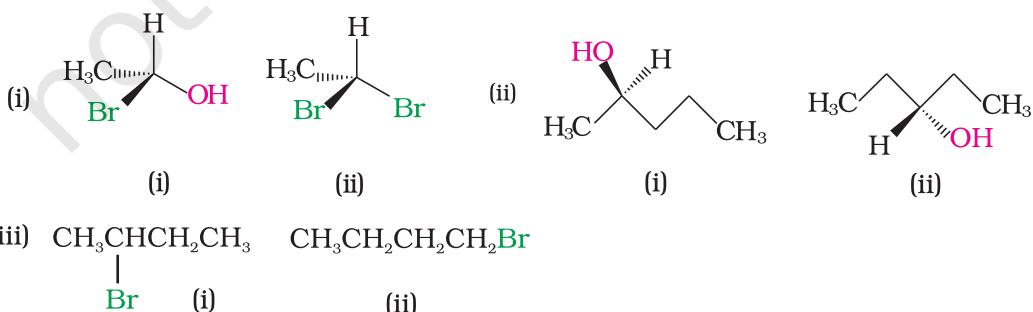
Enantiomers possess identical physical properties namely, melting point, boiling point, refractive index, etc. They only differ with respect to the rotation of plane polarised light. If one of the enantiomer is *dextro rotatory*, the other will be *laevo rotatory*.

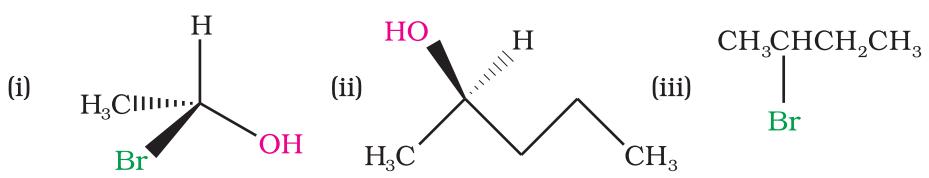
However, the sign of optical rotation is not necessarily related to the absolute (actual) configuration of the molecule.

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  $(\pm)$  before the name, for example  $(\pm)$  butan-2-ol. The process of conversion of enantiomer into a racemic mixture is known as **racemisation**.

### Example 6.8

Identify chiral and achiral molecules in each of the following pair of compounds. (Wedge and Dash representations according to Class XI).

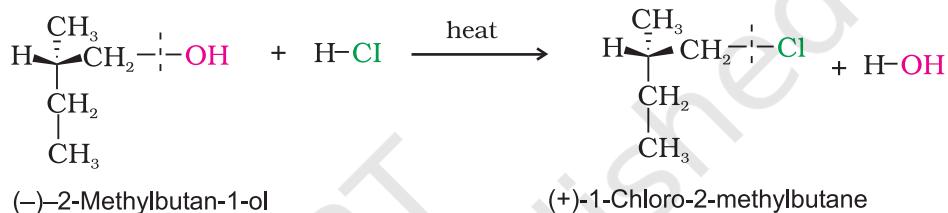




### *Solution*

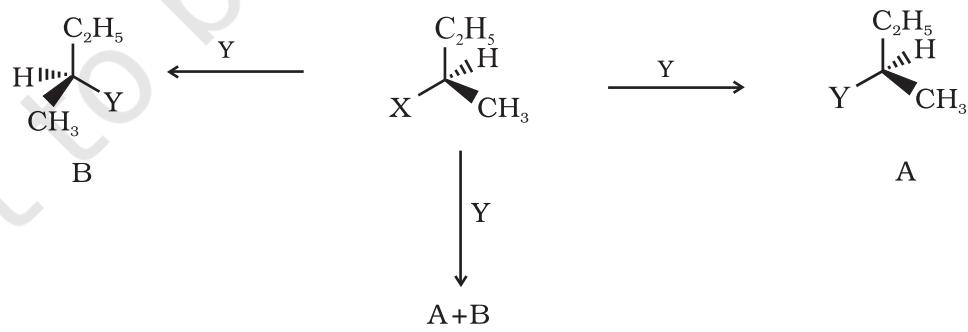
(iii) **Retention:** Retention of configuration is the preservation of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.

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.



It is important to note that configuration at a symmetric centre in the reactant and product is same but the sign of optical rotation has changed in the product. This is so because two different compounds with same configuration at asymmetric centre may have different optical rotation. One may be dextrorotatory (plus sign of optical rotation) while other may be laevorotatory (negative sign of optical rotation).

(iv) *Inversion, retention and racemisation:* There are three outcomes for a reaction at an asymmetric carbon atom, when a bond directly linked to an asymmetric carbon atom is broken. Consider the replacement of a group X by Y in the following reaction;



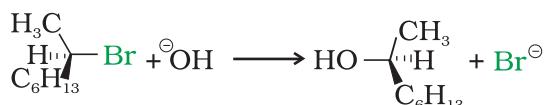
If (A) is the only compound obtained, the process is called retention of configuration. Note that configuration has been rotated in A.

If (B) is the only compound obtained, the process is called inversion of configuration. Configuration has been inverted in B.

If a 50:50 mixture of A and B is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate the plane polarised light in the direction opposite to another.

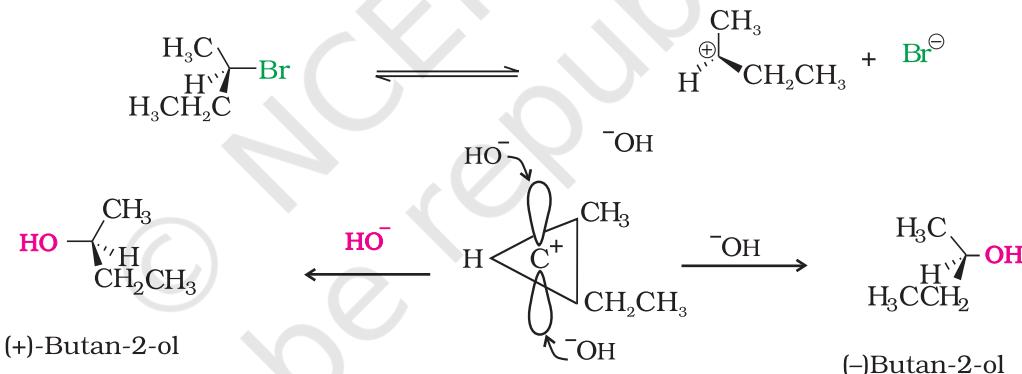
**Now let us have a fresh look at S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms by taking examples of optically active alkyl halides.**

In case of optically active alkyl halides, the product formed as a result of S<sub>N</sub>2 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-bromo-octane 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<sub>N</sub>2 reactions of optically active halides are accompanied by inversion of configuration.

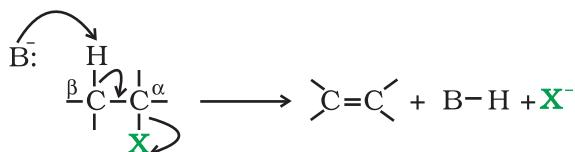
In case of optically active alkyl halides, S<sub>N</sub>1 reactions are accompanied by racemisation. Can you think of the reason why it happens? Actually the carbocation formed in the slow step being sp<sup>2</sup> hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side of the plane of carbocation 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 ( $\pm$ )-butan-2-ol.

## 2. Elimination reactions

When a haloalkane with  $\beta$ -hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from  $\beta$ -carbon and a halogen atom from the  $\alpha$ -carbon atom.



B=Base ; X=Leaving group

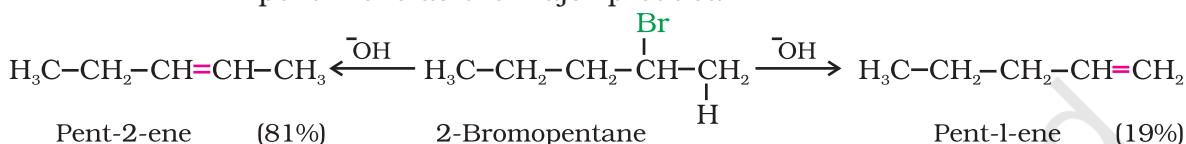
### Location of $\alpha$ and $\beta$ carbon in a molecule

Carbon on which halogen atom is directly attached is called  $\alpha$ -carbon and the carbon atom adjacent to this carbon is called  $\beta$ -carbon.



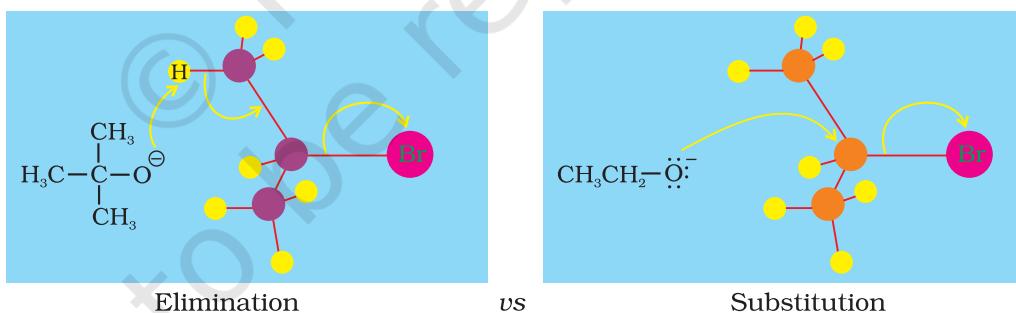
As a result, an alkene is formed as a product. Since  $\beta$ -hydrogen atom is involved in elimination, it is often called  **$\beta$ -elimination**.

If there is possibility of formation of more than one alkene due to the availability of more than one  $\beta$ -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.



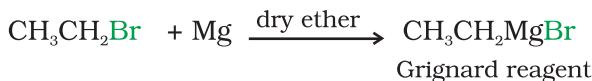
### Elimination versus substitution

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  $\beta$ -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.



### 3. Reaction with metals

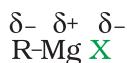
Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organo-metallic compounds**. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide,  $\text{RMgX}$ , referred as **Grignard Reagents**. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.





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.



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.



It is therefore necessary to avoid even traces of moisture from a Grignard reagent. That is why reaction is carried out in dry ether. 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.

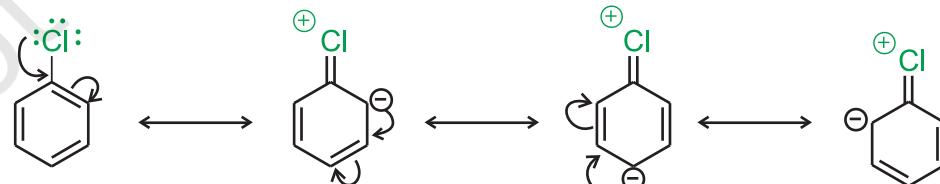


#### **6.7.2 Reactions of Haloarenes**

##### **1. Nucleophilic substitution**

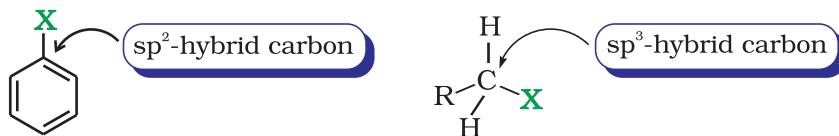
Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

- (i) *Resonance effect* : In haloarenes, the electron pairs on halogen atom are in conjugation with  $\pi$ -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.

- (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.

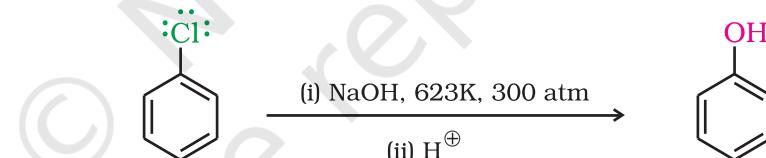


The  $sp^2$  hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than  $sp^3$ -hybridised carbon in haloalkane with less s-character. Thus, C—Cl bond length in haloalkane is 177 pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

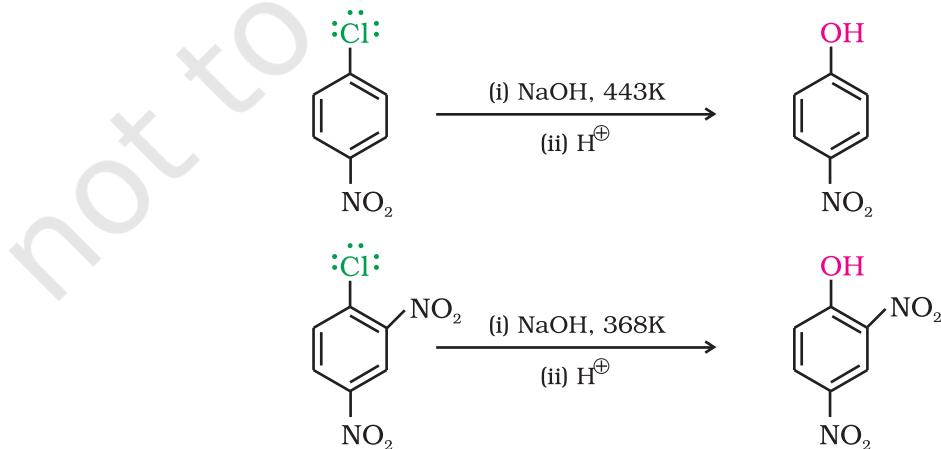
- (iii) *Instability of phenyl cation:* In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore,  $S_N1$  mechanism is ruled out.  
 (iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

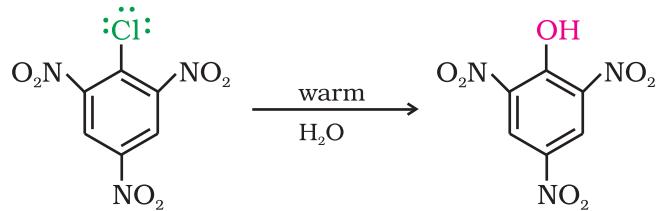
#### **Replacement by hydroxyl group**

Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atmospheres.

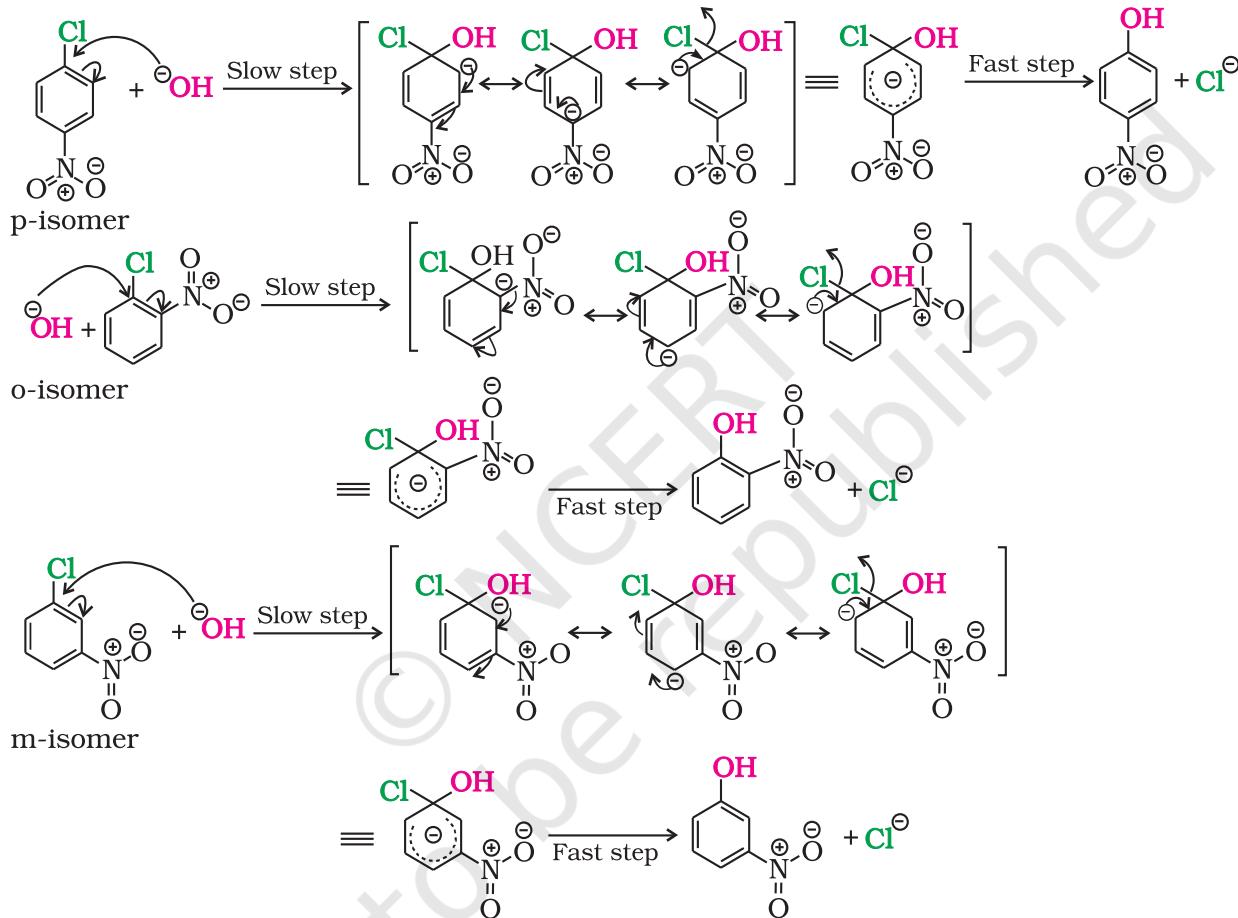


The presence of an electron withdrawing group ( $-NO_2$ ) at *ortho*- and *para*-positions increases the reactivity of haloarenes.





The effect is pronounced when (-NO<sub>2</sub>) 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:

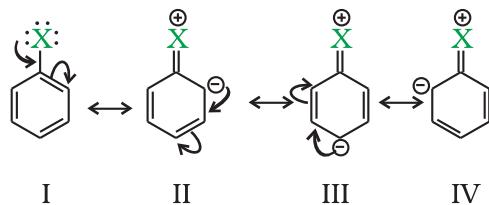


Can you think why does NO<sub>2</sub> group show its effect only at *ortho*- and *para*- positions and not at *meta*- position?

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<sub>2</sub> group while in case of *meta*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the -NO<sub>2</sub> 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<sub>2</sub> group at *meta*-position.

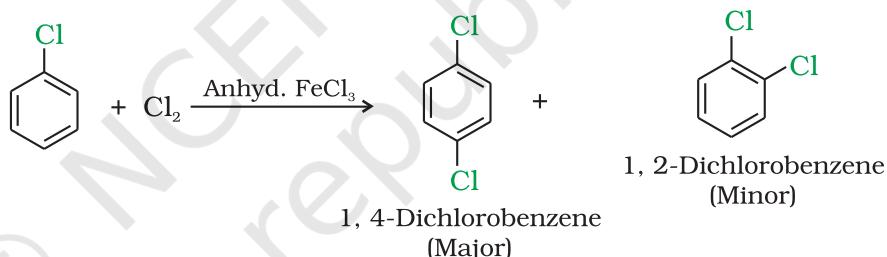
## 2. Electrophilic substitution reactions

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:

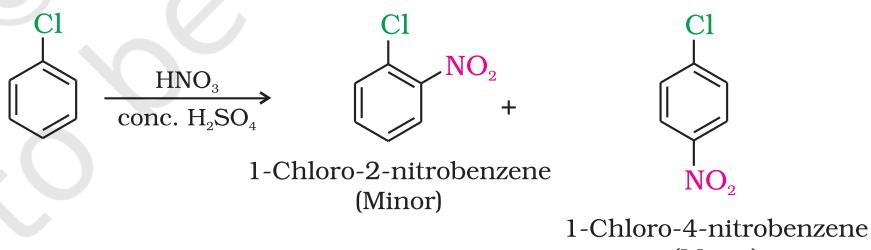


Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its  $-I$  effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

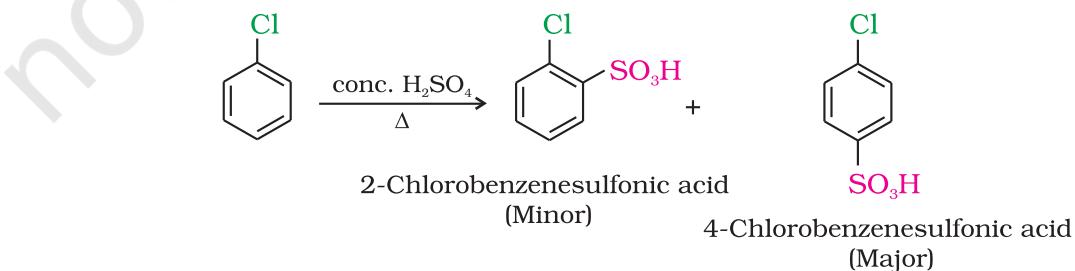
### (i) Halogenation



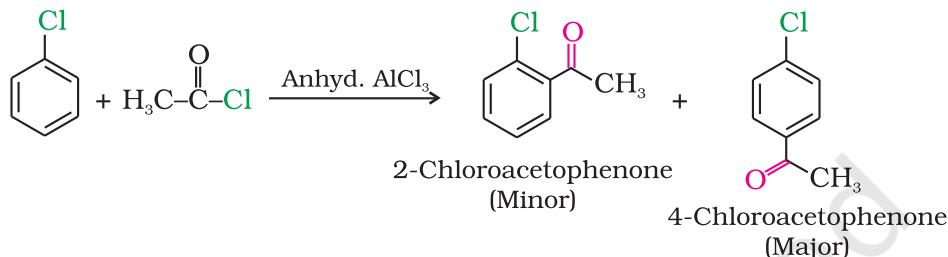
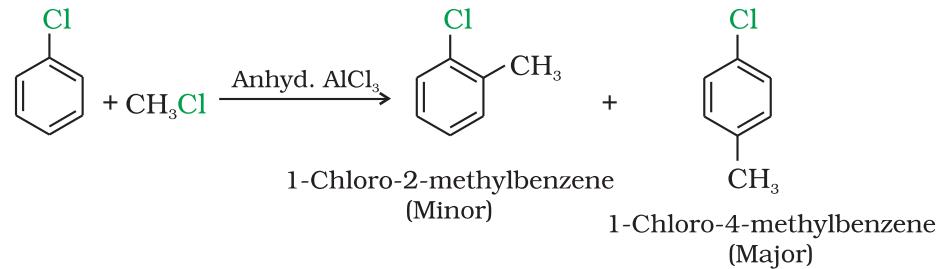
### (ii) Nitration



### (iii) Sulphonation



(iv) Friedel-Crafts reaction

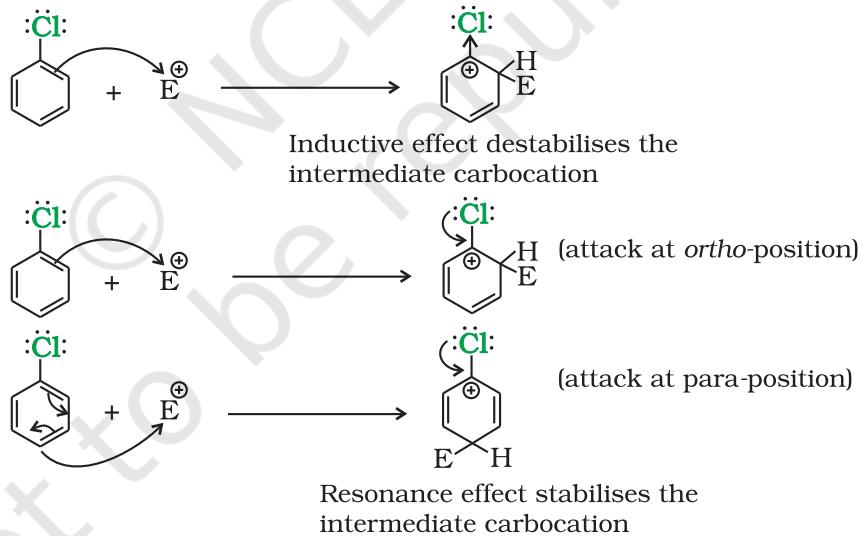


Example 6.9

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.

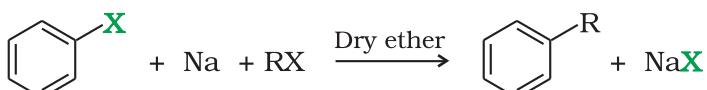


Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect 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.

### 3. Reaction with metals

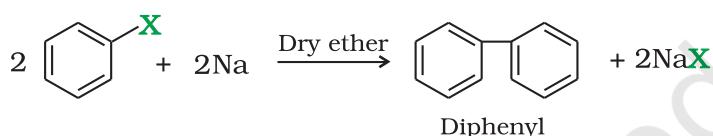
#### **Wurtz-Fittig reaction**

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.



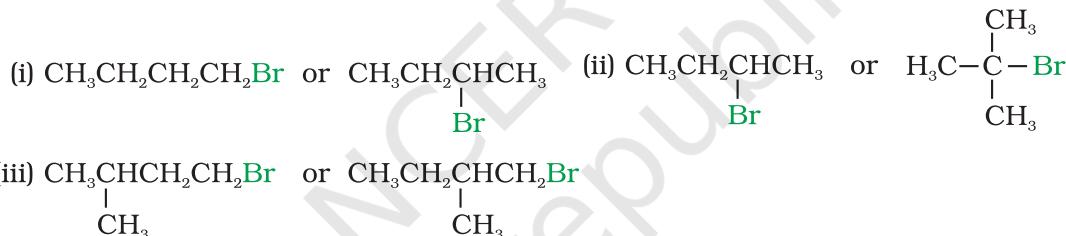
#### **Fittig reaction**

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.

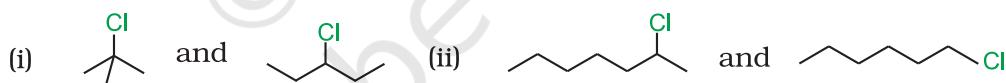


#### Intext Questions

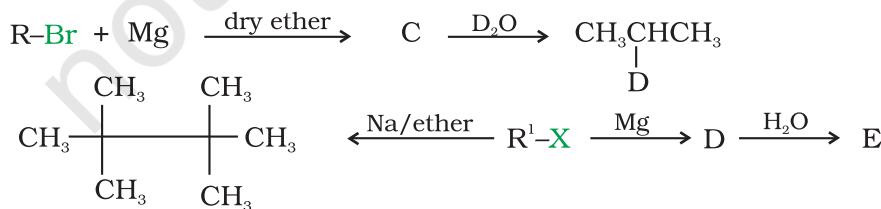
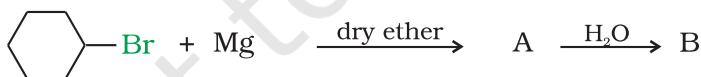
- 6.7** Which alkyl halide from the following pairs would you expect to react more rapidly by an  $S_N2$  mechanism? Explain your answer.



- 6.8** In the following pairs of halogen compounds, which compound undergoes faster  $S_N1$  reaction?



- 6.9** Identify A, B, C, D, E, R and  $R^1$  in the following:



## 6.8 Polyhalogen Compounds

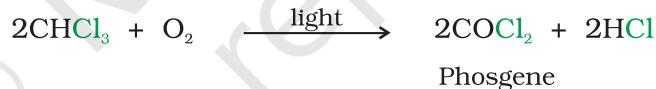
Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

### 6.8.1 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.

### 6.8.2 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.



### 6.8.3 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.

### 6.8.4 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 permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to  $\text{CCl}_4$  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

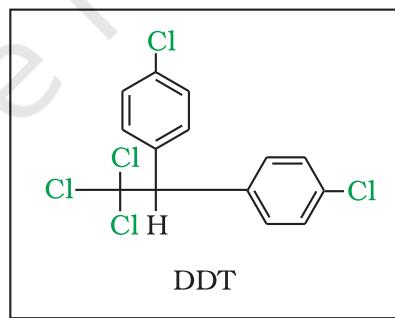
ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

#### 6.8.5 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 ( $\text{CCl}_2\text{F}_2$ ) 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.

#### 6.8.6 **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.



### 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<sub>N</sub>1** and **S<sub>N</sub>2** on the basis of their kinetic properties. **Chirality** has a profound role in understanding the reaction mechanisms of **S<sub>N</sub>1** and **S<sub>N</sub>2** reactions. **S<sub>N</sub>2** reactions of chiral alkyl halides are characterised by the inversion of configuration while **S<sub>N</sub>1** 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

- 6.1** 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)  $p\text{-Cl}C_6H_4CH_2CH(CH_3)_2$   
(xi)  $m\text{-Cl}CH_2C_6H_4CH_2C(CH_3)_3$       (xii)  $o\text{-Br\text{-}}C_6H_4CH(CH_3)CH_2CH_3$
- 6.2** Give the IUPAC names of the following compounds:
- (i)  $CH_3CH(Cl)CH(Br)CH_3$       (ii)  $CHF_2CBrClF$       (iii)  $CICH_2C\equiv CCH_2Br$   
(iv)  $(CCl_3)_3CCl$       (v)  $CH_3C(p\text{-Cl}C_6H_4)_2CH(Br)CH_3$       (vi)  $(CH_3)_3CCH=CClC_6H_4I-p$
- 6.3** 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) 2-Bromobutane      (vi) 4-tert-Butyl-3-iodoheptane  
(vii) 1-Bromo-4-sec-butyl-2-methylbenzene      (viii) 1,4-Dibromobut-2-ene
- 6.4** Which one of the following has the highest dipole moment?
- (i)  $CH_2Cl_2$       (ii)  $CHCl_3$       (iii)  $CCl_4$
- 6.5** 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.
- 6.6** Write the isomers of the compound having formula  $C_4H_9Br$ .
- 6.7** Write the equations for the preparation of 1-iodobutane from  
(i) 1-butanol      (ii) 1-chlorobutane      (iii) but-1-ene.
- 6.8** What are ambident nucleophiles? Explain with an example.

- 6.9** Which compound in each of the following pairs will react faster in  $S_N2$  reaction with  $\text{OH}^-$ ?
- $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$
  - $(\text{CH}_3)_3\text{CCl}$  or  $\text{CH}_3\text{Cl}$
- 6.10** Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:
- 1-Bromo-1-methylcyclohexane
  - 2-Chloro-2-methylbutane
  - 2,2,3-Trimethyl-3-bromopentane.
- 6.11** How will you bring about the following conversions?
- Ethanol to but-1-yne
  - Ethane to bromoethene
  - Propene to 1-nitropropane
  - Toluene to benzyl alcohol
  - Propene to propyne
  - Ethanol to ethyl fluoride
  - Bromomethane to propanone
  - But-1-ene to but-2-ene
  - 1-Chlorobutane to n-octane
  - Benzene to biphenyl.
- 6.12** Explain why
- the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
  - alkyl halides, though polar, are immiscible with water?
  - Grignard reagents should be prepared under anhydrous conditions?
- 6.13** Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.
- 6.14** Write the structure of the major organic product in each of the following reactions:
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow[\text{heat}]{\text{acetone}}$
  - $(\text{CH}_3)_3\text{CBr} + \text{KOH} \xrightarrow[\text{heat}]{\text{ethanol}}$
  - $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{\text{water}}$
  - $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \xrightarrow{\text{aq. ethanol}}$
  - $\text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \longrightarrow$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow$
  - $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{HBr} \xrightarrow{\text{peroxide}}$
  - $\text{CH}_3\text{CH} = \text{C}(\text{CH}_3)_2 + \text{HBr} \longrightarrow$
- 6.15** Write the mechanism of the following reaction:
- $$\text{nBuBr} + \text{KCN} \xrightarrow{\text{EtOH-H}_2\text{O}} \text{nBuCN}$$
- 6.16** Arrange the compounds of each set in order of reactivity towards  $S_N2$  displacement:
- 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
  - 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane
  - 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.
- 6.17** Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ , which is more easily hydrolysed by aqueous KOH.
- 6.18**  $p$ -Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.
- 6.19** How the following conversions can be carried out?
- Propene to propan-1-ol
  - Ethanol to but-1-yne
  - 1-Bromopropane to 2-bromopropane

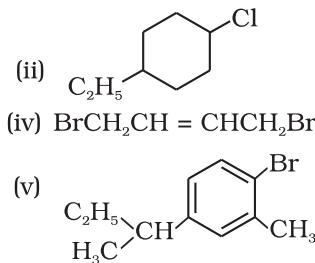
- (iv) Toluene to benzyl alcohol
- (v) Benzene to 4-bromonitrobenzene
- (vi) Benzyl alcohol to 2-phenylethanoic acid
- (vii) Ethanol to propanenitrile
- (viii) Aniline to chlorobenzene
- (ix) 2-Chlorobutane to 3, 4-dimethylhexane
- (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
- (xi) Ethyl chloride 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

- 6.20** 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.
- 6.21** 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.
- 6.22** 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?

### Answers to Some Intext Questions

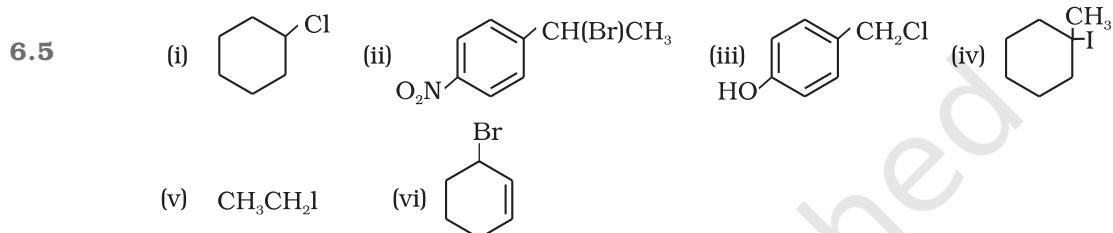
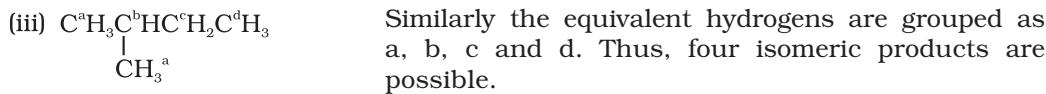
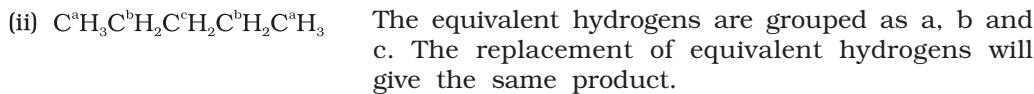
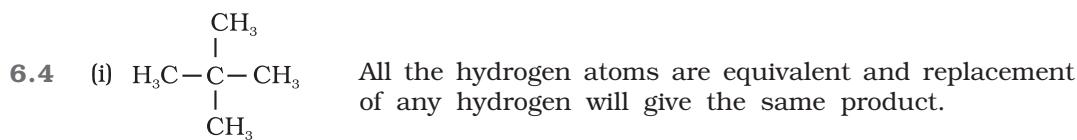
**6.1**

- (i)  $CH_3CH_2CH(CH_3)CHClCH_3$
- (iii)  $CH_3CH_2CH_2\underset{\begin{array}{c} | \\ H_3C-C-CH_3 \end{array}}{CH} CH(I)CH_2CH_3$



- 6.2** (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 acid, HI which is then oxidised by it to  $I_2$ .

- 6.3** (i)  $ClCH_2CH_2CH_2Cl$  (ii)  $ClCH_2CHClCH_3$  (iii)  $Cl_2CHCH_2CH_3$  (iv)  $CH_3CCl_2CH_3$



**6.6** (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.

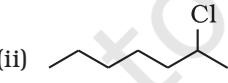
**6.7** (i)  $CH_3CH_2CH_2CH_2Br$  Being primary halide, there won't be any steric hindrance.

(ii)  $CH_3CH_2CH(CH_3)_2Br$  Secondary halide reacts faster than tertiary halide.

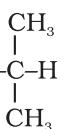
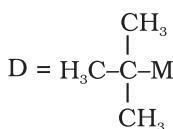
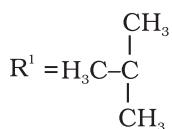
(iii)  $CH_3CH(CH_3)CH_2CH_2Br$  The presence of methyl group closer to the halide group will increase the steric hindrance and decrease the rate.

**6.8** (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.





12086CHI1

Unit

7

# Alcohols, Phenols and Ethers

## 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 alkenes, aldehydes, ketones and carboxylic acids;
- discuss the reactions involved in the preparation of phenols from haloarenes, benzene sulphonic acids, diazonium salts and 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.

*Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.*

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, newspapers, 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 ( $\text{CH}_3\text{OH}$ ) while a phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system ( $\text{C}_6\text{H}_5\text{OH}$ ).

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group ( $\text{R}-\text{O}/\text{Ar}-\text{O}$ ) yields another class of compounds known as 'ethers', for example,  $\text{CH}_3\text{OCH}_3$  (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.

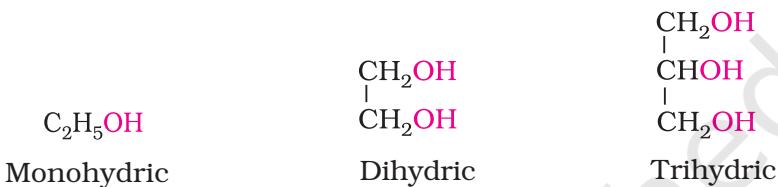
In this unit, we shall discuss the chemistry of three classes of compounds, namely — alcohols, phenols and ethers.

## 7.1 Classification

### 7.1.1 Alcohols— Mono, Di, Tri or Polyhydric alcohols

The classification of compounds makes their study systematic and hence simpler. Therefore, let us first learn how are alcohols, phenols and ethers classified?

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:



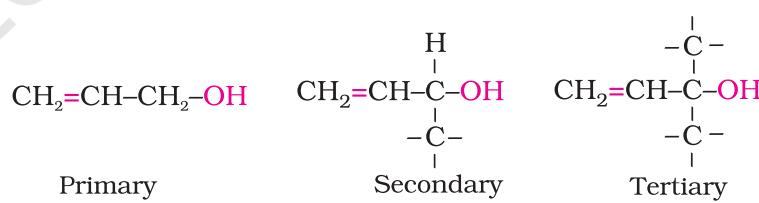
Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

(i) *Compounds containing  $\text{C}_{sp^3}$ —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:

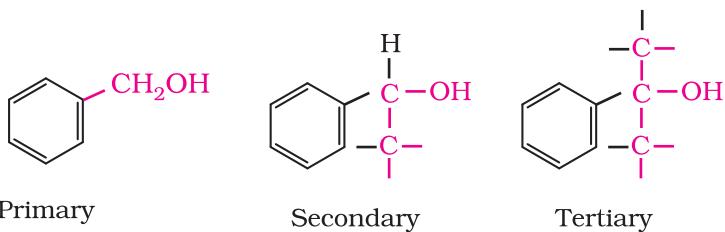
*Primary, secondary and tertiary alcohols*: In these three types of alcohols, the —OH group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:



*Allylic alcohols*: In these alcohols, the —OH group is attached to a  $sp^3$  hybridised carbon adjacent to the carbon-carbon double bond, that is to an allylic carbon. For example



*Benzyllic alcohols*: In these alcohols, the —OH group is attached to a  $sp^3$ —hybridised carbon atom next to an aromatic ring. For example.

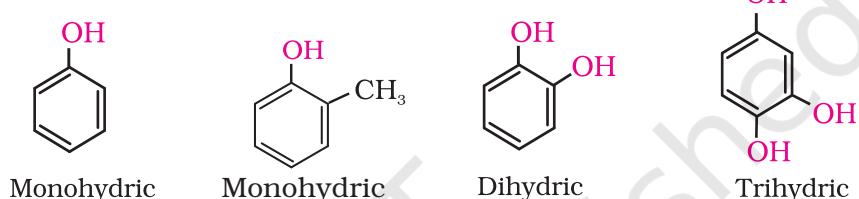


Allylic and benzylic alcohols may be primary, secondary or tertiary.

(ii) *Compounds containing C<sub>sp</sub><sup>2</sup>–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<sub>2</sub> = CH – OH

### 7.1.2 Phenols— Mono, Di and trihydric phenols

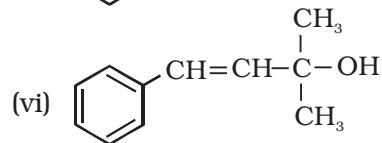
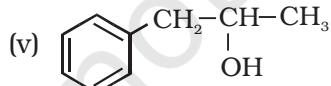
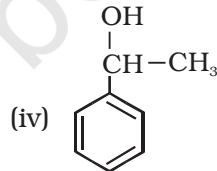
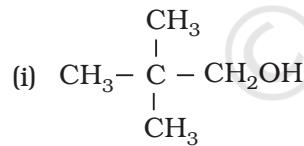


### 7.1.3 Ethers

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<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>, is a symmetrical ether whereas C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>5</sub> are unsymmetrical ethers.

### Intext Questions

**7.1** Classify the following as primary, secondary and tertiary alcohols:



**7.2** Identify allylic alcohols in the above examples.

### 7.2 Nomenclature

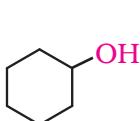
(a) **Alcohols:** The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, CH<sub>3</sub>OH is methyl alcohol.

According to IUPAC system, 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<sub>2</sub>—CH<sub>2</sub>—OH is named as ethane-1, 2-diol. Table 7.1 gives common and IUPAC names of a few alcohols as examples.

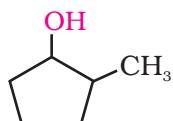
**Table 7.1: Common and IUPAC Names of Some Alcohols**

Compound	Common name	IUPAC name
CH <sub>3</sub> — OH	Methyl alcohol	Methanol
CH <sub>3</sub> — CH <sub>2</sub> — CH <sub>2</sub> — OH	n-Propyl alcohol	Propan-1-ol
CH <sub>3</sub> — CH — CH <sub>3</sub>   OH	Isopropyl alcohol	Propan-2-ol
CH <sub>3</sub> — CH <sub>2</sub> — CH <sub>2</sub> — CH <sub>2</sub> — OH	n-Butyl alcohol	Butan-1-ol
CH <sub>3</sub> — CH — CH <sub>2</sub> — CH <sub>3</sub>   OH	sec-Butyl alcohol	Butan-2-ol
CH <sub>3</sub> — CH — CH <sub>2</sub> — OH   CH <sub>3</sub>	Isobutyl alcohol	2-Methylpropan-1-ol
CH <sub>3</sub>   CH <sub>3</sub> — C — OH   CH <sub>3</sub>	tert-Butyl alcohol	2-Methylpropan-2-ol
HO—H <sub>2</sub> C—CH <sub>2</sub> —OH	Ethylene glycol	Ethane-1,2-diol
CH <sub>2</sub> — CH — CH <sub>2</sub>   OH        OH      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.

<b>Common name</b> Phenol	<b>IUPAC name</b> Phenol	<b>Common name</b> o-Cresol 2-Methylphenol	<b>IUPAC name</b> m-Cresol 3-Methylphenol
<b>Common name</b> <i>p</i> -Cresol 4-Methylphenol			

Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- and 1, 4-benzenediol.

<b>Common name</b> Catechol Benzene-1,2-diol	<b>IUPAC name</b> Resorcinol Benzene-1,3-diol	<b>Common name</b> Hydroquinone or quinol 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,  $\text{CH}_3\text{OC}_2\text{H}_5$  is ethylmethyl ether.

**Table 7.2: Common and IUPAC Names of Some Ethers**

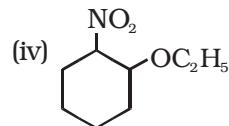
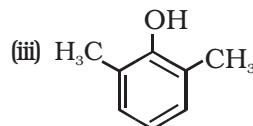
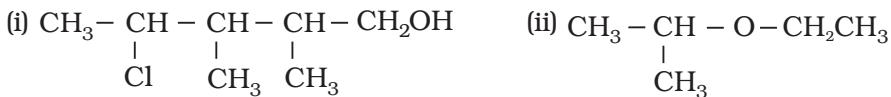
Compound	Common name	IUPAC name
$\text{CH}_3\text{OCH}_3$	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6 - \text{CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	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,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  is diethyl ether.

According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an  $-\text{OR}$  or  $-\text{OAr}$  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 7.2.

### Example 7.1

Give IUPAC names of the following compounds:

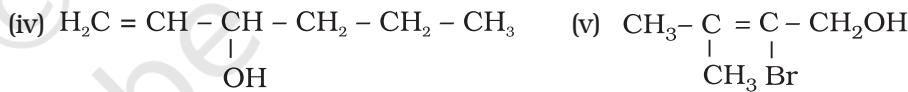
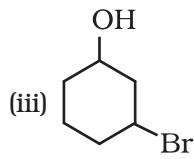
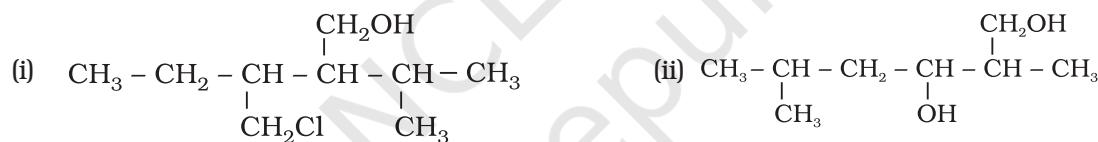


### Solution

- (i) 4-Chloro-2,3-dimethylpentan-1-ol    (ii) 2-Ethoxypropane  
 (iii) 2,6-Dimethylphenol                         (iv) 1-Ethoxy-2-nitrocyclohexane

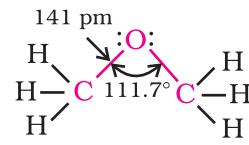
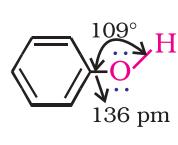
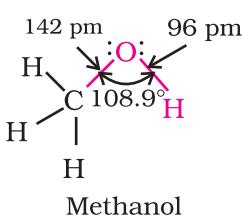
### Intext Question

**7.3** Name the following compounds according to IUPAC system.



### 7.3 Structures of functional Groups

In alcohols, the oxygen of the  $-\text{OH}$  group is attached to carbon by a sigma ( $\sigma$ ) bond formed by the overlap of a  $sp^3$  hybridised orbital of carbon with a  $sp^3$  hybridised orbital of oxygen. Fig. 7.1 depicts structural aspects of methanol, phenol and methoxymethane.



**Fig. 7.1:** Structures of methanol, phenol and methoxymethane

The bond angle  in alcohols is slightly less than the tetrahedral angle ( $109^\circ\text{-}28'$ ). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the  $-\text{OH}$  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 7.4.4) 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 ( $-\text{R}$ ) groups. The  $\text{C}-\text{O}$  bond length (141 pm) is almost the same as in alcohols.

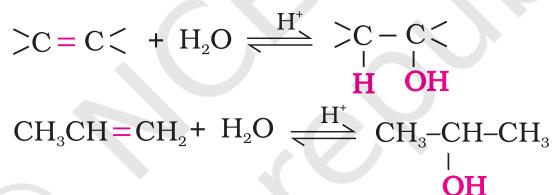
## 7.4 Alcohols and Phenols

### 7.4.1 Preparation of Alcohols

Alcohols are prepared by the following methods:

#### 1. From alkenes

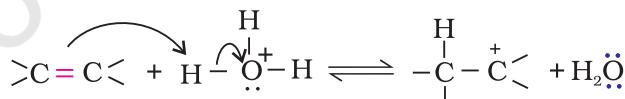
(i) *By acid catalysed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.



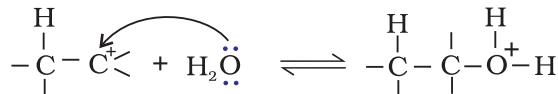
#### Mechanism

The mechanism of the reaction involves the following three steps:

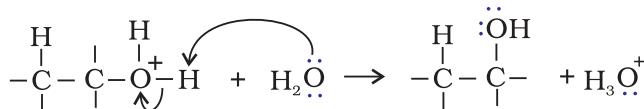
Step 1: Protonation of alkene to form carbocation by electrophilic attack of  $\text{H}_3\text{O}^+$ .



Step 2: Nucleophilic attack of water on carbocation.

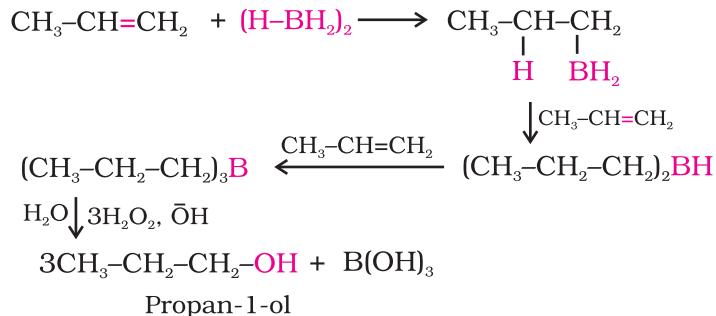


Step 3: Deprotonation to form an alcohol.



*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.*

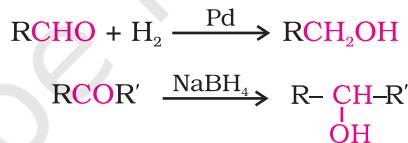
- (ii) *By hydroboration-oxidation:* Diborane ( $\text{BH}_3\text{}_2$ ) reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



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.

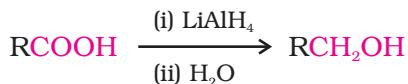
## 2. From carbonyl compounds

- (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 ( $\text{NaBH}_4$ ) or lithium aluminium hydride ( $\text{LiAlH}_4$ ). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



*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.



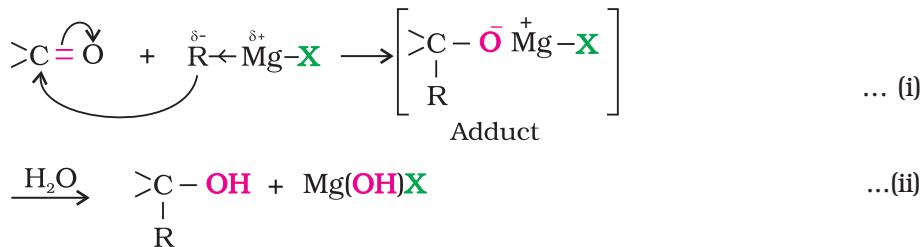
However,  $\text{LiAlH}_4$  is an expensive reagent, and therefore, used for preparing special chemicals only. Commercially, acids are reduced to alcohols by converting them to the esters (Section 7.4.4), followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).



### 3. From Grignard reagents

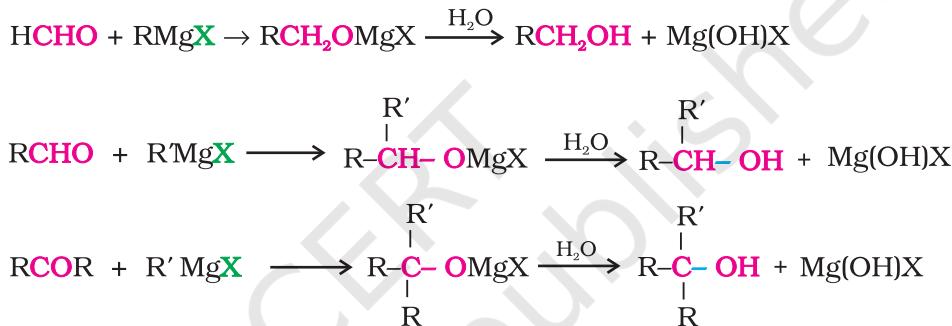
Alcohols are produced by the reaction of Grignard reagents (Unit 6, Class XII) with aldehydes and ketones.

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.



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:

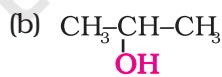
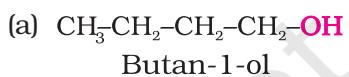


You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

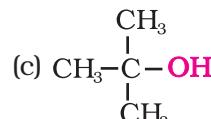
Give the structures and IUPAC names of the products expected from the following reactions:

#### Example 7.2

- (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.



Propan-2-ol



2-Methylpropan-2-ol

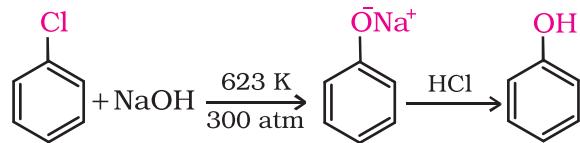
#### Solution

#### 7.4.2 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:

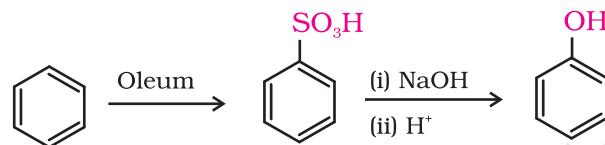
### 1. From haloarenes

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced (Unit 6, Class XII).



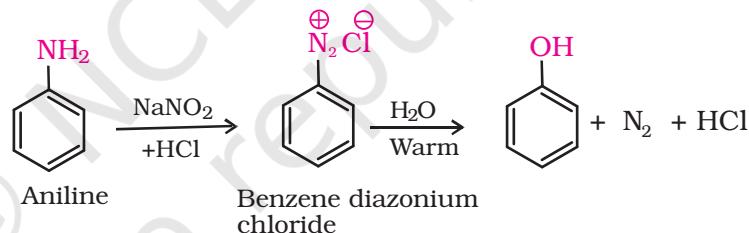
### 2. From benzenesulphonic acid

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

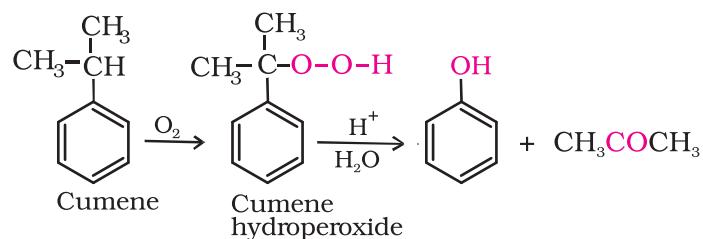
A diazonium salt is formed by treating an aromatic primary amine with nitrous acid (NaNO<sub>2</sub> + HCl) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids (Unit 9, Class XII).



Most of the worldwide production of phenol is from cumene.

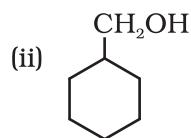
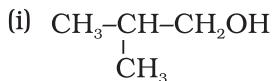
### 4. From cumene

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.

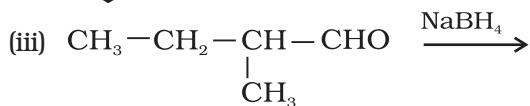
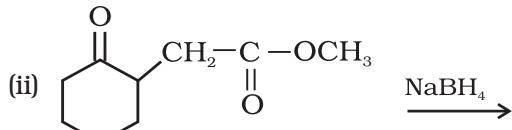
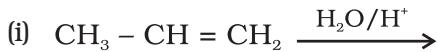


### Intext Questions

**7.4** Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?



**7.5** Write structures of the products of the following reactions:



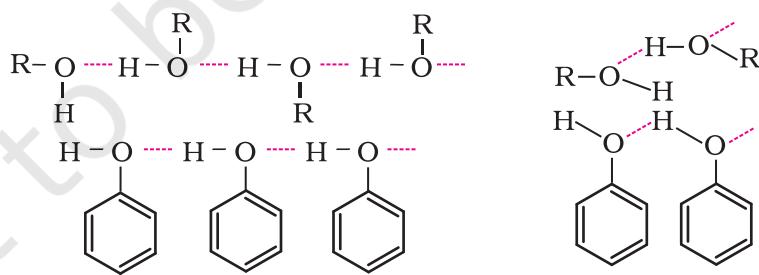
#### 7.4.3 Physical Properties

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.

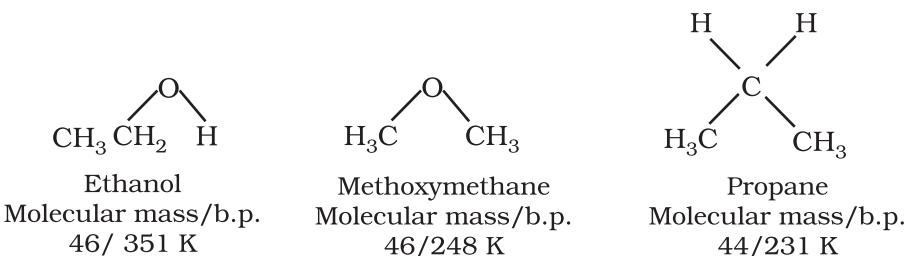
##### Boiling Points

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  $-\text{OH}$  group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



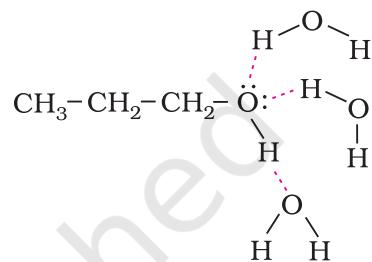
It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.



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 7.3

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.
- (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.
- (b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

### Solution

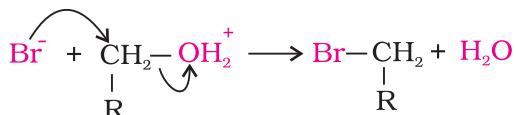
#### 7.4.4 Chemical Reactions

Alcohols are versatile compounds. They react both as nucleophiles and electrophiles. The bond between O–H is broken when alcohols react as nucleophiles.



(ii) The bond between C–O is broken when they react as electrophiles. Protonated alcohols react in this manner.

#### Protonated alcohols as electrophiles

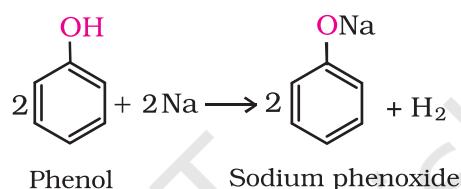
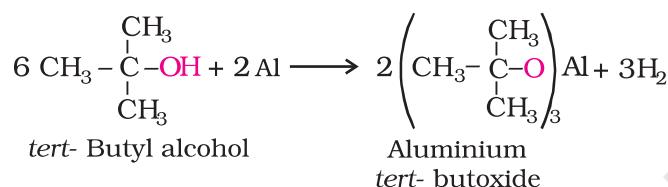
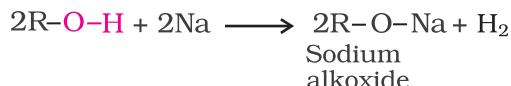


Based on the cleavage of O–H and C–O bonds, the reactions of alcohols and phenols may be divided into two groups:

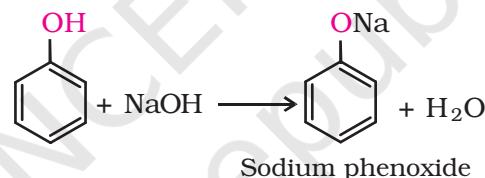
**(a) Reactions involving cleavage of O-H bond**

## **1. Acidity of alcohols and phenols**

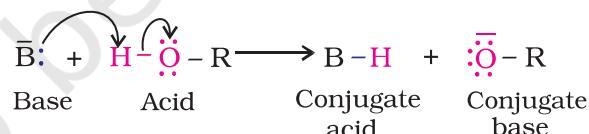
(i) **Reaction with metals:** Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.



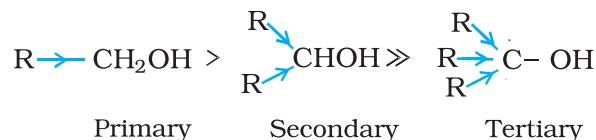
In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



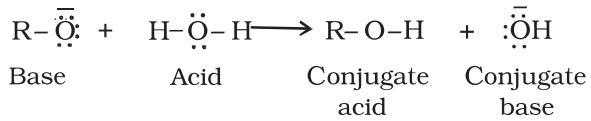
The above reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are Brönsted acids i.e., they can donate a proton to a stronger base ( $B^-$ ).



(ii) **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O-H bond. An electron-releasing group ( $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ) 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:



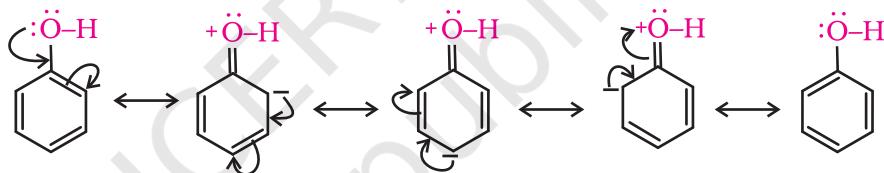
Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.



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).

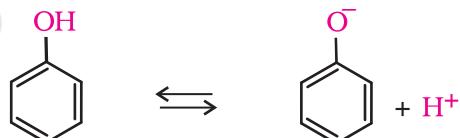
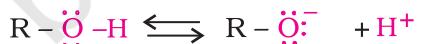
Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

- (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.



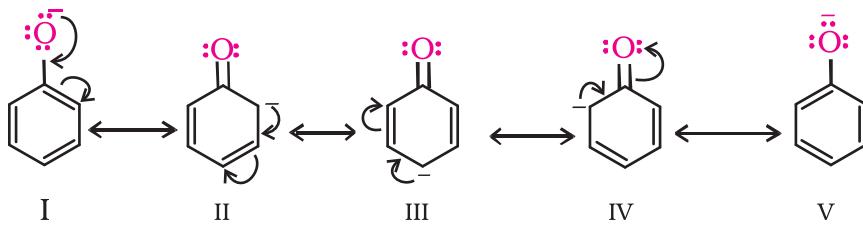
The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how a compound in which hydroxyl group attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group.

The ionisation of an alcohol and a phenol takes place as follows:



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

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.



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 when substituent is at *ortho* or *para* position. 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 7.3:  $pK_a$  Values of some Phenols and Ethanol**

Compound	Formula	$pK_a$
<i>o</i> -Nitrophenol	<i>o</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	7.2
<i>m</i> -Nitrophenol	<i>m</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	8.3
<i>p</i> -Nitrophenol	<i>p</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	7.1
Phenol	C <sub>6</sub> H <sub>5</sub> -OH	10.0
<i>o</i> -Cresol	<i>o</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2
<i>m</i> -Cresol	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -OH	10.1
<i>p</i> -Cresol	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

Arrange the following compounds in increasing order of their acid strength:

**Example 7.4**

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4,6-trinitrophenol.

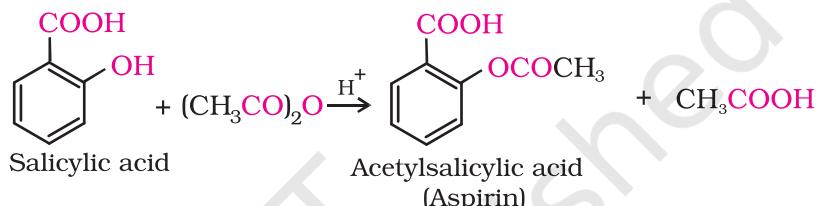
## 2. Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



*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 ( $\text{CH}_3\text{CO}$ ) 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**

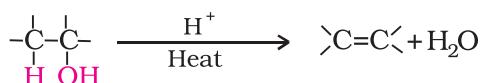
The reactions involving cleavage of C–O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

1. **Reaction with hydrogen halides:** Alcohols react with hydrogen halides to form alkyl halides (Refer Unit 6, Class XII).

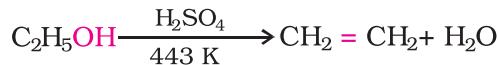


The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (**Lucas test**). Alcohols are soluble in Lucas reagent (conc. HCl and  $\text{ZnCl}_2$ ) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

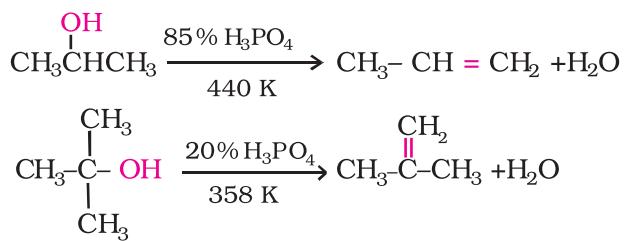
2. **Reaction with phosphorus trihalides:** Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide (Refer Unit 6, Class XII).
3. **Dehydration:** Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , or catalysts such as anhydrous zinc chloride or alumina.



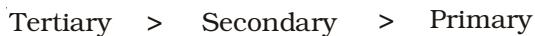
Ethanol undergoes dehydration by heating it with concentrated  $\text{H}_2\text{SO}_4$  at 443 K.



Secondary and tertiary alcohols are dehydrated under milder conditions. For example



Thus, the relative ease of dehydration of alcohols follows the following order:

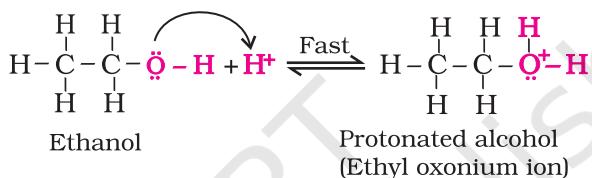


The mechanism of dehydration of ethanol involves the following steps:

*Tertiary carbocations are more stable and therefore are easier to form than secondary and primary carbocations; tertiary alcohols are the easiest to dehydrate.*

### Mechanism

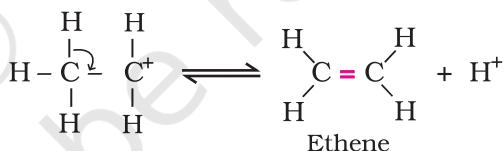
**Step 1:** Formation of protonated alcohol.



**Step 2:** Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

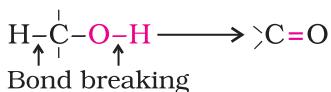


**Step 3:** Formation of ethene by elimination of a proton.

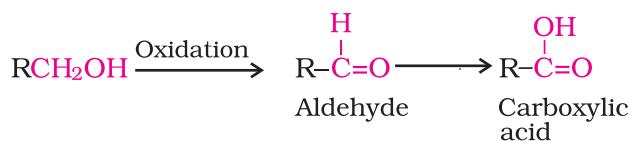


The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

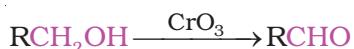
**4. Oxidation:** Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.



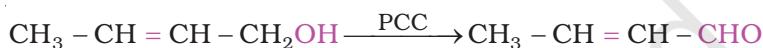
Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.



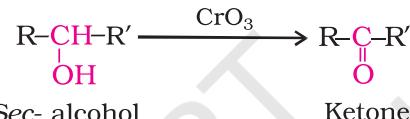
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly.  $\text{CrO}_3$  in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



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.

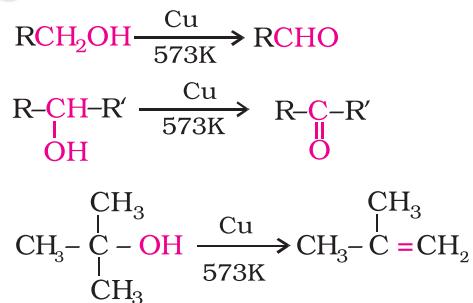


Secondary alcohols are oxidised to ketones by chromic anhydride ( $\text{CrO}_3$ ).



Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ( $\text{KMnO}_4$ ) 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.



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 ( $\text{HCHO}$ ) to acid is swamped allowing time for kidneys to excrete methanol.

### (c) Reactions of phenols

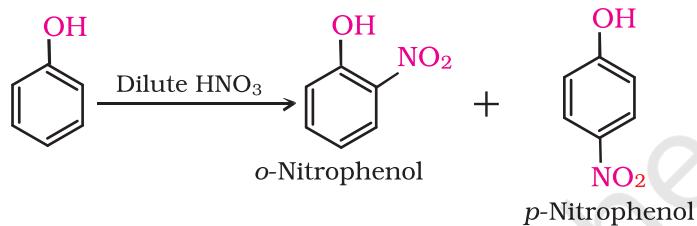
Following reactions are shown by phenols only.

## 1. Electrophilic aromatic substitution

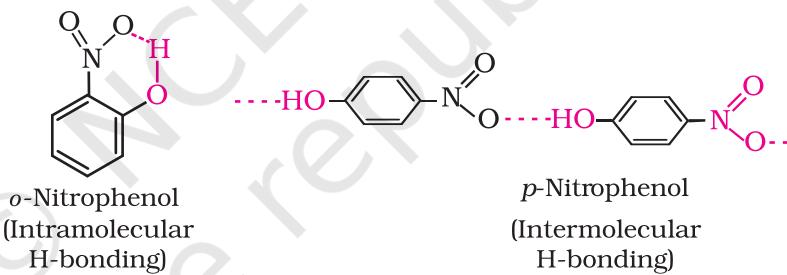
In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions (Unit 9, Class XI). The -OH group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to *ortho* and *para* positions in the ring as these 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.

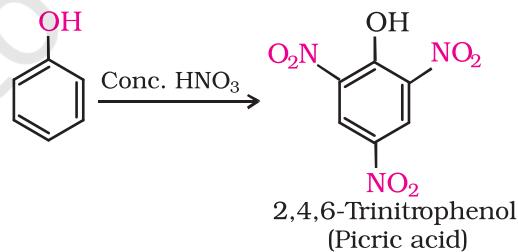


The *ortho* and *para* isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



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.

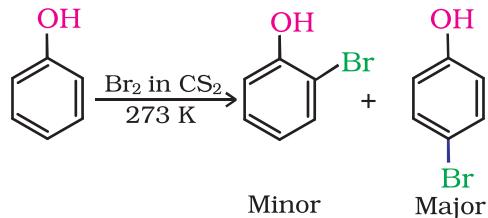
With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



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?

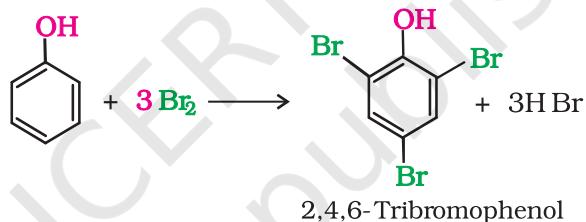
(ii) **Halogenation:** On treating phenol with bromine, different reaction products are formed under different experimental conditions.

- (a) When the reaction is carried out in solvents of low polarity such as  $\text{CHCl}_3$  or  $\text{CS}_2$  and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as  $\text{FeBr}_3$  (Unit 6, 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  $-\text{OH}$  group attached to the benzene ring.

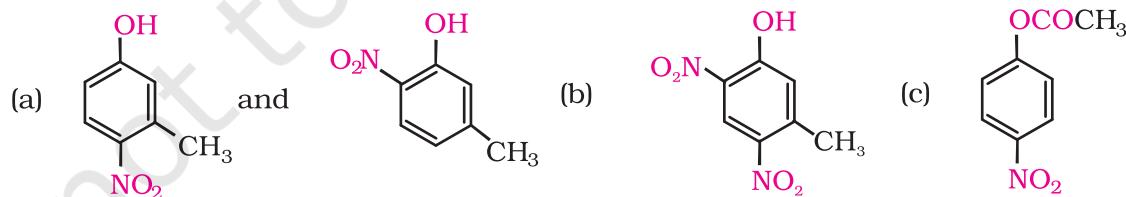
- (b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



**Example 7.5** Write the structures of the major products expected from the following reactions:

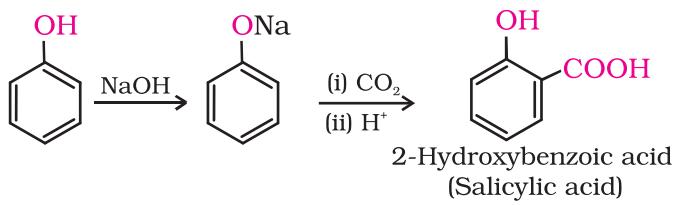
- Mononitration of 3-methylphenol
- Dinitration of 3-methylphenol
- Mononitration of phenyl methanoate.

**Solution** The combined influence of  $-\text{OH}$  and  $-\text{CH}_3$  groups determine the position of the incoming group.



## 2. Kolbe's reaction

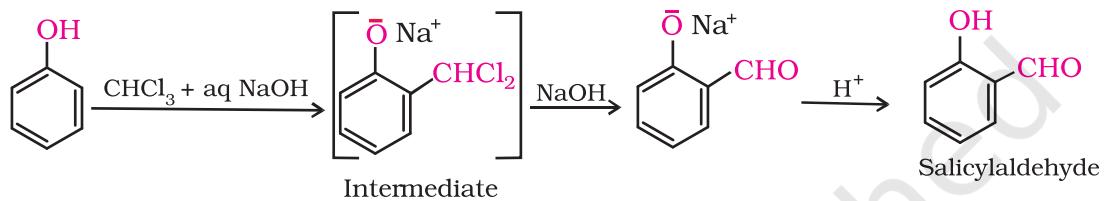
Phenoxyde ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.



### 3. Reimer-Tiemann reaction

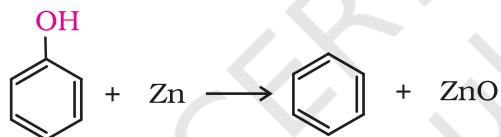
On treating phenol with chloroform in the presence of sodium hydroxide, a -CHO group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*.

The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



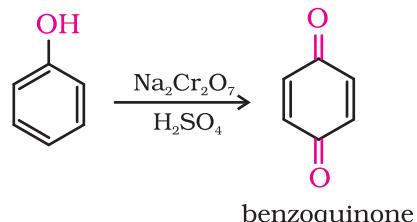
### 4. Reaction of phenol with zinc dust

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.



### Intext Questions

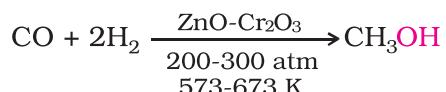
- 7.6 Give structures of the products you would expect when each of the following alcohol reacts with (a)  $\text{HCl} - \text{ZnCl}_2$  (b)  $\text{HBr}$  and (c)  $\text{SOCl}_2$ .
  - (i) Butan-1-ol
  - (ii) 2-Methylbutan-2-ol
- 7.7 Predict the major product of acid catalysed dehydration of
  - (i) 1-methylcyclohexanol and
  - (ii) butan-1-ol
- 7.8 *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.
- 7.9 Write the equations involved in the following reactions:
  - (i) Reimer - Tiemann reaction
  - (ii) Kolbe's reaction

## 7.5 Some Commercially Important Alcohols

Methanol and ethanol are among the two commercially important alcohols.

## 1. Methanol

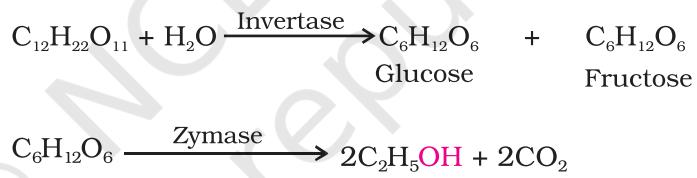
Methanol,  $\text{CH}_3\text{OH}$ , also known as ‘wood spirit’, was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of  $\text{ZnO} - \text{Cr}_2\text{O}_3$  catalyst.



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.



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.

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.

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 7.4).

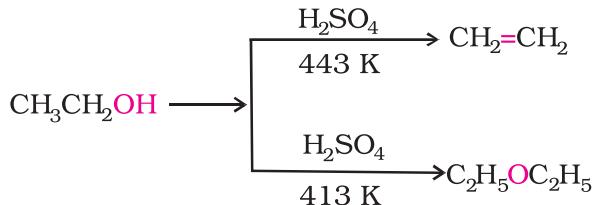
## 7.6 Ethers

### 7.6.1 Preparation of Ethers

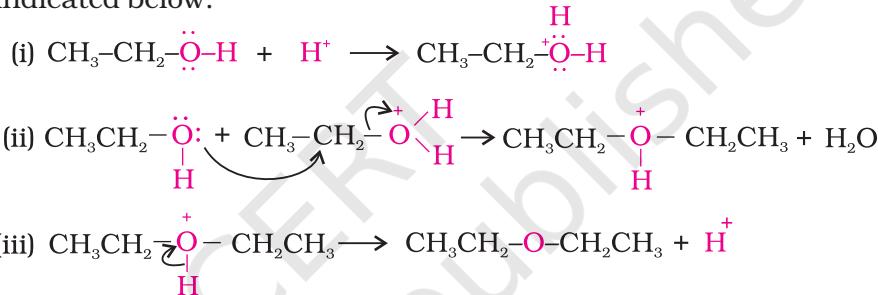
Diethyl ether has been used widely as an inhalation anaesthetic. But due to its slow effect and an unpleasant recovery period, it has been replaced, as an anaesthetic, by other compounds.

#### 1. By dehydration of alcohols

Alcohols undergo dehydration in the presence of protic acids ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ). 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.



The formation of ether is a nucleophilic bimolecular reaction ( $\text{S}_{\text{N}}2$ ) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:



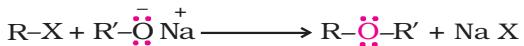
Acidic dehydration of alcohols, to give an alkene is also associated with substitution reaction to give an ether.

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  $\text{S}_{\text{N}}1$  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?

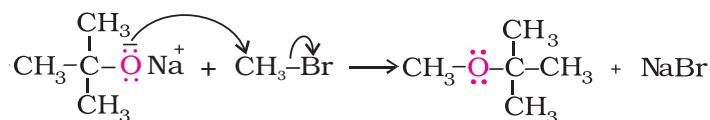
#### 2. Williamson synthesis

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.

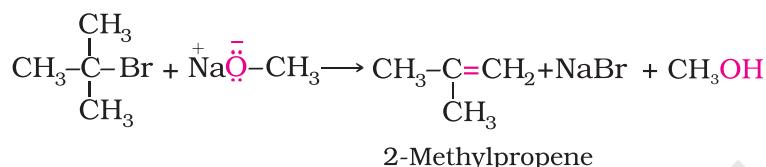


Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves  $\text{S}_{\text{N}}2$  attack of an alkoxide ion on primary alkyl halide.

Alexander William Williamson (1824–1904) was born in London of Scottish parents. In 1849, he became Professor of Chemistry at University College, London.



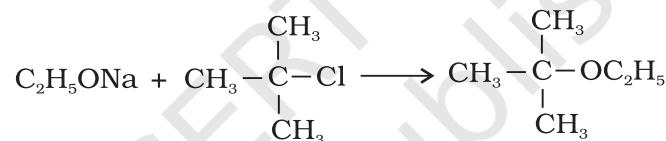
Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of  $\text{CH}_3\text{ONa}$  with  $(\text{CH}_3)_3\text{C}-\text{Br}$  gives exclusively 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 7.6

The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.



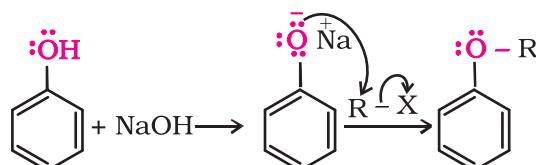
- (i) What would be the major product of this reaction ?
- (ii) Write a suitable reaction for the preparation of t-butylethyl ether.

### 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.



Phenols are also converted to ethers by this method. In this, phenol is used as the phenoxide moiety.



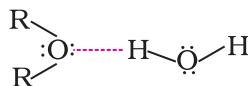
## 7.6.2 Physical Properties

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 <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> n-Pentane	C <sub>2</sub> H <sub>5</sub> -O-C <sub>2</sub> H <sub>5</sub> Ethoxyethane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -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.

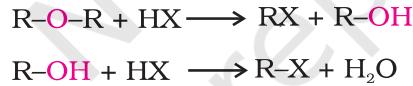
The miscibility of ethers with water resembles those of alcohols of the same molecular mass. Both ethoxyethane and butan-1-ol are miscible to almost the same extent i.e., 7.5 and 9 g per 100 mL water, respectively while pentane is essentially immiscible with water. Can you explain this observation ? This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown:



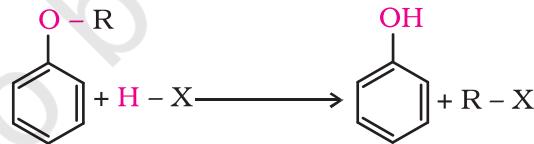
## 7.6.3 Chemical Reactions

### 1. Cleavage of C-O bond in ethers

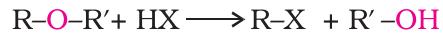
Ethers are the least reactive of the functional groups. The cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.



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.

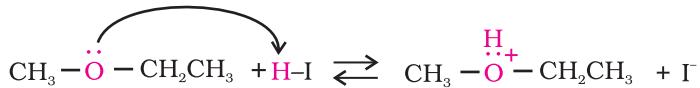


The order of reactivity of hydrogen halides is as follows: HI > HBr > HCl. The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

## Mechanism

The reaction of an ether with concentrated HI starts with protonation of ether molecule.

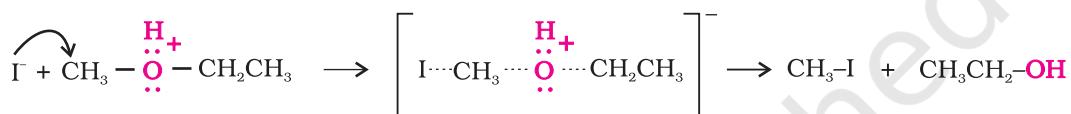
Step 1:



The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

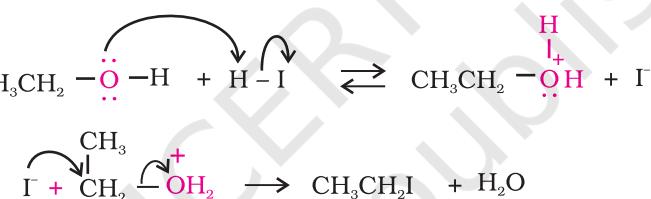
Step 2:

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).

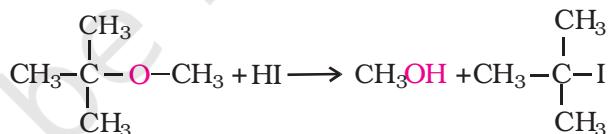


When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

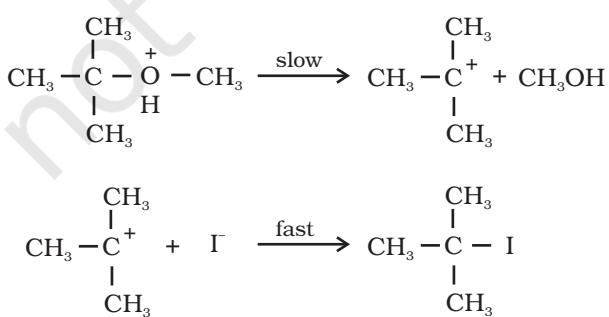
Step 3:



However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



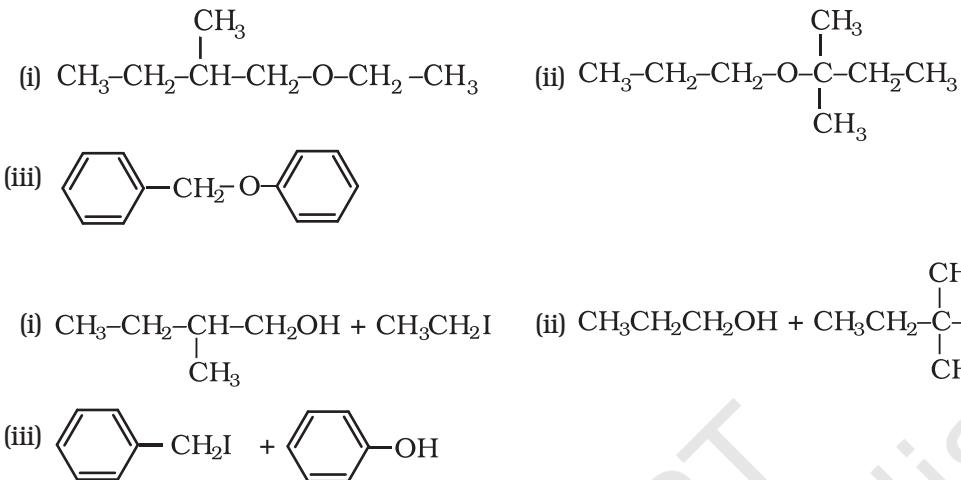
It is because in step 2 of the reaction, the departure of leaving group ( $\text{HO}-\text{CH}_3$ ) creates a more stable carbocation  $[(\text{CH}_3)_3\text{C}^+]$ , and the reaction follows  $S_N1$  mechanism.



In case of anisole, methylphenyl oxonium ion,  $\text{C}_6\text{H}_5-\overset{\text{H}}{\underset{\text{H}}{\text{O}}}-\text{CH}_3$  is formed by protonation of ether. The bond between  $\text{O}-\text{CH}_3$  is weaker than the bond between  $\text{O}-\text{C}_6\text{H}_5$  because the carbon of phenyl group is  $sp^2$  hybridised and there is a partial double bond character.

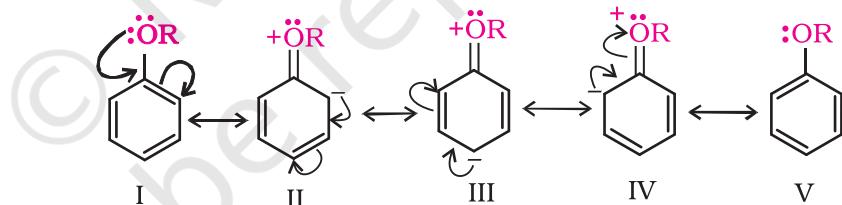
Therefore the attack by  $\Gamma$  ion breaks O-CH<sub>3</sub> bond to form CH<sub>3</sub>I. Phenols do not react further to give halides because the  $sp^2$  hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

Give the major products that are formed by heating each of the following ethers with HI. [Example 7.7](#)

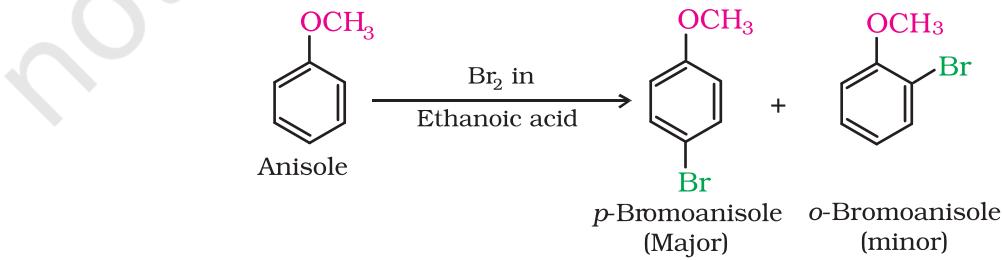


## 2. Electrophilic substitution

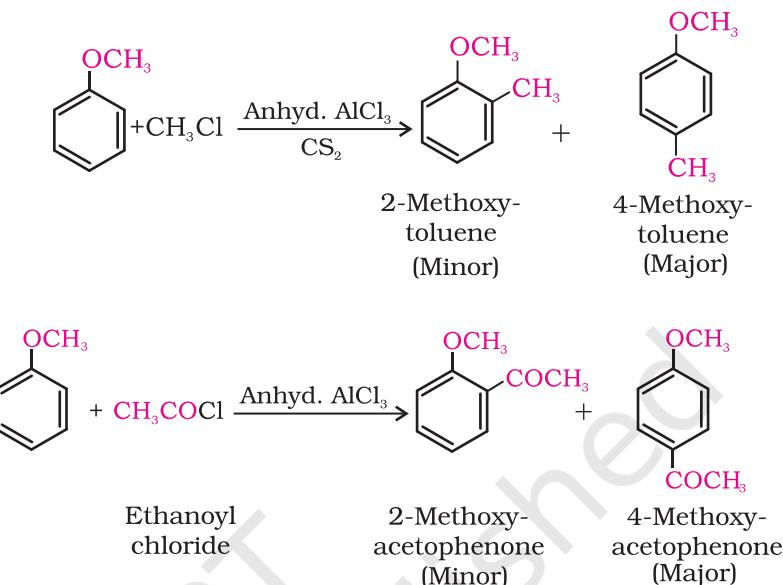
The alkoxy group (-OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.



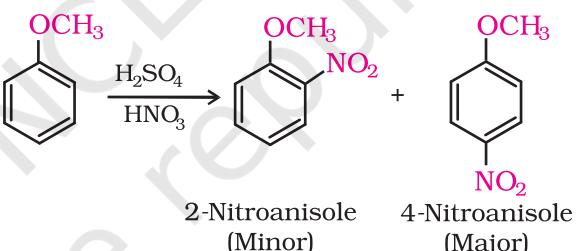
- (i) *Halogenation:* Phenylalkyl ethers undergo usual halogenation in the benzene ring, e.g., anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. *Para* isomer is obtained in 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.

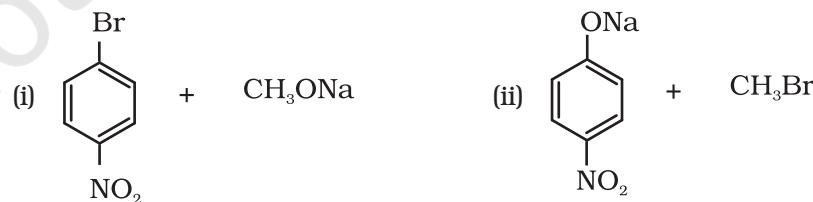


(iii) *Nitration*: Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of *ortho* and *para* nitroanisole.

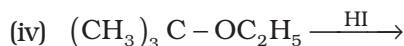
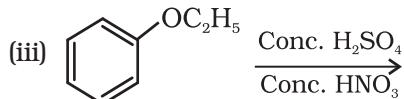
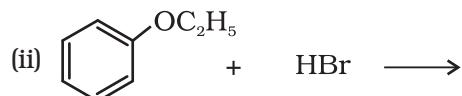
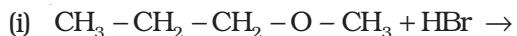


### Intext Questions

- 7.10 Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.
- 7.11 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



**7.12** Predict the products of the following reactions:



### 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  $-\text{OH}$  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  $-\text{OH}$  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.

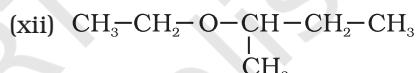
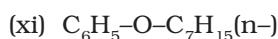
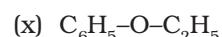
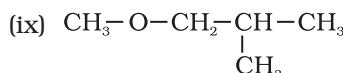
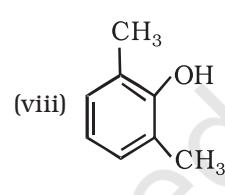
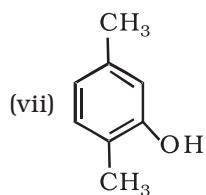
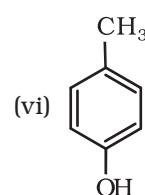
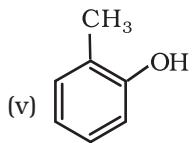
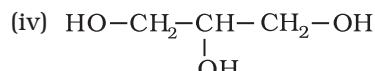
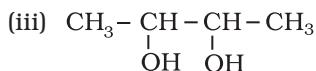
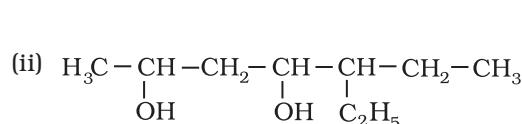
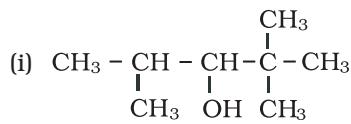
Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation.

The presence of  $-\text{OH}$  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**.

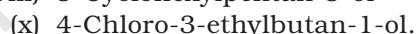
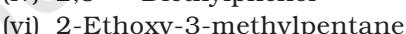
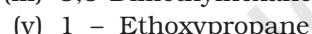
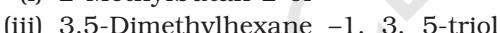
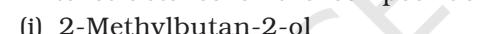
Ethers may be prepared by (i) dehydration of alcohols and (ii) **Williamson synthesis**. The boiling points of ethers resemble those of alkanes while their solubility is comparable to those of alcohols having same molecular mass. The C–O bond in ethers can be cleaved by hydrogen halides. In electrophilic substitution, the alkoxy group activates the aromatic ring and directs the incoming group to *ortho* and *para* positions.

## Exercises

**7.1** Write IUPAC names of the following compounds:



**7.2** Write structures of the compounds whose IUPAC names are as follows:



**7.3** (i) Draw the structures of all isomeric alcohols of molecular formula  $\text{C}_5\text{H}_{12}\text{O}$  and give their IUPAC names.

(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

**7.4** Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

**7.5** Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

**7.6** What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

**7.7** Give the structures and IUPAC names of monohydric phenols of molecular formula,  $\text{C}_7\text{H}_8\text{O}$ .

**7.8** While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

**7.9** Give the equations of reactions for the preparation of phenol from cumene.

**7.10** Write chemical reaction for the preparation of phenol from chlorobenzene.

**7.11** Write the mechanism of hydration of ethene to yield ethanol.

**7.12** You are given benzene, conc.  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . Write the equations for the preparation of phenol using these reagents.

**7.13** Show how will you synthesise:

- 1-phenylethanol from a suitable alkene.
- cyclohexylmethanol using an alkyl halide by an  $S_N2$  reaction.
- pentan-1-ol using a suitable alkyl halide?

**7.14** Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

**7.15** Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol ?

**7.16** Explain how does the -OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

**7.17** Give equations of the following reactions:

- Oxidation of propan-1-ol with alkaline  $KMnO_4$  solution.
- Bromine in  $CS_2$  with phenol.
- Dilute  $HNO_3$  with phenol.
- Treating phenol with chloroform in presence of aqueous NaOH.

**7.18** Explain the following with an example.

- Kolbe's reaction.
- Reimer-Tiemann reaction.
- Williamson ether synthesis.
- Unsymmetrical ether.

**7.19** Write the mechanism of acid dehydration of ethanol to yield ethene.

**7.20** How are the following conversions carried out?

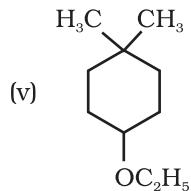
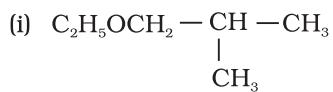
- Propene  $\rightarrow$  Propan-2-ol.
- Benzyl chloride  $\rightarrow$  Benzyl alcohol.
- Ethyl magnesium chloride  $\rightarrow$  Propan-1-ol.
- Methyl magnesium bromide  $\rightarrow$  2-Methylpropan-2-ol.

**7.21** Name the reagents used in the following reactions:

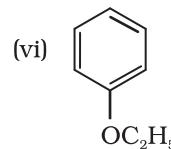
- Oxidation of a primary alcohol to carboxylic acid.
- Oxidation of a primary alcohol to aldehyde.
- Bromination of phenol to 2,4,6-tribromophenol.
- Benzyl alcohol to benzoic acid.
- Dehydration of propan-2-ol to propene.
- Butan-2-one to butan-2-ol.

**7.22** Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

**7.23** Give IUPAC names of the following ethers:

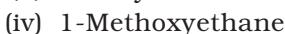
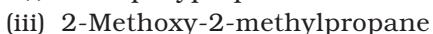


(v)



(vi)

**7.24** Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:



**7.25** Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

**7.26** How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

**7.27** Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

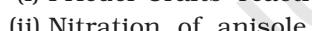
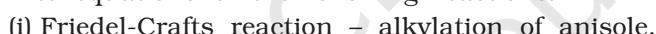
**7.28** Write the equation of the reaction of hydrogen iodide with:



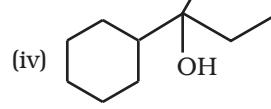
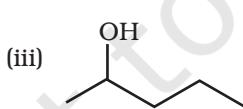
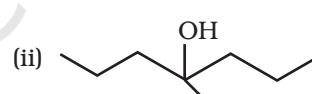
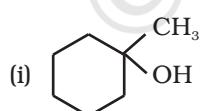
**7.29** Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

**7.30** Write the mechanism of the reaction of HI with methoxymethane.

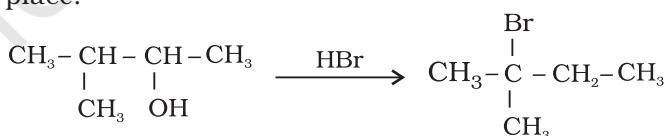
**7.31** Write equations of the following reactions:



**7.32** Show how would you synthesise the following alcohols from appropriate alkenes?



**7.33** When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



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

**7.1** Primary alcohols (i), (ii), (iii)

Secondary alcohols (iv) and (v)

Tertiary alcohols (vi)

**7.2** Allylic alcohols (ii) and (vi)

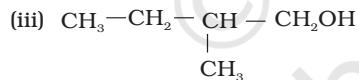
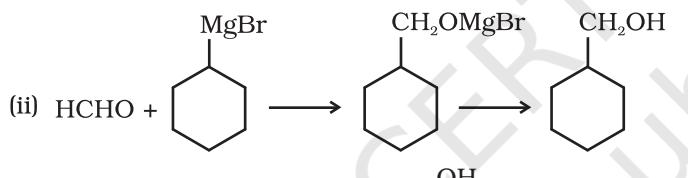
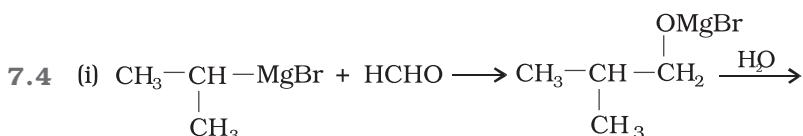
**7.3** (i) 4-Chloro-3-ethyl-2-(1-methylethyl)-butan-1-ol

(ii) 2, 5-Dimethylhexane-1,3-diol

(iii) 3-Bromocyclohexanol

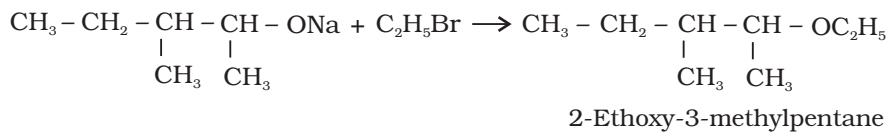
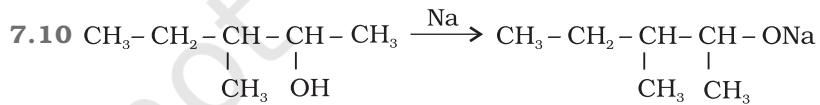
(iv) Hex-1-en-3-ol

(v) 2-Bromo-3-methylbut-2-en-1-ol

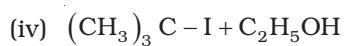
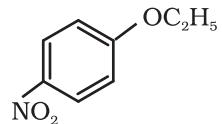
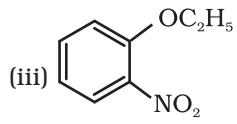
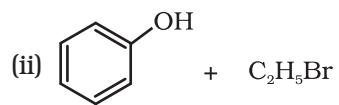
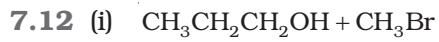


**7.7** (i) 1-Methylcyclohexene

(ii) A Mixture of but-1-ene and but-2-ene. But-2-ene is the major product formed due to rearrangement to give secondary carbocation.



**7.11** (ii)





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Unit

8

# Aldehydes, Ketones and Carboxylic Acids

## Objectives

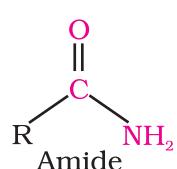
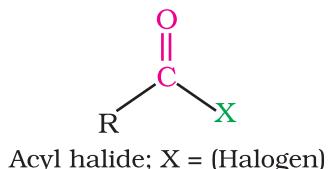
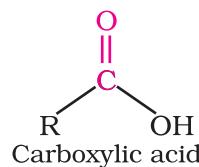
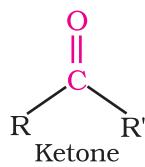
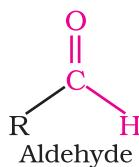
After studying this Unit, you will be able to

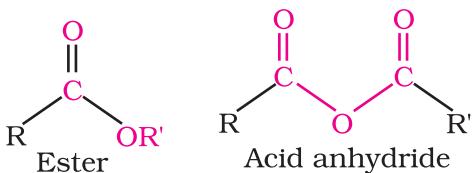
- write the common and IUPAC names of aldehydes, ketones and carboxylic acids;
- write the structures of the compounds containing functional groups namely carbonyl and carboxyl groups;
- describe the important methods of preparation and reactions of these classes of compounds;
- correlate physical properties 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.*

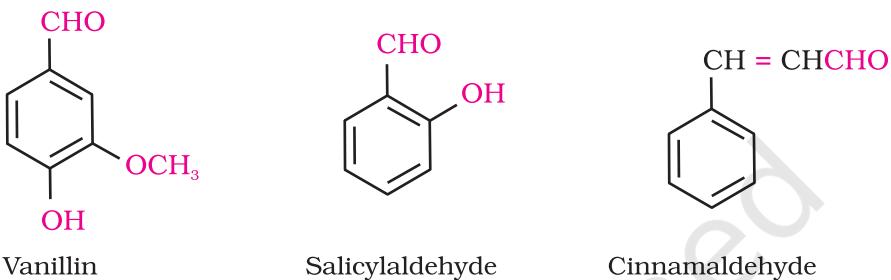
In the previous Unit, you have studied organic compounds with functional groups containing carbon-oxygen single bond. In this Unit, we will study about the organic compounds containing carbon-oxygen double bond ( $>\text{C}=\text{O}$ ) called carbonyl group, which is one of the most important functional 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 carbon of carbonyl group is bonded to carbon or hydrogen and oxygen of hydroxyl moiety (-OH) are known as carboxylic acids, while in compounds where carbon is attached to carbon or hydrogen and nitrogen of  $-\text{NH}_2$  moiety or to halogens are called amides and acyl halides respectively. Esters and anhydrides are derivatives of carboxylic acids. The general formulas of these classes of compounds are given below:





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.



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.

## 8.1 Nomenclature and Structure of Carbonyl Group

### 8.1.1 Nomenclature

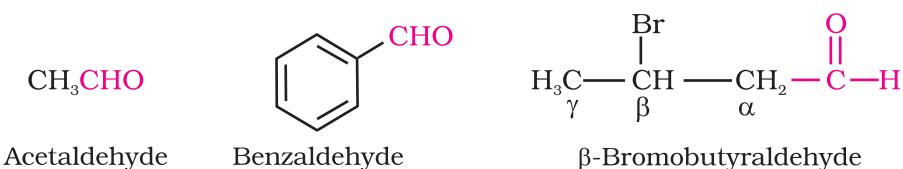
#### I. Aldehydes and ketones

Aldehydes and ketones are the simplest and most important carbonyl compounds.

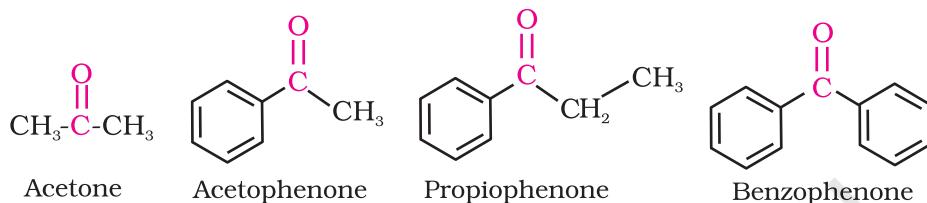
There are two systems of nomenclature of aldehydes and ketones.

##### (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 8.6.1] 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  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc. The  $\alpha$ -carbon being the one directly linked to the aldehyde group,  $\beta$ -carbon the next, and so on. For example

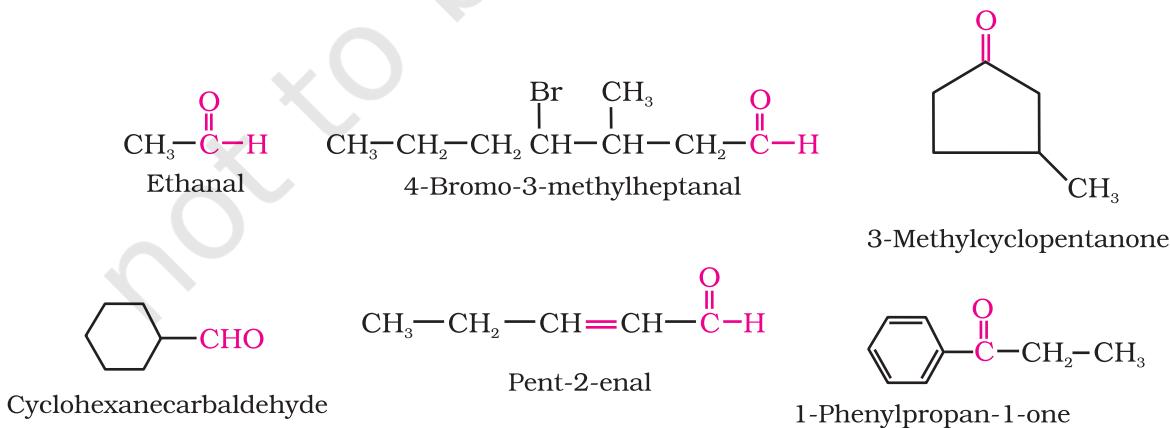


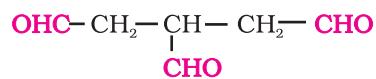
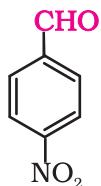
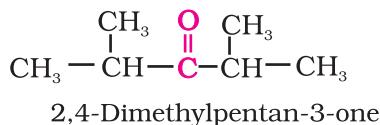
The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. The locations of substituents are indicated by Greek letters,  $\alpha$   $\alpha'$ ,  $\beta$   $\beta'$  and so on beginning with the carbon atoms next to the carbonyl group, indicated as  $\alpha\alpha'$ . Some ketones have historical common names, the simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the name of acyl group as prefix to the word phenone. For example



### (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.





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 8.1.

**Table 8.1: Common and IUPAC Names of Some Aldehydes and Ketones**

Structure	Common name	IUPAC name
<b>Aldehydes</b>		
HCHO	Formaldehyde	Methanal
CH <sub>3</sub> CHO	Acetaldehyde	Ethanal
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ-Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
CH <sub>3</sub> CH(OCH <sub>3</sub> )CHO	α-Methoxypropionaldehyde	2-Methoxypropanal
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	Valeraldehyde	Pentanal
CH <sub>2</sub> =CHCHO	Acrolein	Prop-2-enal
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
<b>Ketones</b>		
CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Methyl n-propyl ketone	Pentan-2-one
(CH <sub>3</sub> ) <sub>2</sub> CHCOCH(CH <sub>3</sub> ) <sub>2</sub>	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
(CH <sub>3</sub> ) <sub>2</sub> C=CHCOCH <sub>3</sub>	Mesityl oxide	4-Methylpent-3-en-2-one

### 8.1.2 Structure of the Carbonyl Group

The carbonyl carbon atom is  $sp^2$ -hybridised and forms three sigma ( $\sigma$ ) bonds. The fourth valence electron of carbon remains in its  $p$ -orbital and forms a  $\pi$ -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  $\pi$ -electron cloud is above and below this plane. The bond angles are approximately  $120^\circ$  as expected of a trigonal coplanar structure (Figure 8.1).

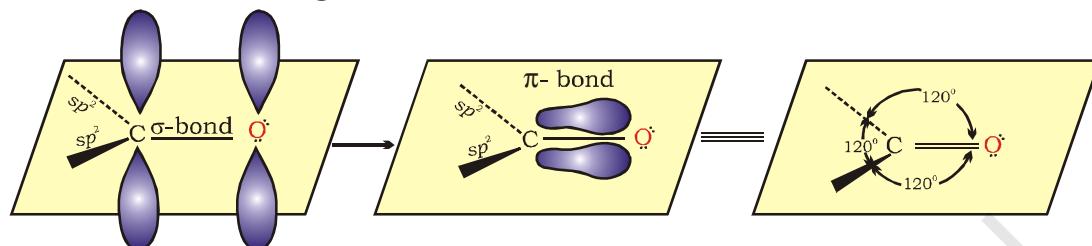
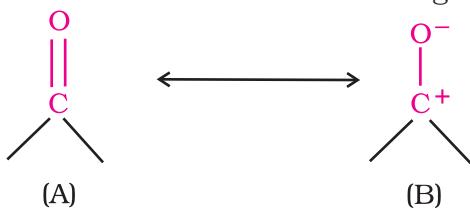


Fig.8.1 Orbital diagram for the formation of carbonyl group

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

8.1 Write the structures of the following compounds.

- |  |                           |
|--|---------------------------|
| (i) $\alpha$ -Methoxypropionaldehyde     | (ii) 3-Hydroxybutanal     |
| (iii) 2-Hydroxycyclopentane carbaldehyde | (iv) 4-Oxopentanal        |
| (v) Di-sec. butyl ketone                 | (vi) 4-Fluoroacetophenone |

## 8.2 Preparation of Aldehydes and Ketones

Some important methods for the preparation of aldehydes and ketones are as follows:

### 8.2.1 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 7, 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 7, 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,

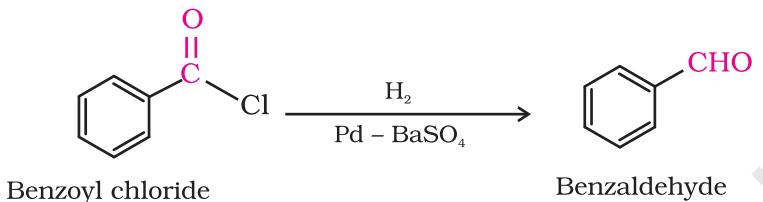
ketones or a mixture of both depending on the substitution pattern of the alkene (Unit 9, Class XI).

- (ii) *By hydration of alkynes:* Addition of water to ethyne in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  gives acetaldehyde. All other alkynes give ketones in this reaction (Unit 9, Class XI).

## **8.2.2 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**.



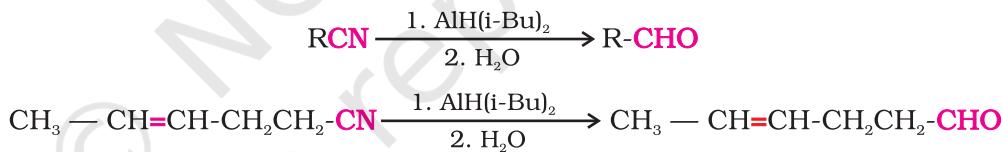
## **2. From nitriles and esters**

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

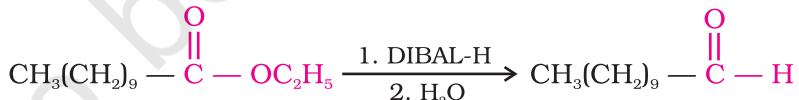


This reaction is called **Stephen** reaction.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



Similarly, esters are also reduced to aldehydes with DIBAL-H.



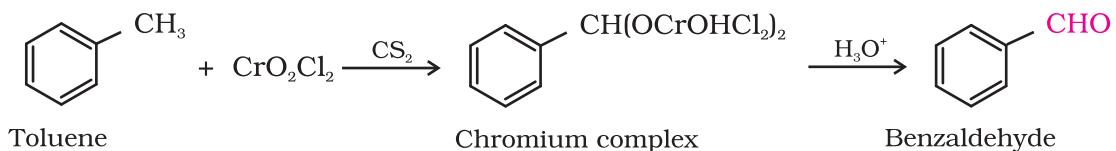
### **3. From hydrocarbons**

Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

- (i) By oxidation of methylbenzene

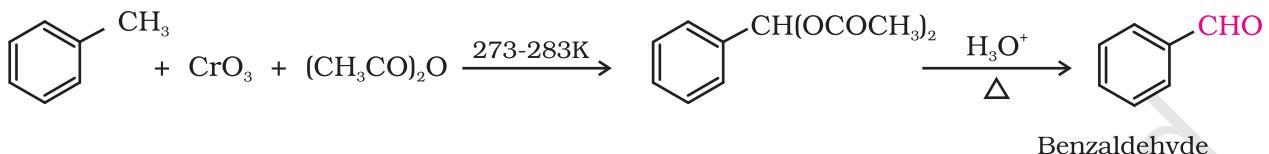
Strong oxidising agents oxidise toluene and its derivatives to benzoic acids. However, it is possible to stop the oxidation at the aldehyde stage with suitable reagents that convert the methyl group to an intermediate that is difficult to oxidise further. The following methods are used for this purpose.

- (a) Use of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



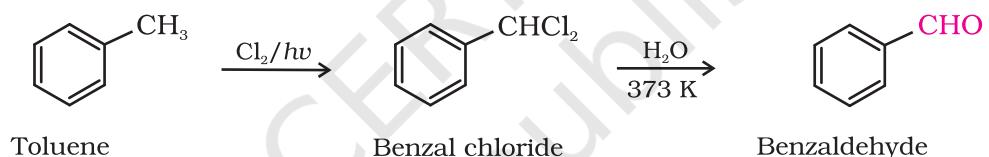
This reaction is called **Etard reaction**.

(b) Use of chromic oxide ( $\text{CrO}_3$ ): 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.



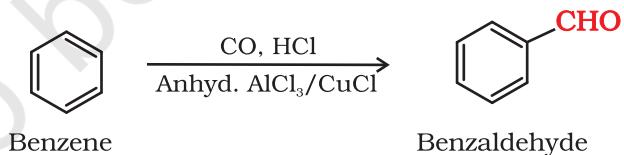
(ii) By side chain chlorination followed by hydrolysis

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.

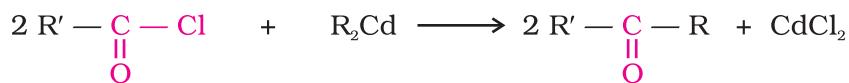
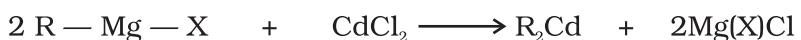


This reaction is known as **Gatterman-Koch reaction**.

### 8.2.3 Preparation of Ketones

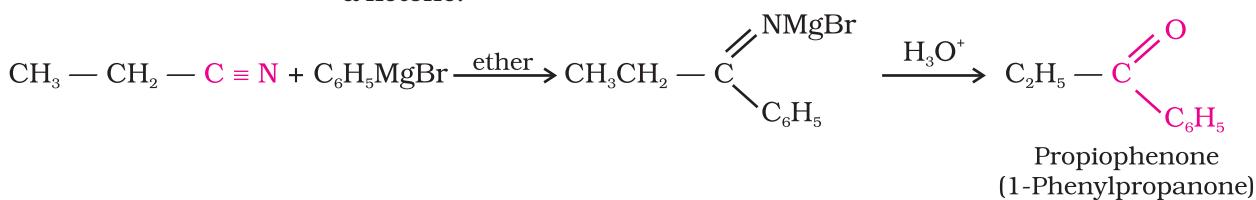
#### 1. From acyl chlorides

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.



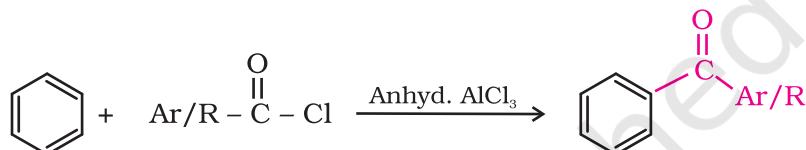
## 2. From nitriles

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



## 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 8.1

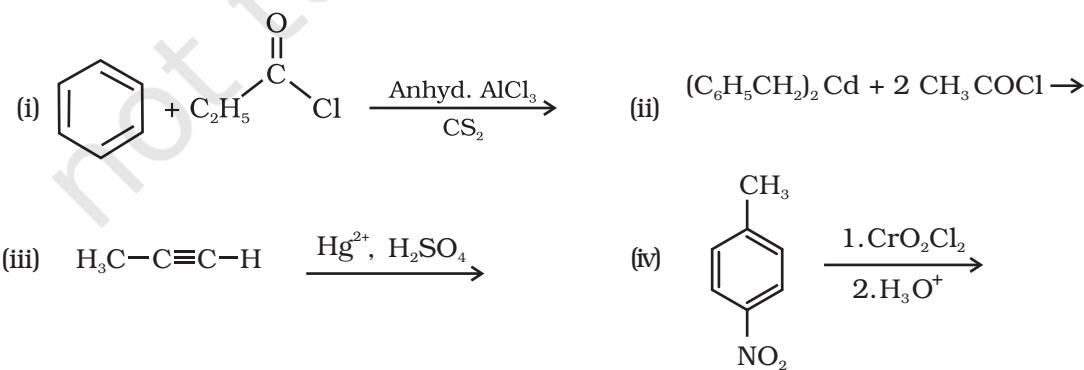
Give names of the reagents to bring about the following transformations:

- |   |  |
|---|--|
| (i) Hexan-1-ol to hexanal   | (ii) Cyclohexanol to cyclohexanone           |
| (iii) <i>p</i> -Fluorotoluene to <i>p</i> -fluorobenzaldehyde   | (iv) Ethanenitrile to ethanal                |
| (v) Allyl alcohol to propenal   | (vi) But-2-ene to ethanal                    |
| (i) $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}$ (PCC)  | (ii) Anhydrous $\text{CrO}_3$                |
| (iii) $\text{CrO}_3$ in the presence of acetic anhydride/<br>1. $\text{CrO}_2\text{Cl}_2$ 2. $\text{HOH}$ | (iv) (Diisobutyl)aluminium hydride (DIBAL-H) |
| (v) PCC   | (vi) $\text{O}_3/\text{H}_2\text{O-Zn}$ dust |

### Solution

### Intext Question

**8.2** Write the structures of products of the following reactions:



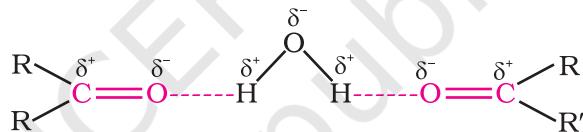
### 8.3 Physical Properties

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.

Arrange the following compounds in the increasing order of their boiling points:



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:



#### Example 8.2

#### Solution

### Intext Question

- 8.3 Arrange the following compounds in increasing order of their boiling points.



## 8.4 Chemical Reactions

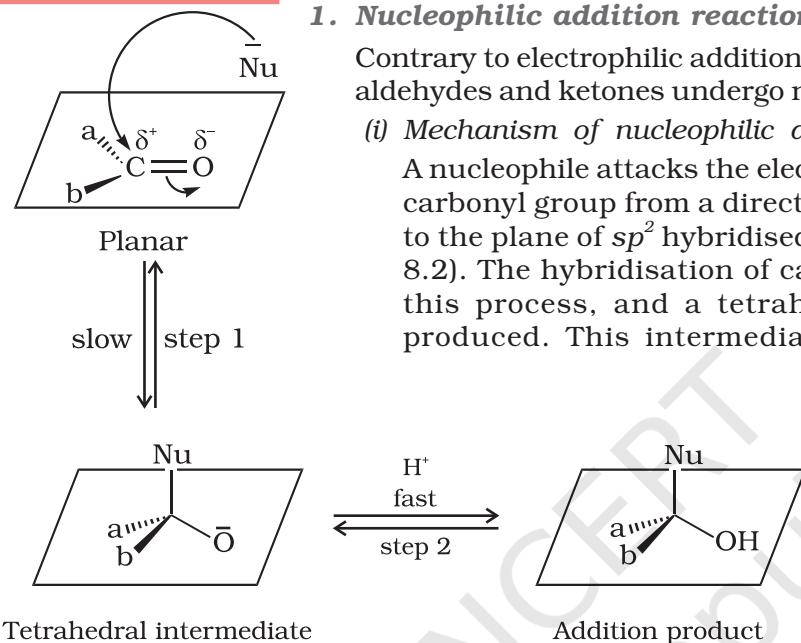


Fig. 8.2: Nucleophilic attack on carbonyl carbon

### (i) Mechanism of nucleophilic addition reactions

Contrary to electrophilic addition reactions observed in alkenes, the aldehydes and ketones undergo nucleophilic addition reactions.

#### (ii) Reactivity

A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of  $\text{sp}^2$  hybridised orbitals of carbonyl carbon (Fig. 8.2). The hybridisation of carbon changes from  $\text{sp}^2$  to  $\text{sp}^3$  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  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon oxygen double bond as shown in Fig. 8.2.

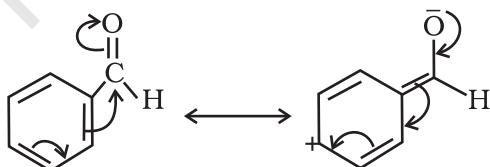
reaction medium to give the electrically neutral product. The net result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon oxygen double bond as shown in Fig. 8.2.

### Example 8.3

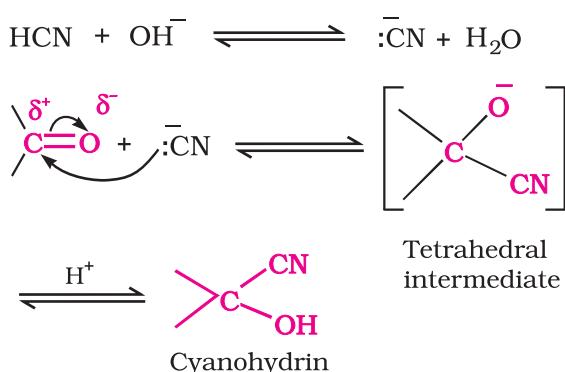
Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

#### 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.



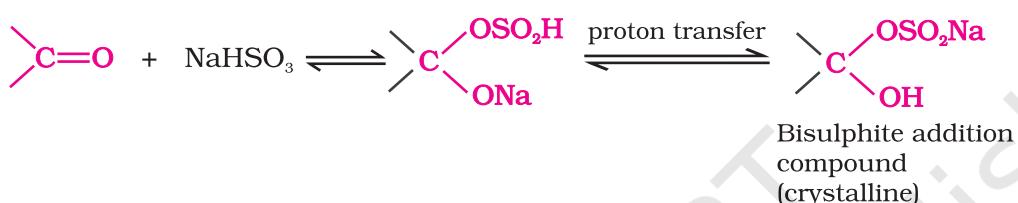
(iii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:



(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 ( $\text{CN}^-$ ) 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.

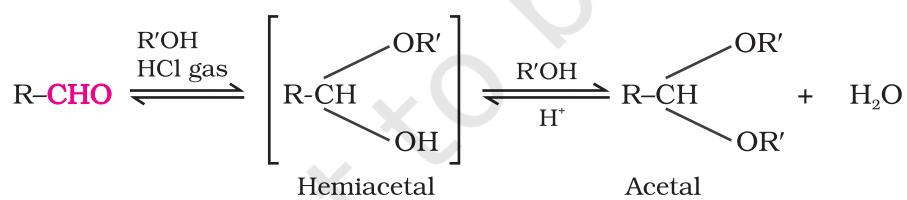


The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most

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 7, Class XII).

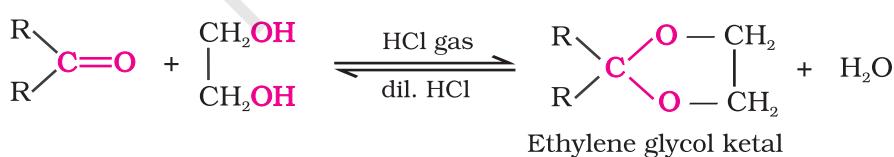
(d) *Addition of alcohols:* Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to



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.

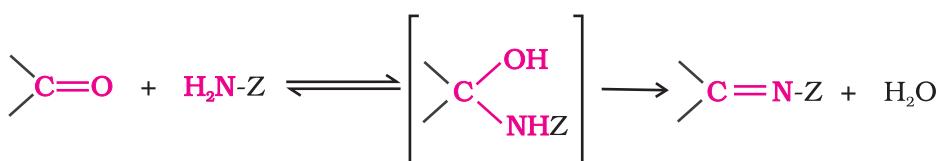
Dry hydrogen chloride protonates the oxygen of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon facilitating



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  $\text{H}_2\text{N-Z}$  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  $>\text{C}=\text{N-Z}$ .



$\text{Z} = \text{Alkyl, aryl, OH, NH}_2, \text{C}_6\text{H}_5\text{NH, NHCONH}_2$ , etc.

**Table 8.2: Some N-Substituted Derivatives of Aldehydes and Ketones ( $>\text{C}=\text{N-Z}$ )**

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$\text{C}=\text{NH}$	Imine
-R	Amine	$\text{C}=\text{NR}$	Substituted imine (Schiff's base)
-OH	Hydroxylamine	$\text{C}=\text{N-OH}$	Oxime
-NH <sub>2</sub>	Hydrazine	$\text{C}=\text{N-NH}_2$	Hydrazone
	Phenylhydrazine	$\text{C}=\text{N-NH-C}_6\text{H}_5$	Phenylhydrazone
	2,4-Dinitrophenylhydrazine	$\text{C}=\text{N-NH-C}_6\text{H}_3(\text{NO}_2)_2-\text{NO}_2$	2,4 Dinitrophenylhydrazone
	Semicarbazide	$\text{C}=\text{N-NH-C}(=\text{O})-\text{NH}_2$	Semicarbazone

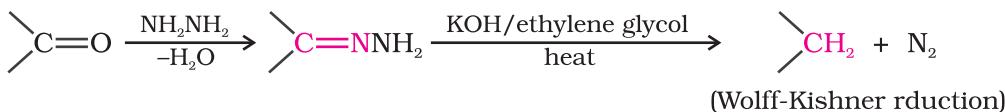
\* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

## 2. Reduction

- (i) *Reduction to alcohols:* Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ( $\text{NaBH}_4$ ) or lithium aluminium hydride ( $\text{LiAlH}_4$ ) as well as by catalytic hydrogenation (Unit 7, Class XII).

- (ii) *Reduction to hydrocarbons:* The carbonyl group of aldehydes and ketones is reduced to  $\text{CH}_2$  group on treatment with zinc-amalgam and concentrated hydrochloric acid [Clemmensen

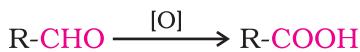
**reduction**] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).



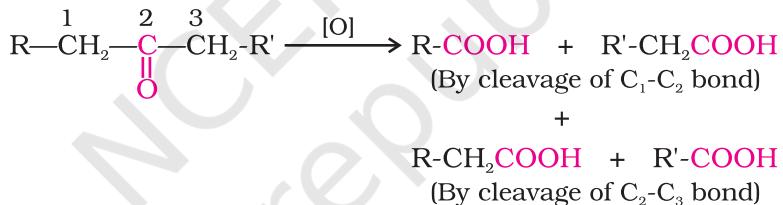
### 3. Oxidation

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.

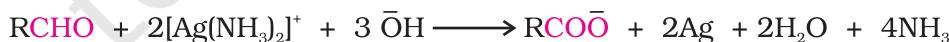


Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

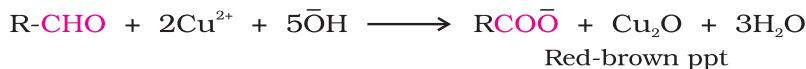


The mild oxidising agents given below are used to distinguish aldehydes from ketones:

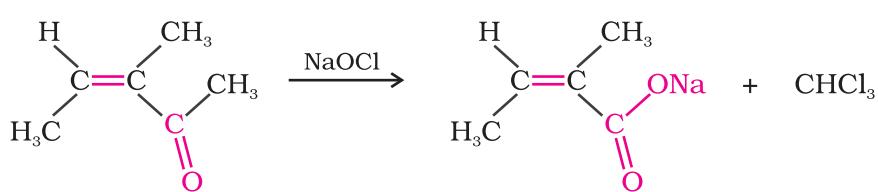
(i) *Tollens' test*: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



(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.



(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  $\text{CH}_3\text{CO}$  group or  $\text{CH}_3\text{CH}(\text{OH})$  group which produces  $\text{CH}_3\text{CO}$  group on oxidation.

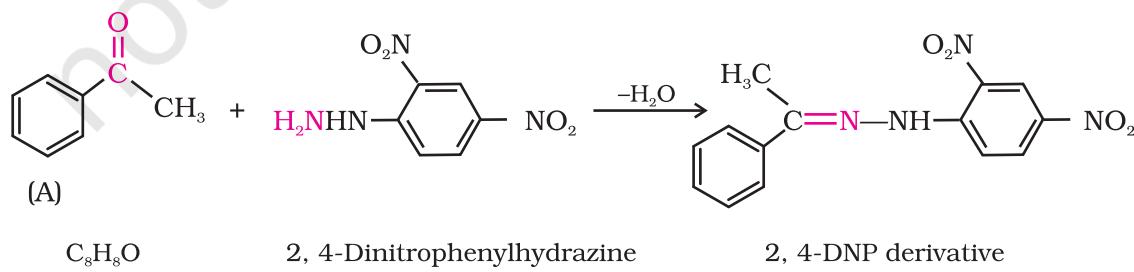
#### Example 8.4

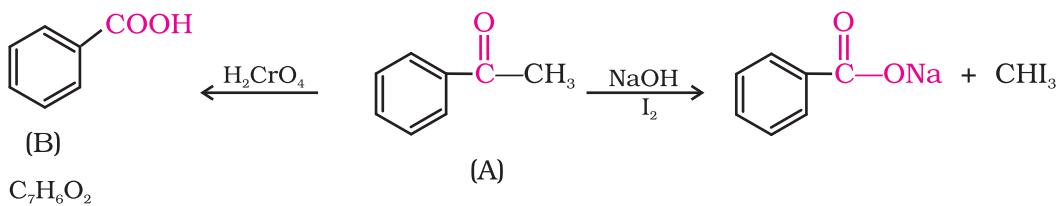
An organic compound (A) with molecular formula  $\text{C}_8\text{H}_8\text{O}$  forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula  $\text{C}_7\text{H}_6\text{O}_2$ . 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:

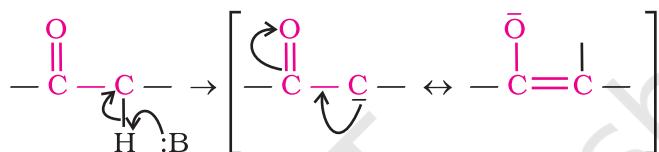




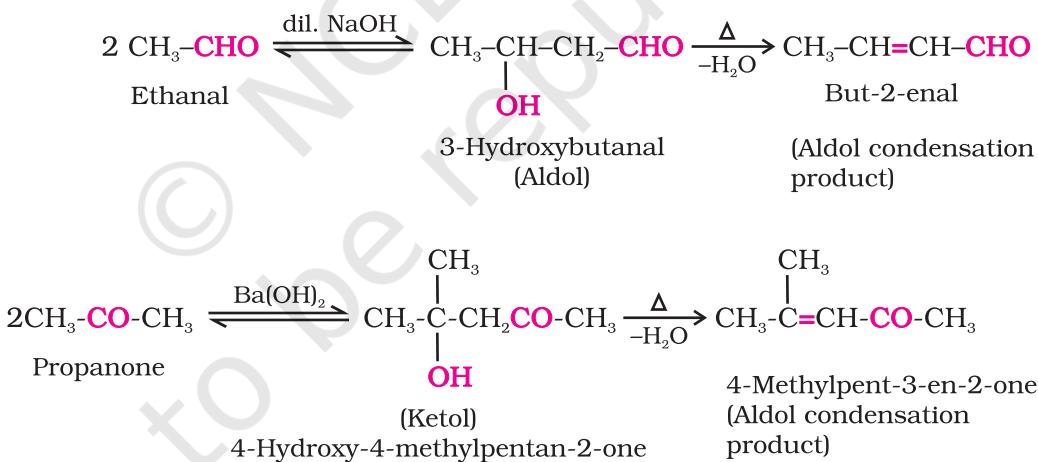
#### 4. Reactions due to $\alpha$ -hydrogen

**Acidity of  $\alpha$ -hydrogens of aldehydes and ketones:** The aldehydes and ketones undergo a number of reactions due to the acidic nature of  $\alpha$ -hydrogen.

The acidity of  $\alpha$ -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

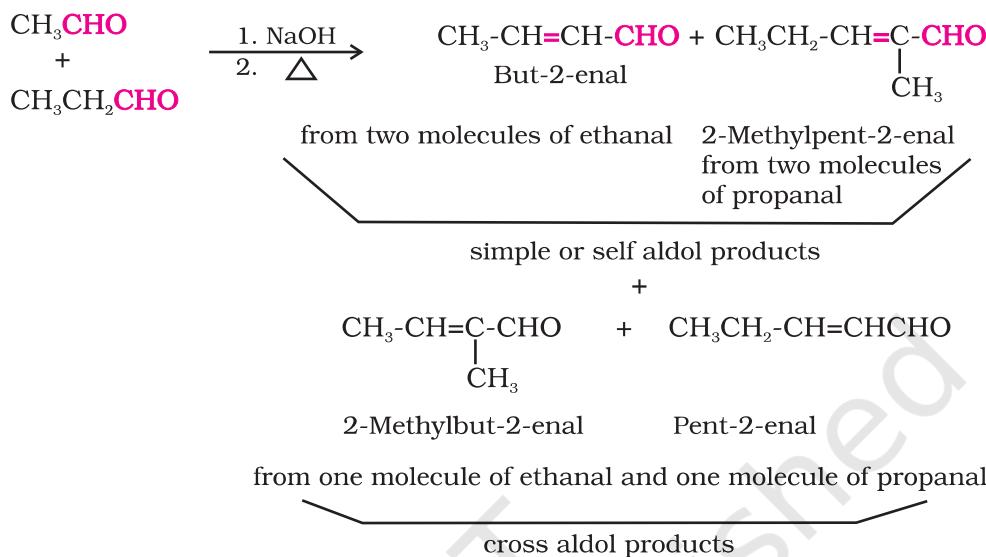


- (i) **Aldol condensation:** Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.

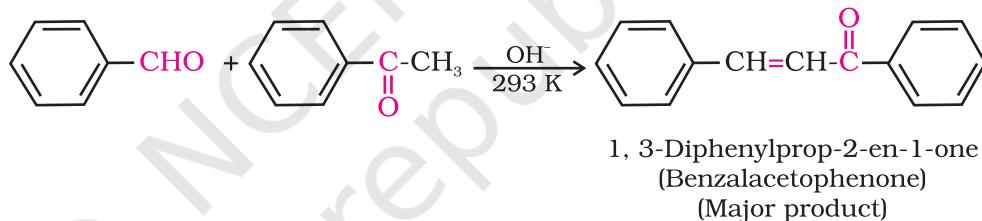


The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give  $\alpha,\beta$ -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation**. 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  $\alpha$ -hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.

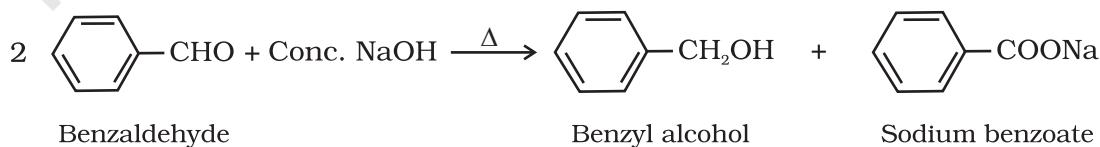
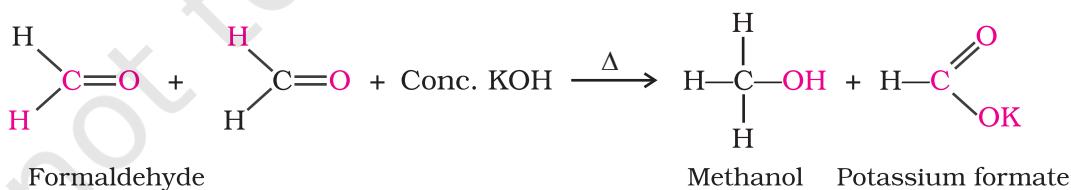


Ketones can also be used as one component in the cross aldol reactions.

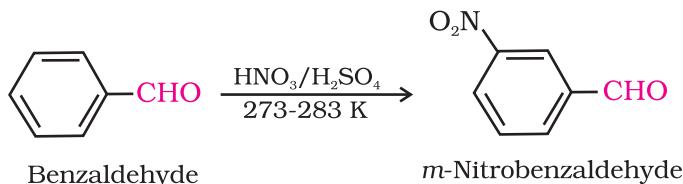


## 5. Other reactions

(i) **Cannizzaro reaction:** Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



- (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.



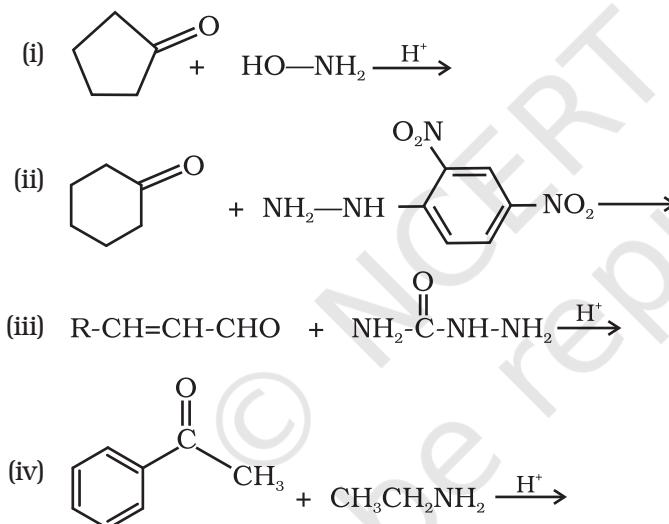
## Intext Questions

- 8.4** 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.

- ### 8.5 Predict the products of the following reactions:



## 8.5 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 ( $\text{RCOOH}$ ) or aromatic ( $\text{ArCOOH}$ ) 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 ( $\text{C}_{12} - \text{C}_{18}$ ) 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.

## **8.6 Nomenclature and Structure of Carboxyl Group**

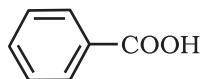
### **8.6.1 Nomenclature**

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 ( $\text{HCOOH}$ ) was first obtained from red ants (Latin: *formica* means ant), acetic acid ( $\text{CH}_3\text{COOH}$ ) from vinegar (Latin: *acetum*, means vinegar), butyric acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ) from rancid butter (Latin: *butyrum*, means butter).

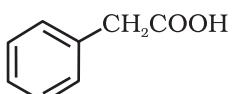
In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending *-e* in the name of the corresponding alkane with *-oic acid*. In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the alkyl chain leaving carboxyl groups is numbered and the number of carboxyl groups is indicated by adding the multiplicative prefix, *dicarboxylic acid*, *tricarboxylic acid*, etc. to the name of parent alkyl chain. 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 8.3.

**Table 8.3 Names and Structures of Some Carboxylic Acids**

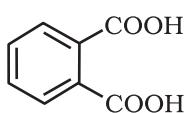
<b>Structure</b>	<b>Common name</b>	<b>IUPAC name</b>
$\text{HCOOH}$	Formic acid	Methanoic acid
$\text{CH}_3\text{COOH}$	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butanoic acid
$(\text{CH}_3)_2\text{CHCOOH}$	Isobutyric acid	2-Methylpropanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC - $\text{CH}_2$ -COOH	Malonic acid	Propanedioic acid
HOOC -( $\text{CH}_2$ ) <sub>2</sub> -COOH	Succinic acid	Butanedioic acid
HOOC -( $\text{CH}_2$ ) <sub>3</sub> -COOH	Glutaric acid	Pentanedioic acid
HOOC -( $\text{CH}_2$ ) <sub>4</sub> -COOH	Adipic acid	Hexanedioic acid
HOOC - $\text{CH}_2$ -CH(COOH)- $\text{CH}_2$ -COOH	Tricarballylic acid or carballylic acid	Propane-1, 2, 3-tricarboxylic acid



Benzoic acid



Phenylacetic acid



Phthalic acid

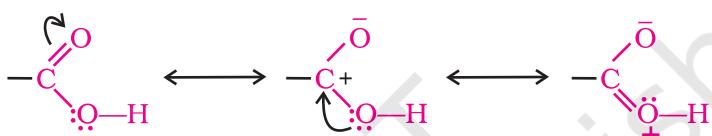
Benzenecarboxylic acid  
(Benzoic acid)

2-Phenylethanoic acid

Benzene-1, 2-dicarboxylic  
acid

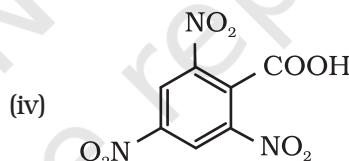
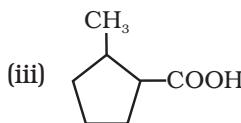
### 8.6.2 Structure of Carboxyl Group

In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about  $120^\circ$ . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



#### Intext Question

8.6 Give the IUPAC names of the following compounds:

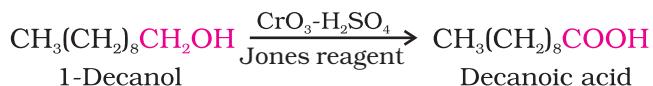


### 8.7 Methods of Preparation of Carboxylic Acids

Some important methods of preparation of carboxylic acids are as follows.

#### 1. From primary alcohols and aldehydes

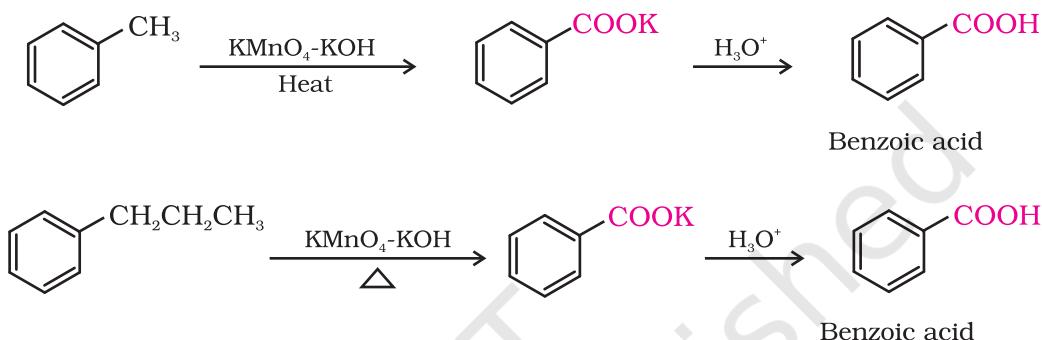
Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ( $\text{KMnO}_4$ ) in neutral, acidic or alkaline media or by potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and chromium trioxide ( $\text{CrO}_3$ ) in acidic media (Jones reagent).



Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents (Section 8.4).

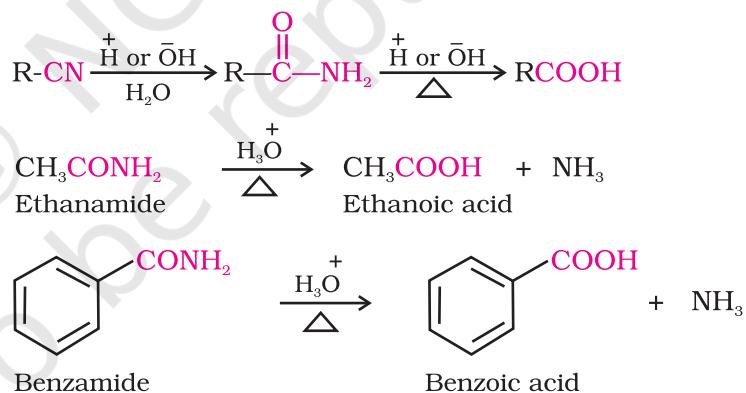
## **2. From alkylbenzenes**

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.



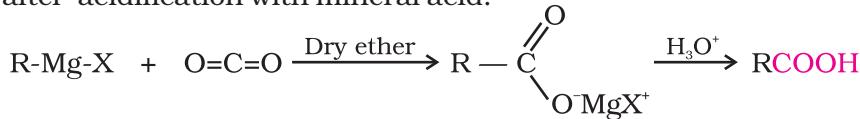
### 3. From nitriles and amides

Nitriles are hydrolysed to amides and then to acids in the presence of H<sup>+</sup> or OH as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



#### **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.

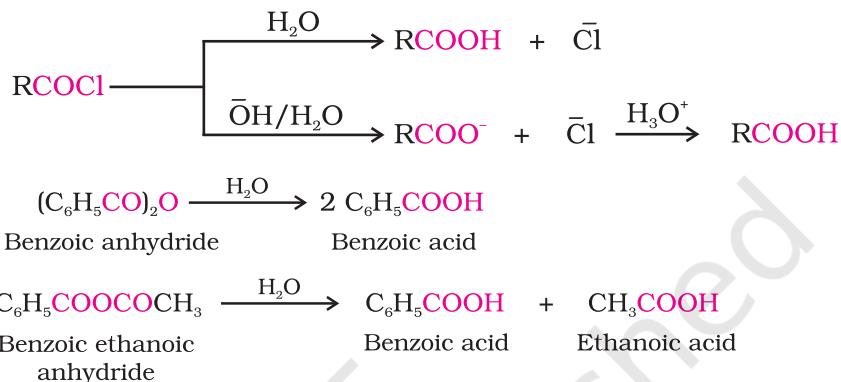


As we know, the Grignard reagents and nitriles can be prepared from alkyl halides (refer Unit 6, Class XII). The above methods

(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).

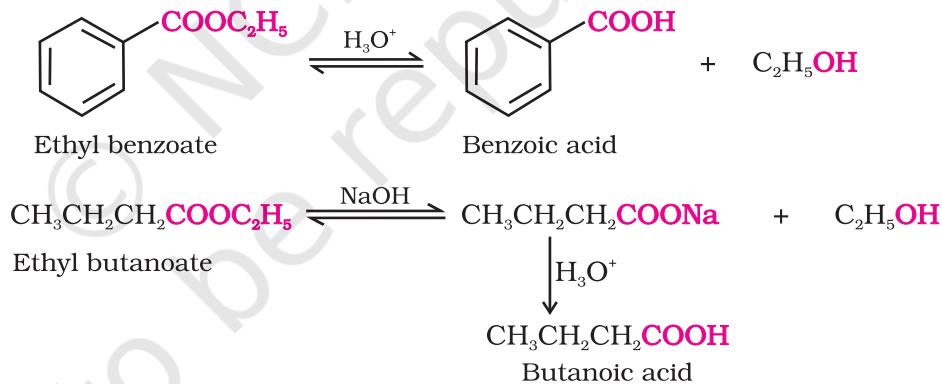
## **5. From acyl halides and anhydrides**

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.



## 6. From esters

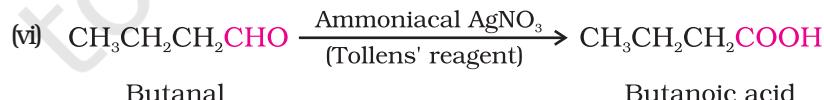
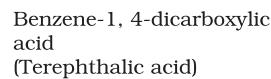
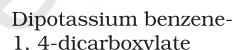
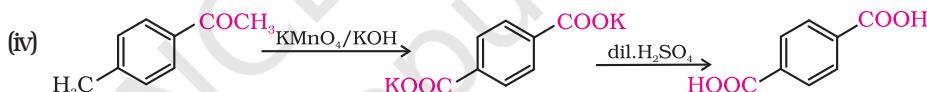
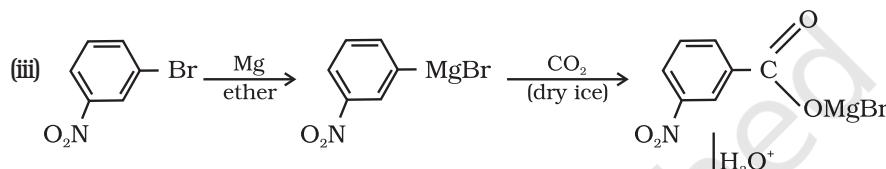
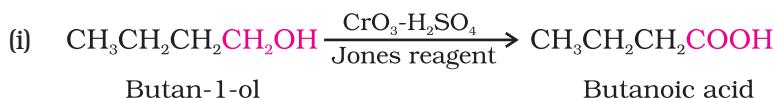
Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



Write chemical reactions to affect the following transformations: **Example 8.5**

- (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.

### Solution

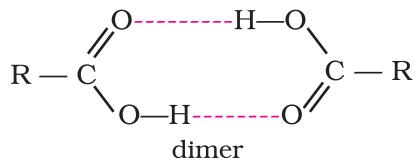


## *Intext Question*

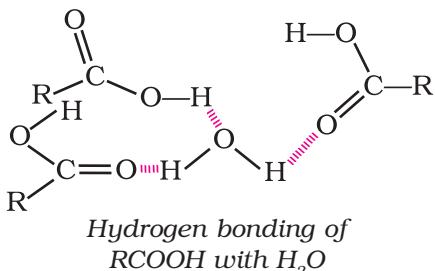
**8.7** Show how each of the following compounds can be converted to benzoic acid.

- (i) Ethylbenzene      (ii) Acetophenone  
(iii) Bromobenzene    (iv) Phenylethene (Styrene)

## 8.8 Physical properties



In vapour state or in aprotic solvent



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.

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.

## 8.9 Chemical Reactions

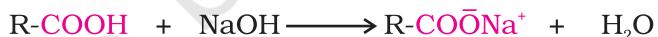
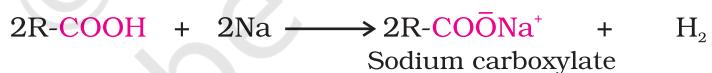
The reaction of carboxylic acids are classified as follows:

### 8.9.1 Reactions Involving Cleavage of O-H Bond

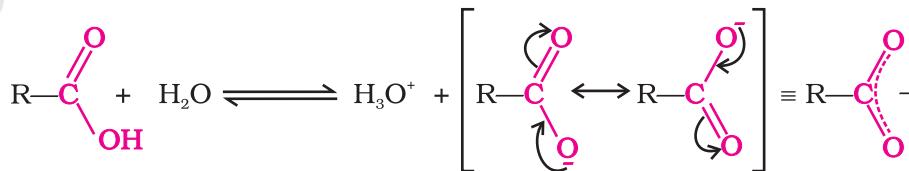
#### Acidity

##### 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.



Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.



For the above reaction:

$$K_{eq} = \frac{[\text{H}_3\overset{+}{\text{O}}] [\text{RCOO}^-]}{[\text{H}_2\text{O}] [\text{RCOOH}]} \quad K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{H}_3\overset{+}{\text{O}}] [\text{RCOO}^-]}{[\text{RCOOH}]}$$

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  $\text{p}K_a$  value rather than its  $K_a$  value.

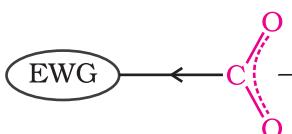
$$\text{p}K_a = -\log K_a$$

The  $\text{p}K_a$  of hydrochloric acid is  $-7.0$ , whereas  $\text{p}K_a$  of trifluoroacetic acid (the strongest carboxylic acid), benzoic acid and acetic acid are  $0.23$ ,  $4.19$  and  $4.76$ , respectively.

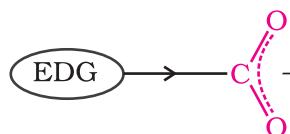
Smaller the  $\text{p}K_a$ , the stronger the acid (the better it is as a proton donor). Strong acids have  $\text{p}K_a$  values  $< 1$ , the acids with  $\text{p}K_a$  values between  $1$  and  $5$  are considered to be moderately strong acids, weak acids have  $\text{p}K_a$  values between  $5$  and  $15$ , and extremely weak acids have  $\text{p}K_a$  values  $> 15$ .

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols ( $\text{p}K_a$  is  $\sim 16$  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 7, 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

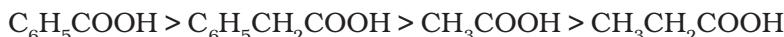


Electron donating group (EDG)  
destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is



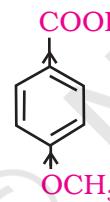
Thus, the following acids are arranged in order of increasing acidity (based on  $pK_a$  values):



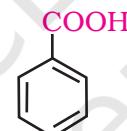
Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:



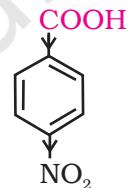
This is because of greater electronegativity of  $sp^2$  hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.



4-Methoxy  
benzoic acid  
( $pK_a = 4.46$ )



Benzoic acid  
( $pK_a = 4.19$ )

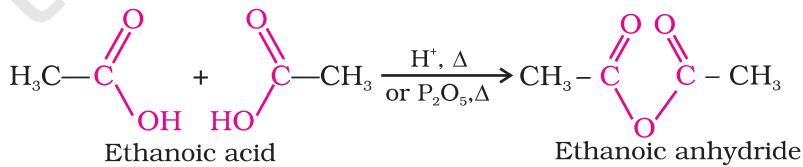


4-Nitrobenzoic  
acid  
( $pK_a = 3.41$ )

### 8.9.2 Reactions Involving Cleavage of C-OH Bond

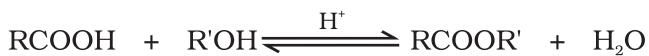
#### 1. Formation of anhydride

Carboxylic acids on heating with mineral acids such as  $\text{H}_2\text{SO}_4$  or with  $\text{P}_2\text{O}_5$  give corresponding anhydride.

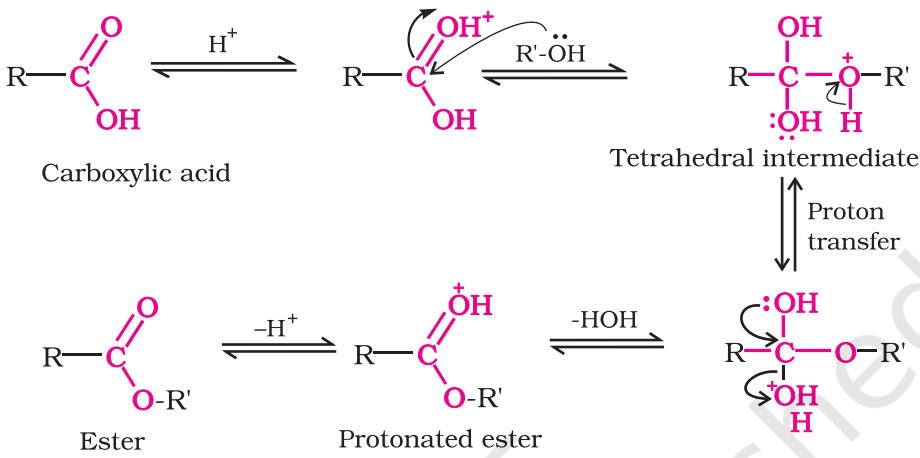


#### 2. Esterification

Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  gas as a catalyst.

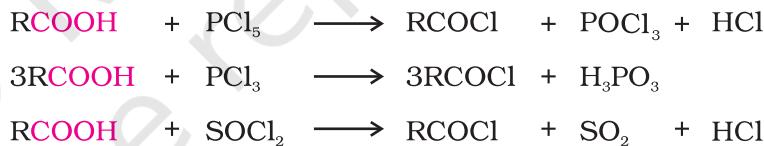


**Mechanism of esterification of carboxylic acids:** The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution. Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol. Proton transfer in the tetrahedral intermediate converts the hydroxyl group into  $-\text{OH}_2^+$  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.



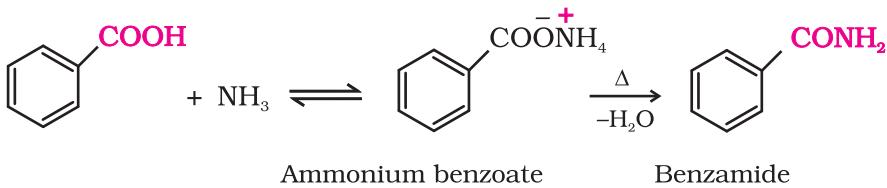
### **3. Reactions with $PCl_5$ , $PCl_3$ and $SOCl_2$**

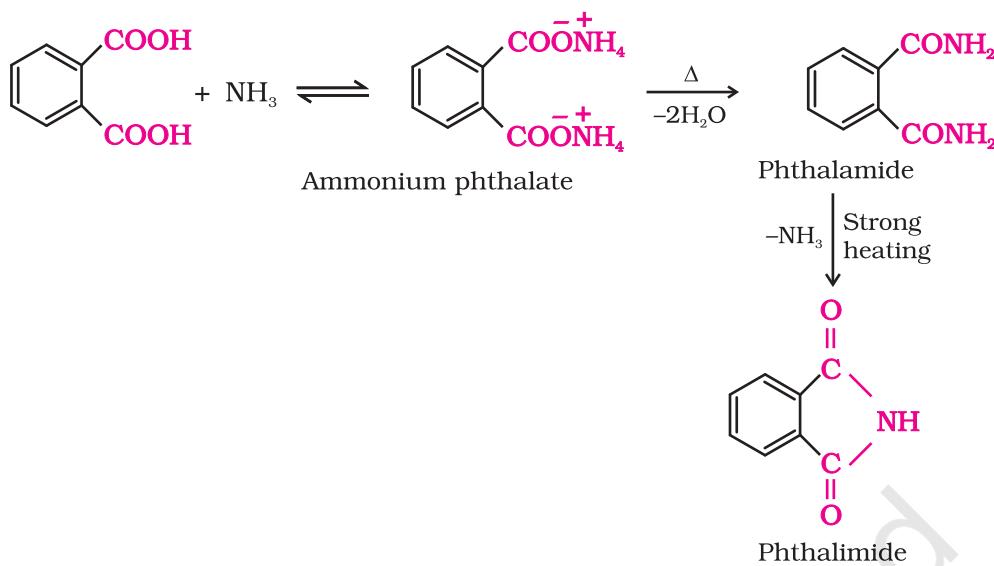
The hydroxyl group of carboxylic acids, behaves like that of alcohols and is easily replaced by chlorine atom on treating with  $\text{PCl}_5$ ,  $\text{PCl}_3$  or  $\text{SOCl}_2$ . Thionyl chloride ( $\text{SOCl}_2$ ) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.



#### **4. Reaction with ammonia**

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. For example:

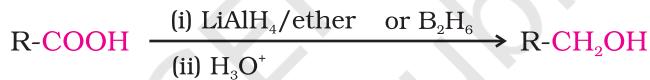




### 8.9.3 Reactions Involving -COOH Group

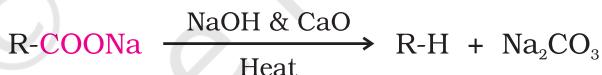
#### 1. Reduction

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.



#### 2. Decarboxylation

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime ( $\text{NaOH}$  and  $\text{CaO}$  in the ratio of 3 : 1). The reaction is known as decarboxylation.

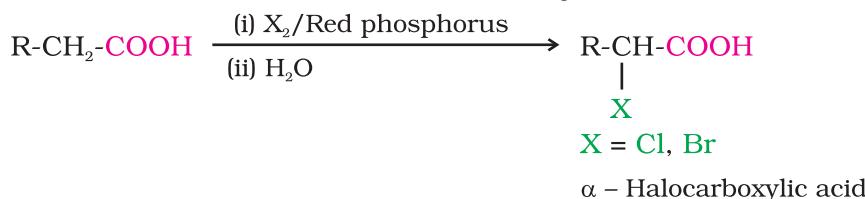


Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis** (Unit 9, Class XI).

### 8.9.4 Substitution Reactions in the Hydrocarbon Part

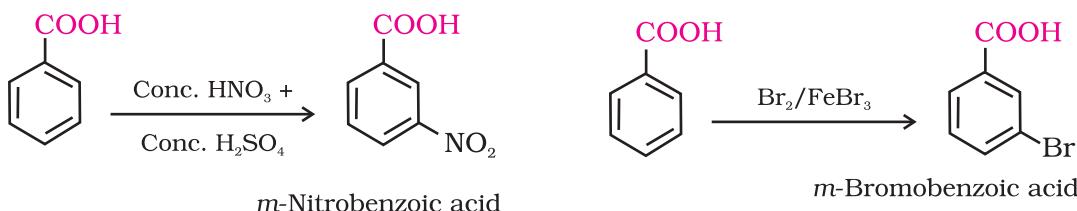
#### 1. Halogenation

Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



## 2. Ring substitution

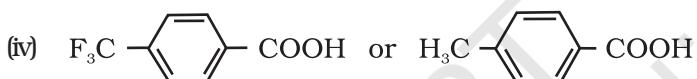
Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They however, do not undergo **Friedel-Crafts reaction** (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).



### In-text Question

8.8 Which acid of each pair shown here would you expect to be stronger?

- (i) CH<sub>3</sub>CO<sub>2</sub>H or CH<sub>2</sub>FCO<sub>2</sub>H
- (ii) CH<sub>2</sub>FCO<sub>2</sub>H or CH<sub>2</sub>ClCO<sub>2</sub>H
- (iii) CH<sub>2</sub>FCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H or CH<sub>3</sub>CHFCH<sub>2</sub>CO<sub>2</sub>H



## 8.10 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<sub>3</sub> 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<sub>3</sub>, alcohols (or diols),

ammonia derivatives, and **Grignard reagents**. The  $\alpha$ -hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one  $\alpha$ -hydrogen, undergo **Aldol condensation** in the presence of a base to give  $\alpha$ -hydroxyaldehydes (aldol) and  $\alpha$ -hydroxyketones(ketol), respectively. Aldehydes having no  $\alpha$ -hydrogen undergo **Cannizzaro reaction** in the presence of concentrated alkali. Aldehydes and ketones are reduced to alcohols with  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$ , 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  $\text{LiAlH}_4$ , or better with diborane in ether solution and also undergo  $\alpha$ -halogenation with  $\text{Cl}_2$  and  $\text{Br}_2$  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*

- 8.1** What is meant by the following terms ? Give an example of the reaction in each case.

  - Cyanohydrin
  - Acetal
  - Semicarbazone
  - Aldol
  - Hemiacetal
  - Oxime
  - Ketal
  - Imine
  - 2,4-DNP-derivative
  - Schiff's base

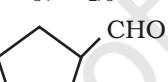
**8.2** Name the following compounds according to IUPAC system of nomenclature:

  - $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHO}$
  - $\text{CH}_3\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{Cl}$
  - $\text{CH}_3\text{CH}=\text{CHCHO}$
  - $\text{CH}_3\text{COCH}_2\text{COCH}_3$
  - $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{COCH}_3$
  - $(\text{CH}_3)_3\text{CCH}_2\text{COOH}$
  - $\text{OHCC}_6\text{H}_4\text{CHO}-p$

**8.3** Draw the structures of the following compounds.

  - 3-Methylbutanal
  - p*-Nitropropiophenone
  - p*-Methylbenzaldehyde
  - 4-Methylpent-3-en-2-one
  - 4-Chloropentan-2-one
  - 3-Bromo-4-phenylpentanoic acid
  - p,p'*-Dihydroxybenzophenone
  - Hex-2-en-4-yneic acid

**8.4** Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

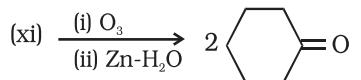
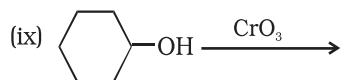
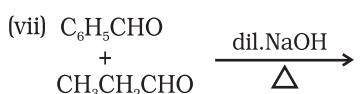
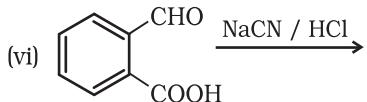
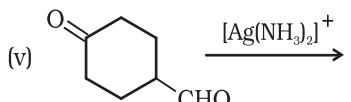
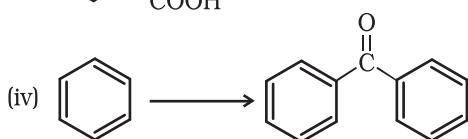
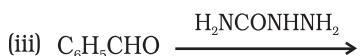
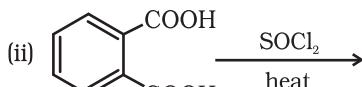
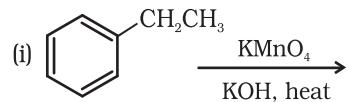
  - $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$
  - $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}(\text{CH}_3)\text{CHO}$
  - $\text{CH}_3(\text{CH}_2)_5\text{CHO}$
  - $\text{Ph-CH=CH-CHO}$
  - 
  - $\text{PhCOPh}$

**8.5** Draw structures of the following derivatives.

  - The 2,4-dinitrophenylhydrazone of benzaldehyde
  - Cyclopropanone oxime
  - Acetaldehydedimethylacetal
  - The semicarbazone of cyclobutanone
  - The ethylene ketal of hexan-3-one
  - The methyl hemiacetal of formaldehyde

- 8.6** Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.
- (i) PhMgBr and then  $\text{H}_3\text{O}^+$
  - (ii) Tollens' reagent
  - (iii) Semicarbazide and weak acid
  - (iv) Excess ethanol and acid
  - (v) Zinc amalgam and dilute hydrochloric acid
- 8.7** 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
- 8.8** How will you convert ethanal into the following compounds?
- (i) Butane-1,3-diol
  - (ii) But-2-enal
  - (iii) But-2-enoic acid
- 8.9** 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.
- 8.10** An organic compound with the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.
- 8.11** An organic compound (A) (molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$ ) 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.
- 8.12** 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)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ ,  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  (acid strength)
  - (iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
- 8.13** 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
- 8.14** 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.
- 8.15** 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  $\alpha$ -Hydroxyphenylacetic acid
  - (ix) Benzoic acid to *m*- Nitrobenzyl alcohol
- 8.16** Describe the following:
- (i) Acetylation
  - (ii) Cannizzaro reaction
  - (iii) Cross aldol condensation
  - (iv) Decarboxylation

**8.17** Complete each synthesis by giving missing starting material, reagent or products



**8.18** Give plausible explanation for each of the following:

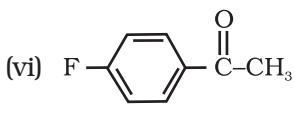
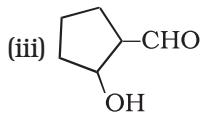
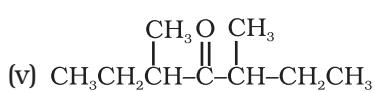
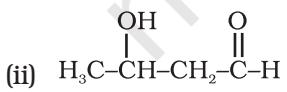
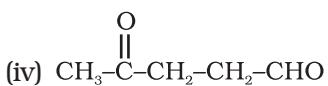
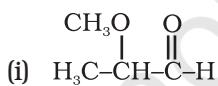
- Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
- There are two  $-\text{NH}_2$  groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
- During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

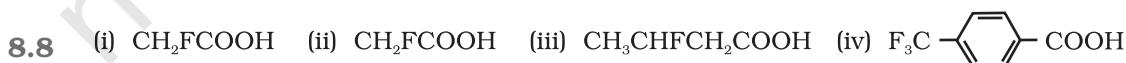
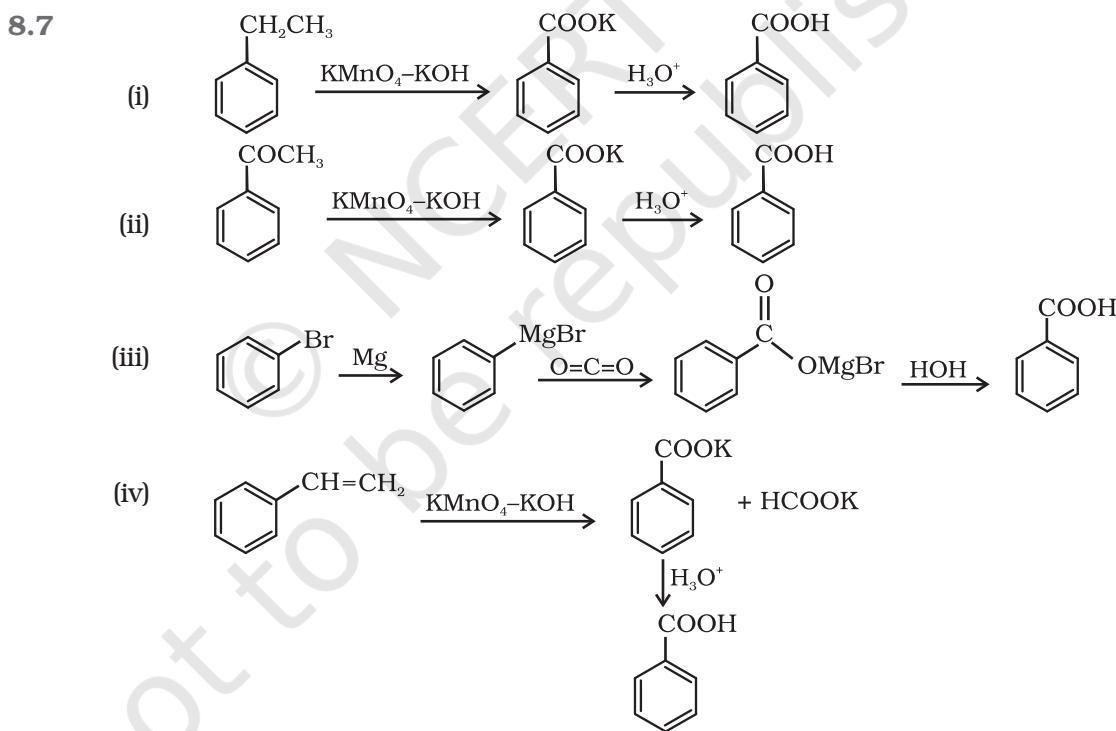
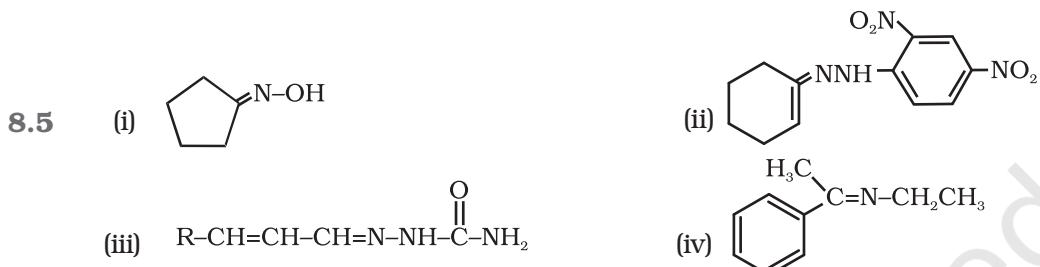
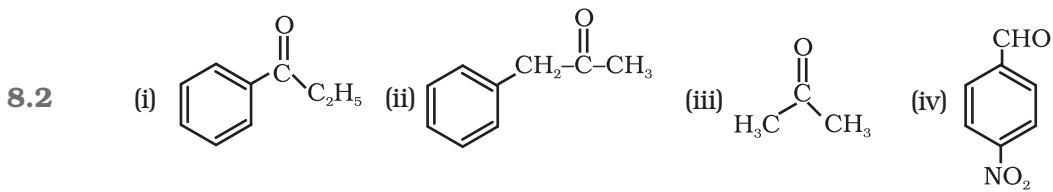
**8.19** An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

**8.20** 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

**8.1**







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## 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.

Unit

9

## Amines

*"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, dye stuffs 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.

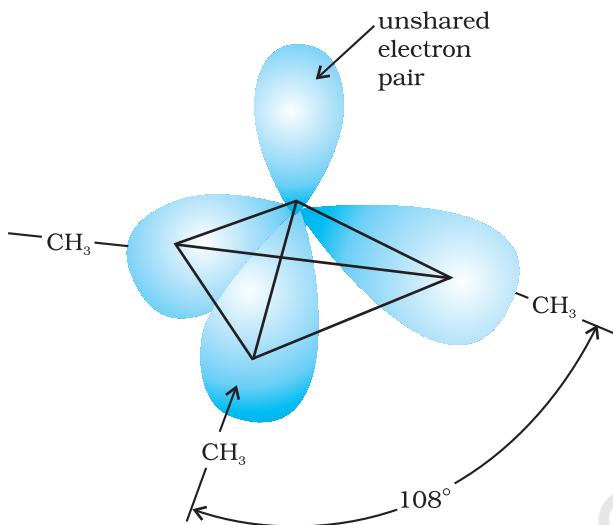
For example:



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

### 9.1 Structure of Amines

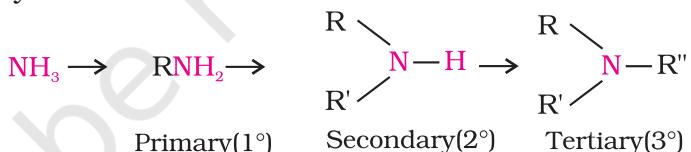
C or H) is less than  $109.5^\circ$ ; for instance, it is  $108^\circ$  in case of trimethylamine as shown in Fig. 9.1.



**Fig. 9.1** Pyramidal shape of trimethylamine

## 9.2 Classification

Amines are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) 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  $\text{RNH}_2$  or  $\text{ArNH}_2$ , a primary amine ( $1^\circ$ ). If two hydrogen atoms of ammonia or one hydrogen atom of  $\text{R-NH}_2$  are replaced by another alkyl/aryl(R') group, what would you get? You get  $\text{R-NHR}'$ , 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.



## 9.3 Nomenclature

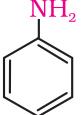
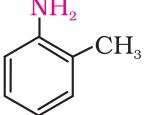
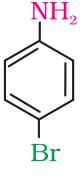
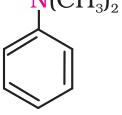
In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g., methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, primary amines are named as **alkanamines**. The name is derived by replacement of 'e' of alkane by the word amine. For example,  $\text{CH}_3\text{NH}_2$  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  $-\text{NH}_2$  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,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  is named as ethane-1, 2-diamine.

To name secondary and tertiary amines, we use locant N to designate substituent attached to a nitrogen atom. For example,  $\text{CH}_3\text{NHCH}_2\text{CH}_3$  is

named as N-methylethanamine and  $(\text{CH}_3\text{CH}_2)_3\text{N}$  is named as N, N-diethylethanamine. More examples are given in Table 9.1.

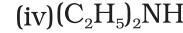
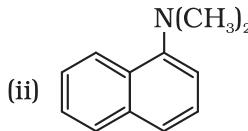
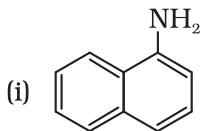
In arylamines,  $-\text{NH}_2$  group is directly attached to the benzene ring.  $\text{C}_6\text{H}_5\text{NH}_2$  is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'. Thus in IUPAC system,  $\text{C}_6\text{H}_5\text{--NH}_2$  is named as benzenamine. Common and IUPAC names of some alkylamines and arylamines are given in Table 9.1.

**Table 9.1: Nomenclature of Some Alkylamines and Arylamines**

Amine	Common name	IUPAC name
$\text{CH}_3\text{--CH}_2\text{--NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--NH}_2$	<i>n</i> -Propylamine	Propan-1-amine
$\text{CH}_3\text{--CH}(\text{NH}_2)\text{--CH}_3$	Isopropylamine	Propan-2-amine
$\text{CH}_3\text{--N}(\text{H})\text{--CH}_2\text{--CH}_3$	Ethylmethylamine	N-Methylethanamine
$\text{CH}_3\text{--N}(\text{CH}_3)\text{--CH}_3$	Trimethylamine	N,N-Dimethylmethanamine
$\text{C}_2\text{H}_5\text{--N}(\text{C}_2\text{H}_5)\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$	<i>N,N</i> -Diethylbutylamine	N,N-Diethylbutan-1-amine
$\text{NH}_2\text{--CH}_2\text{--CH}=\text{CH}_2$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2\text{--}(\text{CH}_2)_6\text{--NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	<i>o</i> -Toluidine	2-Methylaniline
	<i>p</i> -Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	<i>N,N</i> -Dimethylaniline	N,N-Dimethylbenzenamine

## Intext Questions

**9.1** Classify the following amines as primary, secondary or tertiary:



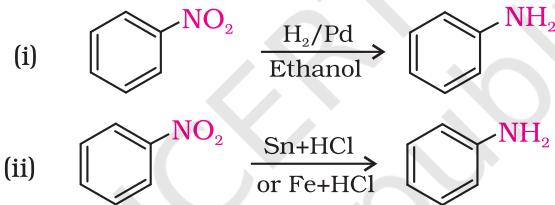
**9.2** (i) Write structures of different isomeric amines corresponding to the molecular formula,  $C_4H_{11}N$ .  
(ii) Write IUPAC names of all the isomers.  
(iii) What type of isomerism is exhibited by different pairs of amines?

## 9.4 Preparation of Amines

Amines are prepared by the following methods:

## **1. Reduction of nitro compounds**

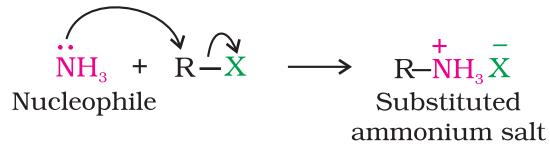
Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

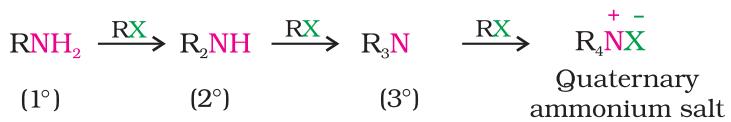


Reduction with iron scrap and hydrochloric acid is preferred because  $\text{FeCl}_2$  formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

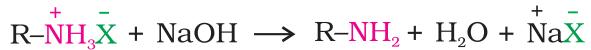
## **2. Ammonolysis of alkyl halides**

You have read (Unit 6, 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<sub>2</sub>) 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.





The free amine can be obtained from the ammonium salt by treatment with a strong base:



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.

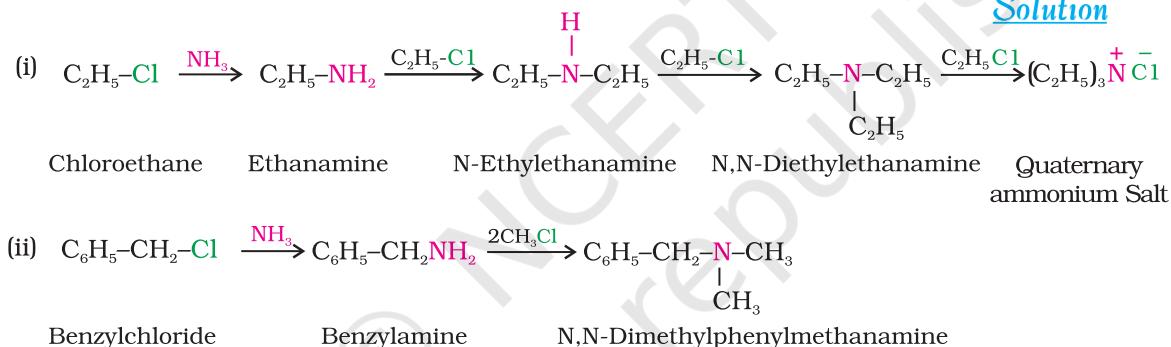
The order of reactivity of halides with amines is  $\text{RI} > \text{RBr} > \text{RCl}$ .

Write chemical equations for the following reactions:

### Example Q.1

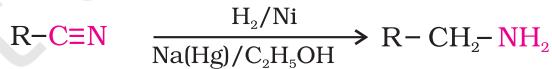
- (i) Reaction of ethanolic  $\text{NH}_3$  with  $\text{C}_2\text{H}_5\text{Cl}$ .
- (ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of  $\text{CH}_3\text{Cl}$ .

### Solution



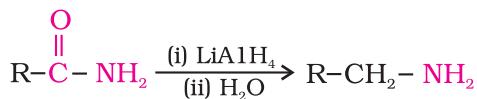
### **3. Reduction of nitriles**

Nitriles on reduction with lithium aluminium hydride ( $\text{LiAlH}_4$ ) 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.



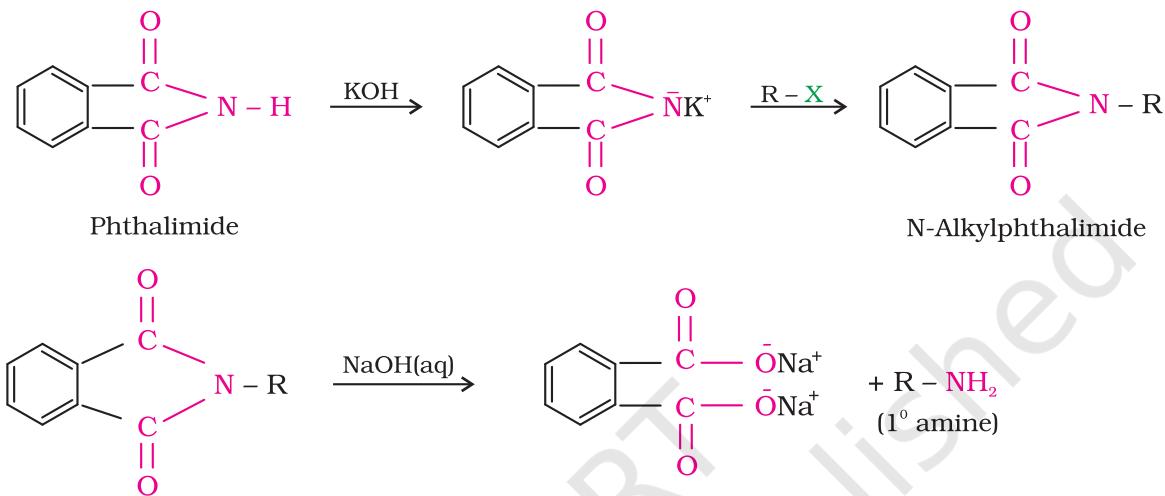
### **4. Reduction of amides**

The amides on reduction with lithium aluminium hydride yield amines.



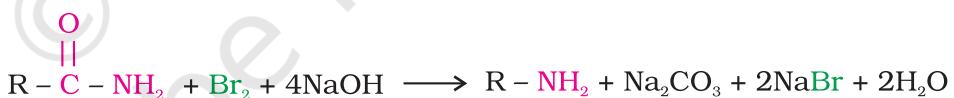
### 5. Gabriel phthalimide synthesis

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.



### 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.



#### Example 9.2

Write chemical equations for the following conversions:

- (i) CH<sub>3</sub>-CH<sub>2</sub>-Cl into CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>
- (ii) C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-Cl into C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>

#### Solution

- (i) CH<sub>3</sub>-CH<sub>2</sub>-Cl  $\xrightarrow{\text{Ethanolic NaCN}}$  CH<sub>3</sub>-CH<sub>2</sub>-C≡N  $\xrightarrow{\text{reduction}}$  CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>  
Chloroethane Propanenitrile Propan-1-amine
- (ii) C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-Cl  $\xrightarrow{\text{Ethanolic NaCN}}$  C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-C≡N  $\xrightarrow{\text{H}_2/\text{Ni}}$  C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>  
Chlorophenylmethane Phenylethanenitrile (Benzyl cyanide) 2-Phenylethanamine

Write structures and IUPAC names of

Example 9.3

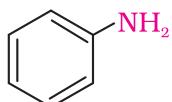
- (i) the amide which gives propanamine by Hoffmann bromamide reaction.  
(ii) the amine produced by the Hoffmann degradation of benzamide.

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:



- (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

**9.3** How will you convert

- (i) Benzene into aniline (ii) Benzene into N, N-dimethylaniline  
(iii)  $\text{Cl}-(\text{CH}_2)_4-\text{Cl}$  into hexan-1,6-diamine?

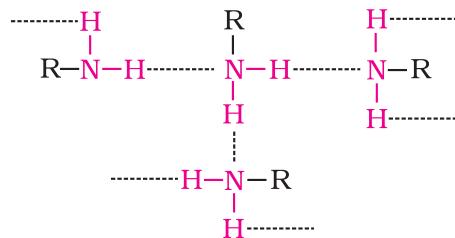
## 9.5 Physical Properties

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. 9.2.



**Fig. 9.2** Intermolecular hydrogen bonding in primary amines

Boiling points of amines, alcohols and alkanes of almost the same molar mass are shown in Table 9.2.

**Table 9.2: Comparison of Boiling Points of Amines, Alcohols and Alkanes of Similar Molecular Masses**

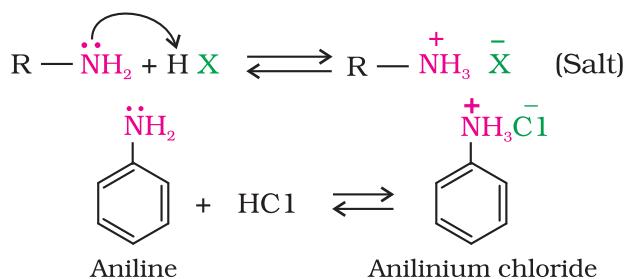
Sl. No.	Compound	Molar mass	b.p./K
1.	n-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	73	350.8
2.	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	73	329.3
3.	C <sub>2</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	73	310.5
4.	C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	72	300.8
5.	n-C <sub>4</sub> H <sub>9</sub> OH	74	390.3

## 9.6 Chemical Reactions

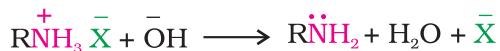
Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also decides the course of reaction of amines; that is why primary ( $\text{--NH}_2$ ), secondary ( $\text{>N--H}$ ) and tertiary amines ( $\text{>N--}$ ) 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.

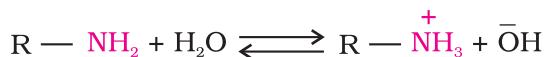


Amine salts on treatment with a base like NaOH, regenerate the parent amine.



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  $\text{p}K_b$  values as explained below:



$$K = \frac{[\text{R}-\text{NH}_3^{\text{+}}][\text{OH}^{-}]}{[\text{R}-\text{NH}_2][\text{H}_2\text{O}]}$$

$$\text{or } K[\text{H}_2\text{O}] = \frac{[\text{R}-\text{NH}_3^{\text{+}}][\text{OH}^{-}]}{[\text{R}-\text{NH}_2]}$$

$$\text{or } K_b = \frac{[\text{R}-\text{NH}_3^{\text{+}}][\text{OH}^{-}]}{[\text{R}-\text{NH}_2]}$$

$$\text{p}K_b = -\log K_b$$

Larger the value of  $K_b$  or smaller the value of  $\text{p}K_b$ , stronger is the base. The  $\text{p}K_b$  values of few amines are given in Table 9.3.

$\text{p}K_b$  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  $\text{p}K_b$  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 9.3:  $\text{p}K_b$  Values of Amines in Aqueous Phase**

Name of amine	$\text{p}K_b$
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

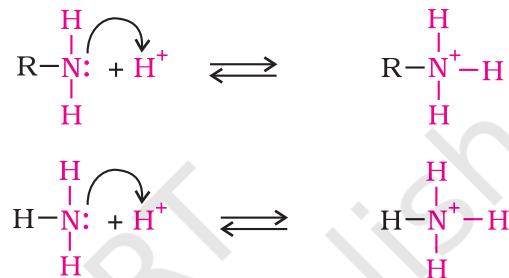
You may find some discrepancies while trying to interpret the  $K_b$  values of amines on the basis of +I or -I effect of the substituents present in amines. Besides inductive effect, there are other effects like solvation effect, steric hinderance, etc., which affect the basic strength of amines. Just ponder over. You may get the answer in the following paragraphs.

### **Structure-basicity relationship of amines**

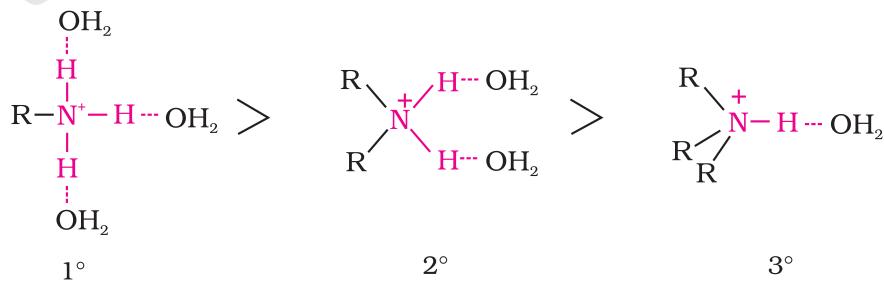
Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

#### **(a) Alkanamines versus ammonia**

Let us consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.

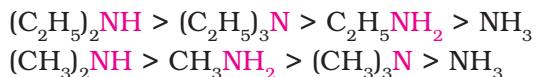


Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive 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 >  $\text{NH}_3$ . The trend is not regular in the aqueous state as evident by their  $pK_b$  values given in Table 9.3. 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:



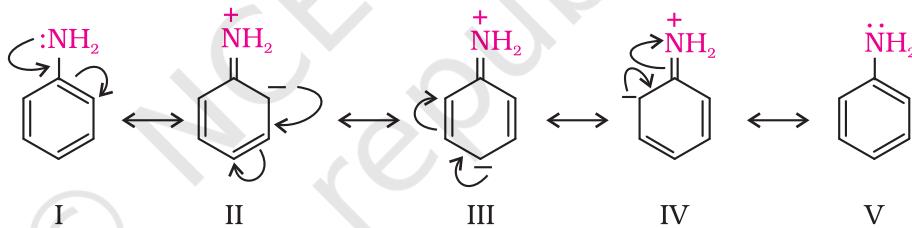
**Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.**

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  $-\text{CH}_3$  group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than  $\text{CH}_3$  group, there will be steric hinderance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from  $-\text{CH}_3$  to  $-\text{C}_2\text{H}_5$  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:

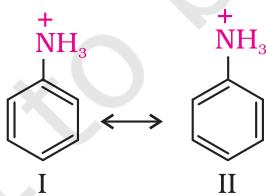


### (b) Arylamines versus ammonia

$\text{pK}_b$  value of aniline is quite high. Why is it so? It is because in aniline or other arylamines, the  $-\text{NH}_2$  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.



On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (Kekulé).



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  $-\text{OCH}_3$ ,  $-\text{CH}_3$  increase basic strength whereas electron withdrawing groups like  $-\text{NO}_2$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{X}$  decrease it.

**Example 9.4** Arrange the following in decreasing order of their basic strength:  
 $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{NH}_3$

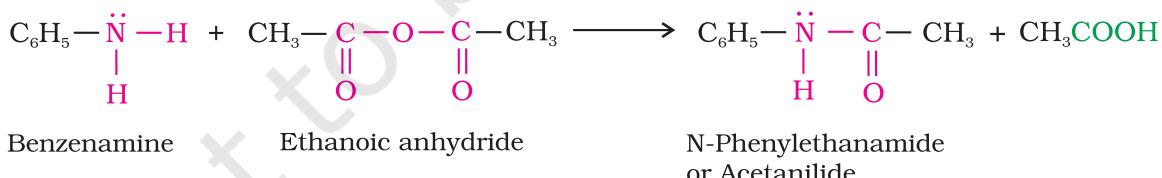
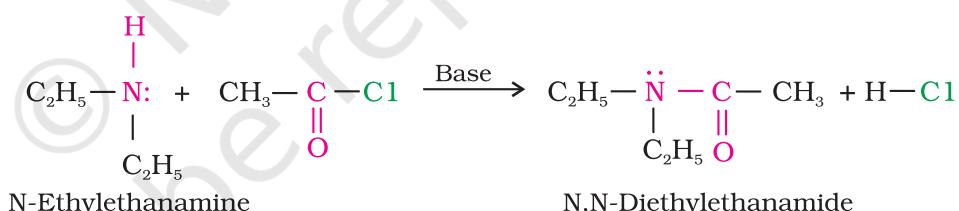
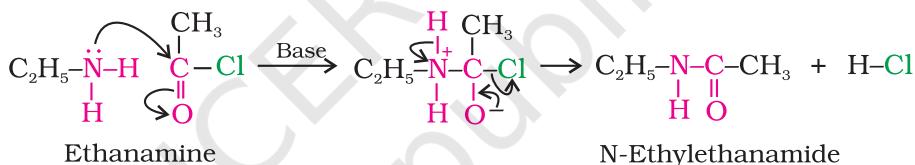
**Solution** The decreasing order of basic strength of the above amines and ammonia follows the following order:  
 $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

## 2. Alkylation

Amines undergo alkylation on reaction with alkyl halides (refer Unit 6, 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  $-\text{NH}_2$  or  $>\text{N}-\text{H}$  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  $\text{HCl}$  so formed and shifts the equilibrium to the right hand side.



Amines also react with benzoyl chloride ( $\text{C}_6\text{H}_5\text{COCl}$ ). This reaction is known as benzoylation.



What do you think is the product of the reaction of amines with carboxylic acids ? They form salts with amines at room temperature.

#### **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.



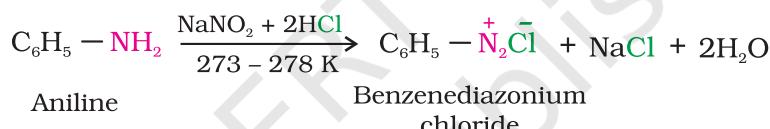
### **5. Reaction with nitrous acid**

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.



- (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 9.7.

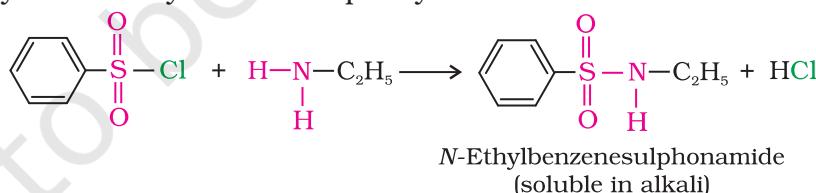


Secondary and tertiary amines react with nitrous acid in a different manner.

## 6. Reaction with arylsulphonyl chloride

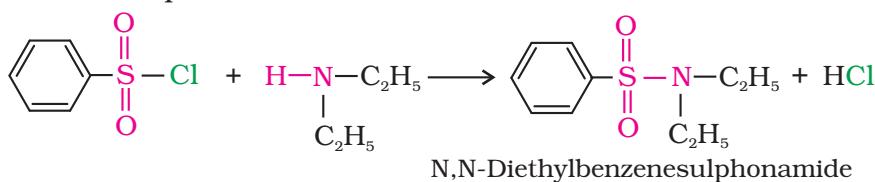
Benzenesulphonyl chloride ( $C_6H_5SO_2Cl$ ), which is also known as **Hinsberg's reagent**, reacts with primary and secondary amines to form sulphonamides.

- (a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



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-diethylbenzenesulphonamide is formed.



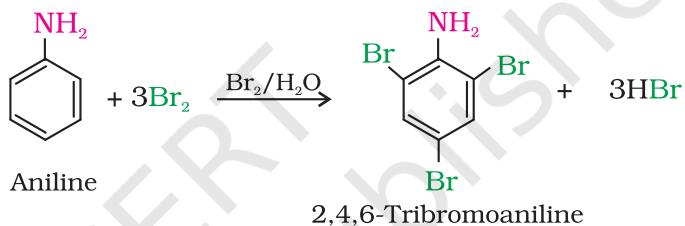
Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(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.

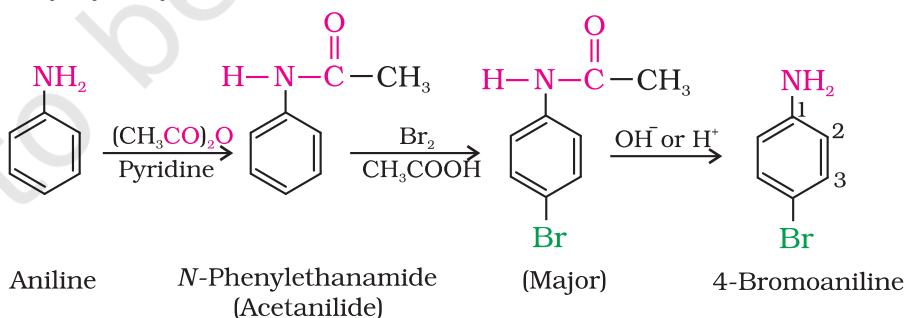
### 7. Electrophilic substitution

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  $-\text{NH}_2$  group become centres of high electron density. Thus  $-\text{NH}_2$  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.



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  $-\text{NH}_2$  group be controlled ? This can be done by protecting the  $-\text{NH}_2$  group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

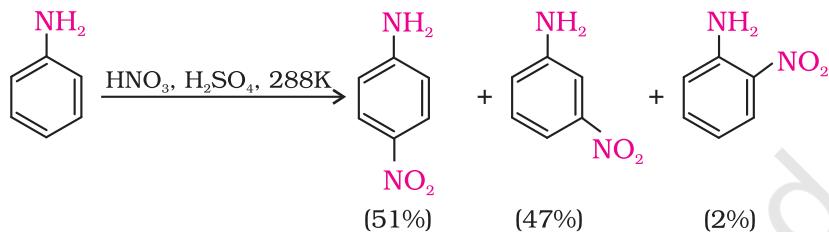


The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

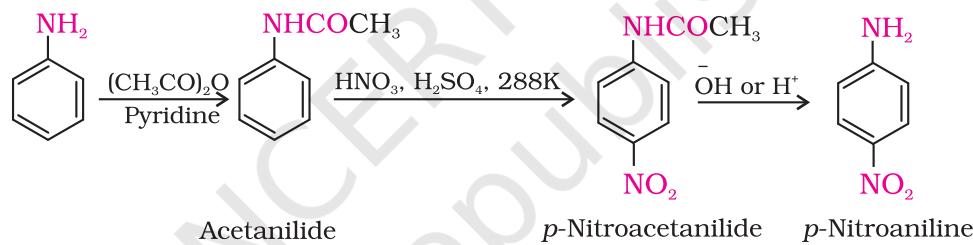


Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of  $-\text{NHCOCH}_3$  group is less than that of amino group.

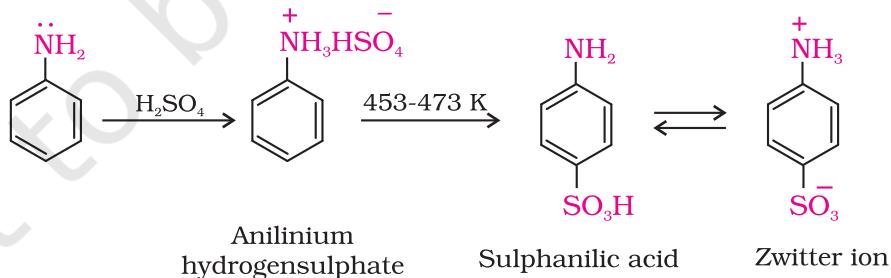
(b) **Nitration:** Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



However, by protecting the  $-\text{NH}_2$  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.

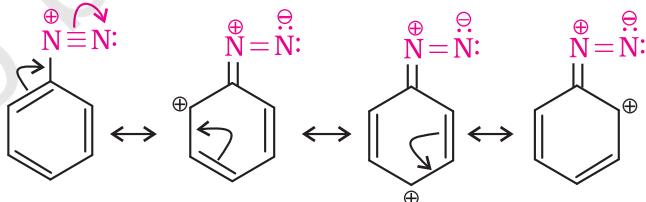
### Intext Questions

- 9.4** Arrange the following in increasing order of their basic strength:
- $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  and  $(\text{C}_2\text{H}_5)_2\text{NH}$
  - $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{C}_6\text{H}_5\text{NH}_2$
  - $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ .
- 9.5** Complete the following acid-base reactions and name the products:
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow$
  - $(\text{C}_2\text{H}_5)_3\text{N} + \text{HCl} \rightarrow$
- 9.6** Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.
- 9.7** Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.
- 9.8** Write structures of different isomers corresponding to the molecular formula,  $\text{C}_3\text{H}_9\text{N}$ . Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

## II. DIAZONIUM SALTS

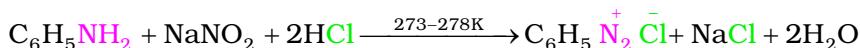
The diazonium salts have the general formula  $\text{R}^+ \text{N}_2^- \text{X}^-$  where R stands for an aryl group and  $\text{X}^-$  ion may be  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ , etc. They are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc. The  $\text{N}_2^+$  group is called diazonium group. For example,  $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$  is named as benzenediazonium chloride and  $\text{C}_6\text{H}_5\text{N}_2^+\text{HSO}_4^-$  is known as benzenediazonium hydrogensulphate.

Primary aliphatic amines form highly unstable alkyl diazonium salts (refer to Section 9.6). 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.



### **9.7 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.



## 9.8 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.

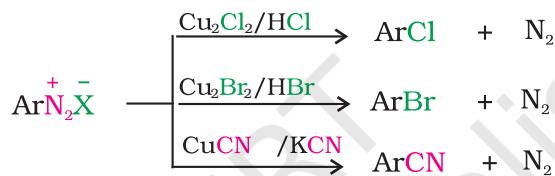
## 9.9 Chemical Reactions

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  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$  and  $\text{OH}^-$  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  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{CN}^-$  nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This reaction is called **Sandmeyer reaction**.

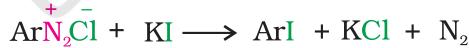


Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gattermann reaction**.



The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

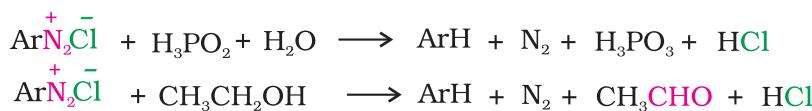
2. *Replacement by iodide ion:* Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.



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.



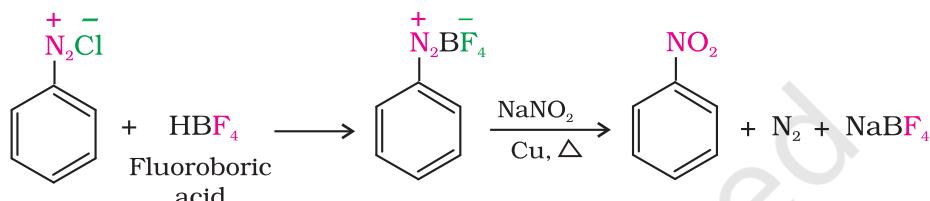
4. *Replacement by H:* Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanal, respectively.



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.

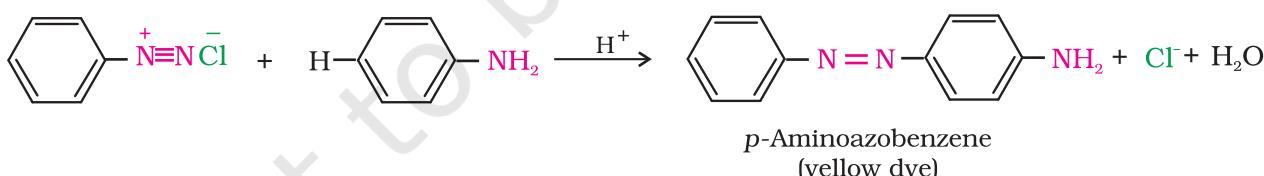
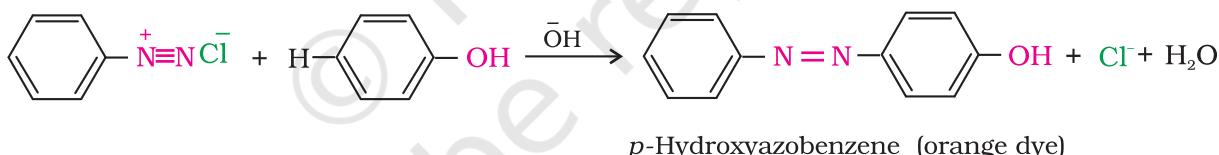


6. *Replacement by  $-\text{NO}_2$  group:* When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by  $-\text{NO}_2$  group.



#### 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  $-\text{N}=\text{N}-$  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.



#### 9.10 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  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ ,  $-\text{CN}$ ,  $-\text{OH}$ ,  $-\text{NO}_2$  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.

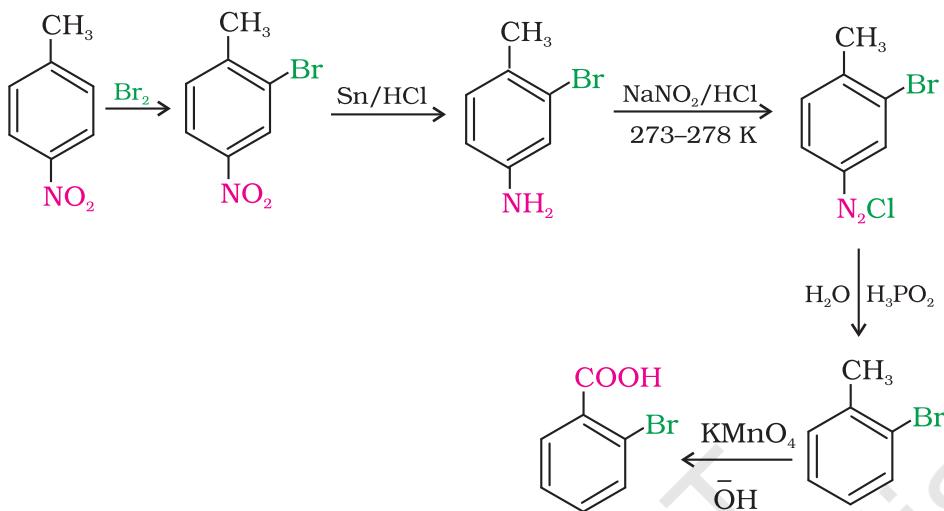
Thus, the replacement of diazo group by other groups is helpful in

preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene.

How will you convert 4-nitrotoluene to 2-bromobenzoic acid ?

### Example 9.5

#### Solution



#### Intext Question

##### 9.9 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  $\text{R}-\text{NH}_2$ , known as **primary amine**. **Secondary amines** are characterised by the structure  $\text{R}_2\text{NH}$  or  $\text{R}-\text{NHR}'$  and **tertiary amines** by  $\text{R}_3\text{N}$ ,  $\text{RNR}'\text{R}''$  or  $\text{R}_2\text{NR}'$ . 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

- 9.1** 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)  $m\text{-BrC}_6H_4NH_2$
- 9.2** 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.
- 9.3** 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.
- 9.4** 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

- (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:  
 $C_6H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $C_2H_5NH_2$ .
- 9.5** 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?
- 9.6** Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.
- 9.7** 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.
- 9.8** 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.
- 9.9** 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)  $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$
  - (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)  $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273 K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

- 9.10** An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with  $\text{Br}_2$  and KOH forms a compound 'C' of molecular formula  $\text{C}_6\text{H}_7\text{N}$ . Write the structures and IUPAC names of compounds A, B and C.
- 9.11** Complete the following reactions:
- $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + \text{alc.KOH} \rightarrow$
  - $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow$
  - $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4 \text{ (conc.)} \rightarrow$
  - $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow$
  - $\text{C}_6\text{H}_5\text{NH}_2 + \text{Br}_2 \text{ (aq)} \rightarrow$
  - $\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow$
  - $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow[\text{(ii)NaNO}_2 / \text{Cu}, \Delta]{\text{(i)HBF}_4} \rightarrow$
- 9.12** Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
- 9.13** Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.
- 9.14** Give plausible explanation for each of the following:
  - Why are amines less acidic than alcohols of comparable molecular masses?
  - Why do primary amines have higher boiling point than tertiary amines?
  - Why are aliphatic amines stronger bases than aromatic amines?

#### **Answers to Some Intext Questions**

- 9.4**
- $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$
  - $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$
  - $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$



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# Unit 10

## Biomolecules

### Objectives

After studying this Unit, you will be able to

- explain the characteristics of biomolecules like carbohydrates, proteins and nucleic acids and hormones;
- classify carbohydrates, proteins, nucleic acids and vitamins on the basis of their structures;
- explain the difference between DNA and RNA;
- describe 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.

### 10.1 Carbohydrates

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. Some common examples of carbohydrates 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. For example 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).

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, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose gives two molecules of only glucose.
- (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*.

### 10.1.2 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 10.1

**Table 10.1: Different Types of Monosaccharides**

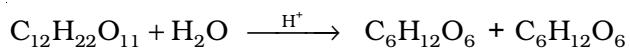
Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

#### 10.1.2.1 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:

1. *From sucrose (Cane sugar):* If sucrose is boiled with dilute HCl or  $\text{H}_2\text{SO}_4$  in alcoholic solution, glucose and fructose are obtained in equal amounts.

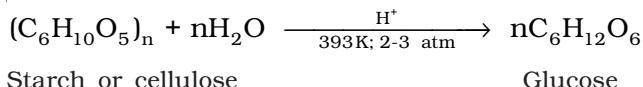
#### Preparation of Glucose



Sucrose

Glucose Fructose

2. *From starch:* Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute  $\text{H}_2\text{SO}_4$  at 393 K under pressure.

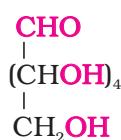


Starch or cellulose

Glucose

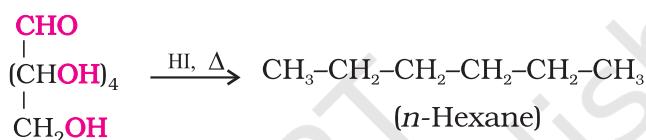
### Structure of Glucose

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:

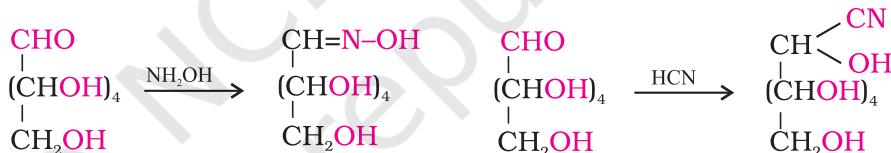


Glucose

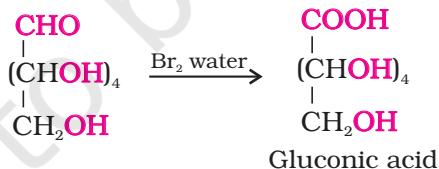
- Its molecular formula was found to be  $\text{C}_6\text{H}_{12}\text{O}_6$ .
- On prolonged heating with  $\text{HI}$ , it forms *n*-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



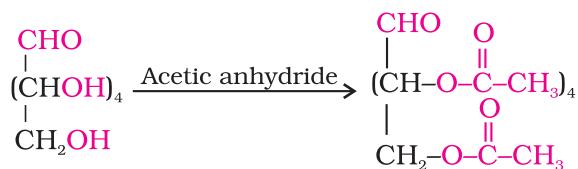
- Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group ( $>\text{C}=\text{O}$ ) in glucose.



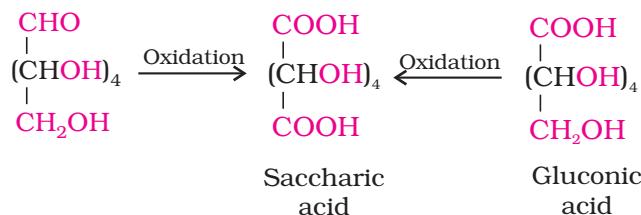
- Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.



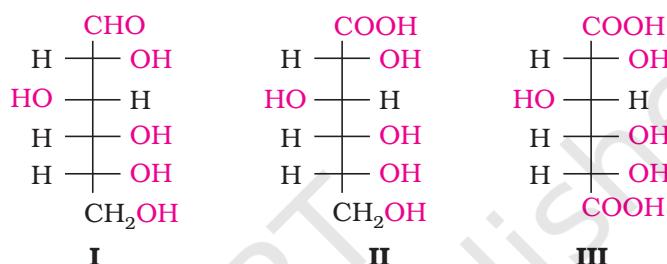
- Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five -OH groups. Since it exists as a stable compound, five -OH groups should be attached to different carbon atoms.



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.

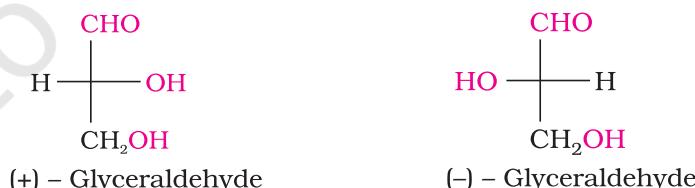


The exact spatial arrangement of different  $-OH$  groups was given by Fischer after studying many other properties. Its configuration is correctly represented as I. So gluconic acid is represented as II and saccharic acid as III.



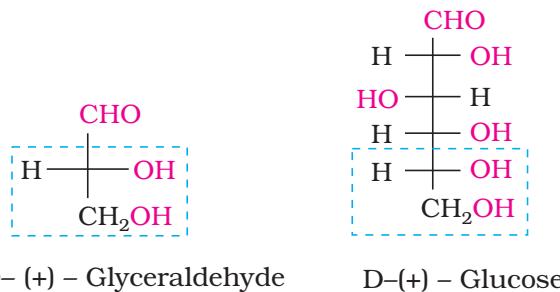
Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule. It should be remembered that 'D' and 'L' have no relation with the optical activity of the compound. They are also not related to letter 'd' and 'l' (see Unit 6). The meaning of D- and L- notations is as follows.

The letters 'D' or 'L' before the name of any compound indicate the relative configuration of a particular stereoisomer of a compound with respect to configuration of some other compound, configuration of which is known. In the case of carbohydrates, 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.



(+) Isomer of glyceraldehyde has 'D' configuration. It means that when its structural formula is written on paper following specific conventions which you will study in higher classes, the  $-OH$  group lies on right hand side in the structure. All those compounds which can be chemically correlated to D (+) isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to L (-) isomer of glyceraldehyde are said to have L-configuration. In L (-) isomer  $-OH$  group is on left hand side as you can see in the structure. 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 (+) glucose is assigned D-configuration. Other asymmetric carbon atoms of glucose are not considered for this comparison. Also, the structure of glucose and glyceraldehyde is written in a way that most oxidised carbon (in this case —CHO) is at the top.

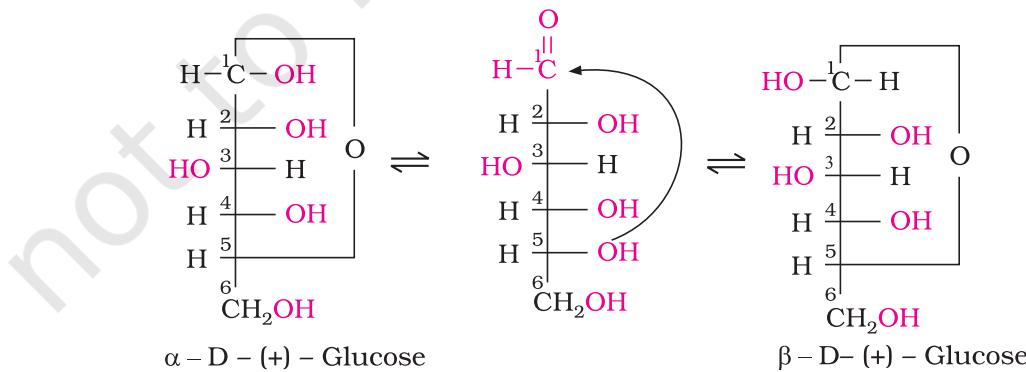


### Cyclic Structure of Glucose

The structure (I) of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

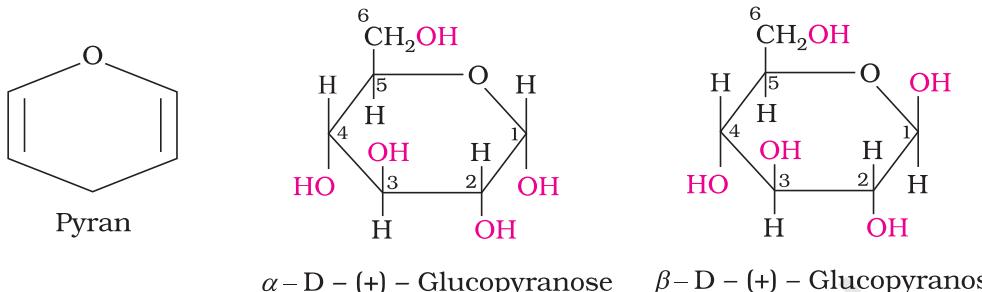
1. Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogensulphite addition product with  $\text{NaHSO}_3$ .
2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.
3. Glucose is found to exist in two different crystalline forms which are named as  $\alpha$  and  $\beta$ . The  $\alpha$ -form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the  $\beta$ -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.



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.,  $\alpha$ -form and  $\beta$ -form, are called **anomers**. The six membered cyclic structure of glucose is called **pyranose structure** ( $\alpha$ - or  $\beta$ -), 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.

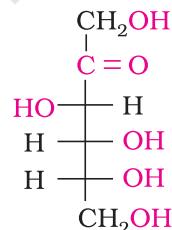


### 10.1.2.2 Fructose

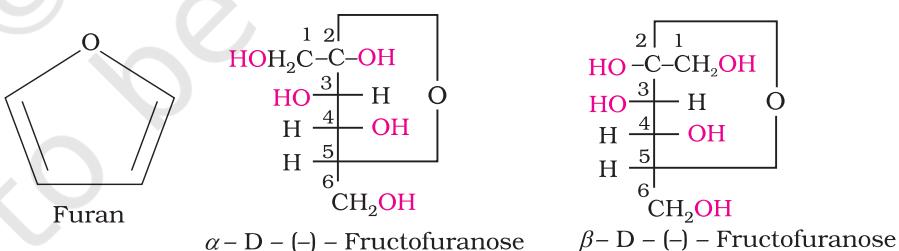
Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose. It is a natural monosaccharide found in fruits, honey and vegetables. In its pure form it is used as a sweetener. It is also an important ketohexose.

#### Structure of Fructose

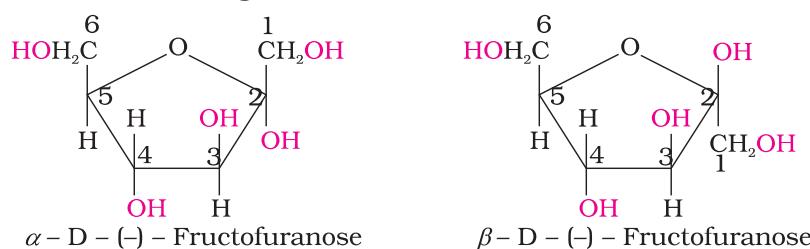
Fructose also has the molecular formula C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(-)-fructose. Its open chain structure is as shown.



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.



The cyclic structures of two anomers of fructose are represented by Haworth structures as given.

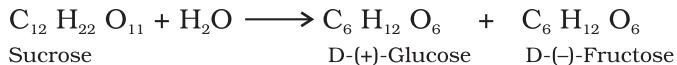


## 10.1.3 Disaccharides

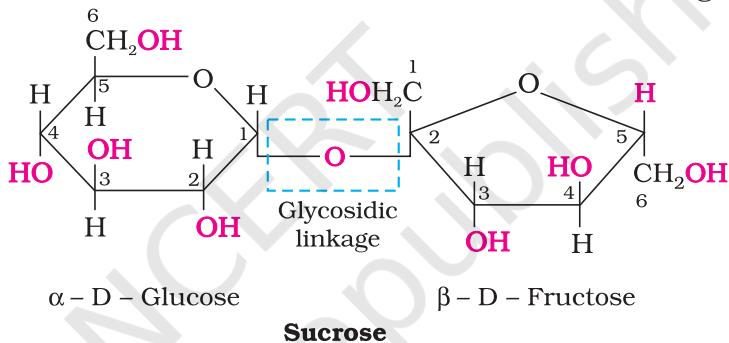
You have already read that disaccharides on hydrolysis with dilute acids or enzymes yield two molecules of either the same or different monosaccharides. The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called *glycosidic linkage*.

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.

- (i) Sucrose: One of the common disaccharides is **sucrose** which on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

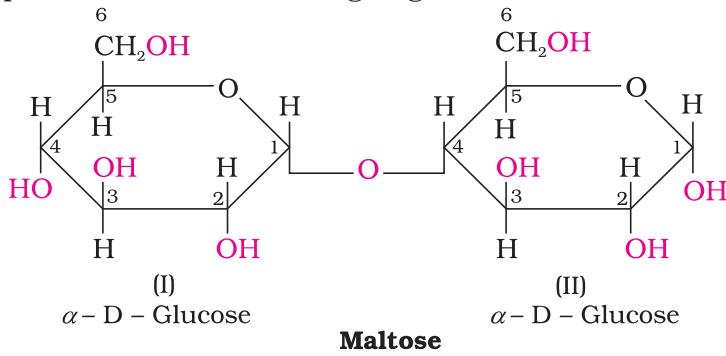


These two monosaccharides are held together by a glycosidic linkage between C1 of  $\alpha$ -D-glucose and C2 of  $\beta$ -D-fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.

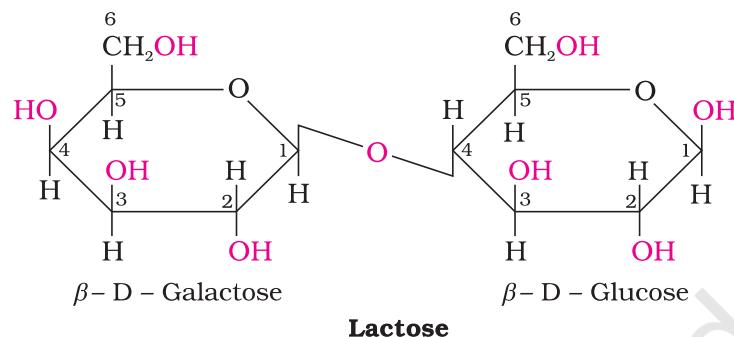


Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose ( $-92.4^\circ$ ) is more than dextrorotation of glucose ( $+52.5^\circ$ ), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and the product is named as **invert sugar**.

- (ii) **Maltose:** Another disaccharide, maltose is composed of two  $\alpha$ -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.



(iii) **Lactose:** It is more commonly known as milk sugar since this disaccharide is found in milk. It is composed of  $\beta$ -D-galactose and  $\beta$ -D-glucose. The linkage is between C1 of galactose and C4 of glucose. Free aldehyde group may be produced at C-1 of glucose unit, hence it is also a reducing sugar.

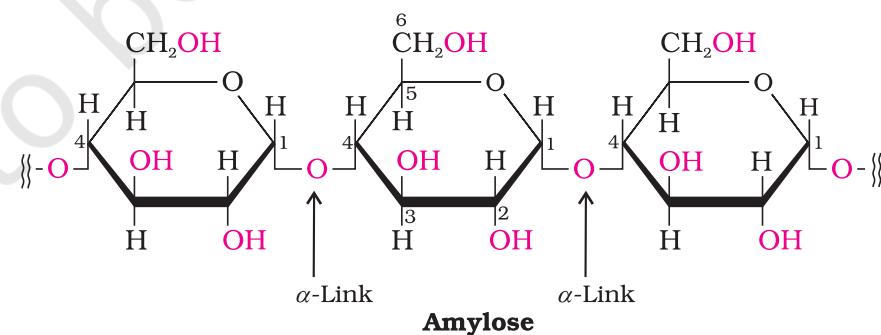


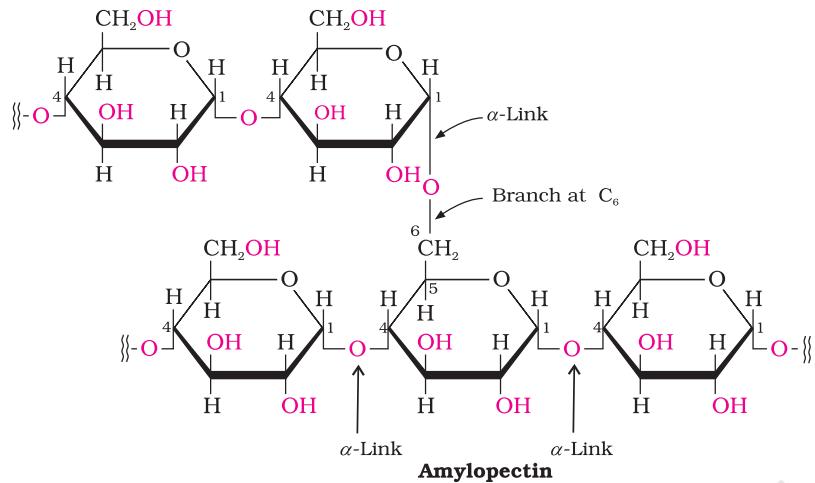
#### 10.1.4 Polysaccharides

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.

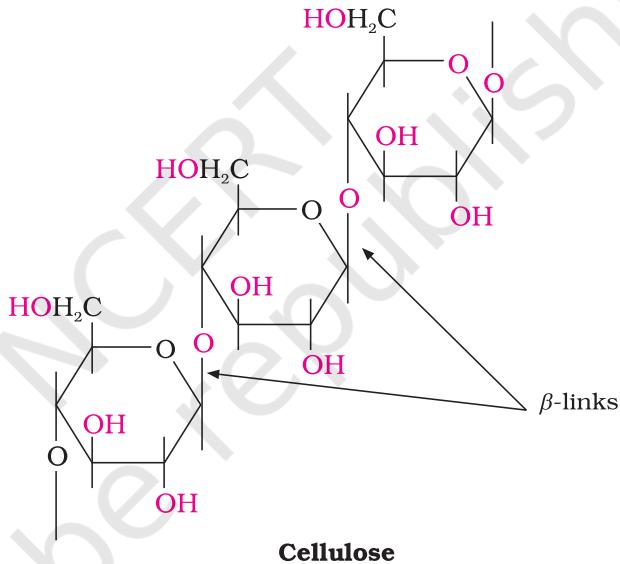
(i) **Starch:** Starch is the main storage polysaccharide of plants. It is the most important dietary source for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of  $\alpha$ -glucose and consists of two components—**Amylose** and **Amylopectin**. Amylose is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000  $\alpha$ -D-(+)-glucose units held together by C1– C4 glycosidic linkage.

Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of  $\alpha$ -D-glucose 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



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.

#### 10.1.5 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 '**Vaidas**' 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 10.5.1, Class XII) are present in nucleic acids. Carbohydrates are found in biosystem in combination with many proteins and lipids.

### Intext Questions

- 10.1 Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six membered ring compounds) are insoluble in water. Explain.
- 10.2 What are the expected products of hydrolysis of lactose?
- 10.3 How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

## 10.2 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  $\alpha$ -amino acids.

### **10.2.1 Amino Acids**

Amino acids contain amino ( $-\text{NH}_2$ ) and carboxyl ( $-\text{COOH}$ ) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and so on. Only  $\alpha$ -amino acids are obtained on hydrolysis of proteins. They may contain other functional groups also.

All  $\alpha$ -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 10.2.

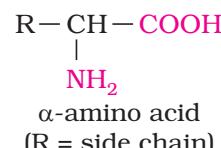
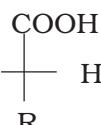
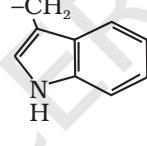
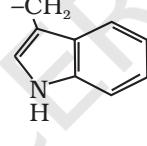
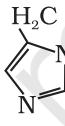


Table 10.2: Natural Amino Acids



Name of the amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-\text{CH}_3$	Ala	A
3. Valine*	$(\text{H}_3\text{C})_2\text{CH}-$	Val	V
4. Leucine*	$(\text{H}_3\text{C})_2\text{CH}-\text{CH}_2-$	Leu	L

5. Isoleucine*	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)-$	Ile	I
6. Arginine*	$\text{HN}=\text{C}-\text{NH}-(\text{CH}_2)_3-$ $\text{NH}_2$	Arg	R
7. Lysine*	$\text{H}_2\text{N}-(\text{CH}_2)_4-$	Lys	K
8. Glutamic acid	$\text{HOOC}-\text{CH}_2-\text{CH}_2-$	Glu	E
9. Aspartic acid	$\text{HOOC}-\text{CH}_2-$	Asp	D
10. Glutamine	$\text{H}_2\text{N}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-$	Gln	Q
11. Asparagine	$\text{H}_2\text{N}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-$	Asn	N
12. Threonine*	$\text{H}_3\text{C}-\text{CHOH}-$	Thr	T
13. Serine	$\text{HO}-\text{CH}_2-$	Ser	S
14. Cysteine	$\text{HS}-\text{CH}_2-$	Cys	C
15. Methionine*	$\text{H}_3\text{C}-\text{S}-\text{CH}_2-\text{CH}_2-$	Met	M
16. Phenylalanine*	$\text{C}_6\text{H}_5-\text{CH}_2-$	Phe	F
17. Tyrosine	$(p)\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-$ $-\text{CH}_2-$ 	Tyr	Y
18. Tryptophan*		Trp	W
19. Histidine*		His	H
20. Proline	$\text{HN}-\text{CH}(\text{CH}_2)-\text{COOH}^a$	Pro	P

\* essential amino acid, a = entire structure

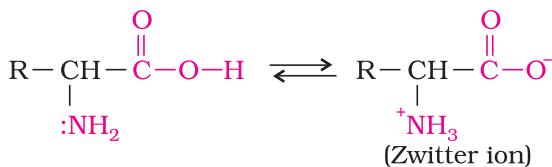
### 10.2.2 Classification of Amino Acids

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 10.2).

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.

$$\xrightarrow{\hspace{1cm}} \text{R}-\underset{\substack{| \\ +\text{NH}_3}}{\text{CH}}-\underset{\substack{|| \\ \text{C}}}{{\text{O}}}-\text{O}^-$$

(Zwitter ion)

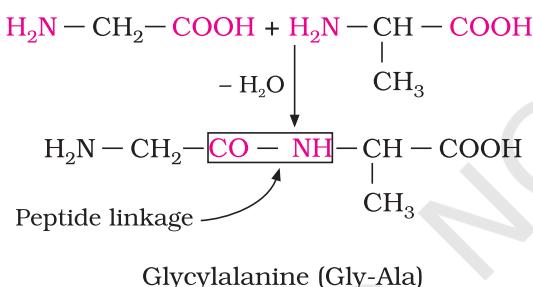


In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

Except glycine, all other naturally occurring  $\alpha$ -amino acids are optically active, since the  $\alpha$ -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.

### 10.2.3 Structure of Proteins

You have already read that proteins are the polymers of  $\alpha$ -amino acids and they are connected to each other by **peptide bond** or **peptide linkage**. Chemically, peptide linkage is an amide formed between  $-\text{COOH}$  group and  $-\text{NH}_2$  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  $-\text{CO}-\text{NH}-$ . 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.



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

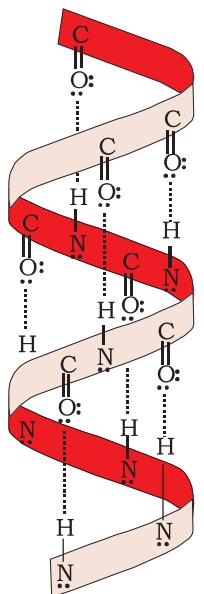
When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

### (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.

(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.



**Fig. 10.1:**  $\alpha$ -Helix structure of proteins

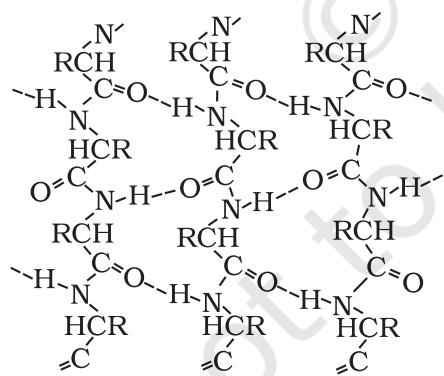
(ii) *Secondary structure of proteins:* The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz.  $\alpha$ -helix and  $\beta$ -pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between  $\text{O}=\text{C}-$  and  $-\text{NH}-$  groups of the peptide bond.

$\alpha$ -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  $-\text{NH}$  group of each amino acid residue hydrogen bonded to the  $>\text{C}=\text{O}$  of an adjacent turn of the helix as shown in Fig. 10.1.

In  $\beta$ -pleated sheet 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  $\beta$ -pleated sheet.

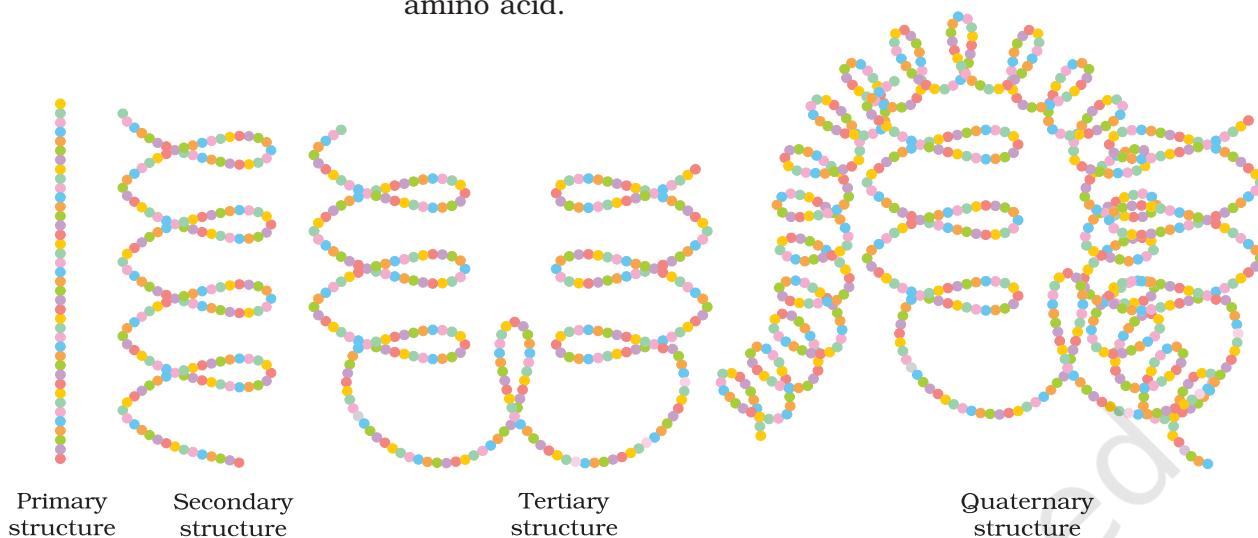
(iii) *Tertiary structure of proteins:* The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the  $2^\circ$  and  $3^\circ$  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.

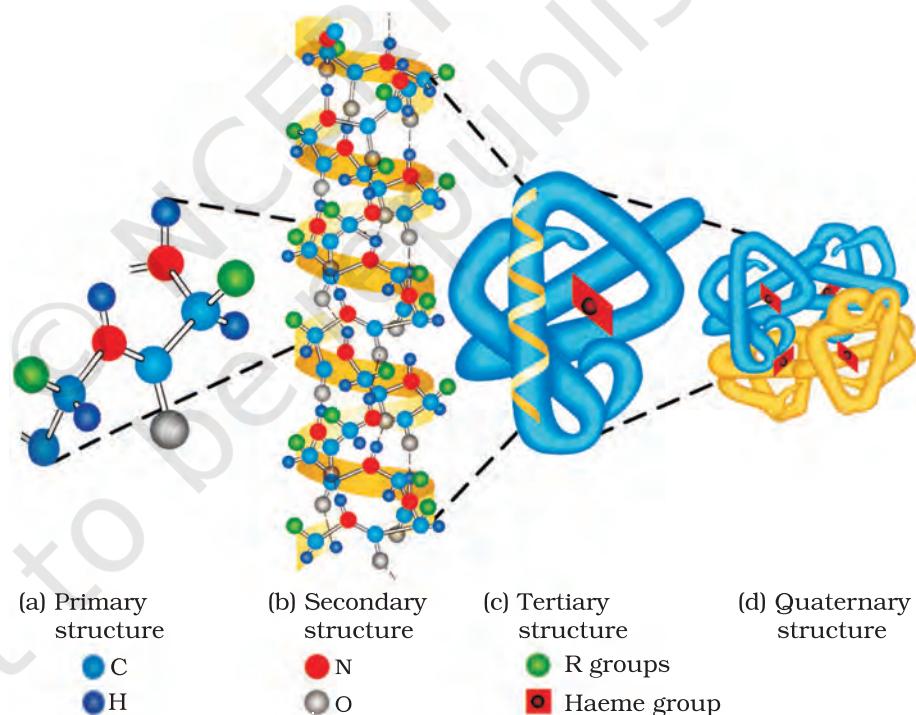


**Fig. 10.2:**  $\beta$ -Pleated sheet structure of proteins

A diagrammatic representation of all these four structures is given in Figure 10.3 where each coloured ball represents an amino acid.



**Fig. 10.3:** Diagrammatic representation of protein structure (two sub-units of two types in quaternary structure)



**Fig. 10.4:** Primary, secondary, tertiary and quaternary structures of haemoglobin

#### 10.2.4 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

protein. During denaturation secondary and tertiary structures are destroyed but primary 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

- 10.4** The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.
- 10.5** Where does the water present in the egg go after boiling the egg?

## 10.3 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*.



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**.

### 10.3.1 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  $6.22 \text{ kJ mol}^{-1}$ , while the activation energy is only  $2.15 \text{ kJ mol}^{-1}$  when hydrolysed by the enzyme, sucrase. Mechanism for the enzyme action has been discussed.

## 10.4 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<sub>1</sub>, B<sub>2</sub>, B<sub>6</sub>, B<sub>12</sub>, 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.

#### 10.4.1 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<sub>12</sub>) in our body.

Some important vitamins, their sources and diseases caused by their deficiency are listed in Table 10.3.

**Table 10.3: 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 <sub>1</sub> (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3.	Vitamin B <sub>2</sub> (Riboflavin)	Milk, eggwhite, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B <sub>6</sub> (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B <sub>12</sub>	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)

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

## 10.5 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.



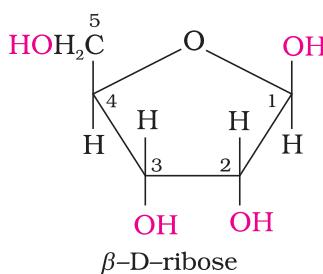
### James Dewey Watson

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;

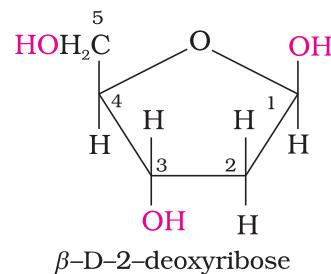
the rungs are each composed of a pair of purine/ pyrimidine bases. This research laid the foundation for the emerging field of **molecular biology**. The complementary pairing of nucleotide bases explains how identical copies of parental DNA pass on to two daughter cells. This research launched a revolution in biology that led to modern recombinant DNA techniques.

### 10.5.1 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  $\beta$ -D-2-deoxyribose whereas in RNA molecule, it is  $\beta$ -D-ribose.



$\beta$ -D-ribose

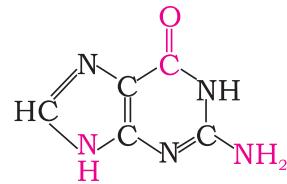


$\beta$ -D-2-deoxyribose

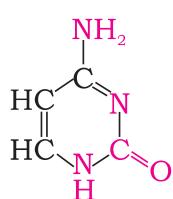
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



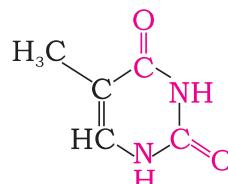
Adenine (A)



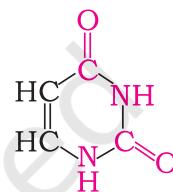
Guanine (G)



Cytosine (C)



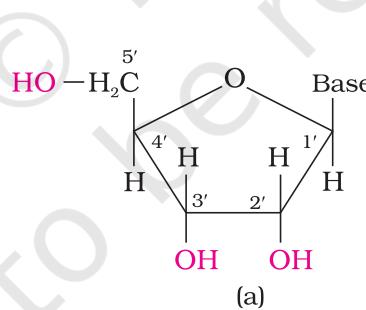
Thymine (T)



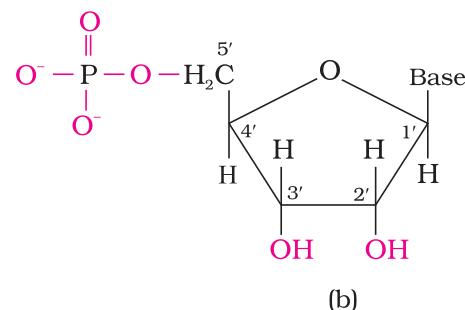
Uracil (U)

### 10.5.2 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. 10.5a). When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide (Fig. 10.5).



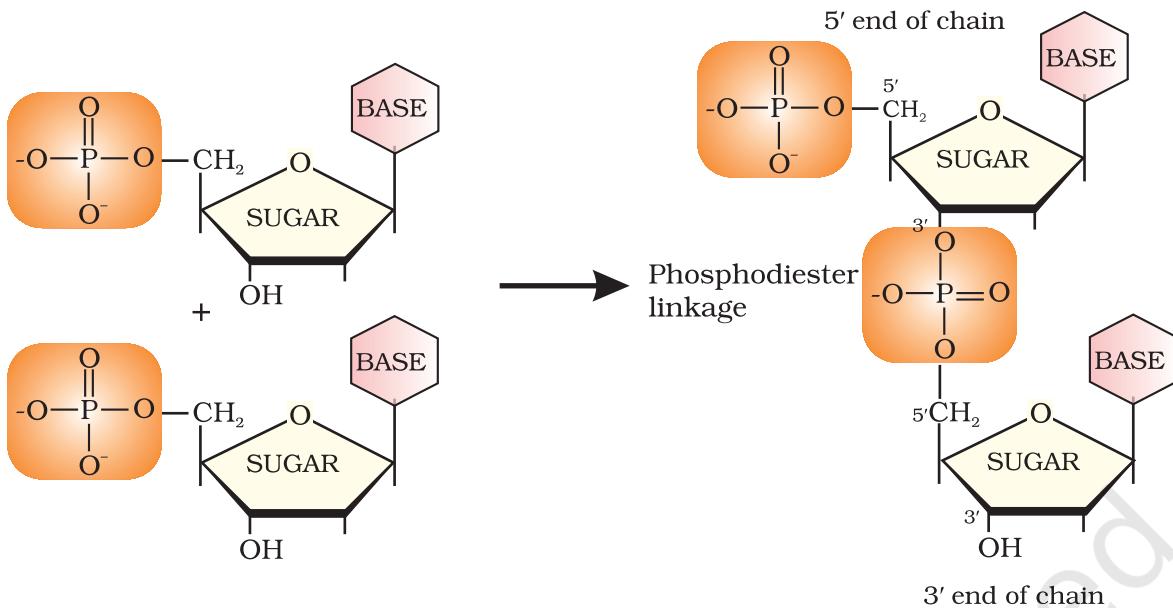
(a)



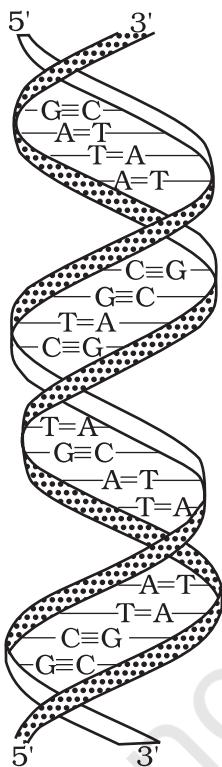
(b)

**Fig. 10.5:** Structure of (a) a nucleoside and (b) a nucleotide

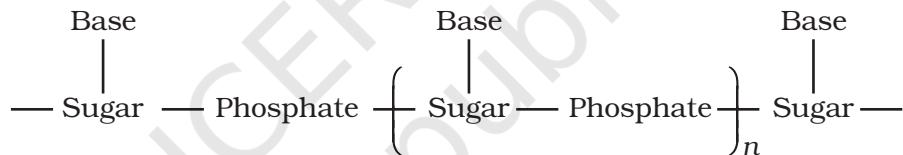
Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig. 10.6.



**Fig. 10.6:** Formation of a dinucleotide



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. 10.7). 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 single stranded helics is present which sometimes foldsback on itself. 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)**.

**Fig. 10.7:** Double strand helix structure for DNA



### 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.

#### 10.5.3 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.

Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are poured directly in the blood stream which transports them to the site of action.

In terms of chemical nature, some of these are steroids, e.g., estrogens and androgens; some are poly peptides for example insulin and endorphins and some others are amino acid derivatives such as epinephrine and norepinephrine.

Hormones have several functions in the body. They help to maintain the balance of biological activities in the body. The role of insulin in keeping the blood glucose level within the narrow limit is an example of this function. Insulin is released in response to the rapid rise in blood glucose level. On the other hand hormone glucagon tends to increase the glucose level in the blood. The two hormones together regulate the glucose level in the blood. Epinephrine and norepinephrine mediate responses to external stimuli. Growth hormones and sex hormones play role in growth and development. Thyroxine produced in the thyroid gland is an iodinated derivative of amino acid tyrosine. Abnormally low level of thyroxine leads

## 10.6 Hormones

to hypothyroidism which is characterised by lethargy and obesity. Increased level of thyroxine causes hyperthyroidism. Low level of iodine in the diet may lead to hypothyroidism and enlargement of the thyroid gland. This condition is largely being controlled by adding sodium iodide to commercial table salt ("Iodised" salt).

Steroid hormones are produced by adrenal cortex and gonads (testes in males and ovaries in females). Hormones released by the adrenal cortex play very important role in the functions of the body. For example, glucocorticoids control the carbohydrate metabolism, modulate inflammatory reactions, and are involved in reactions to stress. The mineralocorticoids control the level of excretion of water and salt by the kidney. If adrenal cortex does not function properly then one of the results may be Addison's disease characterised by hypoglycemia, weakness and increased susceptibility to stress. The disease is fatal unless it is treated by glucocorticoids and mineralocorticoids. Hormones released by gonads are responsible for development of secondary sex characters. Testosterone is the major sex hormone produced in males. It is responsible for development of secondary male characteristics (deep voice, facial hair, general physical constitution) and estradiol is the main female sex hormone. It is responsible for development of secondary female characteristics and participates in the control of menstrual cycle. Progesterone is responsible for preparing the uterus for implantation of fertilised egg.

### Intext Questions

- 10.6 Why cannot vitamin C be stored in our body?
- 10.7 What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?
- 10.8 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?

### 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  **$\alpha$ -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  $\alpha$ -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 majority of **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

- 10.1** What are monosaccharides?
- 10.2** What are reducing sugars?
- 10.3** Write two main functions of carbohydrates in plants.
- 10.4** Classify the following into monosaccharides and disaccharides.  
Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.
- 10.5** What do you understand by the term glycosidic linkage?
- 10.6** What is glycogen? How is it different from starch?
- 10.7** What are the hydrolysis products of  
(i) sucrose and                   (ii) lactose?
- 10.8** What is the basic structural difference between starch and cellulose?
- 10.9** What happens when D-glucose is treated with the following reagents?  
(i) HI                                 (ii) Bromine water                             (iii)  $\text{HNO}_3$
- 10.10** Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.
- 10.11** What are essential and non-essential amino acids? Give two examples of each type.
- 10.12** Define the following as related to proteins  
(i) Peptide linkage                   (ii) Primary structure                   (iii) Denaturation.
- 10.13** What are the common types of secondary structure of proteins?
- 10.14** What type of bonding helps in stabilising the  $\alpha$ -helix structure of proteins?
- 10.15** Differentiate between globular and fibrous proteins.
- 10.16** How do you explain the amphoteric behaviour of amino acids?
- 10.17** What are enzymes?
- 10.18** What is the effect of denaturation on the structure of proteins?
- 10.19** How are vitamins classified? Name the vitamin responsible for the coagulation of blood.
- 10.20** Why are vitamin A and vitamin C essential to us? Give their important sources.
- 10.21** What are nucleic acids? Mention their two important functions.
- 10.22** What is the difference between a nucleoside and a nucleotide?
- 10.23** The two strands in DNA are not identical but are complementary. Explain.
- 10.24** Write the important structural and functional differences between DNA and RNA.
- 10.25** What are the different types of RNA found in the cell?