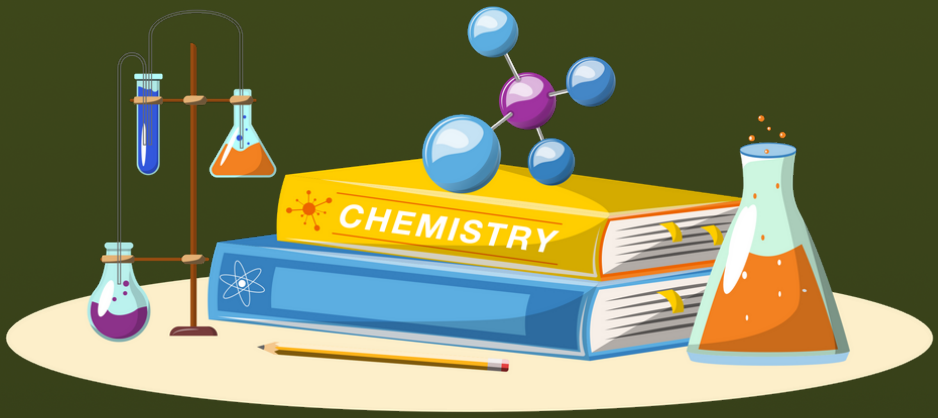
TEXT BOOK FOR

SR.SECONDARY COURSE

CHEMISTRY



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ATOMS, MOLECULES AND CHEMICAL ARITHMETIC

Chemistry is the study of matter and the changes it undergoes. Chemistry is often called the central science, because a basic knowledge of chemistry is essential for the study of biology, physics, geology, ecology, and many other subjects.

Although chemistry is an ancient science, its modern foundation was laid in the nineteenth century, when intellectual and technological advances enabled scientists to break down substances into ever smaller components and consequently to explain many of their physical and chemical characteristics.

Chemistry plays a pivotal role in many areas of science and technology e.g. in health, medicine, energy and environment, food, agriculture and new materails.

As you are aware, atoms and molecules are so small that we cannot see them with our naked eyes or even with the help of a microscope. Any sample of matter which can be studied consists of extremely large number of atoms or molecules. In chemical reactions, atoms or molecules combine with one another in a *definite number ratio.* Therefore, it would be pertinent if we could specify the total number of atoms or molecules in a given sample of a substance. We use many *number units* in our daily life. For example, we express the number of bananas or eggs in terms of 'dozen'. In chemistry we use a number unit called **mole** which is very large.

With the help of **mole concept** it is possible to take a desired number of atoms/ molecules by weighing. Now, in order to study chemical compounds and reactions in the laboratory, it is necessary to have adequate knowledge of the quantitative relationship among the amounts of the reacting substances that take part and products formed in the chemical reaction. This relationship is knows as stoichiometry. **Stoichiometry** (derived from the Greek *Stoicheion* = element and *metron* = measure) is the term we use to refer to all the quntatitative aspects of chemical compounds and reactions. In the present lesson, you will see how chemical formulae are determined and how chemical equations prove useful in predicting the proper amounts of the reactants that must be mixed to carry out a complete reaction. In other words we can take reactants for a reaction in such a way that none of the reacting substances is in excess. This aspect is very vital in chemistry and has wide application in industries.

OBJECTIVES

After reading this lesson you will be able to :

- explain the scope of chemistry;
- explain the atomic theory of matter;
- state the laws of chemical combinaton;
- explain Dalton's atomic theory;
- define the terms element, atoms and molecules.
- state the need of SI units;
- list base SI units;
- explain the relationship between mass and number of particles;
- define Avogadro's constant and state its significance;
- calculate the molar mass of different elements and compounds;
- define molar volume of gases at STP.
- define empirical and molecular formulae;
- differentiate between empirical and molecular formulae;
- calculate precentage by mass of an element in a compound and also work out empirical formula from the percentage composition;
- establish relationship between mole, mass and volume;
- calculate the amount of substances consumed or formed in a chemical reaction using a balanced equation and mole concept, and
- explain the role of limiting reagent in limiting the amount of the products formed.

1.1 SCOPE OF CHEMISTRY

Chemistry plays an important role in all aspects of our life. Let us discuss role of chemistry in some such areas.

1.1.1 Health and Medicine

Three major advances in this century have enabled us to prevent and treat diseases. Public health measures establishing sanitation systems to protect vast numbers of people from infectious diseases; surgery with anesthesia, enabling physicians to cure potentially fatal conditions, such as an inflamed appendix; and the introduction of vaccines and antibiotics that made it possible to prevent diseases spread by microbes. Gene therapy promises to be the fourth revolution in medicine. (A gene is the basic unit of inheritance.) Several thousand known conditions, including cystic fibrosis and hemophilia, are carried by inborn damage to a single gene. Many other ailments, such as cancer, heart disease, AIDS, and arthritis, result to an extent from impairment of one or more genes involved in the body's defenses. In gene therapy, a selected healthy gene is delivered to a patient's cell to cure or ease such disorders. To carry out such a procedure, a doctor must have a sound knowledge of the chemical properties of the molecular components involved.

Chemists in the pharmaceutical industry are researching potent drugs with few or no side effects to treat cancer, AIDS, and many other diseases as well as drugs to increase the number of successful organ transplants. On a broader scale, improved understanding of the mechanism of ageing will lead to a longer and healthier lifespan for the world's population.

11.2 Energy and the Environment

Energy is a by-product of many chemical processes, and as the demand for energy continues to increase, both in technologically advanced countries like the United States and in developing ones like India. Chemists are actively trying to find new energy sources. Currently the major sources of energy are fossil fuels (coal, petroleum, and natural gas). The estimated reserves of these fuels will last us another 50-100 years at the present rate of consumption, so it is urgent that we find alternatives.

Solar energy promises to be a viable source of energy for the future. Every year earth's surface receives about 10 times as much energy from sunlight as is contained in all of the known reserves of coal, oil, natural gas, and uranium combined. But much of this energy is "wasted" because it is reflected back into space. For the past thirty years, intense research efforts have shown that solar energy can be harnessed effectively in two ways. One is the conversion of sunlight directly to electricity using devices called *photovoltaic cells*. The other is to use sunlight to obtain hydrogen from water. The hydrogen can then be fed into *a fuel cell* to generate electricity. Although our understanding of the scientific process of converting solar energy to electricity has advanced, the technology has not yet improved to the point where we can produce electricity on a large scale at an economically acceptable cost. By 2050, however, it has been predicted that solar energy will supply over 50 percent of our power needs.

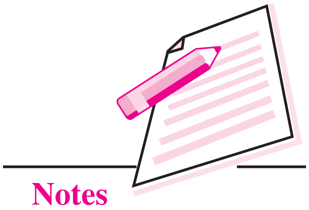
Another potential source of energy is nuclear fission, but because of environmental concerns about the radioactive wastes from fission processes, the future of the nuclear industry is uncertain. Chemists can help to devise better ways to dispose of nuclear waste. Nuclear fusion, the process that occurs in the sun and other stars, generates huge amounts of energy without producing much dangerous radioactive waste. In another 50 years, nuclear fusion will likely be a significant source of energy.

Energy production and energy utilization are closely tied to the quality of our environment. A major disadvantage of burning fossil fuels is that they give off carbon dioxide, which is *a greenhouse gas* (that is, it promotes the heating of Earth's atmosphere), along with sulfur dioxide and nitrogen oxides, which result in acid rain and smog. Harnessing solar energy has no such detrimental effects on the environment. By using fuel-efficient automobiles and more effective catalytic converters, we should be able to drastically reduce harmful auto emissions and improve the air quality in areas with heavy traffic. In addition, electric cars, powered by durable, long-lasting batteries, should be more prevalent in the next century, and their use will help to minimize air pollution.

1.1.3 Materials and Technology

Chemical research and development in the twentieth century have provided us with new materials that have profoundly improved the quality of our lives and helped to advance technology in countless ways. A few examples are polymers (including rubber and nylon), ceramics (such as cookware), liquid crystals (like those in electronic displays), adhesives, and coatings (for example, latex paint).

What is in store for the near future? One likely possibility is room-temperature *superconductors*. Electricity is carried by copper cables, which are not perfect conductors. Consequently, about 20 percent of electrical energy is lost in the form of heat between the power station and our homes. This is a tremendous waste. Superconductors are materials that have no electrical resistance and can therefore conduct electricity with no energy loss.



1.1.4 Food and Agriculture

How can the world's rapidly increasing population be fed? In poor countries, agricultural activities occupy about 80 percent of the workforce and half of an average family budget is spent on foodstuffs. This is a tremendous drain on a nation's resources. The factors that affect agricultural production are the richness of the soil, insects and diseases that damage crops, and weeds that compete for nutrients. Besides irrigation, farmers rely on fertilizers and pesticides to increase crop yield.

1.2 PARTICULATE NATURE OF MATTER

Chemistry deals with study of structure and composition of matter. Since ancient time people have been wondering about nature of matter. Suppose we take a piece of rock and start breaking it into smaller and smaller particles can this process go on far ever resulting in smaller and smaller particles or would it come to stop when such particles are formed which can no longer to broken into still smaller particles? Many people including Greek philosophers Plato and Aristotle believed that matter is continuous and the process of subdivision of matter can go on.

On the other hand, many people believed that the process of subdivision of mater can be repeated only a limited nuimber of times till such particles are obtained which cannot be further subdivided. They believed that mattr is composed of large number of very tiny particles and thus has particle naturew. The smallest indivisible particles of matter were given the name 'atom' from the Greek word "atoms" meaning 'indivisible'. It is generally agreed that the Greek philosopher Leucippus and his student Democritus were the first to propose this idea, about 440 B.C.. However, Maharshi Kanad had propounded the atomic concept of matter earlier (500 BC) and had named the smallest particle of matter as "PARMANU".

1.3 LAWS OF CHEMICAL COMBINATIONS

There was tremendous progress in Chemical Sciences after 18th century. It arose out of an interest in the nature of heat and the way things burn. Major progress was made through the careful use of *chemical balance* to determine the change in mass that occurs in chemical reactions. The great French Chemist Antoine Lavoisier used the balance to study chemical reactions. He heated mercury in a sealed flask that contained air. After several days, a red substance mercury (II) oxide was produced. The gas remaining in the flask was reduced in mass. The remaining gas was neither able to support combustion nor life. The remaining gas in the flask was identified as nitrogen. The gas which combined with mercury was oxygen. Further he carefully performed the experiment by taking a weighed quantity of mercury (II) oxide. After strong heating, he found that mercury (II) oxide, red in colour, was decomposed into mercury and oxygen. He weighed both mercury and oxygen and found that their combined mass was equal to that of the mercury (II) oxide taken. Lavoisier finally came to the conclusion that ***in every chemical reaction, total masses of all the reactants is equal to the masses of all the products***. This law is known as the **law of conservation of mass.**

There was rapid progress in science after chemists began accurate determination of masses of reactants and products. French chemist Claude Berthollet and Joseph Proust worked on the ratio (by mass) of two elements which combine to form a compound. Through a careful work, Proust demonstrated the fundamental law of definite or constant proportions in 1808. **In a given chemical compound, the proportions by mass of the elements that compose it are fixed, independent of the origin of the compound or its mode of preparation.**

In pure water, for instance, the ratio of mass of hydrogen to the mass of oxygen is always 1:8 irrespective of the source of water. In other words, pure water contains 11.11% of hydrogen and 88.89% of oxygen by mass whether water is obtained from well, river or from a pond. Thus, if 9.0 g of water are decomposed, 1.0 g of hydrogen and 8.0 g of oxygen are always obtained. Furthermore, if 3.0 g of hydrogen are mixed with 8.0 g of oxygen and the mixture is ignited, 9.0 g of water are formed and 2.0 g of hydrogen remains unreacted. Similarly sodium chloride contains 60.66% of chlorine and 39.34% of sodium by mass whether we obtained it from salt mines or by crytallising it from water of ocean or inland salt seas or synthesizing it from its elements sodium and chlorine. Of course, the key word in this sentence is ‘pure’. Reproducible experimental results are highlights of scientific thoughts. In fact modern science is based on experimental findings. **Reproducible results indirectly hint for a truth which is hidden**. Scientists always worked for findings this truth and in this manner many theories and laws were discovered. This search for truth plays an important role in the development of science.

The Dalton’s atomic theory not only explained the laws of conservations of mass and law of constant proportions but also predicted the new ones. He deduced **the law of multiple proportions** on the basis of his theory. The law states that **when two elements form more than one compound, the masses of one element in these compound for a fixed mass of the other element are in the ratio of small whole numbers**. For example, carbon and oxygen form two compounds: carbon monoxide and carbon dioxide. Carbon monoxide contains 1.3321 g of oxygen for each 1.0000 g of carbon, whereas carbon dioxide contains 2.6642 g of oxygen for 1.0000 g of carbon. In other words, carbon dioxide contains twice the mass of oxygen as is contained in carbon monoxide

(2.6642 g = 2 × 1.3321 g) for a given mass of carbon. Atomic theory explains this by saying that carbon dioxide contains twice as many oxygen atoms for a given number of carbon atoms as does carbon monoxide. The deduction of *law of multiple proportions* from atomic theory was important in convincing chemists of the validity of the theory.

1.4 DALTON’S ATOMIC THEORY

As we learnt earlier, Lavosier laid the experimental foundation of modern chemistry. But the British chemist John Dalton (1766–1844) provided the basic theory; all matter – whether element, compound, or mixture –is composed of small particles called atoms. The postulates, or basic assumptions of Dalton's theory are presented below in this section.

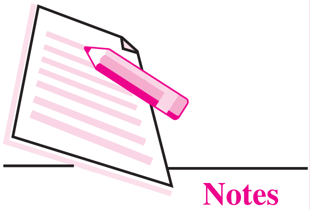
1.4.1 Postulates of Dalton's Atomic Theory

The English scientist John Dalton was by no means the first person to propose the existence of atoms, as we have seen in the previous section, such ideas date back to classical times. Dalton’s major contribution was to arrange those ideas in proper order and give evidence for the existence of atoms. He showed that the mass relationship expressed by Lavoisier and Proust (in the form of law of conservation of mass and law of constant proportions) could be interpreted most suitably by postulating the existence of atoms of the various elements.

In 1803, Dalton published a new system of chemical philosophy in which the following statements comprise the atomic theory of matter:

1. Matter consists of indivisible atoms.
2. All the atoms of a given chemical element are identical in mass and in all other properties.
3. Different chemical elements have different kinds of atoms and in particular such atoms have different masses.
4. Atoms are indestructible and retain their identity in chemical reactions.
5. The formation of a compound from its elements occurs through the combination of atoms of unlike elements in small whole number ratio.

Dalton’s fourth postulate is clearly related to the law of conservation of mass. Every atom of an element has a definite mass. Also in a chemical reaction there is rearrangement of atoms. Therefore after the reaction, mass of the product should remain the same. The fifth postulate is an attempt to explain the law of definite proportions. A compound is a type of matter containing the atoms of



two or more elements in small whole number ratio. Because the atoms have definite mass, the compound must have the elements in definite proportions by mass.

The Dalton's atomic theory not only explained the laws of conservations of mass and law of constant proportions but also predicted the new ones. He deduced **the law of multiple proportions** on the basis of his theory. The law states that **when two elements form more than one compound, the masses of one element in these compound for a fixed mass of the other element are in the ratio of small whole numbers**. For example, carbon and oxygen form two compounds: Carbon monoxide and carbon dioxide. Carbon monoxide contains 1.3321 g of oxygen for each 1.000g of carbon, whereas carbon dioxide contains 2.6642 g of oxygen for 1.0000 g of carbon. In other words, carbon dioxide contains twice the mass of oxygen as is contained in carbon monoxide (2.6642 g = 2 × 1.3321 g) for a given mass of carbon. Atomic theory explains this by saying that carbon dioxide contains twice as many oxygen atoms for a given number of carbon atoms as does carbon monoxide. The deduction of *law of multiple proportions* from atomic theory was important in convincing chemists of the validity of the theory.

1.4.2 What is an Atom?

As you have just seen in the previous section that an atom is the smallest particle of an element that retains its (elements) chemical properties. An atom of one element is different in size and mass from the atoms of the other elements. These atoms were considered 'indivisible' by Indian and Greek 'Philosophers' in the beginning and the name 'atom' was given as mentioned earlier. Today, we know that atoms are not indivisible. They can be broken down into still smaller particles although they lose their chemical identity in this process. But inspite of all these developments atom still remains a **building block** of matter.

1.4.3 Molecules

A ***molecule*** *is* an *aggregate of at least two atoms in a definite arrangement held together by chemical forces* (also called *chemical bonds).* It is smallest particle of matter, an element or a compound, which can exist independently. A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio, in accordance with the law of definite proportions stated. Thus, a molecule is not necessarily a compound, which, by definition, is made up of two or more elements. Hydrogen gas, for example, is a pure element, but it consists of molecules made up of two H atoms each. Water, on the other hand, is a molecular compound that contains hydrogen and oxygen in a ratio of two H atoms and one O atom. Like atoms, molecules are electrically neutral.

The hydrogen molecule, symbolized as $H_{2,}$ is called *a* ***diatomic molecule*** because it *contains only two atoms.* Other elements that normally exist as diatomic molecules are nitrogen (N_2) and oxygen (O_2), as well as the Group 17 elements-fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). Of course, a diatomic molecule can contain atoms of different elements. Examples are hydrogen chloride (HCl) and carbon monoxide (CO).

The vast majority of molecules contain more than two atoms. They can be atoms of the same element, as in ozone (O_3), which is made up of three atoms of oxygen, or they can be combinations of two or more different elements. *Molecules containing more than two atoms* are called ***polyatomic molecules.*** Like ozone, water (H_2O) and ammonia (NH_3) are polyatomic molecules.

1.4.4 Elements

Substances can be either elements or compounds. An ***element*** *is a substance that cannot be separated into simpler substances by chemical means.* To date, 118 elements have been positively identified. Eighty-three of them occur naturally on Earth. The others have been created by scientists via nuclear processes.

For convenience, chemists use symbols of one or two, letters to represent the elements. The first letter of a symbol is *always* capitalized, but the following letter is not. For example, Co is the symbol for the element cobalt, whereas CO is the formula for the carbon monoxide molecule. Table 1.1 shows the names and symbols of some of the more common elements; a complete list of the elements and their symbols appears inside the front cover of this book. The symbols of some elements are derived from their Latin names for example, Au from *auram* (gold), Fe from *ferrurn.* (iron), and Na from *natrium* (sodium) while most of them come from their English names.

Table 1.1: Some Common Elements and Their Symbols

Name	Symbol	Name	Symbol	Name	Symbol
Aluminium	Al	Fluorine	F	Oxygen	0
Arsenic	As	Gold	Au	Phosphorus	P
Barium	Ba	Hydrogen	H	Platinum	Pt
Bismuth	Bi	Iodine	I	Potassium	K
Bromine	Br	Iron	Fe	Silicon	Si

Calcium	Ca	Lead	Pb	Silver	Ag
Carbon	C	Magnesium	Mg	Sodium	Na
Chlorine	Cl	Manganese	Mn	Sulfur	S
Chromium	Cr	Mercury	Hg	Tin	Sn
Cobalt	Co	Nickel	Ni	Tungsten	W
Copper	Cu	Nitrogen	N	Zinc	Zn

Chemists use *chemical formulas* to *express the composition of molecules and ionic compounds in terms of chemical symbols*. By composition we mean not only the elements present but also the ratios in which the atoms are combined.

INTEXT QUESTIONS 1.1

1. Chemistry plays a vital role in many areas of science and technology. What are those areas?
2. Who proposed the particulate nature of matter?
3. What is law of conservation of mass?
4. What is an atom?
5. What is a molecule?
6. Why is the symbol of sodium Na?
7. How is an element different from a compound?

1.5 SI UNITS (REVISITED)

Measurement is needed in every walk of life. As you know that for every measurement a ‘unit’ or a ‘reference standard’ is required. In different countries, different systems of units gradually developed. This created difficulties whenever people of one country had to deal with those of another country. Since scientists had to often use each other’s data, they faced a lot of difficulties. For a practical use, data had to be first converted into local units and then only it could be used.

In 1960, the ‘General Conference of Weights and Measures’, the international authority on units proposed a new system which was based upon the metric system. This system is called the ‘International System of Units’ which is abbreviated as SI units from its French name, Le Système Internationale d’Unitès. You have learned about SI units in your earlier classes also and know that they are based upon seven base units corresponding to seven base physical quantities. Units needed for various other physical quantities can be derived from these base SI units. The seven base SI units are listed in Table 1.2.

Table 1.2: SI Base Units

Physical Quantity	Name of SI Unit	Symbol for SI unit
Length	Metre	m
Mass	Kilogram	kg
Time	Second	s
Electrical current	Ampere	A
Temperature	Kelvin	K
Amount of substance	Mole	mol
Luminous intensity	Candela	cd

For measuring very large or very small quantities, multiples or sub-multiples of these units are used. Each one of them is denoted by a symbol which is **prefixed** to the symbol of the unit. For example, to measure long distances we use the unit **kilometre** which is a multiple of metre, the base unit of length. Here **kilo** is the prefix used for the multiple 10^3. Its symbol is k which is prefixed to the symbol of metre, m . Thus the symbol of kilometre is km and

$$1 \text{ km} = 1.0 \times 10^3 \text{ m} = 1000 \text{ m}$$

Similarly, for measuring small lengths we use centimetre (cm) and millimetre (mm) where

$$1 \text{ cm} = 1.0 \times 10^{-2} \text{ m} = 0.01 \text{ m}$$

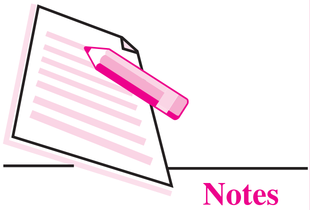
$$1 \text{ mm} = 1.0 \times 10^{-3} \text{ m} = 0.001 \text{ m}$$

Some prefixes used with SI units are listed in Table 1.3.

Table 1.3: Some prefixes used with SI units

Prefix	Symbol	Meaning	Example
Tera	T	10^{12}	1 terametre (Tm) = 1.0×10^{12} m
Giga	G	10^{9}	1 gigametre (Gm) = 1.0×10^{9} m
Mega	M	10^{6}	1 megametre (Mm) = 1.0×10^{6} m
Kilo	k	10^{3}	1 kilometre (km) = 1.0×10^{3} m
Hecta	h	10^{2}	1 hectametre (hm) = 1.0×10^{2} m
Deca	da	10^{1}	1 decametre (dam) = 1.0×10^{1} m
Deci	d	10^{-1}	1 decimetre (dm) = 1.0×10^{-1} m
Centi	c	10^{-2}	1 centimetre (cm) = 1.0×10^{-2} m
Milli	m	10^{-3}	1 millimetre (mm) = 1.0×10^{-3} m
Micro	µ	10^{-6}	1 micrometre (µm) = 1.0×10^{-6} m
Nano	n	10^{-9}	1 nanometre (nm) = 1×10^{-9} m
Pico	p	10^{-12}	1 picometre (pm) = 1×10^{-12}m

Before proceeding further try to answer the following questions:



INTEXT QUESTIONS 1.2

1. Name the SI Unit of mass
2. What symbol will represent 1.0×10^{-6} g ?
3. Name the prefixes used for (i) 10^2 and (ii) 10^{-9}

   (i) ....

   (ii) ....
4. What do the following symbols represent?

   (i) Ms (ii) ms

   (i) ....

   (ii) ....

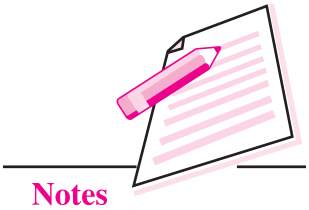
1.6 RELATIONSHIP BETWEEN MASS AND NUMBER OF PARTICLES

Suppose you want to purchase 500 screws. How, do you think, the shopkeeper would give you the desired quantity? By counting the screws individually? No, he would give the screws by weight because it will take a lot of time to count them. If each screw weighs 0.8 g, he would weigh 400 g screws because it is the mass of 500 screws ($0.8 \times 500 = 400$ g). You will be surprised to note that the Reserve Bank of India gives the desired number of coins by weight and not by counting.This process of *counting by weighing* becomes more and more labour saving as the number of items to be counted becomes large. We can carry out the reverse process also. Suppose we take 5000 very tiny springs (used in watches) and weigh them. If the mass of these springs is found to be 1.5 g, we can conclude that mass of each spring is $1.5 \div 5000 = 3 \times 10^{-4}$ g.

Thus, we see that mass and number of identical objects or particles are inter-related. Since atoms and molecules are extremely tiny particles it is impossible to weigh or count them individually. Therefore we need a relationship between the mass and number of atoms and molecules (particles). Such a relationship is provided by 'mole concept'.

1.7 MOLE – A NUMBER UNIT

Mass of an atom or a molecule is an important property. However, while discussing the quantitative aspects of a chemical reaction, the *number* of reacting atoms or molecules is more significant than their masses.



Notes

It is observed experimently that iron and sulphur do not react with each other in a simple mass ratio. When taken in 1:1 ratio by mass (Fe:S), some sulphur is left unreacted and when taken in 2:1 ratio by mass (Fe:S) some iron is left unreacted.

Let us now write the chemical equation of this reaction

$$Fe + S \rightarrow FeS$$

From the above chemical equation, it is clear that 1 atom of iron reacts with 1 atom of sulphur to form 1 molecule of iron (II) sulphide (FeS). It means that if we had taken equal *number* of atoms of iron and sulphur, both of them would have reacted completely. Thus we may conclude that *substances react in a simple ratio by number of atoms or molecules.*

From the above discussion it is clear that the *number* of atoms or molecules of a substance is more relevant than their masses. In order to express their number we need a number unit. One commonly used number unit is 'dozen', which, as you know, means a collection of 12. Other number units that we use are 'score' (20) and 'gross'(144 or 12 dozens). These units are useful in dealing with small numbers only. The atoms and molecules are so small that even in the minute sample of any substance, their number is extremely large. For example, a tiny dust particle contains about 10^{16} molecules. In chemistry such large numbers are commonly represented by a unit known as **mole.** Its symbol is 'mol' and it is defined as.

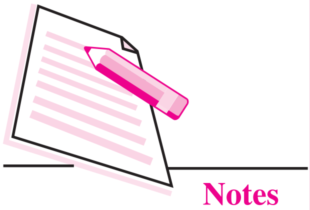
A mole is the amount of a substance that contains as many elementary entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg or 12 g of the carbon-12 isotope.

The term mole has been derived from the Latin word *'moles'* which means a 'heap' or a 'pile'. It was first used by the famous chemist Wilhelm Ostwald more than a hundred years ago.

Here you should remember that one mole always contains the **same number of entities**, no matter what the substance is. Thus *mole* is a number unit for dealing with elementary entities such as atoms, molecules, formula units, electrons etc., just as *dozen* is a number unit for dealing with bananas or oranges. In the next section you will learn more about this number.

1.8 AVOGADRO'S CONSTANT

In the previous section we have learned that a mole of a substance is that amount which contains as many elementary entities as there are atoms in exactly 0.012 kilogram or 12 gram of the carbon-12 isotope. This definition gives us a method by which we can find out the amount of a substance (in moles) if we know the number of elementary entities present in it or *vice versa.* Now the question arises



how many atoms are there in exactly 12 g of carbon-12. This number is determined experimentally and its currently accepted value is 6.022045×10^{23}. Thus 1 mol = 6.022045×10^{23} entities or particles, or atoms or molecules.

For all practical purposes this number is · rounded off to 6.022×10^{23}.

The basic idea of such a number was first conceived by an Italian scientist Amedeo Avogadro. But, he never determined this number. It was determinned later and is known as *Avogadro's constant* in his honour.

This number was earlier known as *Avogadro's number*. This number alongwith the unit, that is, 6.022×10^{23} mol^{-1} is known as Avogadro constant. It is represented by the symbol N_A. Here you should be clear that mathematically a number does not have a unit. Avogadro's number 6.022×10^{23} will not have any unit but Avogradro's constant will have unit of mol^{-1}. Thus Avogradro's constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}.

Significance of Avogadro's Constant

You know that 0.012 kg or 12 g of carbon –12 contains its *one mole* of carbon atoms. A mole may be defined as the amount of a substance that contains 6.022×10^{23} elementary entities like atoms, molecules or other particles. When we say one mole of carbon –12, we mean 6.022×10^{23} atoms of carbon –12 whose mass is exactly 12 g. This mass is called the *molar mass* of carbon-12. The ***molar mass** is defined as the mass (in grams) of 1 mole of a substance*. Similarly, a *mole of any substance* would contain 6.022×10^{23} particles or elementary entities. The nature of elementary entity, however,depends upon the nature of the substance as given below :

S.No.	Type of Substance	Elementary Entity
1.	Elements like Na, K, Cu which exist in atomic form	Atom
2.	Elements like O, N, H, which exist in molecular form (O_2, N_2, H_2)	Molecule
3.	Molecular compounds like NH_3, H_2O, CH_4	Molecule
4.	Ions like Na^+, Cu^{2+}, Ag^+, Cl^-, O^{2-}	Ion
5.	Ionic compounds like NaCl, $NaNO_3$, K_2SO_4	Formula unit

Formula unit of a compound contains as many atoms or ions of different types as is given by its chemical formula. The concept is applicable to all types of compounds. The following examples would clarify the concept.

Formula	Atoms/ions present in one formula unit
H_2O	Two atoms of H and one atom of O
NH_3	One atom of N and three atoms of H
NaCl	One Na^+ ion and one Cl^- ion
$NaNO_3$	One Na^+ ion and one $NO_3{}^-$ ion
K_2SO_4	Two K^+ ions and one SO_4^{2-} ion
$Ba_3(PO_4)_2$	Three Ba^{2+} ions and two PO_4^{3-} ions

Now, let us take the examples of different types of substances and correlate their amounts and the number of elementary entities in them.

1 mole C $= 6.022 \times 10^{23}$ C atoms

1 mole O_2 $= 6.022 \times 10^{23}$ O_2 molecules

1 mole H_2O $= 6.022 \times 10^{23}$ H_2O molecules

1 mole NaCl $= 6.022 \times 10^{23}$ formula units of NaCl

1 mole Ba^{2+} ions $= 6.022 \times 10^{23}$ Ba^{2+} ions

We may choose to take amounts other than one mole and correlate them with number of particles present with the help of relation :

Number of elementary entities = number of moles × Avogadro's constant

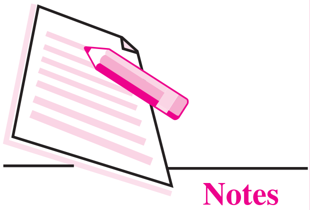
1 mole O_2 $= 1 \times (6.022 \times 10^{23}) = 6.022 \times 10^{23}$ molecules of O_2

0.5 mole O_2 $= 0.5 \times (6.022 \times 10^{23}) = 3.011 \times 10^{23}$ molecules of O_2

0.1 mole O_2 $= 0.1 \times (6.022 \times 10^{23}) = 6.022 \times 10^{22}$ molecules of O_2

INTEXT QUESTIONS 1.3

1. A sample of nitrogen gas consists of 4.22×10^{23} molecules of nitrogen. How many moles of nitrogen gas are there?
2. In a metallic piece of magnesium, 8.46×10^{24} atoms are present. Calculate the amount of magnesium in moles.
3. Calculate the number of Cl_2 molecules and Cl atoms in 0.25 mol of Cl_2 gas.



Notes

1.9 MOLE, MASS AND NUMBER RELATIONSHIPS

You know that 1 mol $= 6.022 \times 10^{23}$ elementary entities

and Molar mass = Mass of 1 mole of substance

$= \text{Mass of } 6.022 \times 10^{23}$ elementary entities.

As discussed earlier the elementary entity can be an atom, a molecule, an ion or a formula unit. As far as mole – number relationship is concerned it is clear that one mole of any substance would contain 6.022×10^{23} particles (elementary entities). For obtaining the molar mass, i.e., mole-mass relationship we have to use atomic mass scale.

1.9.1 Atomic Mass Unit

By inernational agreement, a unit of mass to specify the atomic and molecular masses has been defined. This unit is called *atomic mass unit* and its symbol is 'amu'. The mass of one C-12 atom, is taken as exactly 12 amu. Thus, C-12 atom serves as the *standard.* The **Atomic mass unit** is defined as a mass exactly equal to the 1/12th of the mass of one carbon-12 atom.

$$1 \text{ amu} = \frac{\text{Mass of one C-12 atom}}{12}$$

Atomic mass unit is also called **unified atomic mass unit** whose symbol is 'u'. Another name of atomic mass unit is **dalton** (symbol Da). The latter is mainly used in biological sciences.

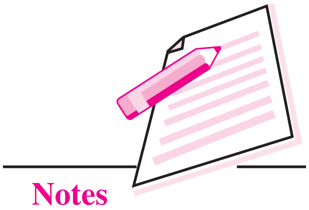
1.9.2 Relative Atomic and Molecular Masses

You are aware that atomic mass scale is a *relative scale* with C-12 atom (also written as ^{12}C) chosen as the standard. Its mass is taken as exactly 12. Relative masses of atoms and molecules are the number of times each atom or molecules is heavier than $\frac{1}{12}$th of the mass of one C-12 atom. Often, we deal with elements and compounds containing isotopes of different elements. Therefore, we prefer to use *average* masses of atoms and molecules. Thus

$$\text{Relative atomic mass} = \frac{\text{Average mass of 1 atom of the element}}{\frac{1}{12}\text{th of the mass of one C-12 atom}}$$

$$\text{and Relative molecular mass} = \frac{\text{Average mass of 1 molecule of the substance}}{\frac{1}{12}\text{th of the mass of one C-12 atom}}$$

Experiments show that one O-16 atom is 1.333 times as heavy as one C-12 atom. Thus



$$\text{Relative atomic mass of O-16} = 1.333 \times 12 = 15.996 \simeq 16.0$$

The relative atomic masses of all elements have been determined in a similar manner. Relative molecular masses can also be determined experimentally in a similar manner . In case we know the molecular formula of a molecule, we can calculate its relative molecular mass by adding the relative atomic masses of all its constituent atoms. Let us calculate the relative molecular mass of water, H_2O.

$$\text{Relative molecular mass of water, } H_2O = (2 \times \text{relative atomic mass of H}) + (\text{relative atomic mass of O})$$

$$= (2 \times 1) + (16) = 2 + 16 = 18$$

The relative atomic and molecular masses are just numbers and dimensionless, unit-less quantities.

1.9.3 Atomic, Molecular and Formula Masses

From the definition of atomic mass unit, we can calculate the atomic masses. Let us again take the example of oxygen-16 whose relative atomic mass is 16. By definition:

$$\text{Relative atomic mass of O-16} = 16 = \frac{\text{mass of one O-16 atom}}{\frac{1}{12}\text{th the mass of one C-12 atom}}$$

$$\text{Since 1 amu} = \frac{1}{12}\text{th the mass of one C-12 atom}$$

$$\therefore \quad 16 = \frac{\text{mass of one O-16 atom}}{1\ \text{amu}}$$

$$\text{Mass of one O-16 atom} = 16\ \text{amu}$$

Or $\quad \text{Atomic mass of O-16} = 16\ \text{amu.}$

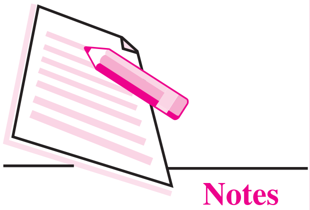
From this example we can see that numerical value of the relative atomic mass and atomic mass is the same. Only, the former has no unit while the latter has the unit *amu*.

Molecular and formula masses can be obtained by adding the atomic or ionic masses of all the constituent atoms or ions of the molecule or formula unit respectively. Let us understand these calculations with the help of following examples.

Example 1.1 : Calculate the molecular mass of ammonia, NH_3.

Solution : One molecule of NH_3 consists of one N atom and three H atoms.

Molecular mass of NH_3 = (Atomic mass of N) + 3 (Atomic mass of H)



Notes

$= [14 + (3 \times 1)]$ amu

$= 17$ amu

Example 1.2 : Calculate the formula mass of sodium chloride (NaCl).

Solution : One formula unit of sodium chloride consists of one Na^+ ion and one Cl^- ion.

Formula mass of NaCl $=$ (Ionic mass of Na^+) + (Ionic mass of Cl^-)

$= 23$ amu + 35.5 amu

$= 58.5$ amu.

You would have noticed in the above example that ionic mass of Na^+ ion has been taken as 23 amu which is the same as the atomic mass of Na atom. Since loss or gain of few electrons does not change the mass significantly, therefore atomic masses are used as ionic masses. Similarly we have taken ionic mass of Cl^- as 35.5 amu which is the same as the atomic mass of Cl^-.

1.9.4 Molar Masses

We know that molar mass is the mass of 1 mol of the substance. Also, 1 mol of any substance is the collection of its 6.022×10^{23} elementary entities. Thus

Molar mass $=$ Mass of 6.022×10^{23} elementary entities.

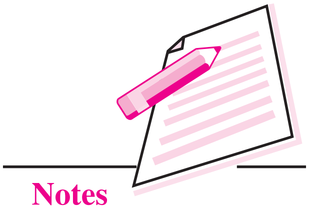
(i) Molar mass of an element

You know that the relative atomic mass of carbon–12 is 12. A 12g sample of it would contain 6.022×10^{23} atoms. Hence the molar mass of C-12 is 12 g mol^{-1}. For getting the molar masses of other elements we can use their relative atomic masses.

Since the relative atomic mass of oxygen -16 is 16, a 16 g sample of it would contain 6.022×10^{23} oxygen atoms and would constitute its one mole. Thus, the molar mass of O–16 is 16 g mol^{-1}. Relative atomic masses of some common elements have been listed in Table 1.4

Table 1.4 : Relative atomic masses of some elements (upto 1st place of decimal)

Element	Relative Atomic Mass	Element	Relative Atomic Mass
Hydrogen, H	1.0	Phosphorus, P	31.0
Carbon, C	12.0	Sulphur, S	32.1
Nitrogen, N	14.0	Chlorine, Cl	35.5
Oxygen, O	16.0	Potassium, K	39.1
Sodium, Na	23.0	Iron, Fe	55.9



Notes

(ii) Molar mass of a molecular substance

The elementary entity in case of a molecular substance is the molecule. Hence, *molar mass of such a substance would be the mass of its* 6.022×10^{23} *molecules*, which can be obtained from its relative molecular mass or by multiplying the molar mass of each element by the number of its moles present in one mole of the substance and then adding them.

Let us take the example of water, H_2O. Its relative molecular mass is 18. Therefore, 18 g of it would contain 6.022×10^{23} molecules. Hence, its molar mass is 18 g mol^{-1} . Alternately we can calculate it as :

$$\begin{aligned}\text{Molar mass of water, } H_2O &= (2 \times \text{molar mass of H}) + (\text{molar mass of O})\\ &= (2 \times 1 \text{ g mol}^{-1}) + (16 \text{ g mol}^{-1})\\ &= 18 \text{ g mol}^{-1}\end{aligned}$$

Table 1.5 lists molecular masses and molar masses of some substances.

Table 1.5 : Molecular masses and molar masses of some substances

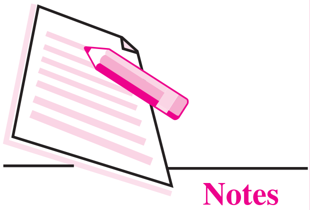
Element or Compound	Molecular mass / amu	Molar mass / (g mol^{-1})
O_2	32.0	32.0
P_4	124.0	124.0
S_8	256.8	256.8
H_2O	18.0	18.0
NH_3	17.0	17.0
HCl	36.5	36.5
CH_2Cl_2	85.0	85.0

(iii) Molar masses of ionic compounds

Molar mass *of an ionic compound is the mass of its* 6.022×10^{23} *formula units.* It can be obtained by adding the molar masses of ions present in the formula unit of the substance. In case of NaCl it is calculated as

$$\begin{aligned}\text{Molar mass of NaCl} &= \text{molar mass of Na}^+ + \text{molar mass of Cl}^-\\ &= (23 \text{ g mol}^{-1}) + (35.5 \text{ g mol}^{-1})\\ &= 58.5 \text{ g mol}^{-1}\end{aligned}$$

Let us take some more examples of ionic compounds and calculate their molar masses.



Example 1.3 : Calculate the molar mass of

(i) K_2SO_4 (ii) $Ba_3(PO_4)_2$

Solution :

(i) Molar mass of K_2SO_4 $= (2 \times \text{molar mass of } K^+) + (\text{molar mass of } SO_4^{2-})$

$= (2 \times \text{molar mass of } K^+) + (\text{molar mass of S} + 4 \times \text{molar mass of O})$

$= [(2 \times 39.1) + (32.1 + 4 \times 16)] \text{ g mol}^{-1}]$

$= (78.2 + 32.1 + 64) \text{ g mol}^{-1} = 174.3 \text{ g mol}^{-1}$

(ii) Molar mass of $Ba_3(PO_4)_2$ $= (3 \times \text{molar mass of } Ba^{2+}) + 2\,(\text{molar mass of } PO_4^{3-})$

$= (3 \times \text{molar mass of } Ba^{2+}) + 2\,(\text{molar mass of P} + 4 \times \text{molar mass of O})$

$= [(3 \times 137.3) + 2\,(31.0 + 4 \times 16.0)] \text{ g mol}^{-1}$

$= (411.9 + 190.0) \text{ g mol}^{-1} = 601.9 \text{ g mol}^{-1}$

Now you have learned about the mole, mass and number relationships for all types of substances. The following examples would illustrate the usefulness of these relationships.

Example 1.4 : Find out the mass of carbon -12 that would contain 1.0×10^{19} carbon-12 atoms.

Solution : Mass of 6.022×10^{23} carbon-12 atoms $= 12$ g

Mass of 1.0×10^{19} carbon-12 atoms $= \dfrac{12 \times 1 \times 10^{19}}{6.022 \times 10^{23}}$ g

$= 1.99 \times 10^{-4}$ g

Example 1.5 : How many molecules are present in 100 g sample of NH_3?

Solution : Molar mass of NH_3 $= (14 + 3) \text{ g mol}^{-1} = 17 \text{ g mol}^{-1}$

$\therefore$ 17 g sample of NH_3 contains 6.022×10^{23} molecules

Therefore, 100 g sample of NH_3 would contain $\dfrac{6.022 \times 10^{23} \text{ molecule}}{17\text{g}} \times 100\text{g}$

$= 35.42 \times 10^{23}$ molecules

$= 3.542 \times 10^{24}$ molecules

Example 1.6 : Molar mass of O is 16 g mol^{-1}. What is the mass of one atom and one molecule of oxygen?

Solution : Mass of 1 mol or 6.022×10^{23} atoms of O = 16 g

$$\therefore \quad \text{Mass of 1atom of O} = \frac{16\text{g}}{6.022 \times 10^{23}}$$

$$= 2.66 \times 10^{-23} \text{ g}$$

Since a molecule of oxygen contains two atoms (O_2),
its mass = $2 \times 2.66 \times 10^{-23}$ g = 5.32×10^{-23} g.

INTEXT QUESTIONS 1.4

1. Calculate the molar mass of hydrogen chloride, HCl.
2. Calculate the molar mass of argon atoms, given that the mass of single atom is 6.634×10^{-26} kg.
3. Calculate the mass of 1.0 mol of potassium nitrate, KNO_3 (atomic masses : K = 39 amu; N = 14 amu, O = 16 amu).
4. The formula of sodium phosphate is Na_3PO_4. What is the mass of 0.146 mol of Na_3PO_4? (atomic masses : Na = 23.0 amu, P = 31.0 amu; O = 16.0 amu).

1.10 MASS, MOLAR MASS AND NUMBER OF MOLES

Mass, molar mass and number of moles of a substance are inter-related quantities. We know that :

Molar mass (M) = Mass of one mole of the substance.

Molar mass of water is 18 g mol^{-1}. If we have 18 g of water, we have 1mol of it. Suppose we have 36 g water (18 × 2), we have 2 mol of it. In general in a sample of water of mass ($n \times 18$) g, the number of moles of water would be n. We may generalize the relation as

$$\text{Number of moles (amount) of a substance} = \frac{\text{mass of the substance}}{\text{molar mass of the substance}}$$

$$n = \frac{m}{M}$$

or

$$m = n \times M$$

These relations are useful in calculations involving moles of substances.

Example 1.7 : In a reaction, 0.5 mol of aluminium is required. Calculate the amount of aluminium required in grams? (atomic mass of Al = 27 amu)

Solution :

$$\begin{aligned} \text{Molar mass of Al} &= 27 \text{ g mol}^{-1} \\ \text{Required mass} &= \text{no. of moles} \times \text{molar mass} \\ &= (0.5 \text{ mol}) \times (27 \text{ g mol}^{-1}) \\ &= 13.5 \text{ g} \end{aligned}$$

1.11 MOLAR VOLUME, V_m

Molar volume *is the volume of one mole of a substance.* It depends upon temperature and pressure. It is related to the density, by the relation.

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$$

In case of gases, we use their volumes at **standard temperature and pressure (STP).** For this purpose **0 ^{0}C** or **273 K** temperature is taken as the **standard temperature** and **1bar** pressure is taken as the **standard pressure**. At STP, the molar volume of an ideal gas is 22.7 litre*. You will study that gases do not behave ideally and therefore their molar volume is not exactly 22.7 L. However, it is very close to 22.7 L and for all practical purposes we take the molar volume of all gases at STP as 22.7 L mol^{-1}.

INTEXT QUESTIONS 1.5

1. How many moles of Cu atoms are present in 3.05 g of copper (Relative atomic mass of Cu = 63.5).
2. A piece of gold has a mass of 12.6 g. How many moles of gold are present in it? (Relative atomic mass of Au = 197)
3. In a combustion reaction of an organic compound, 2.5 mol of CO_2 were produced. What volume would it occupy at STP (273K, 1bar) ?

1.12 MOLCULAR AND EMPIRICAL FORMULAE

In your previous classes, you have studied how to write chemical formula of a sustance. For example, water is represented by H_2O, carbon dioxide is represented

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* Earlier 1 atmosphere pressure was taken as the standard pressure and at STP (273K, 1atm) the molar volume of an ideal gas was taken as 22.4 L mol^{-1}. The difference in the value is due to the change in the standard pressure (1bar) which is slightly less than 1atm.

by CO_2, methane is represented by CH_4, dinitrogen penta oxide is represented by N_2O_5, and so on. You are aware, formula for a molecule uses a symbol and subscript number to indicate the number of each kind of atoms present in the molcule (subscript 1 is always omitted). Such a formula is called **molecular formula** as it represents a molecule of a substance. A molecule of water consists of two hydrogen atoms and one oxygen atom. So its molecular formula is written as H_2O. Thus a **molecular formula shows the actual number of atoms of different elements in a molecule of a compound.**

There is another kind of formula, the empirical formul of a compound, which gives only relative number of atoms of different elements. These numbers are expressed as the simplest ratio. For example, empirical formula of glucose, which consists of carbon, hydrogen and oxygen in the ratio of 1:2:1 is CH_2O (empirical formulae are also called simplest formulae). Molecular formula of a substance is always an integral multiple of its empirical formula (i.e. molecular formula = X_n where X is empirical formula and n is an integer). For example molecular formula of glucose is $C_6H_{12}O_6$ which is $6 \times$ its empirical formula. Thus, while empirical formula gives only a ratio of atoms, the molecular formula gives the actual number of atoms of each element in an individual molecule. In some cases the ratio of atoms shown in a molecular formula cannot be reduced to smaller integers. In such cases molecular and empirical formulae are the same, for example, sucrose $C_{12}H_{22}O_{11}$ which is popularly known as cane-sugar. In case of certain elements, a molecule consists of several atoms for example P_4, S_8, etc. In such cases, empirical formula will be symbol of the element only.

As you know, common salt, which is chemically called sodium chloride is represented as NaCl. This salt is ionic in nature and does not exist in molecular form. Therefore, NaCl is its empirical formula which shows that sodium and chlorine atoms are present in NaCl in the ratio of 1:1. Similar is the case with all ionic substanes. KCl, $NaNO_3$, MgO are examples of empirical formulae as these are all ionic compounds. Table 1.6 provides a few more examples.

Table 1.6: Molecular and Empirical Formulae

Substance	Molecular formula	Empirical formula
Ammonia	NH_3	NH_3
Carbon dioxide	CO_2	CO_2
Ethane	C_2H_6	CH_3
Fructose	$C_6H_{12}O_6$	CH_2O
Sulphur	S_8	S
Benzene	C_6H_6	CH
Sodium chloride	—	NaCl
Calcium oxide	—	CaO

1.13 CHEMICAL COMPOSITION AND FORMULAE

How much carbon is present in one kilogram of methane whose molecular formula is CH_4? How much nitrogen is present in one kilogram of ammonia, NH_3? If we have prepared a substance that is made of 58.8% carbon, 28.4% oxygen, 8.28% nitrogen and 6.56% hydrogen, what is its empirical formula? You have studied **atomic masses, formulae,** and the **mole concept.** Can we solve the problem using these basic concepts? The answer is 'yes'. Atomic masses, formulae and the mole concept are the basic tools needed to solve such problems. What is percentage composition? Let us take up this aspect in a little detail and try to understand.

1.13.1 Percentage Composition

If we know the formula of a compound, we can find out how much of each of the elements is present in a given quantity of the compound. Aluminium is obtained from its oxide. Al_2O_3 (which is found as the ore, bauxite). From the formula we can calculate how much aluminium can be obtained, at least in prinicple, from a given amount of aluminium oxide. Calculation is done by making use of the idea of **percentage composition**

Percentage mass of an element in a compound

$$= \frac{\begin{array}{c}\text{mass of element in one molecular formula or}\\ \text{in one empirical formula}\end{array}}{\begin{array}{c}\text{molecular mass or empirical formula}\\ \text{mass of compound}\end{array}} \times 100$$

$$= \frac{\text{Mass of element in 1mol of compound}}{\text{Molar mass of compound}} \times 100$$

Let us calculate percentage composition of aluminium oxide, Al_2O_3

$$\text{Pecentage of aluminium} = \frac{\text{Mass of aluminium in 1 mol } Al_2O_3}{\text{Molar mass of } Al_2O_3} \times 100$$

Molar mass of $Al_2O_3 = (2 \times 27.0)\ g + (3 \times 16.0)\ g = 102.0\ g$

Since 1 mol of Al_2O_3 contains 2 mol of Al atoms, the mass of Al is $2 \times 27.0\ g = 54.0\ g$ Al

$$\text{Percentage of Aluminium} = \frac{54.0\ g}{102.0\ g} \times 100 = 52.9\ \%$$

We can calculate percentage of oxygen in the same way. One mole of Al_2O_3 contains 3 mole of O atoms, that is, 3×16.0 g oxygen therefore

$$\text{Percentage of oxygen} = \frac{3\times16.0\ g}{102.0\ g} \times 100 = 47.1\%$$

Notes

Example 1.8: Butanoic acid, has the formula $C_4H_8O_2$. What is the elemental analysis of butanoic acid?

Solution : Molecular formula of the butanoic acid is $C_4H_8O_2$.

In one mole of butanoic acid there are 4 mol of carbon atoms, 8 mol of hydrogen atoms and 2 mol of oxygen atoms. Thus, 1 molar mass of butanoic acid will be equal to the sum of 4 × molar mass of carbon atoms, 8 × molar mass of hydrogen atoms, and 2 × molar mass of oxygen atoms.

Molar mass of butanoic acid = $4 \times 12.0\text{ g} + 8 \times 1.0\text{ g} + 2 \times 16.0\text{ g} = 88.0\text{ g}$

$$\text{Percentage of C by mass} = \frac{48.0\text{ g}}{88.0\text{ g}} \times 100 = 54.5\%$$

$$\text{Percentage of H by mass} = \frac{8.0\text{ g}}{88.0\text{ g}} \times 100 = 9.1\%$$

$$\text{Percentage of O by mass} = \frac{32.0\text{ g}}{88.0\text{ g}} \times 100 = 36.4\%$$

The percentage of O in butanoic acid can also be calculated as follows :

Percentage of O by mass = 100 – (Percentage of C by mass + Percentage of H by mass)

$$= 100 - (54.5 + 9.1) = 36.4\%$$

1.14 DETERMINATION OF EMPIRICAL FORMULAE – FORMULA STOICHIOMETRY

We have just seen that if we know the formula of a compound we can calculate the percentage composition. Now the question arises, can we determine the formula of the compound if we know the percentage composition of a compound. The answer will be 'yes', but this formula will not be molecular formula; instead it would be **empirical formula** as it would give simplest ratio of different atoms present in a compound. Normally we determine the percentage composition of different elements present in an **unknown compound** and determine its formula. Let us take a simple example of water. Water consists of 11.11% hydrogen and 88.89% oxygen by mass. From the data, we can determine empirical formula of water. Now if we assume that we have a 100.00 g sample of water, then the percentage composition tells us that 100.0 g of water contains 11.11 g of hydrogen atoms and 88.89 g of oxygen atoms.

From the atomic mass table, we find that 1 mol of hydrogn atoms has a mass of 1.0g, and 1 mol of oxygen atoms has a mass of 16.0 g. Now we can write **unit conversion factors** so that the mass of hydrogen can be converted to moles of H atoms and the mass of oxygen can be converted to moles of O atoms.

$$\text{Moles of H} = \frac{\text{Mass of H}}{\text{Molar mass of H}} = \frac{11.11\text{ g}}{1.0\text{ g mol}^{-1}}$$

Similarly,

$$\text{Moles of O} = \frac{\text{Mass of O}}{\text{Molar mass of O}} = \frac{88.89\text{ g}}{16.0\text{ g mol}^{-1}} = 5.55\text{ mol}$$

Thus in water, the ratio of moles of hydrogen atoms to moles of oxygen atoms is 11.11 : 5.55.

Since a mole of one element contains the same number of atoms as a mole of another element, the ratio of moles of atoms in a compound is also the ratio of the number of atoms. Therefore, the ratio of hydrogen atoms to oxygen atoms is 11.11:5.55. Now by dividing each by the smaller of the two numbers we can convert both numbers to integers

$$\frac{11.11}{5.55} = 2 \text{ and } \frac{5.55}{5.55} = 1$$

Thus ratio hydrogen and oxygen atoms in water is 2 : 1 and empirical formula of water is H_2O.

INTEXT QUESTIONS 1.6

1. For the compound Fe_3O_4, calculate percentage of Fe and O.
2. State percent composition for each of the following:
   (a) C in $SrCO_3$ (b) SO_3 in H_2SO_4
3. What are the empirical formulae of substances having the following molecular formulae?
   H_2O_2, C_6H_{12}, Li_2CO_3, $C_2H_4O_2$, S_8, H_2O, B_2H_6, O_3, S_3O_9, N_2O_3
4. A compound is composed of atoms of only two elements, carbon and oxygen. If the compound contain 53.1% carbon, what is its empirical formula.

1.15 CHEMICAL EQUATION AND REACTION STOICHIOMETRY

You have studied that a reaction can be represented in the form of a chemical equation. A balanced chemical equation carries a wealth of information qualitative as well as quantitative. Let us consider the following equation and learn what all information it carries.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad ...(1.1)$$

1. Qualitative Information

Qualitatively the equation (2.1) tells that iron reacts with oxygen to form iron oxide.

2. Quantitative Information

Quantitatively a balanced chemical equation specifies numerical relationship among the quantities of its reactants and products. These relationships can be expressed in terms of :

(i) **Microscopic quantities,** namely, atoms, molecules and formula units.

(ii) **Macroscopic quantities**, namely, moles, masses and volumes *(in case of gaseous substances)* of reactants and products.

Now let us again take the reaction (1.1) given earlier and get the quantitative information out of it.

1.15.1 Microscopic Quantitative Information

The reaction (1.1)

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad ...(1.2)$$

tells that *4 atoms* of iron react with 3 *molecules* of oxygen to form 2 *formula units* of iron oxide. Often this information is written below each reactant and product for ready reference as shown below:

$$\underset{\text{4 atoms of Fe}}{4Fe(s)} \quad + \quad \underset{\text{3 molecules of } O_2}{3O_2(g)} \quad \rightarrow \quad \underset{\text{2 formula units of } Fe_2O_3}{2Fe_2O_3(s)} \qquad ...(1.2a)$$

1.15.2 Macroscopic Quantitative Information

The microscopic quantitative information discussed in the previous section can be converted into macroscopic information with the help of mole concept which you have learnt in unit 1.

(a) Mole Relationships

We know that Avogadro number of elementary entities like atoms, molecules, ions or formula units of a substance constitute one mole of it. Let us multiply the number of atoms, molecules and formula masses obtained in the previous section (Eq.2.1a) by Avogadro's constant, N_A

$$\begin{array}{lclcl} 4\ Fe(s) & + & 3O_2(g) & \rightarrow & 2Fe_2O_3(s) \qquad ..(1.3) \\ \textbf{4 atoms of Fe} & & \textbf{3 molecules of } \mathbf{O_2} & & \textbf{2 formula units of } \mathbf{Fe_2O_3} \\ 4 \times N_A \text{ atoms of Fe} & & 3 \times N_A \text{ molecules of } O_2 & & 2 \times N_A \text{ formula units of } Fe_2O_3 \\ \textbf{4 mol of Fe} & & \textbf{3 mol of } \mathbf{O_2} & & \textbf{2 mol of } \mathbf{Fe_2O_3} \end{array}$$

We may rewrite the above equation as

$$\begin{array}{lcccr} 4Fe(s) & + & 3O_2(g) & \rightarrow & 2Fe_2O_3(s) \quad ...(1.3a) \\ \textbf{4 mol of Fe} & & \textbf{3 mol of } \mathbf{O_2} & & \textbf{2 mol of } \mathbf{Fe_2O_3} \end{array}$$

The above equation (1.3a) gives us the mole relationship between reactants and products. Here *4 mol of Fe* react with *3 mol of* O_2 and produce *2 mol of* Fe_2O_3.

(b) Mass Relationships

The mole relationships which you have learnt in the previous section, can be converted into mass relationship by using the fact that mass of one mole of any substance is equal to its *molar mass* which can be calculated from its formula with the help of relative atomic masses of its constituent elements.

In the reaction that we are discussing, the relative atomic masses of iron and oxygen are 55.8 and 16.0 respectively. Therefore

(i) molar mass of Fe $= 55.8 \text{ g mol}^{-1}$

(ii) molar mass of O_2 $= 2 \times 16.0 = 32 \text{ g mol}^{-1}$

(iii) molar mass of Fe_2O_3 $= (2 \times 55.8 + 3 \times 16.0) \text{ g mol}^{-1}$
$= 159.6 \text{ g mol}^{-1}$

Using these molar masses we can convert the mole relationship given by equation 2.1b into mass relationship as given below :

$$\begin{array}{llll} 4Fe(s) & + \quad 3O_2(g) & \rightarrow & 2Fe_2O_3(s) \\ \textbf{4 mol Fe} & \textbf{3 mol } \mathbf{O_2} & & \textbf{2 mol } \mathbf{Fe_2O_3} \\ (4 \times 55.8) \text{ g Fe} & (3 \times 32) \text{ g } O^2 & & (2 \times 159.6) \text{ g } Fe_2O_3 \\ 223.2 \text{ g Fe} & 96 \text{ g } O_2 & & 319.2 \text{ g } Fe_2O_3 \end{array}$$

Thus 223.2 g iron would react with 96 g oxygen and produce 319.2 g iron oxide, We may rewrite the above equation as

$$\begin{array}{lcccr} 4Fe(s) & + & 3O_2(g) & \rightarrow & 2Fe_2O_3(s) \quad (1.3b) \\ \textbf{223.2 g Fe} & & \textbf{96 g } \mathbf{O_2} & & \textbf{319.2 g } \mathbf{Fe_2O_3} \end{array}$$

(c) Volume Relationships

We know that one mole of *any gas* occupies a volume of 22.7 L* at STP (standard temperature and pressure, 0°C and 1 bar pressure). We can use this information to arrive at volume relationships between gaseous substances. The reaction that we are considering involves only one gaseous substance, O_2. We may rewrite the equation (2.1b) as

$$\begin{array}{lcccr} 4Fe(s) & + & 3O_2(g) & \rightarrow & 2Fe_2O_3(s) \quad (2.1b) \\ \textbf{4 mol} & & \textbf{3 mol} & & \textbf{2 mol.} \\ & & (3 \times 22.7) \text{ L at STP} & & \\ & & 68.1 \text{ L at STP} & & \end{array}$$

---

* Earlier, the standard pressure was taken as 1 atmosphere and the volume of one mole of gas at STP was taken as 22.4 L.

Thus 4 mol of iron would react with 68.1 L of oxygen at STP to produce 2 mol of iron oxide. (The volume relationship becomes more useful for reactions involving 2 or more gaseous substances).

We can express microscopic as well macroscopic quantitative relationships involved in the above reaction as shown below:

$4Fe(s)$	+	$3O_2(s)$	→	$2Fe_2O_3(s)$
4 atoms		**3 molecules**		**2 formula units**
4 mol		3 mol		2 mol
223.2 g		96 g		319.2 g
–		68.1 L at STP		–

We may use even mixed relations. For example, we may say 4 mol of iron would react with 68.1 L (at STP) of oxygen to produce 319.2 g of iron oxide.

Let us understand these relationships with two more examples.

(a) Let us work out the mole, mass and volume relationships for the reaction involved in manufacture of ammonia by Haber's process.

Microscopic relationship	$N_2(g)$ +	$3H_2(g)$ $\longrightarrow$	$2NH_3(g)$	...(2.2)
Microscopic relationships	1 Molecule	3 Molecules	2 Molecules	
(i) Moles	1 mol	3 mol	2 mol	
(ii) Mass	28 g	$(3 \times 2.0) = 6.0$ g	$(2 \times 17.0) = 34$ g	
(iii) Volume	1×22.7 L	(3×22.7)	(2×22.7)	
	$= 22.7$ L	$= 68.1$ L	$= 45.4$ L	
or	1 vol	3 vol	2 vol	

(b) Let us take one more reaction, the combustion reaction of butane and work out the different types of relationships. The reaction is :

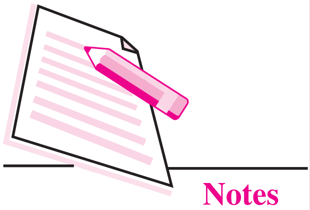
$2C_4H_{10}(g)$	+	$13O_2(g)$	→	$8CO_2(g)$	+	$10H_2O(g)$
2 molecules		13 molecules		8 molecules		10 molecules
2 mol		13 mol		8 mol		10 mol
$2 \times (4 \times 12 + 10 \times 1)$ g		(13×32) g		$8 \times (12 + 2 \times 16)$ g		$10 \times (2 \times 1 + 16)$ g
116 g		416 g		352 g		180 g
$2 \times 22.7 = 45.4$ L		$13 \times 22.7 = 295.1$ L		$8 \times 22.7 = 181.6$ L		$10 \times 22.7 = 227$ L
2 vol		13 vol		8 vol		10 vol

Now let us use the mole, mass and volume relationships to make some calculations.

Example 1.9 : In the manufacture of ammonia by Haber process, nitrogen reacts with hydrogen at high temprature and high pressure in the presence of a catalyst and gives ammonia.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

How much hydrogen would be needed to produce one metric ton of ammonia?



Solution : We should first find out the mass relationships for the reaction.

$$\begin{array}{lclcl} N_2(g) & + & 3H_2(g) & \longrightarrow & 2NH_3(g) \\ \textbf{1 mol} & & \textbf{3 mol} & & \textbf{2 mol} \\ 1 \times 28g = 28\ g & & 3 \times 2g = 6.0\ g & & 2 \times 17g = 34\ g \end{array}$$

We know that :

$$1 \text{ metric ton} = 1000 \text{ kg} = 10^3 \text{ kg} = 10^6 \text{ g}$$

From the mass relationship 34 g NH_3 requires 6.0 g H_2 for its manufacture.

$$\therefore\ 10^6 g\ NH_3 \text{ would require } \frac{6.0 \times 10^6}{34} g = 1.76 \times 10^5 g \text{ of } H_2.$$

Thus 1 metric ton of ammonia will be obtained by using 1.176×10^5g of Hydrogen.

Example 1.10: In a rocket motor fuelled by butane, C_4H_{10}, how many kg of O_2 should be provided with each kg of butane to provide for complete combustion?

Solution : The combustion reaction of butane is

$$\begin{array}{lclclcl} 2C_4H_{10}(g) & + & 13O_2(g) & \longrightarrow & 8CO_2(g) & + & 10H_2O(g) \\ \textbf{2 mol} & & \textbf{13 mol} & & & & \\ \mathbf{2 \times 58 = 116\ g} & & \mathbf{13 \times 32 = 416\ g} & & & & \end{array}$$

Thus, to completely burn 116 g butane, oxygen required is 416g.

Therefore, to completely burn 1 kg (1000 g) butane, oxygen required will be

$$= \frac{416 \times 1000}{116} g\ O_2$$

$$= 3586\ g\ O_2$$

$$= 3.586\ kg\ O_2 \approx 3.59\ kg\ O_2$$

Example 1.11: When lead sulphide; PbS and lead oxide, PbO, are heated together the products are lead metal and sulphur dioxide, SO_2 ,

$$PbS(s) + 2PbO(s) \xrightarrow{\text{heat}} 3Pb\ (1) + SO_2(g)$$

If 14.0 g of lead oxide reacts according to the above equation, how many (a) moles of lead (b) grams of lead, (c) atoms of lead and (d) grams of sulphur dioxide are formed?

(Atomic mass : Pb = 207.0, S = 32.1 ; O =16.0)

Solution : For each part of the question we will use the balanced equation

$$\begin{array}{lclclcl} PbS(s) & + & 2PbO(s) & \xrightarrow{\text{heat}} & 3Pb\ (1) & + & SO_2(g) \\ \textbf{1mol} & & \textbf{2mol} & & \textbf{3 mol} & & \textbf{1mol} \end{array}$$

Now formula mass of PbO = (207.0 + 16.0) = 223.0 amu

Thus, one mole of lead oxide formula units have a mass of 223.0 g. Therefore,

14.0 g of PbO is $\dfrac{14.0\ \text{g PbO}}{223.0\ \text{g mol}^{-1}\ \text{PbO}} = 6.28 \times 10^{-2}\ \text{mol PbO}$

(a) The balanced equation shows that 2 mol of PbO form 3 mol of Pb. Therefore, 6.28×10^{-2} mol of PbO form

$$6.28 \times 10^{-2}\ \text{mol PbO} \times \frac{3\ \text{mol Pb}}{2\ \text{mol PbO}} = 9.42 \times 10^{-2}\ \text{mol Pb}$$

(b) The atomic mass of Pb is 207.0 ; this tells us that one mol of lead has a mass 207.0 g. Thus, 9.42×10^{-2} mol of Pb has a mass of

$$9.42 \times 10^{-2}\ \text{mol Pb} \times \frac{207.0\ \text{g Pb}}{1\text{mol Pb}} = 19.5\ \text{g Pb}$$

(c) 9.42×10^{-2} mol of Pb is

9.42×10^{-2} mol of Pb $\times\ 6.022 \times 10^{23}$ atoms mol^{-1} = 5.67×10^{22} Pb atoms

(d) The balanced equation shows that 2 mol of PbO form 1 mol of SO_2.

Therefore, 6.28×10^{-2} mol of PbO formula unit forms

$$6.28 \times 10^{-2}\ \text{mol PbO} \times \frac{1\text{mol SO}_2}{2\text{mol PbO}}$$

$$= 3.14 \times 10^{-2}\ \text{mol SO}_2$$

Now the relative molecular mass of SO_2 = 32.1 + 2(16.0) = 64.1

Molar mass of SO_2 = 64.1 g mol^{-1}

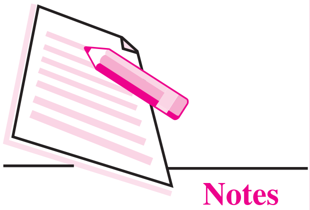
Therefore, 3.14×10^{-2} mol of SO_2 molecules have a mass of 3.14×10^{-2} mol $\times$ 64.1 g mol^{-1} = 2.01 g

INTEXT QUESTIONS 1.7

1. How many grams of NH_3 can be made according to the reaction

   $N_2(g) + 3H_2(g) \longrightarrow 2NH_3\ (g)$

   from (a) 0.207 mol of N_2 (b) 22.6 g of H_2



2. In reaction

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(\ell)$$

How many (a) moles of O_2 are consumed and (b) moles of H_2O are formed when 4.16 X 10^{-2} mol of C_2H_4 react?

1.16 LIMITING REAGENT

We generally find that substances which react with each other are not present in exactly the same proportionin a reaction mixture as stated by a balanced chemical equation. For example, if 2 mol each of hydrogen and oxygen are mixed and a spark is passed through the mixture, water is formed, according to the equation

$$\underset{\textbf{2 mol}}{2H_2} + \underset{\textbf{1mol}}{O_2} \longrightarrow \underset{\textbf{2 mol}}{2H_2O}$$

Here, 2 mol of hydrogen react with only 1 mol of oxygen, and 1 mol of oxygen therefore remains unreacted. In this example hydrogen is said to be the **limiting reagent or reactant** because its amount becomes zero and the reaction therefore stops before the other reactant; that is, the oxygen is used up completly. The amount of hydrogen present initially limits the amount of product that is formed.

Example 1.12: 3 mol of sulphur dioxide SO_2 is mixed with 2 mol of oxygen O_2, and after reaction is over sulphur trioxide, SO_3 is obtained.

(i) Which is the limiting reagent?

(ii) What is the maximum amount of SO_3 that can be formed?

Solution : (i) We must first write the balanced equation

$$2SO_2 + O_2 \rightarrow 2SO_3$$

According to the above equation

(a) 2 mol of SO_3 can be formal from 2 mol of SO_2.

∴ Amount of SO_3 that can be formed from 3 mol of SO_2.

$$= (3 \text{ mol } SO_2) \times \frac{2\text{mol } SO_3}{2\text{mol } SO_2} = 3 \text{ mol } SO_3$$

(b) 2 mol of SO_3 can be formed from 1 mol of O_2. Therefore, the amount of SO_3 that can be formed from 2 mol of O_2.

$$= (2 \text{ mol } O_2) \times \frac{2\text{mol } SO_3}{1\text{mol } O_2} = 4 \text{ mol } SO_3$$

According to the definition, the limiting reactant is that reactant which gives the smallest amount. In this case SO_2 is the limiting reactant.

(ii) The maximum amount of product that can be obtained is the amount formed by the limiting reagent. Thus a the maximum amount of SO_3 that can be obtained is 3 mol.

Example 1.13: 2.3 g of sodium metal is introduced into a 2L flask filled with chlorine gas at STP (273 K, 1bar). After the reaction is over, find :

(i) What is the limiting reagent in this reaction?

(ii) How many moles of sodium chloride are formed?

(iii) Which substance is left unconsumed at the end of the reaction? Find out its mass in grams.

(iv) What percentage of the substance present in excess is converted into sodium chloride?

(Given : Na = 23, Cl = 35.5)

Solution :

$$\begin{array}{llllll} & 2\text{ Na (s)} & + & \text{Cl}_2\text{(g)} & \longrightarrow & 2\text{NaCl (s)} \\ & \textbf{2mol} & & \textbf{1 mol} & & \textbf{2 mol} \\ \text{or} & & & 22.7\text{ L at STP} & & \end{array}$$

(i) Moles of sodium introduced $= \dfrac{2.3\,\text{g}}{23\,\text{g mol}^{-1}} = 0.1$ mol

From the above equation, it is clear that 2 mol NaCl is formed from 2 mol Na

Therefore 0.1 mol Na can produce $= \dfrac{2 \times 0.1}{2} = 0.1$ mol NaCl

Molar volume at STP = 22.7 L

Therefore moles of chlorine in 2 L volume at STP $= \dfrac{2\text{L}}{22.7\,\text{Lmol}^{-1}} = 0.088$ mol

From equation : 1 mol Cl_2 can produce 2 mol NaCl

Therefore 0.088 mol Cl_2 can produce $2 \times 0.088 = 0.176$ mol NaCl.

Since sodium produces less amount of NaCl, it is the limiting reagent.

(ii) Sodium being the limiting reagent, as calculated in (i), the moles of NaCl produced = 0.1 mol

(iii) From above equation, 2 mol NaCl is produced from 1 mol Cl_2

Therefore 0.1 mol NaCl is produced from $\dfrac{1 \times 0.1}{2} = 0.05$ mol Cl_2

Initial moles of $Cl_2 = 0.088$ mol

Moles of Cl_2 left unconsumed = (0.088 – 0.05) mol = 0.038 mol

Therefore, mass of Cl_2 left unconsumed = $0.038 \text{ g} \times 71.0 \text{ g mol}^{-1} = 2.698 \text{ g}$

(because molar mass of $Cl_2 = 2 \times 35.5 = 71.0 \text{ g mol}^{-1}$)

(iv) Moles of Cl_2 consumed = 0.05 mol out of 0.088 mol

$$\therefore \text{ Percent of } Cl_2 \text{ consumed and converted into NaCl} = \frac{0.05}{0.088} \times 100 = 56.8\ \%$$

Example 1.14: 2.0 g mixture of $MgCO_3$ and $CaCO_3$ are heated till no further loss of weight takes place. The residue weighs 1.04 g. Find the percentage composition of the mixture. (Mg = 24, Ca = 40, C = 12, O = 16)

Solution : Mixture of $MgCO_3$ and $CaCO_3$ taken = 2.0 g

Let the mass of $MgCO_3$ be = x g

Therefore the mass of $CaCO_3$ = $(2.0 - x)$ g

The decomposition reactions are

$$\begin{array}{llll} MgCO_3\,(s) & \rightarrow\ MgO(s) & +\ CO_2(g) & \text{(i)} \\ \textbf{(24+12+48) g} & \textbf{(24+16) g} & & \\ \textbf{84 g} & \textbf{40 g (Residue)} & & \\ CaCO_3\,(s) & \rightarrow\ CaO(s) & +\ CO_2(g) & \text{(ii)} \\ \textbf{(40 + 12 + 48) g} & \textbf{(40 + 16) g} & & \\ \textbf{100 g} & \textbf{56 g (Residue)} & & \end{array}$$

From the equation (i)

84 g $MgCO_3$ leaves a residue = 40 g

$$x \text{ g } MgCO_3 \text{ will leave residue} = \frac{40x}{84} \text{ g}$$

From the equation (ii)

100 g $CaCO_3$ leaves a residue = 56 g

$$(2.0 - x) \text{ g } CaCO_3 \text{ will leave residue} = \frac{56 \times (2.0 - x)}{100} \text{ g}$$

$$\text{Total mass of the residue} = \frac{40x}{84} + \frac{56 \times (2.0 - x)}{100} = 1.04 \text{ g (given)}$$

$$\begin{aligned} 40 \times 100x + 84 \times 56 \times 2 - 84 \times 56x &= 84 \times 100 \times 1.04 \\ 4000x + 9408 - 4704x &= 8736 \\ 9408 - 8736 &= (4704 - 4000)x \\ 672 &= 704x \end{aligned}$$

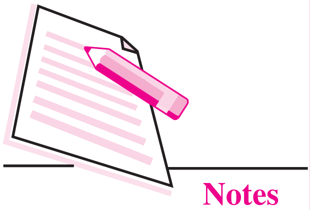
Therefore, mass of $MgCO_3$ in the mixture $= x = \frac{672}{704} = 0.96$ g

Therefore, percentage of $MgCO_3 = \frac{0.96}{2.0} \times 100 = 48\ \%$

and percentage of $CaCO_3 = 100 - 48 = 52\ \%$

WHAT YOU HAVE LEARNT

- Chemistry plays an important role in many aspects of our life like health and medicine, energy and environment, materials and technology, food and agriculture.
- Matter has particulate matter.
- According to the law of conservation of mass, in any chemical reaction, the total mass of all the reactants is equal to the total mass of all the products.
- According to the law of definite proportion, in a chemical compound, the proportions by mass of the elements that compose it are fixed and independent of the origin of the compound or its mode of preparation.
- According to the law of multiple proportions when two elements form two or more compounds, the masses of one element that combine with a fixed mass of the other element are in the ratio of small whole numbers.
- John dalton gave the atomic theory in which he proposed that it is the smallest indivisible particle of matter. Atoms of the same element are all identicle while atoms of different elements differ. Atoms of different elements combine in a simple whole number ratio to form a molecule.
- An atom is the smallest particle of an element that retains its chemical properties.
- A molecule is the smallest particle of matter which can exist independently.
- An element is a substance that cannot be separated into simipler substnaces by chemical means.
- Mole is the amount of a substance which contains as may elementary entities as there are atoms present in 0.012 kg or 12 g of C-12. Thus mole denotes a number.
- The number of elementary entities present in one mole of a substance is 6.022×10^{23}.



- The mass of one mole of a substance is called its molar mass It is numerically equal to relative atomic mass or relative molecular mass expressed in grams per mole (g mol^{-1}) or kilogram per mole (kg mol^{-1}).
- Molar volume is the volume occupied by one mole of a substance. One mole of an ideal gas at standard pressure and temperature, STP (273 K and 1 bar) occupies 22.7 litres.
- In ionic substances, molar mass is numerically equal to the formula mass of the compound expressed in grams.
- If the molar mass of a substance is known, then the amount of a substance present in a sample having a definite mass can be calculated. If M is the molar mass, then, the amount of substance n, present in a sample of mass m is expressed as $n = \frac{m}{M}$.
- A chemical formula is used not only to represent the name of a compound but also to indicate its composition in terms of (i) relative number of atoms and (ii) relative number of moles of atoms.
- A molecular formula of a substance shows(i) the number of atoms of different elements in one molecule.(ii) the number of moles of atoms of different elements in one mole of molecule.
- An empirical formula shows only a ratio of (i) number of atoms, and (ii) moles of atoms in a compound.
- Molecular formula is always an integral multiple of the empirical formula.
- The empirical formula of a compound can be determined from its chemical analysis.
- In order to determine a compound's molecular formula, molecular mass also must be known.
- Stoichiometry is the quantitative study of the composition of chemical compounds (compound or formula stoichiometry) and of the substances consumed and formed in chemical reactions (reaction or equation stoichiometry).
- Chemical equations specify not only the identities of substances consumed and formed in a reaction, but also the relative quantities of these substances in terms of (a) atoms, molecules, and formula units and (b) moles of these entities.
- A balanced chemical equation demonstrates that all the atoms present in the reactants are accounted for in the product; atoms are neither created nor destroyed in a reaction.

- The stoichiometric ratios among the moles of reactants shown in a balanced equation are useful for determining which substance is entirely consumed and which substance(s) is (are) left over.

TERMINAL EXERCISE

1. How many atoms are present in a piece of iron that has a mass of 65.0 g/ (atomic mass; Fe = 55.9 amu).
2. A piece of phosphorus has a mass of 99.2 g. How many moles of phosphorus, P_4 are present in it? (atomic mass, P = 31.0 amu)
3. Mass of 8.46×10^{24} atoms of fluorine is 266.95 g. Calculate the atomic mass of fluorine.
4. A sample of magnesium consists of 1.92×10^{22} Mg atoms. What is the mass of the sample in grams? (atomic mass = 24.3 amu)
5. Calculate the molar mass in g mol^{-1} for each of the following:
   (i) Sodium hydroxide, NaOH
   (ii) Copper Sulphate $CuSO_4 .5H_2O$.
   (iii) Sodium Carbonate, $Na_2CO_3 .10H_2O$
6. For 150 gram sample of phosphorus trichloride (PCl_3), calculate each of the following:
   (i) Mass of one PCl_3 molecule.
   (ii) The number of moles of PCl_3 and Cl in the sample.
   (iii) The number of grams of Cl atoms in the sample.
   (iv) The number of molecules of PCl_3 in the sample.
7. Find out the mass of carbon-12, that would contain 1×10^{19} atoms.
8. How many atoms are present in 100 g sample of C-12 atom?
9. How many moles of $CaCO_3$ would weigh 5 g?
10. If you require 1.0×10^{23} molecules of nitrogen for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$.
    (i) What is the mass (in grams) of N_2 required?
    (ii) How many moles of NH_3 would be formed in the above reaction from 1.0×10^{23} molecules of N_2?
    (iii) What volume would NH_3 gas formed in (ii) occupy at STP?

11. Write empirical formulae of the following compounds:

    CO, Na_2SO_3, C_4H_{10}, H_2O_2, $KC1$

12. The empirical formula of glucose is CH_2O which has a formula mass of 30 amu. If the molecular mass of glucose is 180 amu. Determine the molecular formula of glucose

13. What is ratio of masses of oxygen that are combined with 1.0 gram of nitrogen in the compound NO and N_2O_3?

14. A compound containing sulphur and oxygen on analysis reveals that it contains 50.1% sulphur and 49.9% oxygen by mass. What is the simplest formula of the compound?

15. Hydrocarbons are organic compound composed of hydrogen and carbon. A, 0.1647 g sample of a pure hydrocarbon on burning in a combustion tube produced 0.5694 g of CO_2 and 0.0845 g of H_2O. Determine the percentage of these elements in the hydrocarbon.

16. On combustion 2.4 g of a compound of carbon, hydrogen and oxygen gave 3.52 g of CO_2 and 1.44 g of H_2O. The molecular mass of the compound was found to be 60.0 amu.

    (a) What are the masses of carbon, hydrogen and oxygen in 2.4 g of the compound?

    (b) What are the empirical and molecular formulae of the compound?

17. (i) What mass of oxygen is required to react completely with 24 g of CH_4 in the following reaction?

    $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(1)$

    (ii) How much mass of CH_4 would react with 96 g of oxygen.

18. In the reaction $H_2 + C1_2 \rightarrow 2HC1$

    How many grams of chlorine, $C1_2$ are needed to react completely with 0.245 g of hydrogen, H_2, to give hydrogen chloride, HC1? How much HC1 is formed?

19. 3.65 g of H_2 and 26.7 g of O_2 are mixed and reacted. How many grams of H_2O are formed?

20. Caustic soda NaOH can be commercially prepared by the reaction of Na_2CO_3 with slaked line, $Ca(OH)_2$. How many grams of NaOH can be obtained by treating 2.0 kg of Na_2CO_3 with $Ca(OH)_2$?

21. A portable hydrogen generator utilizes the reaction

    $CaH_2 + H_2O \rightarrow Ca(OH)_2 + 2H_2$

    How many grams of H_2 can be produced by a 100 g cartridge of CaH_2?

22. The reaction $2Al + 3MnO \rightarrow Al_2O_3 + 3Mn$ proceeds till the limiting substance is consumed. A mixture of 220 g Al and 400 g MnO was heated to initiate the reaction. Which initial substance remained in excess and by how much ? (Al = 27, Mn = 55).

23. $KClO_4$ may be prepared by means of following series of reactions

    $Cl_2 + 2KOH \rightarrow KCl + KClO + H_2O$

    $3KClO \rightarrow 2KCl + KClO_3$

    $4KClO_3 \rightarrow 3KClO_4 + KCl$

    How much Cl_2 is needed to prepare 400 g $KClO_4$ by the above sequence?

    (K = 39, Cl = 35.5, O = 16, H = 1)

24. 2.0 g of a mixture of Na_2CO_3 and $NaHCO_3$ was heated when its weight reduced to 1.876 g. Determine the percentage composition of the mixture.

25. Calculate the weight of 60 % sulphuric acid required to decompose 150 g of chalk (calcium carbonate). Given Ca = 40, C = 12, O = 16, S = 32)

ANSWERS TO INTEXT QUESTIONS

1.1

1. Health, medicine, energy, food, agriculture etc.
2. Leucippus and his student Democritus
3. In every chemical reaction total masses of all the reactants is equal to the masses of all the products.
4. An atom is extremely small particles of matter that retains its identity during chemical reaction.
5. Molecule is an aggregate of at least two atoms in a definite arragement held togethrer its chemical forces.
6. It is derived from the Latin name of sodium i.e. Natrium
7. An elements comprises of atoms of one type only while a compound comprises atoms of two or more types combined in a simple but fixed ratio.

1.2

1. Kilogram
2. μg
3. (i) h (ii) n

4. (i) Megasecond, 10^6 s

   (ii) millisecond, 10^{-3} s.

1.3

1. Moles of N_2 gas = $\dfrac{4.22 \times 10^{23} \text{ molecules}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}}$ = 0.70 mol

2. Amount of magnesium (moles) = $\dfrac{8.46 \times 10^{24} \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}}$ = 14.05 mol

3. No. of Cl_2 molecules in 0.25 mol Cl_2 = $0.25 \times 6.022 \times 10^{23}$ molecules

   = 1.5055×10^{23} molecules

   Since each Cl_2 molecule has 2 Cl atoms, the number of Cl atoms = $2 \times 1.5055 \times 10^{23} = 3.011 \times 10^{23}$ atoms.

1.4

1. Molar mass of hydrogen chloride = molar mass of HCl

   = 1 mol of H + 1 mol of Cl

   = 1.0 g mol^{-1} + 35.5 g mol^{-1}

   = 36.5 g mol^{-1}

2. Molar mass of argon atoms = mass of 1 mol of argon

   = mass of 6.022×10^{23} atoms of argon.

   = 6.634×10^{-26} kg $\times 6.022 \times 10^{23}$ mol^{-1}

   = 39.95×10^{-3} kg mol^{-1}

   = 39.95 g mol^{-1}

3. Molar mass of KNO_3 = mass of 1 mol of K + mass of 1 mol of N + mass of 3 mol of O.

   Since molar mass of an element is numerically equal to its atomic mass but has the units of g mol^{-1} in place of amu = 39.1 g + 14.0 g + 3 × 16.0 g

   ∴ Molar mass of KNO_3 = 39.1 g + 14.0 g + 48.0 g = 101.1 g mol^{-1}

4. Mass of 1 mol of Na_3PO_4 = 3 × (mass of 1mol of Na) + mass of 1 mol of P + 4 × (mass of 1mol of oxygen)

   = 3 (23.0 g) + 31.0 g + 4(16.0) g

   = 69.0 g + 31.0 g + 64.0 g = 164.0 g

   ∴ Mass of 0.146 mol of Na_3PO_4 = 0.146 × 164.0 g = 23.94 g

1.5

1. Moles of Cu atoms in 3.05 g copper $= \dfrac{3.05\text{ g}}{63.5\text{ g mol}^{-1}} = 0.048$ mol

2. Moles of gold, Au $= \dfrac{12.6\text{ g}}{197\text{ g mol}^{-1}} = 0.064$ mol

3. Molar volume of any gas at STP (298 K, 1 bar) = 22.7 L

   ∴ Volume occupied by 2.5 mol CO_2 at STP = 2.5 × 22.7 L = 56.75 L

1.6

1. Molar mass of Fe_3O_4 $= 3 \times 56.0 + 4 \times 16.0$

   $= (168.0 + 64.0) = 232.0\text{ g mol}^{-1}$

   Percentage of Fe $= \dfrac{168.0}{232.0} \times 100 = 72.41\%$

   Percentage of O $= \dfrac{64.0}{232.0} \times 100 = 27.59\%$

2. (a) Molar mass of $SrCO_3 = 87.6 + 12.0 + 48.0 = 147.6\text{ g mol}^{-1}$

   Percentage of carbon C in $SrCO_3 = \dfrac{12.0}{147.6} \times 100 = 8.13\%$

   (b) Molar mass of $H_2SO_4 = 2.0 + 32.1 + 64.0 = 98.1\text{ g mol}^{-1}$

   Molar mass of $SO_3 = 32.1 + 48.0 = 80.1\text{ g mol}^{-1}$

   Percentage of SO_3 in $H_2SO_4 = \dfrac{80.1 \times 100}{98.1} = 81.65\%$

3.

Substance	**Empirical formula**
H_2O_2	HO
C_6H_{12}	CH_2
Li_2CO_3	Li_2CO_3
$C_2H_4O_2$	CH_2O
S_8	S
H_2O	H_2O
B_2H_6	BH_3
O_3	O_3
S_3O_9	SO_3
N_2O_3	N_2O_3

4. Percentage of carbon = 53.1%

Percentage of Oxygen = 46.9%

Suppose we take 100 g of the substance then moles of carbon

$$= \frac{53.1}{12.0} \text{ g} = 4.43 \text{ mol}$$

$$\text{mole of oxygen} = \frac{46.0}{16.0} = 2.93 \text{ mol}$$

$$\text{molar ratio of C and O} = \frac{4.43}{2.93} : \frac{2.93}{2.93}$$

$$= 1.50 : 1 \quad \text{or} \quad 3 : 2$$

Empirical formula of the compound is C_3O_2

1.7

1. In equation

$$\underset{\textbf{1 mol}}{N_2(g)} + \underset{\textbf{3 mol}}{3H_2(g)} \rightarrow \underset{\textbf{2 mol}}{2NH_3(g)}$$

0.207 mol of N_2 gives 0.414 mol of NH_3

0.414 mol of NH_3 = 0.414 mol × 17.0 g mol^{-1} = 7.038 g of NH_3

$$22.6 \text{ g of hydrogen} = \frac{22.6}{2.0} = 11.3 \text{ mol of hydrogen}$$

$$11.3 \text{ mol of hydrogen will give } \frac{2}{3} \times 11.3 \text{ mol of } NH_3 = 7.53 \text{ mol}$$

Therefore, mass of NH_3 = 7.53 mol × 17.0 g mol^{-1} = 128.01 g

2. $$\underset{\textbf{1 mol}}{C_2H_4(g)} + \underset{\textbf{3 mol}}{3O_2(g)} \rightarrow \underset{\textbf{2 mol}}{2CO_2(g)} + \underset{\textbf{2 mol}}{2H_2O(g)}$$

(a) 4.16×10^{-2} mol of C_2H_4 will consume $3 \times 4.16 \times 10^{-2}$ mol of oxygen

$$= 12.48 \times 10^{-2} = 1.248 \times 10^{-1} \text{ mol of } O_2$$

(b) moles of H_2O formed = $2 \times 4.16 \times 10^{-2}$ mol

$$= 8.32 \times 10^{-2} \text{ mol of } H_2O$$

313en02

2

ATOMIC STRUCTURE

Chemistry has been defined as the study of matter in terms of its structure, composition and the properties. As you are aware, matter is made up of atoms, and therefore an understanding of the structure of atom is very important. You have studied in your earlier classes that the earliest concept of atom (smallest indivisible part of matter) was given by ancient Indian and Greek philosophers (600-400 BC). At that time there were no experimental evidence. The origin of the concept of atom was based on their thoughts on 'What would happen if we continuously keep dividing matter'. John Dalton revived the concept of atom in the beginning of nineteenth century in terms of his **atomic theory** which successfully explained the laws of chemical combination. Later experiments showed that the atom is not indivisible but has an internal structure.

In this lesson you will learn about the internal structure of an atom which will help you to understand the correlations between its structure and properties. You would learn about these in the later lessons.

OBJECTIVES

After reading this lesson you will be able to :

- explain the atomic number, isotopes and isobars;
- recognize the fundamental particles of atom;
- describe Rutherford's experiment and explain its results;
- define electromagnetic radiation;
- list and define the characteristic parameters of electromagnetic radiation;
- discuss line spectrum of hydrogen;
- explain Bohr's postulates and discuss his model;
- draw energy level diagram of hydrogen atom showing different series of lines in its spectrum;

- to explain the stability of half filled and completely filled orbitals;
- explain wave particle duality of matter and radiation;
- formulate Heisenberg's uncertainty principle;
- explain the need for quantum mechanical model;
- draw probability pictures of an electron in an atom;
- list quantum numbers and discuss their significance;
- draw the shapes of s, p and d orbitals;
- recognize nodal plane;
- explain Pauli's exclusion principle;
- define Aufbau principle;
- explain Hund's rule of maximum multiplicity; and
- explain the stability of half filled and fully filled orbital.

2.1 DISCOVERY OF FUNDAMENTAL PARTICLES OF ATOM

In 1897 J.J. Thomson discovered **electron** as a constituent of atom. He determined that an electron had a negative charge and had very little mass as compared to that of the atom. Since an atom was found to be electrically neutral it was inferred that some source of positive charge must be present in the atom. This soon led to the experimental discovery of the proton, which is a positively charged subatomic particle. Proton was found approximately 1840 times heavier than an electron. Further experiments revealed that the atomic masses were more than that expected from the presence of just protons and electrons in the atom. For example, the mass of helium atom was expected to be double that of hydrogen atom but was actually found to be almost four times the mass of hydrogen atom. This suggested the presence of neutral particles with mass comparable to that of protons in the atom. Sir James Chadwick in 1932 discovered this neutral particle and called **it neutron** subsequently. Thus we may conclude that atoms are not indivisible but are made up of three fundamental particles whose characteristics are given in Table 2.1.

Table 2.1 Fundamental particles of atom and their characteristics

Particle	Symbol	Mass/ kg	Actual Charge / C	Relative charge
Electron	*e*	$9.109\ 389 \times 10^{-31}$	$-\ 1.602\ 177 \times 10^{-19}$	-1
Proton	*p*	$1.672\ 623 \times 10^{-27}$	$1.602\ 177 \times 10^{-19}$	$+1$
Neutron	*n*	$1.674\ 928 \times 10^{-27}$	0	0

Since atoms are made up of still smaller particles, they must have an internal structure. In the next section we shall take up some of the earlier ideas about the internal structure of atom.

INTEXT QUESTION 2.1

1. Compare the mass of an electron with that of the proton.
2. What is a fundamental particle?
3. What is the name given to neutral particles in the atom?

2.2 ATOMIC NUMBER, MASS NUMBER, ISOTOPES AND ISOBARS

All atoms can be identified by the number of protons and neutrons they contain. The *atomic number (Z) is the number of protons in the nucleus of each atom. of an element.* In, a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its atomic number. For example, the atomic number of nitrogen is 7. This means that each neutral nitrogen atom has 7 protons and 7 electrons. Or, viewed another way, every atom in the universe that contains 7 protons is correctly named "nitrogen."

The *mass number (A) is the total number of neutrons and, protons present in the nucleus of an atom of an element.* Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contains both protons and neu-trons. In general the mass number is given by

mass number = number of protons + number of neutrons = atomic number + number of neutrons

The number of neutrons in an atom is equal to the difference between the mass mem-ber and the atomic number, or (A - Z). For example, the mass number of fluorine is 19 and the atomic number is 9 (indicating 9 protons in the nucleus). Thus the number of neutrons in an atom of fluorine is 19 - 9 = 10. Note that the atomic number, num-ber of neutrons, and mass number all must be positive integers (whole numbers).

Atoms of a given element do not all have the same mass. Most elements have two or more *isotopes, atoms that have the same atomic number but different mass numbers.* For example, there are three isotopes of hydrogen. One, simply known as hydrogen, has one proton and no neutrons. The *deturium* isotope contains one proton and one neutron, and *tritium* has one proton and two neutrons. The accepted way to denote the atomic number and mass number of an atom of an element (X) is as follows:

mass number

$$^{A}_{Z}X$$

atomic number

Thus, for the isotopes of hydrogen, we write

$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$
hydrogen	deuterium	tritium

As another example, consider two common isotopes of uranium with mass numbers of 235 and 238, respectively:

$$^{235}_{92}U \qquad ^{238}_{92}U$$

The first isotope is used in nuclear reactors and atomic bombs, whereas the second isotope lacks the properties necessary for these applications. With the exception of hydrogen, which has different names for each of its isotopes, isotopes of elements are identified by their mass numbers. Thus the above two isotopes are called uranium-235 (pronounced "uranium two thirty-five") and uranium-238 (pronounced "uranium two thirty-eight").

The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemistries, forming the same types of compounds and displaying similar reactivities.

The following example shows how to calculate the number of protons, neutrons, and electrons using atomic numbers and mass numbers.

Example 2.1: Give the number of protons, neutrons, and electrons in each of the following species:

(a) $^{17}_{8}O$ (b) $^{199}_{80}Hg$ (c) $^{200}_{80}Hg$

Solution:

(a) The atomic number is 8, so there are 8 protons. The mass number is 17, SO the number of neutrons is 17 - 8 = 9. The number of electrons is the same as the number of protons, that is, 8.

(b) The atomic number is 80, so there are 80 protons. The mass number is 199, so the number of neutrons is 199 - 80 = 119. The number of electrons is 80.

(c) Here the number of protons is the same as in (b), or 80. The number of neutrons is 200 - 80 = 120. The number of electrons is also the same as in (b), 80. The species in (b) and (c) are chemically similar isotopes of mercury.

2.3 EARLIER MODELS

Once it was established that the atom is not indivisible, the scientists made attempts to understand the structure of the atom. A number of models have been proposed for the internal structure of the atom. The first attempt to describe the structure of atom in terms of a model was made by J.J Thomson.

2.3.1 Thomson's Model

On the basis of his experiments on discharge tubes, Thomson proposed that atoms could be considered as a large positively charged body with a number of small negatively charged electrons scattered throughout it. This model (Fig. 2.1) was called as plum pudding model of the atom.

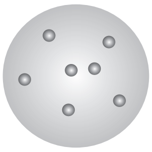


Fig. 2.1 : A pictorial representation of Thomson's plum-pudding model

The electrons represent the plums in the pudding made of positive charge. It is sometimes also called as **watermelon model**. In this, the juicy pulp of the watermelon represents the positive charge and the seeds represent the electrons.

J.J.Thomson
(1856-1940)
Won Nobel prize in Physics in 1906

Ernest Rutherford
(1871-1937)
Won Nobel prize in Chemistry in 1908

2.3.2 Rutherford's Experiment

Ernest Rutherford performed an experiment called 'Gold Foil Experiment' or 'á-ray scattering experiment' to test the structure of an atom as proposed by Thomson. In this experiment a beam of fast moving alpha particles (positively charged helium ions) was passed through a very thin foil of gold. He expected that the alpha particles would just pass straight through the gold foil and could be detected by a photographic plate. But, the actual results of the experiment (Fig. 2.2) were quite surprising. It was observed that most of the α-particles did pass straight through the foil but a number of particles were deflected from their path. Some of these deflected slightly while a few deflected through large angles and about 1 in 10,000 á- particles suffered a rebound.

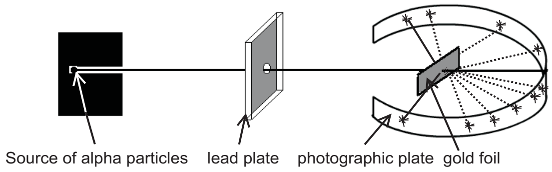


Fig 2.2: *Schematic representation of Rutherford's α-ray scattering experiment.*

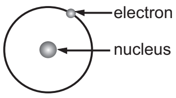


Fig 2.3 : *Schematic representation of Rutherford's model*

These results led Rutherford to conclude that :

- the atom contained some dense and positively charged region located at the center of the atom that he called as **nucleus**.
- all the positive charge of the atom and most of its mass was contained in the nucleus.
- the rest of the atom would be empty space which contained the much smaller and negatively charged electrons (Fig. 2.3).

The model proposed by Rutherford explained the observation in the α-ray scattering experiments as shown below in Fig 2.4.

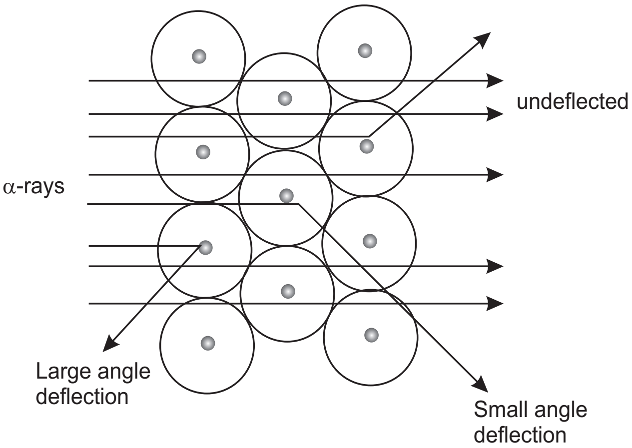


Fig 2.4 : *Explanation of the results of á- ray scattering experiment.*

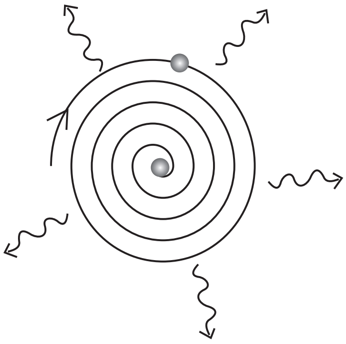


Fig. 2.5 : *Failure of Rutherford's model*

However, there was a problem with the Rutherford's model. According to the

Maxwell's theory of electromagnetic radiation, a charged particle undergoing acceleration would continuously emit radiation and lose energy. Since the electron in the atom is also a charged particle and is under acceleration, it is expected to continuously lose energy. As a consequence, the electron moving around the nucleus would approach the nucleus by a spiral path (Fig. 2.5) and the atom would collapse. However, since it does not happen we can say that the Rutherford's model failed to explain the stability of the atom.

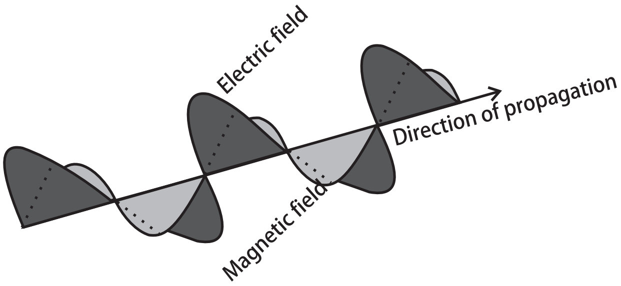
The next attempt to suggest a model for atom was made by Neils Bohr, a student of Rutherford. This model used the concept of quantisation of energy of electrons in the atom. Since this fact was suggested by line spectrum of hydrogen atom it is worthwhile to understand the meaning of a spectrum. For this we begin with the understanding of the nature of an electromagnetic radiation.

INTEXT QUESTION 2.2

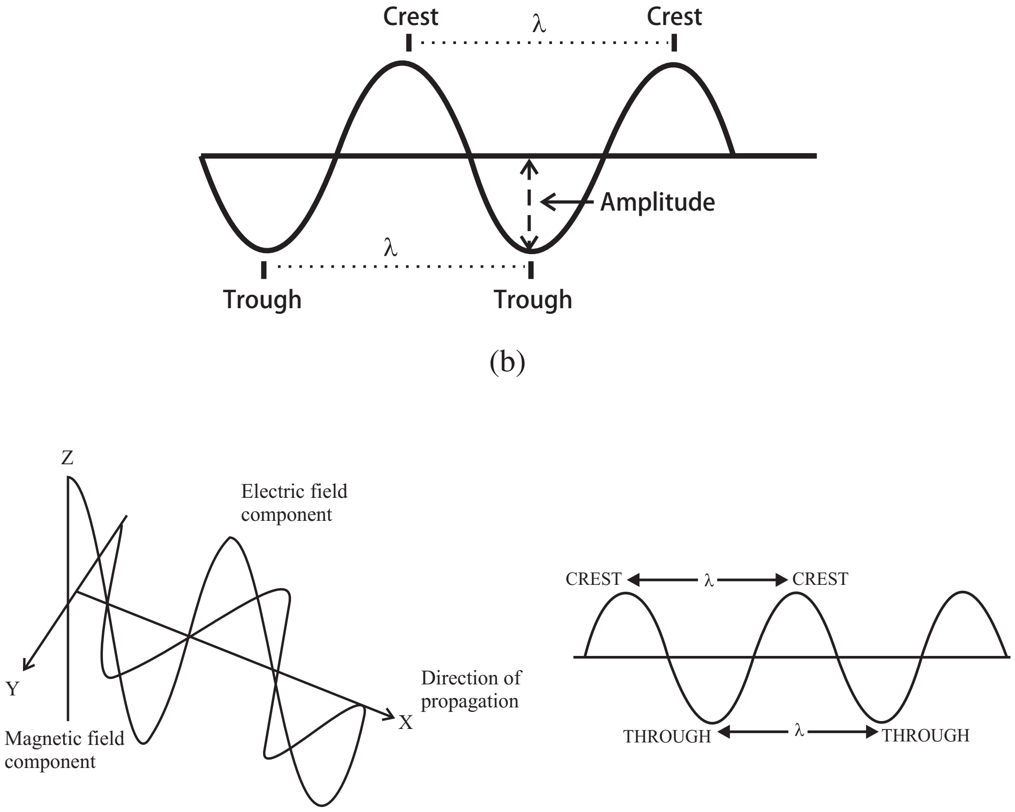
1. List the three constituent particles of an atom.
2. What was the aim of Rutherford's α-rays scattering experiment?
3. Briefly describe Rutherford's model of an atom.
4. On what basis was the Rutherford's model rejected?

2.4 ELECTROMAGNETIC RADIATIONS

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. These do not require any medium to propagate. Visible light, radiant heat, radio waves, X-rays and gamma radiation are some of the examples of electromagnetic radiations. According to the Maxwell's theory, an electromagnetic radiation can be visualised as oscillating electric and magnetic fields. These travel as waves in the planes perpendicular to each other and also to the direction of propagation (Fig. 2.6 (a)). These radiations travel with the velocity of light (3.0×10^8 m s^{-1}).



(a)



(b)

Fig. 2.6 : *(a) An electromagnetic wave showing electric and magnetic fields travelling in planes perpendicular to each other and also to the direction of propagation (b) Characteristics of electromagnetic wave*

2.4.1 Characteristic Parameters of Electromagnetic Radiations

The electromagnetic radiations are characterized by a number of parameters. These are

Amplitude: This refers to the **maximum height to which the wave oscillates**. It equals the height of the crests or depth of the troughs.

Wavelength : It is the linear **distance between two consecutive wave-crests or wave- troughs** as shown in Fig. 2.6(b). It is represented by a Greek letter lambda (λ) and is expressed in terms of m, cm, nm or Angstrom (1Å = 10^{-10} m).

Frequency: It is defined as the **number of wave crests or wave troughs that pass through a given point per second**. It is represented by a Greek letter nu (ν) and is expressed in terms of s^{-1}(second inverse or per second). It is also called as Hz (Hertz).

Wave number: It equals **the number of waves per unit length**. It is denoted as $\bar{\nu}$ (nu bar) and is equal to the reciprocal of the wavelength. The SI unit of $\bar{\nu}$ is m^{-1} (meter inverse). However, sometimes it is also expressed as cm^{-1} (centimeter inverse).

$$\overline{\nu} = \frac{1}{\lambda} \qquad \text{.... (2.1)}$$

Velocity: It is defined as the linear **distance travelled by the wave in one second**. The velocity in meters per second can be obtained by multiplying frequency in Hertz (s^{-1}) with wavelength in meters.

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

The velocity of a radiation depends on the medium. In vacuum the velocity is equal to 3.00 x 10^8 m s^{-1}.

The electromagnetic radiations also show the characteristics of particles. These are called as *quanta*. These quanta are actually bundles of energy. A quantum of visible light is called a *photon*. The energy of the quantum (or photon) is proportional to the frequency of the radiation. The two are related as

$$E = h\nu \qquad \text{... (2.3)}$$

The energy of the quantum can also be related to the wavelength or wave number as

$$E = h\frac{c}{\lambda} \text{ or } E = hc\overline{\nu} \qquad \text{... (2.4)}$$

the energy of photon can be readily calculated from these equations if we know the frequency, wavelength or wave number.

Example 2.2 : A microwave radiation has a frequency of 12 gigahertz. Calculate the energy of the photon corresponding to this radiation. ($h = 6.626 \times 10^{-34}$ J s and 1 gigahertz = 10^9 Hz.).

Solution: The energy is given by the expression, $E = h\nu$

Substituting the values we get,

$$E = 6.626 \times 10^{-34} \text{ Js} \times 1.2 \times 10^{10} \text{ s}^{-1} = 7.95 \times 10^{-24} \text{ J}$$

Example 2.3 : The green light has a wavelength of 535 nm. Calculate the energy of a photon of green light.

Solution: We know that

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^{8} \text{ ms}^{-1})}{535 \times 10^{-9} \text{ m}} = 3.71 \times 10^{-19} \text{ J}$$

2.4.2 Electromagnetic Spectrum

Depending on their characteristics (wavelength , frequency and wave number) electromagnetic radiations are of many types and constitute what is called as an electromagnetic spectrum (Fig. 2.7). The part of the spectrum that we can see is called visible spectrum and is a very small part of the overall spectrum.

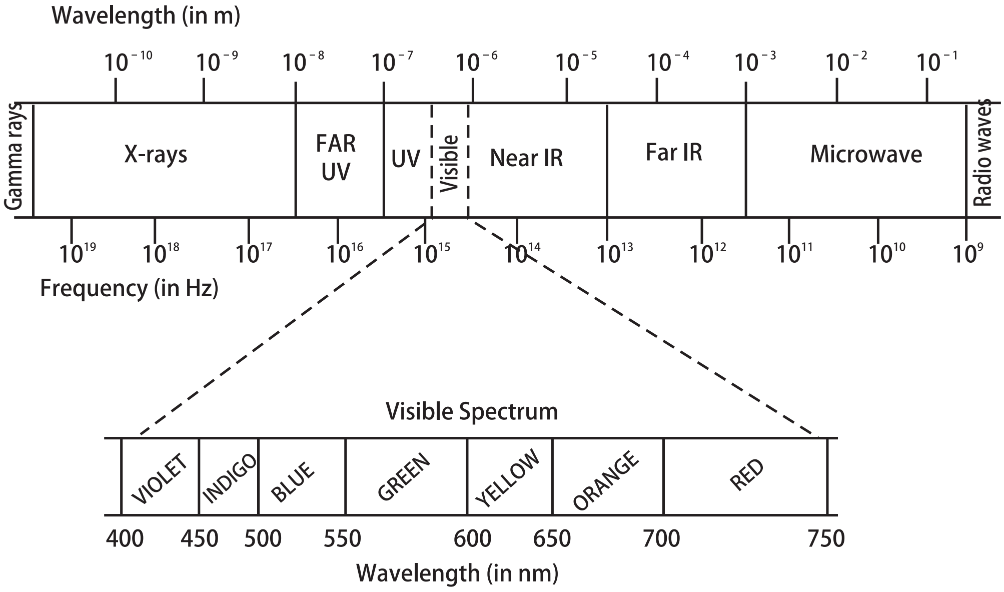


Fig. 2.7: *The electromagnetic spectrum*

INTEXT QUESTION 2.3

1. What is an electromagnetic radiation?
2. List any three characteristics of electromagnetic radiation.
3. What is wave number? How is it related to wave length?
4. What is the difference between a 'quantum' and a ' photon'?

2.5 LINE SPECTRUM

You know that when we pass a beam of sunlight through a prism we get a range of colours from violet to red (VIBGYOR) in the form of a spectrum (like rainbow). This is called a ***continuous spectrum*** because the wavelengths of the light varies continuously that is without any break. Let us take another example. You are

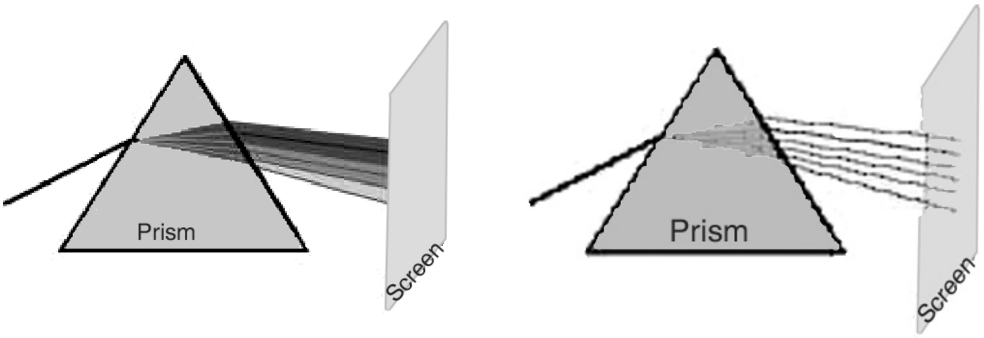


Fig. 2.8: *a) a Continuous spectrum* *b) a Line spectrum*

aware of the flame tests for identifying cations in the qualitative analysis. Compounds of sodium impart a bright yellow colour to the flame, copper gives a green flame while strontium gives a crimson red coloured flame. If we pass such a light through a prism it gets separated into a set of lines. This is called as a *line spectrum.* Fig. 2.8 differentiates between a continuous and a line spectrum.

2.5.1 Line Spectrum of Hydrogen Atom

When an electric discharge is passed through a discharge tube containing hydrogen gas at low pressure, it emits some light. When this light is passed through a prism it splits up into a set of five lines. This spectrum is called the *line spectrum of hydrogen* (Fig. 2.9).

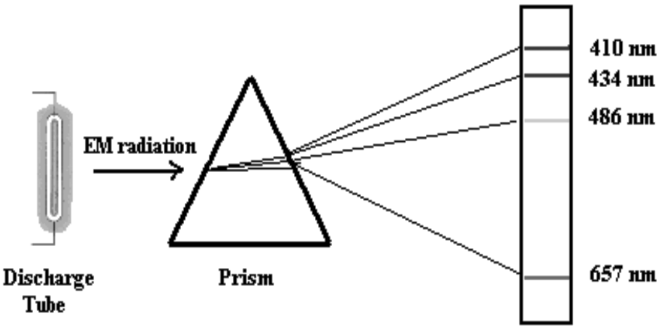


Fig. 2.9: *A schematic diagram showing line spectrum of hydrogen in the visible range*

Johann Balmer (1825-1898)

On careful analysis of the hydrogen spectrum it was found to consist of a few sets of lines in the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. These spectral emission lines could be expressed in the form of a general formula as:

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\ \text{cm}^{-1}\ ;\ R_H = 109677\ \text{cm}^{-1} \qquad \ldots(2.5)$$

Where n_1 and n_2 are positive integers ($n_1 < n_2$) and R_H is called Rydberg's constant. The different sets of lines observed in the hydrogen atom spectrum named after their discoverers and the values of n_1 and n_2 are given in the Table 2.2.

Table 2.2 : Summary of the emission lines observed in hydrogen spectrum

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4…..	Ultraviolet
Balmer	2	3,4,5…..	Visible
Paschen	3	4,5,6…..	Infrared
Bracket	4	5,6,7…..	Infrared
Pfund	5	6,7,8…..	Infrared

The line spectrum of hydrogen atom was explained by Bohr's model, which is discussed in section 2.5.

Example 2.4 : Calculate the wavelength of the Balmer line corresponding to $n_2 = 3$.

Solution: According to Balmer series $\bar{v} = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$

where $R_H = 109{,}677\ \text{cm}^{-1}$

$$\text{For } n_2 = 3\ ;\ \bar{v} = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 109{,}677 \left(\frac{5}{36} \right)$$

$$\text{Since,} \quad \lambda = \frac{1}{\bar{v}} ; \lambda = \frac{36}{109{,}677 \times 5}$$

$$= 6.56 \times 10^{-5}\ \text{cm}$$

$$= 656\ \text{nm}$$

2.6 BOHR'S MODEL

In 1913, Niels Bohr (1885-1962) proposed another model of the atom where electrons move around the nucleus in circular paths. Bohr's atomic model is built upon a set of postulates, which are as follows :

1. The electrons move in a definite circular paths around the nucleus (Fig 2.10). He called these circular paths as **orbits** and postulated that ***as long as the electron is in a given orbit its energy does not change*** (or energy remains fixed). These orbits were therefore referred to as **stationary orbits** or **stationary states** or **non radiating orbits.**

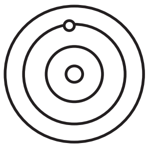


Fig. 2.10: *Bohr's model*

Bohr won the Nobel Prize in Physics in 1922 for his work.

2. The ***electron can change its orbit by absorbing or releasing energy***. An electron at a lower (initial) state of energy, E_i can go to a higher (final) state of energy, E_f by absorbing a single photon of energy as given by

$$E = hv = E_f - E_i \qquad ...(2.6)$$

Similarly, when electron changes its orbit from a higher (initial) state of energy E_i to a lower (final) state of energy E_f , a single photon of energy hί is released (Fig. 2.11).

Fig. 2.11 : *Absorption and emission of photon causes the electron to change its energy level.*

3. The **angular momentum of an electron** of mass m_e moving in a circular orbit of radius r and velocity v is an integral multiple of $h/2\pi$.

$$m_e vr = \frac{nh}{2\pi} \qquad \text{... (2.7)}$$

where n is a positive integer, known as the **principal quantum number**.

Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates :

Energy of the orbit, $E_n = -R_H\left(\frac{1}{n^2}\right)$ ...(2.8)

Bohr could correlate R_H to other properties as $R_H = \frac{mz^2e^4}{8h^2\varepsilon_0^2}$; ...(2.9)

where,

m = mass of the electron

z = nuclear charge

e = electronic charge

h = Planck's constant

ε_0 = permitivitty of the medium

The negative sign in the energy expression means that there is an attractive interaction between the nucleus and the electron. This means that certain amount of energy (called ionisation energy) would be required to remove the electron from the influence of the nucleus in the atom. You may note here that the energies of the Bohr orbits are inversely proportional to the square of the **quantum number** n. As n increases the value of the energy increases (becomes lesser negative or more positive). It means that as we go farther from the nucleus the energy of the orbit goes on increasing.

2.6.1 Explanation of Line Spectrum of Hydrogen Atom

As per the second postulate mentioned above, the energy emitted in the transition of a single electron from an initial stationary state of energy E_i to a final stationary state of energy E_f is given as $h\nu = E_i - E_f$. Substituting the expressions for energy from eq. 2.8 we can get the formula given in eq.2.5. Thus Bohr's model provides an explanation for the observed line spectrum of hydrogen as summarized in

Table 2.2. Fig. 2.12 shows the energy level diagram for hydrogen atom and the transitions responsible for the observed line spectrum.

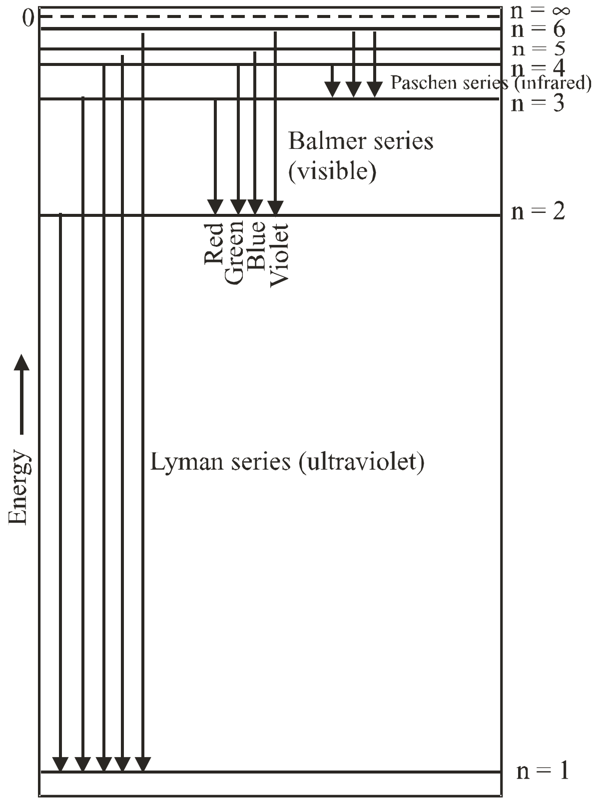


Fig. 2.12: *Energy level diagram for H-atom, showing various transitions responsible for the observed line spectrum*

INTEXT QUESTION 2.4

1. What is the difference between a line spectrum and a continuous spectrum?
2. What are the main postulates of Bohr's model?
3. How does the energy of a Bohr orbit vary with the principle quantum number 'n'.

2.7 WAVE – PARTICLE DUALITY

In section 2.3 you have learnt about the wave nature of light. As you are aware that some of the properties of light e.g., diffraction and interference can be explained on the basis of its wave nature. On the other hand some other properties like photoelectric effect and scattering of light can be explained only on the basis of particle nature of light. Thus light has a dual nature possessing the properties of both a wave and a particle, i.e., light could under some conditions behave like a particle and under other conditions behave as a wave.

In 1923 a young French physicist, Louis de Broglie, argued that if light can show wave as well as particle nature, why should particles of matter (e.g., electron) not possess wave like characteristics? He proposed that matter particles should indeed have a wave nature and said that a particle of mass m moving with a velocity v has an associated wavelength, λ (some times called *de Broglie wavelength)* given by the formula;

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p} \qquad \text{...(2.10)}$$

Where p ($= mv$) is the momentum of the particle. The de Broglie wavelength of a body is inversely proportional to its momentum. Since the magnitude of h is very small, the wavelength of the objects of our everyday world would be too small to be observed. Let us make a calculation to see this.

Example 2.5 : Calculate the de Broglie wavelength associated with a cricket ball weighing 380 g thrown at a speed of 140 km per hour.

Solution: Mass of the cricket ball = 380 g = 380×10^{-3} kg = 0.38 kg

Speed or Velocity = 140 km/hr = $(140 \times 1000)/3600$

$$= 38.89 \text{ m s}^{-1}$$

The wavelength associated with the cricket ball will be

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\text{JS}}{(0.380\,kg)\,(38.89\text{m s}^{-1})}$$

$$= 4.48 \times 10^{-35}\text{ m} \quad (\text{J} = \text{kg m}^2\text{ s}^{-2})$$

de-Broglie (1892-1987)
de-Broglie proposed the theory of wave-particle dualism as a part of his PhD thesis in 1924. He got the physics Nobel prize in 1929

If the electrons show wave nature then a beam of these electrons is expected to show diffraction which is a property of waves. In 1927 G.P. Thomson and C.J. Davisson demonstrated the diffraction of electron waves by the crystal lattice of nickel (Fig. 2.13). Thus electrons also show a dual nature. That is, sometimes these show particle nature while at some other times they show wave nature.

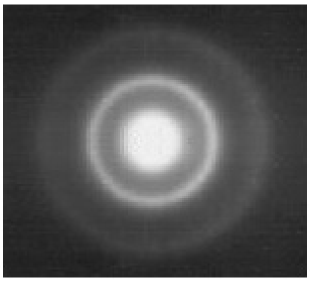


Fig. 2.13: *Electron diffraction pattern from nickel crystal*

2.8 HEISENBERG'S UNCERTAINTY PRINCIPLE

Werner Heisenberg (1901-1976) Heisenberg got the physics. Nobel prize in 1932

An important consequence of the wave-particle duality of matter and radiation was discovered by Werner Heisenberg in 1927 and is called the **uncertainty principle**. According to this principle it is not possible to simultaneously measure both the ***position*** and ***momentum (or velocity)*** of an electron accurately. In simple words we may state that more accurately you measure a particle's position, the less accurately you're able to measure its momentum, and vice versa. Mathematically, the Heisenberg principle can be expressed in terms of an inequality

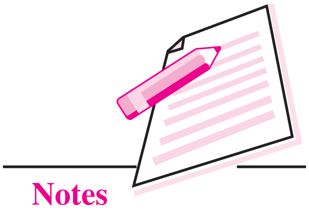
$$\ddot{A}x\ \ddot{A}p \geq \frac{h}{4\pi} \qquad \ldots(2.11)$$

Where $\ddot{A}x$ and $\ddot{A}p$ are the uncertainities in the measurements of position and momentum respectively. If the position of an object is known exactly (i.e., $\ddot{A}x = 0$), then the uncertainty in the momentum must be infinite, meaning that we cannot say anything about the velocity. Similarly, if the velocity is known exactly, then the position would be entirely uncertain and the particle could be anywhere. It means that we cannot say anything about the position of the particle. In actual practice none of the two properties can be measured with certainty. Due to the small value of the Planck's constant, h (6.626×10^{-34} J s) this principle is not relevant while making measurements of large objects like car, bus or aeroplane etc.. It is relevant, only when you are making measurements on very small objects such as electrons.

Heisenberg's principle questioned the validity of Bohr's model. It is so because according to Bohr's model we can precisely calculate the radius of the orbit (i.e., the position of the electron) and the velocity of electron in it. But it is not possible according to Heisenberg's principle. It motivated many scientists to develop newer models of the atom using the dual nature of the electron. This resulted into the development of a Quantum mechanical model or *Wave Mechanical Model* of the atom discussed in the next section.

INTEXT QUESTION 2.5

1. What do you understand by wave-particle duality?
2. Name the experiment that established the wave nature of electron.
3. Compute the de-Broglie wavelength associated with an electron moving with a velocity of 100 km /second? ($m_e = 9.1 \times 10^{-31}$kg)
4. State Heisenberg's Uncertainty Principle?



2.9 WAVE MECHANICAL MODEL OF ATOM

Wave Mechanical Model of atom was proposed by Erwin Schrödinger- an Austrian physicist in 1926. This model is basically a formalism or a mathematical recipe, which is based on some postulates that have no foundation in classical physics. The correctness of these postulates can be justified in terms of the correctness of the results predicted by them. According to this model, the motion of electron inside an atom could be described in terms of a mathematical function called, **wave function**, ø (Greek letter, psi). The wave functions are assumed to contain all the information about the electron and are obtained by solving a differential equation called Schrödinger wave equation (SWE). The square of the wave function $ø^2$ is a measure of the probability of finding an electron in a three dimensional space around the nucleus.

On solving the SWE for hydrogen atom we get a number of wave functions, which are characterized by three quantum numbers viz.,

- Principal quantum number, n
- Azimuthal quantum number, l
- Magnetic quantum number, m_l

These quantum numbers arise in the process of logically solving the wave equation. Every electron in an atom has a unique (different) set of quantum numbers which help to describe the three dimensional region where there is maximum probability of finding the electron. This region is called as ***atomic orbital*** or simply ***orbital***.

2.9.1 Significance of Quantum Numbers

The three quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. There is an additional quantum number which does not arise from the Schrödinger wave equation but is introduced to account for electron spin. The fourth quantum number thus help in designating the electrons present in the atom. Let us understand the significance of each of these quantum numbers.

Principal quantum number, *n*

The principal quantum number, *n* describes the energy level (or principal shell) of the electron within the atom. n can have only positive non zero integral values (i.e., n = 1,2,3,4……). This means that in an atom, the electron can have only certain energies. Thus we may say that n quantizes energy of the electron. The principal quantum number also determines the mean distance of the electron from the nucleus, i.e., its size. Greater the value of ***n***, farther is the electron from the nucleus.

Each principal shell can accommodate a maximum of $2n^2$ electrons, i.e.,

n =1 number of electrons : 2
n =2 number of electrons : 8
n =3 number of electrons : 18 and so on…

Azimuthal quantum number, *l*

The azimuthal quantum number, *l* is related to the geometrical shape of the orbital. The value of *l* may be zero or a positive integer less than or equal to (n–1) (n is the principal quantum number), i.e., *l* = 0,1,2,3…… (n–1). Different values of *l* correspond to different types of **subshells** and each subshell contains orbitals of a given shape.

***l* = 0** , corresponds to **s**-subshell and contains the orbital with **spherical shape** called as ***s* orbital**.

***l* = 1**, corresponds to **p**-subshell and contains the orbitals with a **dumb-bell shape** called as ***p*-orbitals**. There are three p-orbitals in each p-subshell

***l* = 2** , corresponds to **d**-subshell and contains the orbitals with a **cloverleaf shape** called as ***d*-orbitals.**

***l* = 3** , corresponds to **f**-subshell and contain ***f*-orbitals.** There are seven *f*-orbitals in each *f*-subshell.

The shapes of s, p and d orbitals will be discussed in the next subsection (3, 8, 2).

Magnetic quantum number, m_l

The quantum number, m_l, describes the direction or orientation of the orbital in space. The quantum number m_l may have any integral value from – *l* to + *l* . For example, for *l* = 1 ; m_l can have the values as –1,0 and 1.

Magnetic spin quantum number, m_s

The quantum number, m_s, describes the spin of the electron i.e., whether it is clockwise or anticlockwise. The quantum number, m_s does not arise while solving SWE. The clockwise and anticlockwise direction of electron spin has arbitrarily been assigned the values as +1/2 and –1/2 respectively.

To sum up, let us take an example of an electron belonging to the third shell (n = 3). This electron can be in an *s*-subshell (*l* = 0) or a *p*-subshell (*l* = 1) or a *d*-subshell (*l* = 2). If it happens to be in a *p*-subshell it may be in any of the three possible *p* orbitals (corresponding to $m_l = –1, 0 + 1$ directed along *x* , *y* or *z*– axis. And within the orbital it may have clockwise (m_s = + ½)or anti-clockwise (m_s = -½) direction of electron spin. The possible values of different quantum numbers for an electron belonging to the third shell are given in Table 2.3.

Table 2.3 : The quantum numbers for an electron belonging to the third shell

Principal quantum number, n	Azimuthal quantum number, l	Magnetic quantum number, m_l	Magnetic spin quantum number, m_s
3	0	0	+1/2
			−1/2
	1	−1	+1/2
			−1/2
		0	+1/2
			−1/2
		+1	+1/2
			−1/2
	2	−2	+1/2
			−1/2
		−1	+1/2
			−1/2
		0	+1/2
			−1/2
		+1	+1/2
			−1/2
		+2	+1/2
			−1/2

You may note here that the third shell can contain a maximum of 18 electrons and each of them, has a distinct set of four quantum numbers.

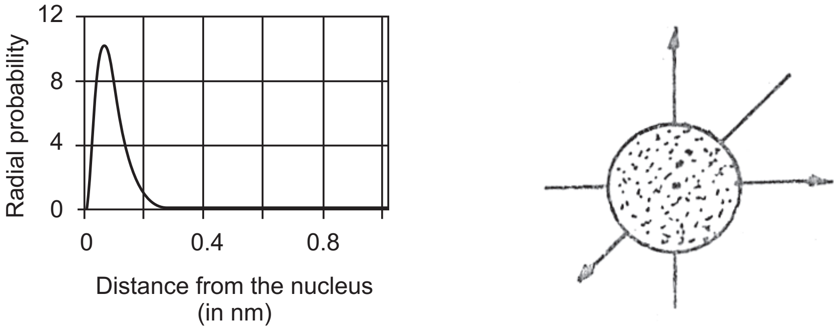
INTEXT QUESTION 2.6

1. What do you understand by a Wave Function?
2. What is the difference between an orbit and an orbital?
3. What are quantum numbers? List different quantum numbers obtained from Schrödinger Wave Equation?
4. Give the significance of the principal, azimuthal and magnetic quantum numbers?

2.9.2 Shapes of Orbitals

We have defined an orbital as "***the three dimensional region of space around the nucleus where there is maximum probability of finding the electron***". Let us try to understand the meaning of an orbital by taking the example of 1*s* orbital

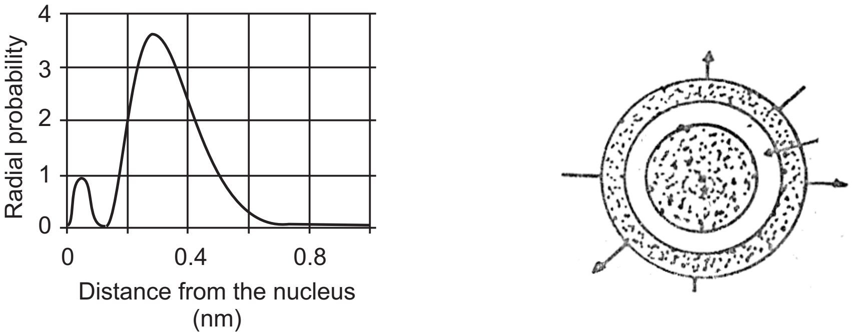
($n = 1$; $l = 0$). This can be understood in terms of a radial probability curve. Such a curve gives the variation of the probability of finding the electron as a function of distance from the nucleus. For 1s orbital the radial probability curve (Fig. 2.14 (a)) shows that the probability of finding the electron in 1s orbital increases as we move away from the nucleus and reaches a maximum at a certain distance (= 0.0529 nm or 52.9 pm for hydrogen atom) and then decreases as we go further away from it and at a certain distance it becomes close to zero. The curve shows the radial probability for a given direction. The probability would be same for all possible directions. If we put all such curves together it would give a spherical distribution of the electron probability. Since the radial probability does not become zero at any distance, we cannot specify the size of the sphere. Therefore, the orbital is represented as a boundary surface diagram, which may be thought as a region of space, which contains 95 % of the probability of finding the electron, as indicated in Fig.2.14(b). Thus the 1s orbital is represented as a sphere.



(a) (b)

Fig. 2.14: *(a) Radial probability curve for 1s orbital (b) Boundary surface diagram for 1s orbital*

Similarly, the Fig. 2.15 (a) gives the radial probability curve for a 2s orbital while the Fig. 2.15 (b) shows the boundary surface diagram for the same. You can note two things here. First you may note that for a 2s orbital the boundary surface diagram is bigger as compared to a 1*s* orbital. Secondly, the radial probability curve shows two maxima. The probability initially increases, reaches a maximum then it decreases and comes close to zero. It increases again and decreases as we



(a) (b)

Fig.3.15: *(a) Radial probability curve for 2s orbital (b) Boundary surface diagram for 2s orbital*

move further away from the nucleus. The region where the probability comes close to zero (before increasing again) is called a ***spherical node***. There are *n–l–*1 spherical nodes in an orbital.

A node is a region in space where the probability of finding the electron is close to zero.

p*- orbital :** Now when we draw the shape of a *p*-orbital (n =1 ; l =1) we get a shape as shown in the Fig. 2.16. This picture shows the shape of one of the three possible *p*-orbitals which is directed towards the z-axis; p_z. You may note that the probability picture for a p_z orbital consists of two lobes ; one along the positive z-axis and the other along the negative z-axis. Another important feature of a p-orbital is the absence of the electron probability in the XY- plane. Such a plane is called a ***nodal plane. The shapes of the three p-orbitals are given in Fig.2.17.

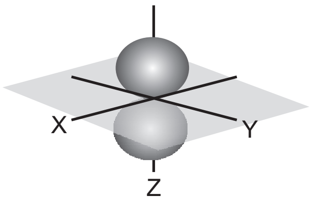


Fig. 2.16 : *A p orbital surface diagrams (Shapes)*

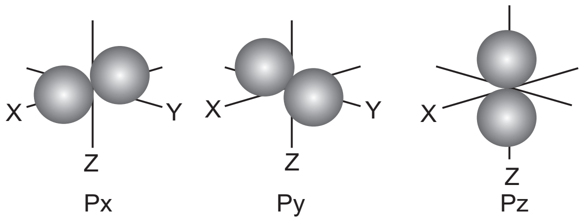


Fig. 2.17: *The boundary showing a nodal plane of the p-orbitals*

The Fig.2.18 gives the shapes of five possible *d*-orbitals. The d-orbitals also contain nodal planes. The five d- orbitals have different shapes but they all have same energies i.e., these are degenerate.

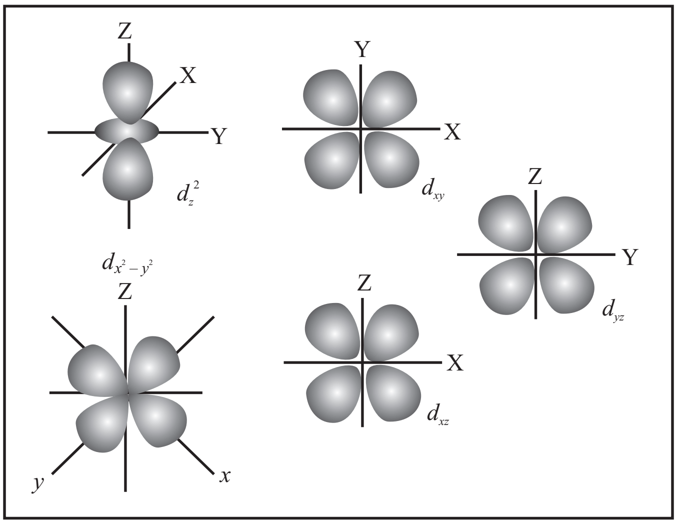


Fig. 2.18: *The boundary surface diagrams (shapes) of the five d-orbitals*

INTEXT QUESTIONS 2.7

1. What are the shapes of *s*,*p* and *d* orbitals?
2. Describe the shape of a 2*s* orbital. How is it different from that of a 1*s* orbital?
3. What do you understand by
   (i) a spherical node?
   (ii) a nodal plane?
4. How many spherical nodes will be there in 3*s* orbital ?

2.10 ELECTRONIC CONFIGURATION OF ELEMENTS

You have so far learnt that an atom consists of a positively charged nucleus surrounded by electrons present in orbitals of different shapes and sizes. These orbitals are part of different shells and sub-shells and are characterized by the three quantum numbers viz. n,l and m_l. Let us now take up the distribution of electrons in these shells and sub-shells. Such a distribution of electrons is called **Electronic Configuration** and is governed by three basic rules or principles.

2.10.1 Aufbau (or building up) Principle

This principle is concerned with the energy of the atom and states that the electrons should occupy. The electrons occupy the orbitals in such a way that the energy of atom is minimum. In other words **the electrons in an atom are filled in the increasing order of their energies**. Now, how does one know the increasing order of the orbital energies? You have learnt above that the principal quantum number determines the energy of the orbitals. Higher the value of n higher the energy. This is true only for hydrogen atom. For other atoms, we need to consider both n and l. This means that **different sub-shells in a given shell have different energies**. The order of orbital energies can be determined by the following $(n + l)$ rules.

Rule 1: An orbital with a lower value for $(n + l)$ has lower energy. For example, the 4*s* orbital $(n + l = 4+0=4)$ will be filled before a 3*d* orbital $(n + l = 3 + 2 =5)$.

Rule 2: If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of n will be filled first. For example, the 3*d* orbital $(n + l = 3+2=5)$ will be filled before a 4*p* orbital $(n + l = 4 + 1 =5)$.

Following these rules the increasing order of the orbital energies comes out to be

1*s* < 2*s* < 2*p* < 3*s* < 3*p* < 4*s* < 3*d* < 4*p* < 5*s* < 4*d* < 5*p* < 6*s*

2.10.2 Pauli's Exclusion Principle

This principle concerns the spin of electrons present in an orbital. According to the Pauli's principle, ***no two electrons can have all the four quantum numbers to be same***. For example, if a given electron in an atom has the set of four quantum numbers as $n = 2$, $l = 1$, $m_l = 1$ and $m_s = +\frac{1}{2}$ then no other electron in the atom can have the same set of quantum numbers.

As you know that an orbital is characterized by three quantum numbers so the electrons occupying a given orbital would have same values of these three quantum numbers. These electrons are distinguished in terms of their spin quantum number, m_s. Since the spin quantum number can have only two values so ***only two electrons can occupy a given orbital***. In fact this fourth quantum number was introduced through Pauli's principle only.

3.10.3 Hund's Rule

This rule concerns the distribution of electrons in a set of orbitals of the same energy, *i.e.* constituents of a subshell. According to this rule if a number of orbitals of the same sub-shell are available then the electrons distribute in such a way that each orbital is first singly occupied with same spin. For example, the six electrons in carbon distribute as

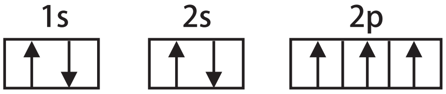
$1s^2\ 2s^2\ 2p^1_x\ 2p^1_y 2p^0_z$ and not as $1s^2\ 2s^2\ 2p^2_x\ 2p^0_y 2p^0_z$

Since electrons repel each other, they remain as far as possible from one another by occupying different orbitals.

The rules discussed above can be used to write the electronic configuration of different elements. There are two common ways of representing the electronic configurations. These are

a) **Orbital notation method**: In this method the filled orbitals are written in the order of increasing energies . The respective electrons in them are indicated as superscripts as shown in the example given below. For example, the electronic configuration of nitrogen atom (atomic number 7) is written as $1s^2 2s^2 2p^1_x\ 2p^1_y 2p^1_z$.

b) **Orbital diagram method**: In this method the filled orbitals are represented by circles or boxes and are written in the order of increasing energies. The respective electrons are indicated as arrows whose direction represents their spin. For example, the electronic configuration of nitrogen in the orbital diagram notation can be written as



Electronic configurations can also be written in a short hand form . In this method the **last completed orbital shell** is represented in terms of a noble gas. For example, the electronic configuration of lithium and sodium can be written as

Li $[He]2s^1$

Na $[Ne]3s^1$

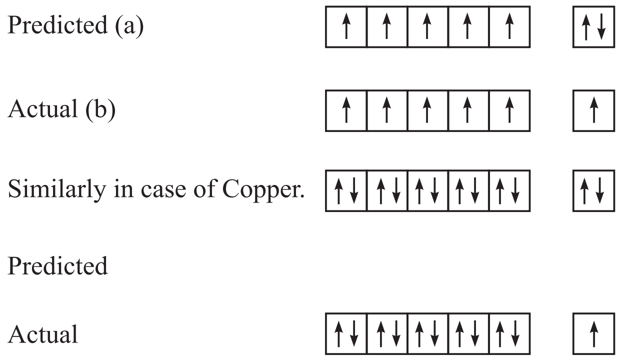
The electrons in the noble gas configuration are termed as ***core electrons*** while the ones in the outer shell are called ***valence electrons.***

2.11 STABILITY OF COMPLETELY FILLED AND HALF FILLED SUBSHELLS

Aufbau principle helps to determine the electronic configuration of an atom in a periodic table but in certain cases it fails to predict the correct electronic configuration where the energies of neighbouring subshells are quite close e.g., $4s$, $3d$; $5s$, $4d$; $4f$, $5d$ etc. There is shifting of energy due to electron-electron interactions e.g., in chromium, the Aufbau predicted configuration is $3d^4$ $4s^2$ but the actual configuration is$3d^5$ $4s^1$. Similarly in copper, the Aufbau predicted configuration is $3d^9$ $4s^2$ but the actual configuration is $3d^{10}$ $4s^1$. This is due to extra stability of half filled or completed filled orbitals.

1. Symmetry of Orbitals

We know that symmetry leads to stability. Sometimes if we add or remove the electron to make symmetrical distribution of the electrons in the orbital thus the electronic configuration become more stable e.g., the Au'fbau predicted electronic configuration of Chromium is $[Ar]$ $4s^2 3d^4$ but its actual configuration is $[Ar]$ $4s^1$ $3d^5$.

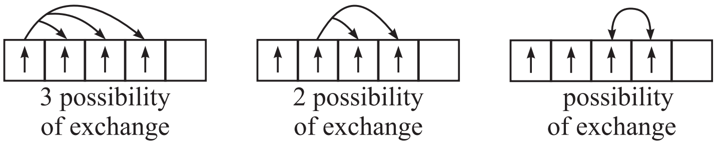


The half filled or completely filled 3d orbital is more symmetrical and more stable.

2. Exchange Energy

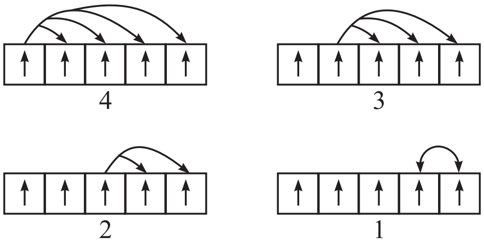
The stability of half filled and completely filled orbtails is expained by exchange energy i.e., (shifting of or exchange of electrons from one orbital to another of the same subshell). Larger the number of electrons witht the same spin larger is the exchange energy. Larger the exchange energy. Larger the exchange energy stabler is the electronic configuration. Consider the outer electron configuration of Cr which is according to Aufbau is $3d^44s^2$ but in reality it is $3d^5\ 4s^1$. In $3d^4\ 4s^2$ there are 4 electrons with same spin whereas in $3d^5\ 4s^1$ there are 6 electrons with same spin therefore exchange energy is larger in the latter case the preferred configuration of Cr is $3d^5\ 4s^1$. Consider the electronic configuration of chromium Cr – $3d^44s^2$

There are no. of possible ways by which electrons can exchange their position in $3d$ subshell.



In $3d^4$ arrangements, electron can exchange in 3 + 2 + 1, $\lambda' = 6$ ways, ie.e there are six possibility of exchange electrons with parallel spins.

In $3d^5$ electronic configuration the electron can exchange in 4 + 3 + 2 + 1 = 10 ways or there are ten possibility of exchange electrons.



Thus there is increase in exhange energy from $3d^4\ 4s^2$ to $3d^5\ 4s^1$ configuration. Greater the exchange energy, greater is the stability of this configuration.

INTEXT QUESTION 2.8

1. What do you understand by the electronic configuration of an atom?
2. What is Pauli's exclusion principle?
3. What is Aufbau principle? What are $(n + l)$ rules?
4. Which of the following orbitals will be filled first?
    i) $2p$ or $3s$ ii) $3d$ or $4s$
5. The electronic configuration of Cr is $(Ar)3d^54s^1$ not $3d^44s^2$.

WHAT YOU HAVE LEARNT

- Atoms are made up of three fundamental particles namely, electrons, protons and neutrons.

- J.J Thomson made the first attempt to describe the structure of an atom in terms of a model called **plum pudding model.** According to this atoms can be considered as a large positively charged body (pudding) in which a number of small negatively charged electrons (plums) are scattered..
- According to the Rutherford's model, the positive charge of the atom and most of its mass is contained in the nucleus and the rest of the atom is empty space which contains the negatively charged electrons.
- Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.
- The electromagnetic radiations are characterized by a number of parameters like, amplitude, wavelength, frequency, wave number and velocity.
- Hydrogen gas gives a line spectrum consisting of distinct lines suggesting the quantization of energy in hydrogen atom.
- In 1913, Niels Bohr proposed 'Planetary Model' for atom. According to the model the electrons move in definite circular paths of fixed energy around a central stationary nucleus. The electrons can change their orbits by absorbing or emitting a photon of energy (= hí) equal to the difference of the energies of the orbits.
- Bohr's model did explain for the stability of atom and the line spectrum of hydrogen. The model however was unable to explain the spectra of atoms other than hydrogen.
- Louis de Broglie, argued for the dual nature of electron and proposed that matter particles should have a wave nature. The associated wavelength is given by the formula; $\lambda = \frac{h}{mv}$ or $\lambda = \frac{h}{p}$
- This was experimentally verified by Thomson and Davisson by diffraction of electron waves passing through the crystal lattice of nickel.
- The wave-particle duality of matter led Werner Heisenberg to propose the **uncertainty principle**. According to which it is not possible to measure simultaneously both the ***position*** and ***momentum*** of a particle with a infinite precision.
- The dual nature of electron and Heisenberg's uncertainty principle led to the development of wave mechanical model.
- According to the wave mechanical model, the motion of electron inside the atom can be described in terms of a mathematical function called, wave function, ø. This wave function contains all the information about the system and can be found by solving a wave equation called Schrodinger wave equation.

- The square of the wave function, $\o^2$ is a measure of the probability of finding the electron in a certain three dimensional space around the nucleus. This region is called as ***atomic orbital*** or simply ***orbital***.
- These wave functions are characterized by three quantum numbers. These quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. Every electron in an atom has a unique set of quantum numbers.
- The principal quantum number n concerns the quantisation of the energy of the electron while the azimuthal quantum number **,** l is related to the shape of the orbital. The magnetic quantum number m_l describes the direction or orientation of the orbital in space.
- An additional quantum number, m_s is introduced to account for electron spin. This quantum number does not follow from the wave mechanical model and describes the spin of the electron.
- Different orbitals have different shapes. An s orbital is spherical; *p*-orbitals are dumb-bell shaped ; *d*-orbitals have cloverleaf shape while *f*-orbitals have a eight lobed shape.
- **Electronic Configuration.** Why are half filled and fully filled orbital more stable
- The distribution of electrons in the shells and subshells is called **Electronic Configuration.** It is governed by three rules which are Aufbau principle ; Pauli's exclusion principle and Hund's Rule of maximum multiplicity.
- According to Aufbau principle the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules.
- According to the Pauli's exclusion principle, no two electrons can have all the four quantum numbers to be same.
- While filling electrons in the orbitals of same subshell, according to Hund's rule, each orbital is first singly occupied with same spin then the pairing up takes place.
- Half filled and fully filled orbital are more stable.

TERMINAL EXERCISE

1. (a) What are the three fundamental particles that constitute an atom?

   (b) Compare the charge and mass of an electron and of a proton.

2. What do you think is the most significant contribution of Rutherford to the development of atomic structure?

3. What experimental evidence shows the dual nature of light?
   (a) Compute the energy of a FM radio signal transmitted at a frequency of 100 MHz.
   (b) What is the energy of a wave of red light with l = 670 nm?
4. In what way was the Bohr's model better than the Rutherford's model?
5. What are the drawbacks of Bohr's Model?
6. What led to the development of Wave Mechanical Model of the atom?
7. What do you understand by an orbital? Draw the shapes of s and p orbitals.
8. Explain the Hund's rule of maximum multiplicity with the help of an example.

ANSWERS TO INTEXT QUESTIONS

2.1

1 Proton is heavier than electron. The ratio of their masses is

$$= m_p/m_e = \frac{1.672\,623\times10^{-27}\,\text{kg}}{9.109\,389\times10^{-31}\,\text{kg}}$$

$$= 1836$$

2 Main constituent particles like proton, neutron and electron etc. present in the atom come in the category of fundamental particles.

3. Neutron

2.2

1 Electron, proton and neutron

2 The aim of Rutherford's experiment was to test the Thomson's plum-pudding model.

3 According to Rutherford's model for atom, the positive charge of the atom and most of its mass is contained in the nucleus. The rest of the atom is empty space which contains the much smaller and negatively charged electrons.

4 Rutherford's model was rejected because it could not explain the stability of the atom.

2.3

1. Electromagnetic radiation is a kind of energy which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.

2. The different characteristics of electromagnetic radiation are
   - i) Amplitude,
   - ii) Wavelength,
   - iii) Frequency,
   - iv) Wave number and
   - v) Velocity
3. The wave number is defined as the number of waves per centimeter. It is equal to the reciprocal of the wavelength.
4. A quantum of visible light is called photon. The energy of the quantum (or photon) is proportional to the frequency of radiation.

2.4

1. A line spectrum consists of a series of discrete lines of characteristic wavelengths while a continuous spectrum contains a broad band of radiations containing all possible wavelengths in the range i.e., the wavelengths of the radiation varies continuously.
2. The main postulates of Bohr's model are
   - i) The electrons move in a definite circular paths called as **stationary orbits** or **stationary states** around a central stationary nucleus.
   - ii) The electrons can change their orbits by absorbing or emitting a photon of energy (= hí) equal to the difference of the energies of the orbits.
   - iii) The angular momentum of the electron is quantised.
3. The energy of a Bohr's orbit increases with an increase in the value of the principal quantum number, n. In fact it becomes lesser and lesser negative.

2.5

1. The wave-particle duality refers to the fact that light and the material particles like electrons could sometimes behave as a particle and as a wave at other times.
2. The wave nature of electron was established by the diffraction of electron waves by the crystal lattice of nickel.
3. Mass of the electron = 9.1×10^{-31} kg

   Speed or Velocity = 100 km s^{-1} = 10^5 m s^{-1}

Using equation , the wavelength associated with the electron will be

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.1 \times 10^{-31} \text{ kg})(10^{5} \text{ m s}^{-1})} = 7.28 \times 10^{-9} m$$

4. According to Heisenberg's Uncertainty Principle it is not possible to measure both the *position* and *momentum* of a particle with any degree of certainity. More accurately we measure a particle's position, the less accurately we are able to measure it's momentum, and vice versa.

2.6

1. It is a mathematical function that describes the motion of an electron inside the atom. It contains all the information about the system and can be found by solving a wave equation called Schrödinger wave equation.
2. An orbit refers to definite circular paths of fixed energy around a central stationary nucleus while an orbital refers to the three dimensional region of space around the nucleus where there is a probability of finding the electron.
3. The quantum numbers are integers that characterize the wavefunctions. These are obtained in the process of solving Schrödinger wave equation and every electron in an atom has a different set of quantum numbers. The three quantum numbers obtained from Schrödinger Wave Equation are
   (i) The principal quantum number, n
   (ii) Azimuthal quantum number, l and
   (iii) The magnetic quantum number m_l
4. The principal quantum number, n is concerned with the energy of the electron in a shell. The quantum number l is related to the geometrical shape of the orbital and the quantum, number, m_l describes the orientation of the orbital in space.

2.7

1. s orbital : spherical;
   p orbitals : dumb-bell shaped ;
   d orbitals : cloverleaf shaped.
2. The 2s orbital is spherical in shape similar to the 1s orbital . However there are two differences. Firstly, the size of a 2s orbital is bigger as compared to a 1s orbital and secondly, it contains a spherical node.
3. (i) It is a spherical region of zero probability in an *s* orbital (other than 1*s*).

(ii) It is a planar region in an orbital (other than *s* orbitals)where the probability of finding the electron is zero.

4. The 3s orbital will have **two** spherical nodes.

4. Because half filled d-orbital is more stable as compared to partially filled orbital.

2.8

1. The distribution of electrons in the shells and subshells of an atom is called *Electronic Configuration.*
2. Pauli's principle states that in an atom no two electrons can have same set of the four quantum numbers.
3. Aufbau principle states that the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules.

   There are two ($n+l$) rules. These are

   An orbital with a lower value for $(n + l)$ is filled first.

   If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of n will be filled first
4. (i) 2p : $(n + l)$ for $2p = 2 + 1 = 3$; for $3s$ $(n + l) = 3 + 0 = 3$; Rule 2

   (ii) $4s$: $(n + l)$ for $4s = 4 + 0 = 4$; for $3d$ $(n + l) = 3 + 2 = 5$; Rule 1

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3

PERIODIC TABLE AND PERIODICITY IN PROPERTIES

We have seen different heaps of onions and potatoes at vegetable shop. Imagine, they are lying mixed and you want to buy 1 kg of onion. What will happen? You will have to wait for long to sort that and then weigh them. When you possess a variety of material substances, you have to keep them classified for an easy access and quick use. You cannot afford to mix clothes with eatables, cosmetics or books. Classification assures you that your eatbles are in the kitchen, books on the study table or rack and your cosmetics are on the dressing table. Shopkeepers, business houses, storekeepers, administrators, managers, information technology experts and scientists etc. have to keep their materials duly classified.

Chemists faced a similar problem when they were to handle a large number of elements. The study of their physical and chemical properties and keeping a systematic record of them had been a great challenge to chemists. Classification of elements finally could be possible due to pioneering work of a few chemists. In the present lesson we shall discuss the need, genesis of classification and periodic trends in physical and chemical properties of elements.

OBJECTIVES

After reading this lesson, you will be able to:

- recongise the need for classification of elements;
- recall the earlier attempts on classification of elements;
- define modern periodic law;
- name the elements with atomic number greater than 100 according to IUPAC nomenclature;

- co-relate the sequence of arrangements of elements in periodic table with electronic configuration of the elements;
- recall the designations of the groups (1-18) in the periodic table;
- locate the classifiction of elements into s-, p-, d- and f- blocks of the periodic table; and
- explain the basis of periodic variations of
  (a) atomic size
  (b) ionic size
  (c) ionization enthalpy
  (d) electron gain enthalpy within a group or a period.
  (e) valence

3.1 EARLY ATTEMPTS

Attempts were made to classify elements ever since the discovery of metals or may be even earlier. J.W. Dobereiner in 1817 discovered that when closely related elements are grouped in a set of three, the atomic weight of the middle element was almost the arithmetical mean of the other two elements in that group e.g.,

Element	Lithium	Sodium	Potassium
Atomic weight	6.94	22.99	39.10
Mean atomic weight	------	23.02	-------

He called such a group of three elements a triad. He could group only a few elements due to lack of knowledge of correct atomic weights of the elements at that time.

In 1863, J.A.R. Newlands, developed a system of classification of elements and entitled it as **Law of Octaves**. He arranged the elements is such a way that every eighth element had similar properties, like the notes of music. The law could not apply to a large number of known elements. However, the law indicated very clearly the recurrence of similar properties among the arranged elements. Thus the periodicity was visualised for the first time in a meaningful way.

Periodicity: Re-occurrence of properties after regular intervals.

More significant results were obtained when Lother Meyer's work reflecting the periodicity was found to be based on physical properties of the elements. He clearly showed that certain propertics showed a periodic trend.

3.2 MENDELEEV'S PERIODIC TABLE

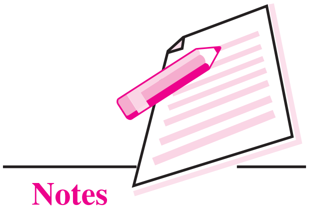
In 1869, Mendeleav, a Russian Chemist made a thorough study of the relation between the atomic weights of the elements and their physical and chemical properties. He then constructed a table in which elements were arranged in order of their increasing atomic weights. It was also found that every eighth element had properties similar to that of the first element. Thus, there was a periodic occurrence of elements with similer properties.

One of the most striking applications of Mendeleev's classification of elements was that in his periodic table (Table 3.1) he left gaps for elements which were yet to be discovered. He also predicted the properties of these elements. However, Mendeleev's periodic table did not provide any place for isotopes and noble gases which were discovered later on.

Table 3.1 Mendeleev's Table of 1871

Group	**I**		**II**		**III**		**IV**		**V**		**VI**		**VII**		**VIII**		
Oxide	R_2O		RO		R_2O_3		RO_2		R_2O_5		RO_3		R_2O_7		RO_4		
Hydride	RH		RH_2		RH_3		RH_4		RH_3		RH_2		RH				
Periods ↓	A	B	A	B	A	B	A	B	A	B	A	B	A	B	Transition series		
1	H 1,008																
2	Li 6.939		Be 9.012		B 10.81		C 12.011		N 14.007		O 15.999		F 18.998				
3	Na 22.99		Mg 24.31		Al 29.98		Sl 28.09		P 30.974		S 32.06		Cl 35.453				
4 First series:	K 39.102		Ca 40.08			Sc 44.96		Ti 47.90		V 50.94		Cr 50.20		Mn 54.94	Fe 55.85	Co 58.93	Ni 58.71
Second series:		Cu 63.54		Zn 65.37	Ga 69.72		Ge 72.59		As 74.92		Se 78.96		Br 79.909				
5 First series:	Rb 85.47		Sr 87.62			Y 88.91		Zr 91.22		Nb 92.91		Mo 95.94		Tc 99	Ru 101.07	Rh 102.91	Pd 106.4
Second series:		Ag 107.87		Cd 112.40	In 114.82		Sn 118.69		Sb 121.75		Te 127.60		I 126.90				
6 First series:	Cs 132.90		Ba 137.34			La 138.91		Hf 178.49		Ta 180.95		W 183.85			Os 190.2	Ir 192.2	Pt 195.09
Second series:		Au 196.97		Hg 200.59	Tl 204.37		Pb 207.19		Bi 208.98								

The extent of knowledge regarding the chemical properties of the elements and his insight into the system of periodicty possessed by the elements under certain arrangement have no parallel in the history of chemistry. This work laid strong foundation of the fundamental principles of the periodic law. One of his most important conclusions was that the elements if arranged according to their atomic weights, exhibit an evident systematic reoccurence of properties (periodicity of properties) and even the properties of some elements were listed much before their discovery. Mendeleev's periodic Table (Table 3.1) was quite useful till the discovery of atomic number. There existed certain inherent defects which opposed the system.



3.3 MODERN APPROACH

Atomic number was discovered in 1913 by a team lead by Mosely. The periodic table based on atomic number is termed as Modern Periodic Table. Moseley arranged all the elements according to increasing atomic number and showed that the properties of elements are periodic function of their atomic numbers.

Modern periodic law: The properties of the elements are periodic function of their atomic numbers.

3.4 LONG FORM OF PERIODIC TABLE

The arrangement of elements in the long form of periodic table is a perfect matching of electronic configuration of the elements on one hand and physical and chemical properties of the elements on the other. Some important considerations of the modern atomic structure applied to the classification of elements are discussed below:

(i) An atom loses electron(s) from or gains electron(s) in the outermost shell of an atom during a chemical reaction.

(ii) The sharing of an electron or electrons by an atom with other atom or atoms is largely through the outer most shell. Thus the electrons in the outermost shell of an atom largely determine the chemical properties of the elements.

We may therefore conclude that the elements possessing identical outer electronic comfiguration should possess similar physical and chemical properties and therefore they should be placed together for an easy and systematic study.

Keeping in mind the reasoning given above, when all the known elements are arranged in a table according to their increasing atomic number, the properties of the elements show periodicity (reappear at definite intervals). The periodicity is shown in Table in 3.2.

3.5 STRUCTURAL FEATURES OF THE LONG FORM OF PERIODIC TABLE

(i) In this table there are 18 vertical columns called **GROUPS**. They are numbered from 1 to 18. Every group has a unique configuration.

(ii) There are seven horizontal rows. These rows are called **PERIODS**. Thus the periodic table has seven periods, numbered from 1 to 7.

(iii) There are a total of 114 elements known to us till today. Of all the known elements 90 are naturally occurring and others are made through nuclear transformations or are synthesised artificially. Either way they are **Man-made Elements**, but you will find the term specifically applied to **transuranic elements** (elements listed after uranium) only.

(iv) First period consists of only two elements (very short period). Second and third periods consist of only eight elements each (short periods). Fourth and fifth periods consist of 18 elements each (long periods). Sixth period consists of 32 elements (long period). Seventh period is yet incomplete and more and more elements are likely to be added as the scientific research advances.

(v) There are also nick names given to the groups or a cluster of groups on the basis of the similarity of their properties, as given below:

Group 1 elements except hydrogen, are called **Alkali Metals**

Group 2 elements are called **Alkaline Earth Metals.**

Group 3 to 12 elements are called **Transition Metals**.

Group 16 elements are called **Chalcogens**

Group 17 elements are called **Halogens**

Group 18 elements are called **Noble Gases**.

Apart from what has been said above elements with atomic numbers 58 to 71 are called *Lanthanoids* – or Inner Transition elements (First series). Elements from atomic numbers 90 to 103 are called actinoids – Inner Transition elements (Second series). All elements except transition and inner transition elements are also collectively called **Main Group Elements.**

3.6 POSITION OF METALS, NON-METALS AND METALLOIDS

In order to locate the position of metals, non-metals and metalloids in the periodic table, you may draw a diagonal line joining the element boron (At. no. 5) with that of tellurium (At. no. 52) and passing through silicon and arsenic. Now we are in a position to make the following observations.

(i) The elements above the diagonal line and to the far right are non-metals (except selenium which shows slightly metallic character also). The non-metallic character is more marked the farther an element is from the diagonal line and up.

(ii) The elements below the diagonal line and to the left are metals. (Hydrogen is a non-metal and is an exception)The metallic character is more marked the farther an element is from the diagonal line and down. All lanthanoids and actinoids are metals.

(iii) The elements along the diagonal line are metalloids and possess the characteristics of metals as well as of non-metals. In addition germanium, antimony and selenium also show the characteristics of metalloids.

GROUPS

REPRESENTATIVE ELEMENTS

TRANSITION ELEMENTS

20 ← Atomic number (Z)
Calcium ← Name of element
Ca ← Symbol of element
40.08 ← Atomic weight or mass number (A)

PERIODS	Group IA 1	2	IIIA 3	IVA 4	VA 5	VIA 6	VIIA 7	VIIIA 8	9	10	IB 11	IIB 12	13	14	15	16	17	18 Noble Gases	
P 1	1 Hydrogen H 1.0079	IIA 2											IIIB 13	IVB 14	VB 15	VIB 16	VIIB 17	2 Helium He 4.00260	2
E 2	3 Lithium Li 6.941	4 Beryllium Be 9.01218											5 Baron B 10.81	6 Carbon C 12.011	7 Ntrogen N 14.0067	8 Oxygen O 15.9994	9 Fluorine F 18.9984	10 Neon Ne 20.179	2 8
R 3	11 Sodium Na 22.9898	12 Magnesium Mg 24.305											13 Aluminium Al 26.9815	14 Silicon Si 28.0855	15 Phosphorus P 30.9738	16 Sulfur S 32.06	17 Chrorine Cl 35.453	18 Argon Ar 39.948	2 8 8
I 4	19 Potassium K 39.0.983	20 Calcium Ca 40.08	21 Scandium Sc 44.9559	22 Titanium Ti 47.88	23 Vandadium V 50.9415	24 Chromium Cr 51996	25 Manganese Mn 54.9380	26 Iron Fe 55.847	27 Cobalt Co 58.9332	28 Nickel Ni 58.69	29 Copper Cu 63.546	30 Zinc Zn 65.39	31 Gallium Ga 69.72	32 Germanium Ge 72.59	33 Arsenic As 74.9216	34 Slenium Se 78.96	35 Bromine Br 79.904	36 Krypton Kr 83.80	2 8 18 8
O 5	37 Rubidium Rb 85.4678	38 Strontium Sr 87.62	39 Yttrium Y 88.9059	40 Zirconium Zr 91.224	41 Niobium Nb 92.9064	42 Molybdenum Mo 95.94	43 Technetium Tc 98.91	44 Ruthenium Ru 101.07	45 Rhoidium Rh 102.906	46 Palladium Pd 106.42	47 Silver Ag 107.868	48 Cadmium Cd 112.41	49 Indium In 114.82	50 Tin Sn 118.71	51 Antimony Sb 121.75	52 Tellurium Te 127.60	53 Iodine I 126.905	54 Zenon Xe 131.29	2 8 18 18 8
D 6	55 Cesium Cs 132.905	56 Barium Ba 137.33	57 Lanthanum La 138.906	72 Hafnium Hf 178.49	73 Tantalum Ta 180.948	74 Wolfram (Tungsten) W 183.85	75 Rhenium Re 186.207	76 Osmium Os 190.2	77 Indium Ir 192.22	78 Platinum Pt 195.08	79 Gold Au 196.967	80 Mercury Hg 200.59	81 Thallium Tl 204.383	82 Lead Pb 207.2	83 Bismuth Bi 208.980	84 Polorium Po (209)	85 Astatine At (210)	86 Radon Rn (222)	2 8 18 32 18 8
S 7	87 Francium Fr (223)	88 Radium Ra 226.025	89 Actinium Ac 227.028	104 unnil- quadium Unq (261)	105 Unnil- pentium Unp (262)	106 Unnil- hexium Unh (263)	107 Unnil- septium Uns (262)	108 Unnil- octium Uno (265)	109 Unnil- ennium Une (266)										2 8 18 32 32 8

Lanthanide Series 6*	58 Cerium Ce 140.12	59 Praseo- dymium Pr 140.908	60 Neodymium Nd 144.24	61 Promethium Pm (145)	62 Samarium Sm 150.36	63 Europium Eu 151.96	64 Gadolinium Gd 157.25	65 Terbium Tb 158.925	66 Dysprosium Dy 162.50	67 Holmium Ho 164.930	68 Erbium Er 167.26	69 Thulium Tm 168.934	70 Ytterbium Yb 173.04	71 Lutetium Lu 174.967	2 8 18 32 9 2
Actinide Series 7**	90 Thorium Th 232.038	91 Protactinium Pa 231.03	92 Uranium U 238.029	93 Neptunium Np 237.048	94 Plotonium Pu 239	95 Americium Am (243)	96 Curium Cm (247)	97 Berkelium Bk (247)	98 Californium Cf (252)	99 Einsteinium Es (252)	100 Fermium Fm (257)	101 Mendelevium Md (256)	102 Nobelium No (259)	103 Lawrencium Lr (260)	2 8 18 32 32 9 2

INTEXT QUESTIONS 3.1

1. Classify the elements of group 14, 15 and 16 into metals, non-metals and metalloids.
2. Compare the metallic character of aluminium and potassium.
3. Name the group number for the following type of clements
   (i) Alkaline earth metals
   (ii) Alkali metals
   (iii) Transition metals
   (iv) Halogens
   (v) Noble gases.
4. Name five man made elements.

3.7 CATAGORISATION OF ELEMENTS INTO '*s*', '*p*', '*d*', AND '*f*' BLOCKS

Grouping of elements in the periodic table can be done in another way also, which is more related to their electronic configuration. Under this categorisation, the location of the **differentiating electron** (the last electron) is most important. If, for example, the electron has gone to '*s*-subshell', the elements will fall in '*s*-block' and if the last electron goes to '*p*-subshell', then the element will belong to *p*-block. Similarly if the defferentiating electron enters the '*d*-subshell', of an atom, then the elements comprising all such atoms will belong to *d*-block.

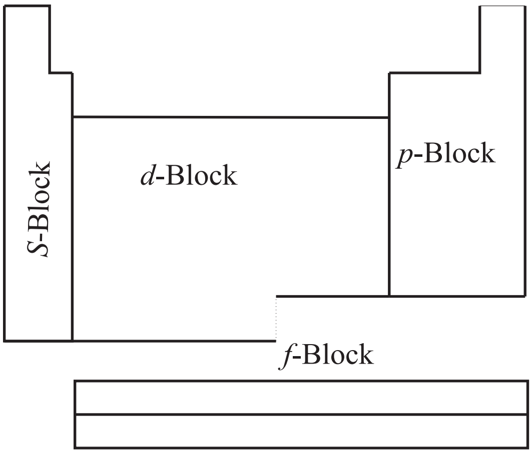


Fig. 3.1 : *Blockwise categorization of elements.*

There are minor exceptions in Mn and Zn configurations. You will study more about the reasons for such exceptions in Lesson 23.

The grouping of elements explained above can be related to the type of elements discussed earlier:

(i) *s*-block elements: All alkali metals and alkaline earth metals.

(ii) *p*-block elements: All elements of group number 13 to group number 18.

(iii) *d*-block elements: All elements from group no. 3 to group no. 12 except Lanthanoids and Actinoides.

(iv) *f*-block elements: Lanthanoids (atomic number 58 to 71) and Actinoids (atomic number 90 to 103)

This is shown in Fig. 3.1.

Nomenclature of Elements with Atomic Numbers greater than 100

The naming of the new elements was earlier left entirely to its discoverer. The suggested names were then later ratified by IUPAC. But due to certain disputes that arose over the original discoverer of some of the elements of atomic numbers greater than 104, the IUPAC in 1994 appointed a Commission on Nomenclature of Inorganic Chemisty (CNIC). After consultation with the Commission and the chemists around the world, the IUPAC in 1997 recommeded a nomenclature to be followed for naming the new elements with atomic numbers greater than 103 until their names are fully recognised.

- The names are derived directly from the atomic number of the element using the following numerical roots for 0 and numbers 1–9.

  0 = nil
  1 = un
  2 = bi
  3 = tri
  4 = quad
  5 = pent
  6 = hex
  7 = sept
  8 = oct
  9 = enn

- The roots are put together in the order of the digits which make up the atomic number and 'ium' is added at the end.

- Names, thus derives, and the IUPAC approved names of some elements with atomic numbers greater than 103 are listed in Table 3.3.

Table 3.3 : Nomenclature of elements with atomic numbers greater than 103

Atomic number	Name	Symbol	IUPAC approved name	IUPAC symbol
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	Ununnillium	Uun	–	–
111	Unununnium	Uuu	–	–
112	Ununbium	Uub	–	–
113	Ununtrium	Uul	–	–
114	Ununquadium	Uuq	–	–
115	Ununpentium	Uup	–	–

3.8 PERIODICITY IN ATOMIC PROPERTIES

The term periodicity is used to indicate that some characteristic properties occur in the periodic table after definite intervals, however with a varying magnitude. Thus after starting from a certain point on the periodic table, we are almost certain that the movement in a particular direction will show steady increase or decrease of a said property.

3.9 ATOMIC SIZE

In homonuclear diatomic molecules the distance from the centre of one nuclus to the centre of another nucleus gives the bond length and half of this bond length is atomic radius (Fig. 3.2). The first member of each period is the largest in size. Thus we can say that the group 1 atom are the largest in their respective horizontal rows. Similarly, atoms of group 2 elements are large but are definitely smaller than the corresponding atoms of group 1. This is due to the reason that the extra charge on the nucleus draws the electrons inward resulting in smaller size for the atoms under reference. This trend of decrease in size of atoms, continues from left to right. An example is shown in Fig. 3.3. However, there may be some exceptions and there will be other reasons to explain them.

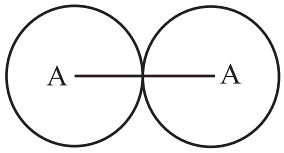


Fig 3.2 : *Atomic radius* = $\frac{1}{2} d_{A-A} = r$

Fig. 3.3: *From left to right, size of atoms decrease in the perodic table*

In going down the group of elements (in any particular column) the atomic size increases at each step.

This increase may be explained in terms of a new electron shell being added, when we pass from one element to another in a group.

3.10 IONIC SIZE

An ion is formed when an atom undergoes a loss or gain of electrons.

$$M\ (g) \longrightarrow M^+\ (g) + e^- \qquad \text{(cation formation)}$$

$$M\ (g) + e^- \longrightarrow M^-\ (g) \qquad \text{(anion formation)}$$

A cation is formed when an atom loses the most loosely bound electron from its outermost shell. The atom acquires a positive charge and becomes an ion (a cation). A cation is smaller than its atom. On the removal of an electron, the positive charge of the nucleus acts on lesser number of electrons than in the neutral atom and thus greater pull is exerted by the nucleus, resulting in a smaller size of the cation.

An anion is bigger than its atom because on receipt of an electron in the outermost orbit the number of negative charges increase and it outweighs the positive charges. Thus the hold of the nucleus on the shells decrease resulting in an increase in the size of the anion.

A cation is always smaller than its atom and an anion is always bigger than its atom e.g. Na^+ is smaller than Na, Cl^- is bigger than Cl.

- In the main groups, the ionic radii increase on descending the group. *e.g.*, $Li^+ = 0.76$ Å, $Na^+ = 1.02$ Å, $K^+ = 1.38$ Å, etc. It is due to the addition of extra shell at each step.
- There is a decrease in the ionic radii of the positive ions on moving from left to right across a period in the periodic table. e.g., $Na^+ = 1.02$ Å, $Mg^{2+} = 0.72$ Å, $Al^{3+} = 0.535$ Å, etc. It is due to the increase in the number of charges on the nucleus and also due to the increase in the charge on the ion.
- The ionic radii of the negative ions, also decrease on moving from left to right across a period. e.g., $O^{2-} = 1.40$ Å, $F^- = 1.33$ Å, etc. This is partly due to increase in the number of charges on the nucleus and also due to the decreasing charge on the ion.

INTEXT QUESTION 3.2

1. Write the names of the elements with atomic numbers 105, 109, 112, 115 according to IUPAC nomenclature.
2. Arrange the following in the order of increasing size
   Na^+, Al^{3+}, O^{2-}, F^-
3. How does the size of atoms vary from left to right in a period and on descending a group in the periodic table?

3.11 IONIZATION ENTHALPY

Ionization Enthalpy is the energy required to remove the most loosely bound electron from an isolated atom in the gaseous state for one mole of an element. It is expressed in kJ mol^{-1} (kilojules per mole).

$$M(g) + IE \rightarrow M^+(g) + e^-$$

As we move from left to right in the periodic table, there is a nearly regular increase in the magnitude of the ionization enthalpy of elements.

Similarly, on moving down a group the magnitude of the ionization enthalpy indicates a regular decline. The ionization enthalpy of the first member of any group is the highest within that group and the ionization enthalpy of the last member in the same group, is the least. This is shown in table 3.4.

Table 3.4: First ionization enthalpies of the elements (in kJ mol^{-1})

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H • 1311																	He • 2372
2	Li • 520	Be • 899											B • 801	C • 1086	N • 1403	O • 1410	F • 1681	Ne • 2081
3	Na • 496	Mg • 737											Al • 577	Si • 786	P • 1012	S • 999	Cl • 1255	Ar • 1521
4	K • 419	Ca • 590	Se • 631	Ti • 656	V • 650	Cr • 652	Mn • 717	Fe • 762	Co • 758	Ni • 736	Cu • 745	Zn • 906	Ga • 579	Ge • 760	As • 947	Se • 941	Br • 1142	Kr • 1351
5	Rb • 403	Sr • 549	Y • 616	Zr • 674	Nb • 664	Mo • 685	Te • 703	Ru • 711	Rn • 720	Pd • 804	Ag • 731	Cd • 876	In • 558	Sn • 708	Sb • 834	Te • 869	I • 1191	Xe • 1170
6	Cs • 376	Ba • 503	La • 541	Hf • 760	Ta • 760	W • 770	Re • 759	Os • 840	Ti • 900	Pt • 870	Au • 889	Hg • 1007	Tl • 589	Pb • 1007	Bi • 589	Po • 715	At • 703	Rn • 813
7	Fr	Ra 912	Ac 1037															

The variation in the magnitude of ionization enthalpy of elements in the periodic table is mainly dependent on the following factors:

(a) The size of the atom

(b) The magnitude of the nuclear charge on the atom,

(c) The extent of screening

(d) The type of orbital involved (s, p, d, or f).

- In small atoms, the electrons are tightly held whereas in large atoms the electron are less strongly held. Thus, the ionization enthalpy decreases as the size of the atom increases.
- When an electron is removed from an atom, the effective nuclear charge, i.e., the ratio of the number of charges on the nucleus to the number of electrons, increases. As a result the remaining electrons come closer to the nucleus and are held more tightly. The removal of a second electron, therefore, requires more energy. e.g., Mg^+ is smaller than the Mg atom The remaining electrons in Mg^+ are more tightly held. The second ionisation enthalpy is, therefore, more than the first ionisation enthalpy.
- Since the orbitals (*s, p, d* and *f*) have different shapes, the ionization enthalpy depends on the type of electrons removed. e.g. an electron in an *s* orbital is more tighly held as compared to an electron in a *p* orbital. It is because an *s* electron is nearer to the nucleus as compared to a *p* electron. Similarly a *p*-electron is more tightly held than a *d*-electron, and a *d*-electron is more tightly held than a *f*-electron. If all other factors are equal, the ionization enthalpies are in the order $s > p > d > f$.

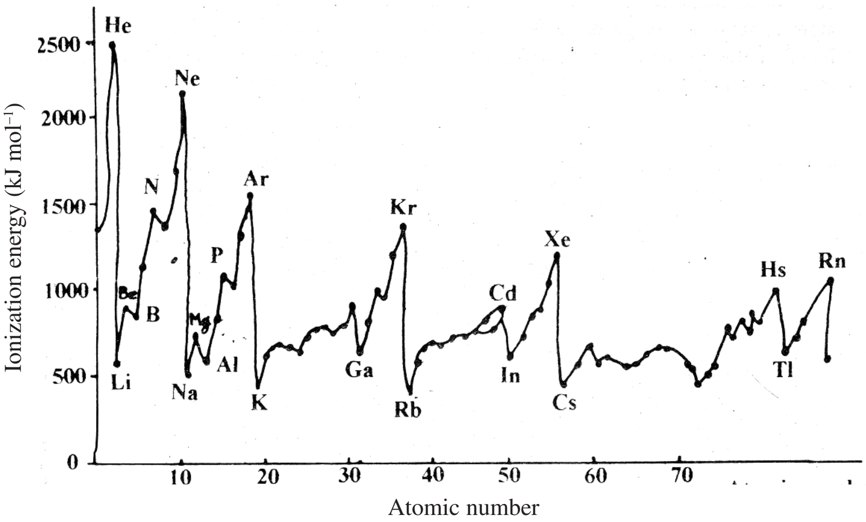


Fig 3.4 : *Variation of ioniztion enthalpy of elements.*

These factors taken together contribute largely to decide the extent of the force of attraction between the nucleus and the electrons around it. The resultant of these factors thus determine the magnitude of ionization enthalpy of any element. You can see the variation in the magnitude of the ionization enthalpy of elements with atomic number in the Fig. 3.4.

It is clear from Fig. 3.4 that

(i) the metals of group 1 (Li, Na, K, Rb, etc.) have the lowest ionization enthalpies in their respective periods.

(ii) the noble gases (He, Ne, Ar, Kr, Xe and Rn) have the highest ionization enthalpies in their respective periods. It is because the energy required to remove an electron from a stable fully filled shell is very large.

(iii) The values of ionization energies do not increase smoothly. e.g. the first ionization enthalpy of B (boron) is lower than that of Be (beryllium); the ionization enthalpy of Al (aluminium) is lower than that of Mg (magnesium); the first ionization enthalpy of O(oxygen) is lower than that of N (nitrogen). It can be explained as follows.

- The first ionization enthalpies of Be and Mg are higher than those of their preceding elements because the elecrons are removed from the fully filled s-orbitals.
- The first ionization enthalpy of N is higher than that of O because from N, the electron is to be removed from a half-filled *p*-orbitals

Ionization enthalpy is the energy required to remove the most loosely bound electron form an atom (in the gaseous state) for one mole of an element. It is an absolute value and can be determined experimentally.

3.12 ELECTRON GAIN ENTHALPY

Every atom, in general, has a tendency to gain or loose electrons in order to acquire a noble gas configuration. The atom which have five, six or seven electrons in their outermost shell show tendency to accept electrons and attain the nearest noble gas configuration. Halogens, for example, have seven electrons in their outermost orbit. Thus they show a tendency to accept one more electron and attain the nearest noble gas configuration. The energy change (ΔE) for this process is called **electron gain enthalpy** of that atom.

Electron gain enthalpy is the energy released for one mole of neutral atoms in a gaseous state when electron is accepted by each atom.

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

where X represents an atom.

$$\mathrm{Cl\ (g)} + e^- \longrightarrow \mathrm{Cl^-\ (g)}: \Delta E = -349\ \mathrm{kJ\ mol^{-1}}$$

The negative value shows release of energy and hence tendency to greater stabilisation. The electron gain enthalpy becomes more in negative from left to right in a period. This is because it is easier to add an electron to a smaller atom since the added electron would be closer to the positively charged nucleus. Halogens release maximum energy when they accept an electron. On the other hand, metals do not accept electrons and show a high positive value for ΔE. Thus electron gain enthalpy can be positive or negative.

Electron gain enthalpies becomes less in negative as we go down the group showing that the electropositive character of the atoms increases. This is because the size of the atom increases down the group and the electron added goes to the higher shells. Electron affinity values for some elements are shown in table 3.5, along with their position in the periodic table. The electron gain enthalpy of chlorine is more in negative value as compared to that of fluroine. This is due to the small size of the F atom. As the electron approaches the small F atom, it expriences a repulsion from other electrons.

Table 3.5: Electeron gain enthalpy in kJ mol^{-1}

	Group							
Period	**1**	**2**	**13**	**14**	**15**	**16**	**17**	**18**
1	H –73							He +98
2	Li –59.6	Be (0)	B –26.7	C –154	N –7	O –111	F –328	Ne +116
3	Na –53						Cl –349	Ar + 96
4	K –48						Br –325	Kr + 96
5	Rb –47						I –295	Xe + 77
6								Rn + 68

3.13 ELECTRONEGATIVITY

It is an indicator of the extent of attraction by which electrons of the bond pair are attracted by an atom linked by this bond. The value of electronegativity is assigned arbitrarily to one atom such as hydrogen. Then the value of electronegativity is assigned to all other atoms with respect to hydrogen. One such scale is the **Pauling Scale of electronegativity** (Table 3.6).

Electronegativity is defined as a measure of the ability of an atom to attract the electron pair in a covalent bond to itself.

In a homonuclear diatomic molecule such as hydrogen (H_2) or fluorine (F_2), the electron pair of the covalent bond in each molecule experiences equal attraction by each atom. Thus none of the two atoms is able to shift the bond pair of electrons to itself. However in a heteronuclear diatomic molecule, the bond pair electrons get shifted towards the atom which is more electronegative than the other. For example, in HF or HCl the bond pair of electrons are not shared equally but the more electronegative atom F or Cl is able to shift the bond pair towards itself, resulting in the polarization of the molecule.

A large difference between electronegativities of the two atoms indicates highly ionic character of the bond between them, for example in Cs^+F^-. On the other hand, zero difference in the electronegativities between the two atoms indicates that the percentage ionic character is zero. Therefore the molecule is purly covalent e.g. H_2, Cl_2, N_2 etc.

Table 3.6 : Electronegativities of elements on Pauling scale.

Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Se	Ge	As	Sc	Br
0.8	1.0	1.3	1.7	1.8	2.1	2.5
Cs	Ba					
0.7	0.9					

The most electronegative elements have been placed on the farthest right hand upper corner (noble gases are not included). The value of electronegativity decreases as we go down in any group and increases from left to right in the period. Thus fluorine is the most electronegative and caesium is the least electronegative element. (We have not considered Francium being radioactive).

3.14 CONCEPT OF VALENCE OR VALENCY

You that that different elements have different number of electrons in the outermost or the valence shell. These electrons in the outermost shell are known as valence electrons. **The number of valence electrons determines the combining capacity of an atom in an element.** Valence is the number of chemical bonds that an atom can form with univalent atoms. Since hydrogen is a univalent atom, the valence of an element can be taken by the number of atoms of hydrogen with which one atom of the element can combine. For example, in H_2O, NH_3, and CH_4 the valencies of oxygen, nitrogen and carbon are 2, 3 and 4, respectively.

The elements having a completely filled outermost shell in their atoms show little or no chemical activity. In other words, their combining capacity or valency is zero. The elements with completely filled valence shells are said to have stable electronic configuration. The main group elements can have a maximum of eight electrons in their valence shell. This is called **octet rule**; you will learn more about it in lesson 7. You will learn that the combining capacity or the tendency of an atom to react with other atoms to form molecules depends on the ease with which it can achieve octet in its outermost shell. The valencies of the elements can be calculated from the electronic configuration by applying the octet rule.

- If the number of valence electrons is four or less then the valency is equal to the number of the valence electrons.
- In cases when the number of valence electrons is more than four then generally the valency is equal to 8 minus the number of valence electrons.

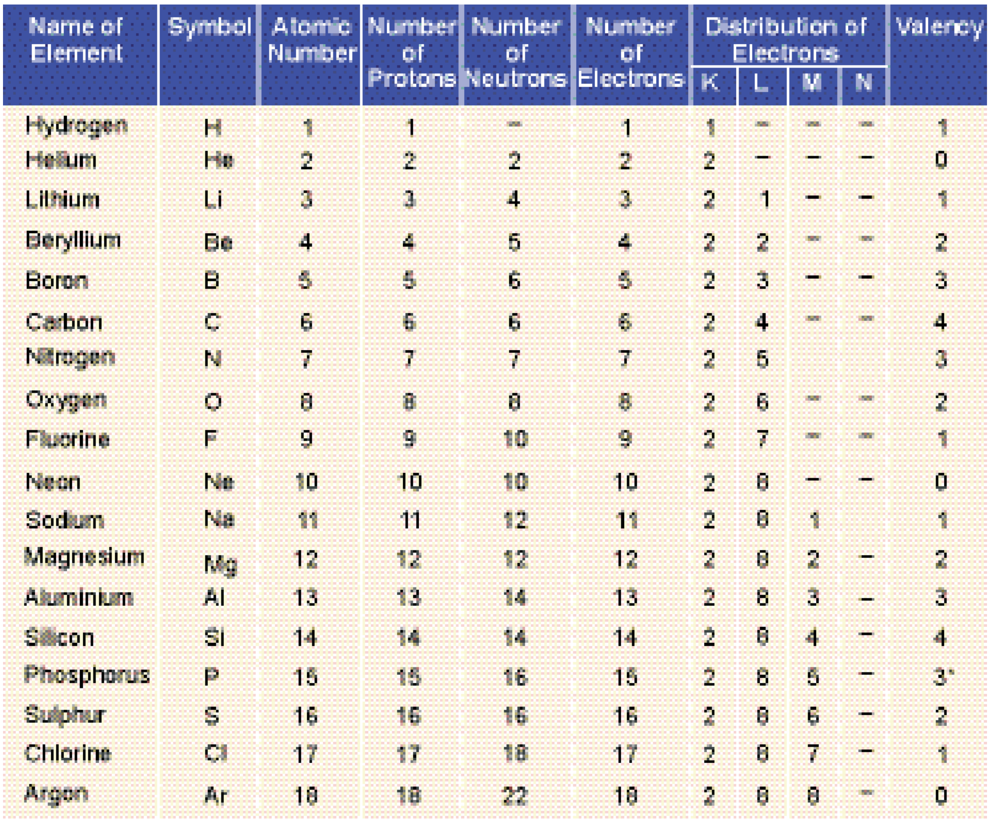
Thus,

Valency = Number of valence electrons (for 4 or lesser valence electrons)

Valency = 8 - Number of valence electrons (for more than 4 valence electrons)

The composition and electronic configuration of the elements having the atomic numbers from 1 to 18, along with their valencies is given in Table 3.7.

Table 3.7: The composition, electron distribution and common valency of the elements with atomic number from 1 to 18



Name of Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Number of Electrons	Distribution of Electrons				Valency
						K	L	M	N	
Hydrogen	H	1	1	–	1	1	–	–	–	1
Helium	He	2	2	2	2	2	–	–	–	0
Lithium	Li	3	3	4	3	2	1	–	–	1
Beryllium	Be	4	4	5	4	2	2	–	–	2
Boron	B	5	5	6	5	2	3	–	–	3
Carbon	C	6	6	6	6	2	4	–	–	4
Nitrogen	N	7	7	7	7	2	5			3
Oxygen	O	8	8	8	8	2	6	–	–	2
Fluorine	F	9	9	10	9	2	7	–	–	1
Neon	Ne	10	10	10	10	2	8	–	–	0
Sodium	Na	11	11	12	11	2	8	1		1
Magnesium	Mg	12	12	12	12	2	8	2	–	2
Aluminium	Al	13	13	14	13	2	8	3	–	3
Silicon	Si	14	14	14	14	2	8	4	–	4
Phosphorus	P	15	15	16	15	2	8	5	–	3*
Sulphur	S	16	16	16	16	2	8	6	–	2
Chlorine	Cl	17	17	18	17	2	8	7	–	1
Argon	Ar	18	18	22	18	2	8	8	–	0

*However, the elements in the 3rd and higher periods may show higher valencie, than predicted by octect rule since more than 8 electrons can be accommodate in their outermost shells due to available *d* orbitas,.

3.14.1 Electron Configurations and the Periodic Table

By this time you can see a pattern develop among the ground state electron configurations of the atoms. This pattern explains the periodic table. Consider helium, neon, argon, and krypton, elements in Group 18 of the periodic table. Neon, argon, and krypton have configurations in which a p subshell has just filled. (Helium has a filled 1s subshell; no lp subshell is possible.)

helium	$1s^2$
neon	$1s^2\ 2s^22p^6$
argon	$1s^22s^22p^63s^23p^6$
krypton	$1s^22s^22p^6\ 3s^23p^63d^{10}4s^241)^6$

These elements are the members of the group called *noble gases* because of their relative unreactivity.

Look now at the configurations of beryllium, magnesium, and calcium, members of the group of *alkaline earth metals* (Group 2), which are similar, moderately reactive elements.

beryllium	$1s^22s^2$	or	$[He]2s^2$
magnesium	$1s^22s^22p^63s^2$	or	$[Ne]3s^2$
calcium	$Is^22s^22p^6\ 3s^23p^64s^2$	or	$[Ar]4s^2$

Each of these configurations consists of a **noble gas core,** that is, *an inner shell configuration corresponding to one of the noble gases, plus* two outer electrons with an ns^2 configuration.

The elements boron, aluminum, and gallium (Group 13) also have similarities. Their configurations are

boron	$Is\ ^2\ 2s^22p^l$	or	$[He]2s^22p^I$
aluminum	$ls^2\ 2s^22p^6\ 3s^23p^l$	or	$[Ne]3s^23p^1$
gallium	$2s^2\ 2s^22p^6\ 3s^2\ 3p^6\ 3d^{10}4s^2\ 4p^l$	or	$[Ar]3d1^04s^24p^1$

Boron and aluminum have noble-gas cores plus three electrons with the configuration $ns^2\ np^1$. Gallium has an additional filled 3d subshell. *The noble-gas core together with $(n - 1)d^{10}$ electrons is* often referred to as a **pseudo-noble gas core,** because these electrons usually are not involved in chemical reactions.

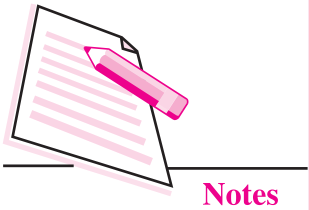
An electron in a core outside the noble-gas or pseudo-noble-gas core is called a **valence electron.** Such electrons are primarily involved in chemical reactions, and similarities among the configurations of valence electrons (the valence-shell *configurations)* account for similarities in the chemical properties among the groups of elements.

INTEXT QUESTIONS 3.3

1. What is the correlation between atomic size and ionization enthalpy.
2. Which species, in each pair is expected to have higher ionization enthalpy.
   - (i) $_{3}$Li, $_{11}$Na
   - (ii) $_{7}$N, $_{15}$P
   - (iii) ^{20}Ca, ^{12}Mg
   - (iv) $_{13}$Al, $_{14}$Si
   - (v) $_{17}$Cl, $_{18}$Ar
   - (vi) $_{18}$Ar, $_{19}$K
   - (vii) $_{13}$Al, $_{14}$C
3. Account for the fact that there is a decrease in first ionization enthalpy from Be to B and Mg to Al.
4. Why is the ionization enthalpy of the noble gases highest in their respective periods?
5. Name the most electronegative element.

WHAT YOU HAVE LEARNT

- The classification of elements makes their study systematic.
- The arrangement of elements in the long form of the periodic table depends on their electornic configuration.
- The properties of the elements are the periodic function of their atomic number.
- All the known elements are arranged in 18 groups in the long form of periodic table
- There are seven horizontal rows (periods) in the long from of the periodic table.
- Elements of groups 1 and 2 are known as alkali metals and alkaline earth metals respectively.
- Elements of groups 17 and 18 are known as halogens and noble gases respectively.
- *s, p, d* and *f* are the four blocks in the periodic table classified on the basis of their outer most electrons residing in *s, p, d* or *f* sub-shell.
- The elements can be classified into metals, non-metals and metalloids on the basis of their properties and their position in the periodic table.
- The atomic size, ionic size, ionization enthalpy, electron gain enthalpy and electronegativity and valence show regular trends along a group and a period.
- Valence can be explained.



TERMINAL EXERCISE

1. Define modern periodic law.
2. Refer the periodic table given in Table 3.2 and answer the following questions.
   - (i) The elements placed in group number 18 are called ....
   - (ii) Alkali and alkaline earth metals are collectively called .... block metals.
   - (iii) The general configuration for halogens is ....
   - (iv) Name a *p*-block element which is a gas other than a noble gas or a hologen.
   - (v) Name the groups that comprise the '*s*' block of elements.
   - (vi) Element number 118 has not yet been established, to which block, will it belong?
   - (vii) How many elements should be there in total if all the 7*s*, 7*p*, 6*d* and 5*f*, blocks are to be full?
3. Describe the variation of electron affinity and ionization enthalpy in the periodic table.
4. Define the following:
   - (a) Electron gain enthalpy
   - (b) Ionization enthalpy
   - (c) Ionic radius
   - (d) Electronegativity.
5. What is electronegativity? How is it related to the type of bond formed?
6. Why is the electron gain enthalpy of Cl more in negative value as compared to that of F?

ANSWERS TO INTEXT QUESTIONS

3.1

1.	Metals	Non metals	Metalloids
	Sn, Pb	C	Si, Ge
	Sb, Bi	N, P	As
	Te, Po	O, S	Se

2. Potassium is more metallic than aluminum.

3. (i) 2 (ii) 1 (iii) 3 - 12 (iv) 17 (v) 18

4. Np, Lr, No, Rf, Hs.

3.2

1. (i) Unnilpentium,

   (ii) unnilennium,

   (iii) Ununbium,

   (iv) Ununpentium

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

3. The atomic size decreases from left to right across a period and increases on moving down the group.

3.3

1. Ionization enthalpy decreases with increase in atomic size and vice-versa.

2. (i) $_{3}Li$ (ii) $_{7}N$ (iii) $_{12}Mg$

   (iv) $_{14}Si$ (v) $_{12}Ar$ (vi) $_{18}Ar$ (vii) $_{6}C$

3. The electronic configureation of Be is $1s^2\ 2s^2$ whereas that of B is $1s^2\ 2s^2\ 2p^1$. In case of Be, the electron is to be removed from completely filled *s* orbital whereas in case of B it is to be removed from a singly occupied *p* orbital. Fully-filled orbitals are more stable. Hence, ionization enthalpy decreases from Be to B. Similarily it decreases from Mg to Al.

4. The noble gases have fully filled shells and are stable. Hence, they have the highest ionization enthalpies in their respective periods.

5. Fluorine.

313en04

4

CHEMICAL BONDING

In lesson 2, you have learnt about the structure of atom while in the lesson 3, you studied about the classification of elements and periodicity in properties . You know that molecules are obtained by the combination of two or more than two atoms of the same or different elements. In this lesson you will study

- Why do atoms combine?
- What are the different ways in which the atoms can combine?, and
- What are the shapes of different molecules?

The answers to these questions are of fundamental importance to the study of chemistry, as you would discover while studying the later parts of this course.

OBJECTIVES

After reading this lesson you will be able to

- explain the formation of bond in terms of potential energy diagram and octet rule;
- list different types of bonds;
- define ionic bond and cite some examples;
- write Lewis structures of some simple molecules;
- list the characteristics of ionic compounds;
- explain Born Haber Cycle;
- define covalent bond and cite some examples;
- list the characteristics of covalent compounds;
- state valence shell electron pair repulsion (VSEPR) theory;

- explain bond polarity and dipole moment;
- explain bond parameters;
- predict the geometry of molecules with the help of VSEPR theory;
- explain the hybridisation of atomic orbitals involving s, p and d orbitals and illustrate with examples;
- tabulate the geometry of some molecules showing sp, sp^2, sp^3, dsp^2, and dsp^3 hybridisation;
- explain the formation of σ and π bonds in CH_4, C_2H_4 and C_2H_2 ;
- explain resonance;
- explain molecular orbital theory;
- write the molecular orbital configuration of H_2, N_2, O_2 and F_2 molecules;
- define bond length and bond order and relate them and
- explain hydrogen bonding with the help of examples.

4.1 VALENCE ELECTRONS

The electrons in the outer most shell take part in the bond formation and determine the combining capacity or the 'valency' of the atom. Therefore, the outer most shell of any atom is called its **valence shell** and the electrons present in the valence shell are called the **valence electrons**.

4.2 WHAT IS A CHEMICAL BOND?

When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combined or a bond is formed between the two. The bond is called a **chemical bond.** Thus *a chemical bond may be visualised as an effect that leads to the decrease in the energy*. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the constituent atoms.

A question arises, " How do atoms achieve the decrease in energy to form the bond". The answer lies in the electronic configuration. As you are aware, the noble gases do not react with other elements to form compounds. This is due to their stable electronic configuration with eight electrons (two in case of helium) in their outermost shells. The formation of a bond between two atoms may be visualised in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons. Accordingly, there are different types of chemical bonds, like,

- Ionic or electrovalent bond
- Covalent bond
- Co-ordinate covalent bond

In addition to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

4.3 IONIC OR ELECTOVALENT BOND

According to Kossel's theory, in the process of formation of ionic bond the atoms acquire the noble gas electronic configuration by the gain or loss of electrons. Let us consider the formation of NaCl in terms of Kossel's Theory.

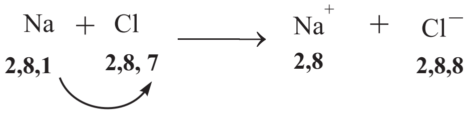
The electronic configuration of sodium atom (atomic number 11) is 2,8,1. Since it is highly electropositive, it readily loses an electron to attain the stable configuration of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na^+) in the process

$$\underset{\mathbf{2,8,1}}{\mathrm{Na}} \longrightarrow \underset{\mathbf{2,8}}{\mathrm{Na}^+} + e^- \; ; \qquad \underset{\textbf{(}\boldsymbol{\Delta}\textbf{H is enthalpy change)}}{\Delta H = 493.8 \text{ kJ mol}^{-1}}$$

On the other hand, a chlorine atom (electronic configuration: 2,8,7) requires one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl^-) in the process.

$$\underset{\mathbf{2,8,7}}{\mathrm{Cl}} + e^- \longrightarrow \underset{\mathbf{2,8,8}}{\mathrm{Cl}^-} \; ; \qquad \Delta H = -379.5 \text{ kJ mol}^{-1}$$

According to **Kossel's** theory, there is a **transfer** of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.



$$\underset{\mathbf{2,8,1}}{\mathrm{Na}} + \underset{\mathbf{2,8,\,7}}{\mathrm{Cl}} \longrightarrow \underset{\mathbf{2,8}}{\mathrm{Na}^+} + \underset{\mathbf{2,8,8}}{\mathrm{Cl}^-}$$

The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an **electrovalent** or an **ionic bond**. Thus *the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together*. The compounds so formed are termed as ionic or electrovalent compounds.

4.3.1 Energetics of Ionic Compound Formation

We have just described the formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. You may raise a question here that when **more energy is required** (ionisation energy) to form a sodium ion from sodium atom, **than that released** (electron affinity) in the formation of chloride ion from chlorine atom then how do we say that the formation of NaCl is accompanied by a decrease in energy? Your question is quite justified but let us assure you that there is no anomaly. Let us look at the whole process somewhat closely to clarify your doubts.

Born Harber Cycle

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

a) **Sublimation** of solid sodium to gaseous sodium atoms.

$$\mathrm{Na(s)} \longrightarrow \mathrm{Na(g)}\,; \qquad \Delta H = 108.7\ \mathrm{kJ\ mol^{-1}}$$

b) **Ionization** of gaseous sodium atom to give sodium ion.

$$\mathrm{Na(g)} \longrightarrow \mathrm{Na^{+}(g)} + e^{-}\,; \qquad \Delta H = 493.8\ \mathrm{kJ\ mol^{-1}}$$

c) **Dissociation** of gaseous chlorine molecule into chlorine atoms

$$\frac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{Cl(g)}\,; \qquad \Delta H = 120.9\ \mathrm{kJ\ mol^{-1}}$$

d) Conversion of gaseous chlorine atom to chloride ion **(addition of electron)**

$$\mathrm{Cl(g)} + e^{-} \longrightarrow \mathrm{Cl^{-}(g)}\,; \qquad \Delta H = -379.5\ \mathrm{kJ\ mol^{-1}}$$

e) Formation of NaCl from sodium and chloride ions.(**Crystal or lattice formation**).

$$\mathrm{Na^{+}(g)} + \mathrm{Cl^{-}(g)} \longrightarrow \mathrm{Na^{+}Cl^{-}(s)}\,; \qquad \Delta H = -754.8\ \mathrm{kJ\ mol^{-1}}$$

The energy released in this step is **lattice energy**.

The net reaction would be

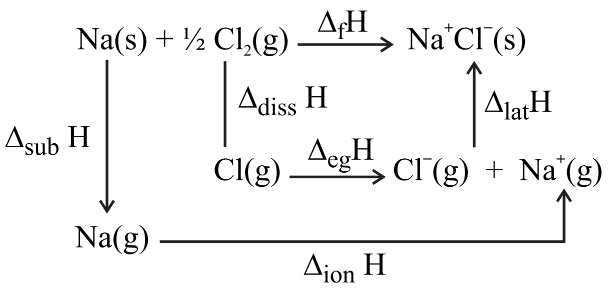
$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{Na^{+}Cl^{-}(s)}\,; \quad \Delta H = -410.9\ \mathrm{kJ\ mol^{-1}}$$

The overall energy change can be computed by taking the sum of all the energy changes:

$$\Delta H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9\ \mathrm{kJ\ mol^{-1}}$$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Born Haber Cycle



Of the five different types of energies involved, two (sublimation and dissociation energies) generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. On the basis of the above discussion we can say that the formation of an ionic compound is favoured by

i. Low ionisation energy of the metal,

ii. High electron affinity of the other element (non-metal), and

iii. High lattice energy

4.3.2 Characteristic Properties of Ionic Compounds

- These exist as crystalline solids in which the ions are arranged in a regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explains bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. Secondly, this theory is incapable of explaining the formation of molecules like, SO_2 or O_2, etc. For example in case of O_2, there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

4.4 COVALENT BOND

Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration is achieved, is different. Lewis proposed that this is achieved by "sharing of a pair of electrons" between the two atoms. Both the atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shown as

$$H\cdot + \cdot H \longrightarrow H : H \longrightarrow H—H$$

This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for 'bonding' between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called covalent compounds.

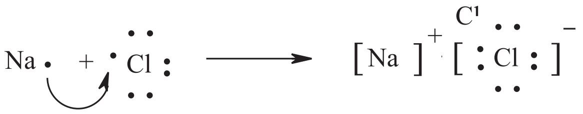
4.4.1 Lewis Structure

In the process of suggesting the process of chemical bonding Lewis provided a very convenient way of representing bonding in simple molecules. This is called **Lewis electron-dot structures** or simply **Lewis structures**.

In Lewis structure each element is represented by a **Lewis symbol**. This symbol consists of the normal chemical symbol of the element surrounded by number of dots representing the electrons in the valence shell. Since the electrons are represented by dots, these are called electron-dot structures. The Lewis symbols of some elements are as:

You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols

In terms of Lewis symbols the ionic bond formation in NaCl can be represented as

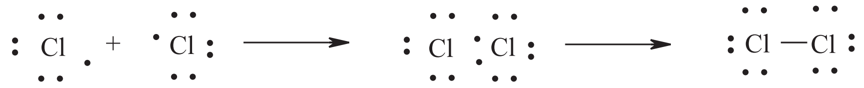


and the covalent bond formation in HFl is represented as

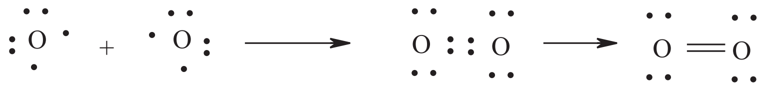
Sometimes the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as

In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no difference between electrons; it is just a presentation for the sake of convenience.

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as



Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.

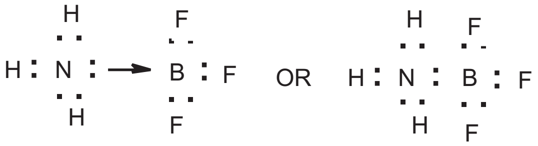


You may have noticed that in the process of bond formation, the elements of second period acquire eight electrons in their valence shell. This is called '**Octet rule**'. You may also note that in case of H_2 and Cl_2 the atoms are linked by a single line while in case of O_2 the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said to be joined by a single bond. And when, two pairs of electrons are shared (as in case of O_2), the two atoms are said to be bound by a double bond. In nitrogen (N_2) the two atoms are joined by a triple bond as they share three pairs of electrons.

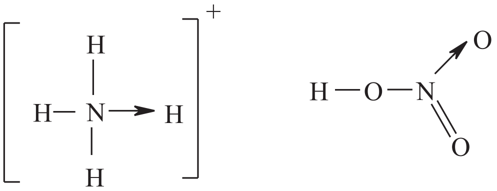
In a Lewis representation the electrons shown to be involved in the bond formation are called bonding electrons; the pair of electrons is called *'bond pair'* and the pairs of electrons not involved in the bonding process are called *'lone pairs'*. The nature of the electron pair plays an important role in determining the shapes of the molecules. This aspect is discussed later in Section 4.4.

4.4.2 Coordinate Covalent Bond

You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair, However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion) A common example is the formation of a bond between boron trifluoride (BF_3) and ammonia (NH_3). BF_3 is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electrons on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electrons to electron deficient $BF_{3.}$ Such electron donor-acceptor bonds are called **coordinate covalent** or **dative bonds**.



A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is identical to a covalent bond in terms of its polarity and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed. HNO_3 and NH_4^+ ion are some more common examples of formation of a coordinate bond.



INTEXT QUESTION 4.1

1. Define electrovalent bond.
2. Show the formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.
3. What do you understand by a polar covalent bond? Give two examples.
4. What is a coordinate covalent bond ? How is it different from a covalent bond?

4.4.3 Characteristic properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

4.4.4 Polar Covalent Bond

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule this shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more towards more electronegative chlorine atom. As a result of this unequal sharing of the electron pair , the bond acquires polarity or partial ionic character.

$$\mathrm{H}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\qquad \mathrm{H}^{\delta+-}\ \mathrm{C\,l}^{\delta-}$$

In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus , though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

4.4.5 Bond Polarity and Dipole Moment

A covalent bond is formed by sharing of a pair of electrons by the two atoms-each one of which contributes one electron. If the two atoms have the same electronegativity, then the sharing of the two bonded atoms is equal, see Fig. 4.1. This situation is encountered when both the atoms are of the same element as in H_2, Cl_2, O_2, N_2 etc. Such a bond is pure covalent bond. It is *non-polar* in nature. However, if the electronegativities of the two bonded atoms are different as in HCl, then the shared pair of electrons lies more towards the more electronegative atom i.e. chlorine. As a result, a small negative charge $(\delta-)$ develops on Cl atom and an equal positive charge $(\delta+)$ develops on H atom. The covalent bond in HCl is a *polar covalent bond*. It is not a pure covalent bond as it has some ionic character.

$$\underset{\text{(a)}}{\mathrm{H} : \mathrm{H}}\qquad \underset{\text{(b)}}{\overset{\delta+\ \ \delta-}{\mathrm{H} : \mathrm{Cl}}}$$

Fig. 4.1: Non-polar or pure covalent bond; (b) polar covalent bond

The extent of shift of the shared pair of electrons and hence the magnitude of ionic character depends upon the difference in electronegativities of the two bonded atoms. If it is 1.7, then the bond has 50% ionic character. If it is less than 1.7, then ionic character is less than 50% and if the difference is more than 1.7, then the ionic character is more than 50%.

Dipole Moment

Charge separation in a covalent bond results in the formation of an electrical dipole (two equal but opposite charges with a small distance between them). Each electrical dipole is characterized by its **dipole moment** which is defined as

Dipole Moment (μ) = Magnitude of charge (Q) × Distance of Separation (r)

It is commonly measured in the unit **'debye',** symbol D. The SI unit of dipole moment is Coulomb-metre (Cm). The two units are related as

$$1\text{D} = 3.336 \times 10^{-30}\ \text{cm}$$

The dipole moment depends upon the difference in electronegativities of the two bonded atoms. It can be seen from the data given below

Bond	Electronegativity of halogen atom	Dipole moment/D
H–F	4.0	1.90
H–Cl	3.0	1.04
H–Br	2.8	0.79
H–I	2.5	0.38

Dipole moment is a vector quantity since it has direction and magnitude both. By convention, the symbol ($+\!\!\!\longrightarrow$) is used to represent the dipole moment with tail on the positive centre and the head pointing towards the negative centre. The dipole moment of HCl is represented as

$$\overset{+\!\!\!\longrightarrow}{\mathrm{H - Cl}}$$

Like forces, dipole moment vectors can be added and subtracted. By doing so, the overall dipole moment of a molecule can be calculated. Let us consider some examples to understand it.

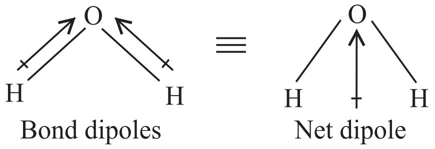
(i) **Carbon dioxide, CO_2**

CO_2 molecule is a linear triatomic molecule. Each C = O bond is polar with the oxygen atom having the negative end of the bond dipole

$$\overset{\longleftarrow\!\!\!+\quad +\!\!\!\longrightarrow}{\mathrm{O = C = O}}$$

The dipole moments of both the C = O bonds have the same magnitude but are in opposite directions hence they cancel each other. The net dipole moment of CO_2 is zero.

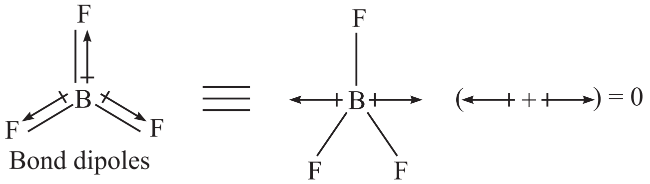
(ii) **Water, H_2O**



H_2O is a non-linear or bent diatomic molecule. Each H–O bond is a polar covalent bond and has a dipole moment. Although dipole moments of both the bonds are equal is magnitude, but due to non-linear shape, they do not cancel each other. The net dipole moment of H_2O molecule is 1.85D (or 6.17×10^{-30} cm)

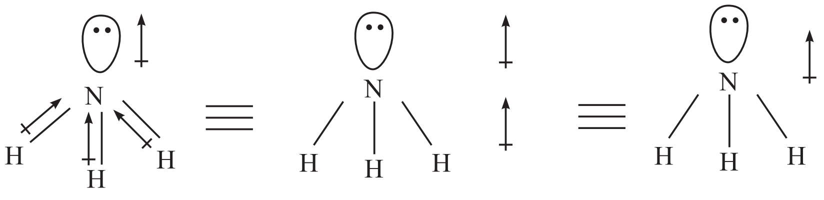
(iii) **Boron trifluoride, BF_3**

The net dipole moment for BF_3 is zero due to its symmetrical planar structure as shown below, although the B–F bonds are polar.



(iv) **Ammonia, NH_3**

NH_3 has a pyramidal structure which makes the arrangement of three N–H bonds unsymmetrical. In each N–H bond, nitrogen is the negative centre and hydrogen is the positive centre. In addition to three N–H bonds, nitrogen atom has a lone pair of electrons. which also has an orbital dipole moment in which the electron pair is the negative centre.



Bond and orbital dipoles

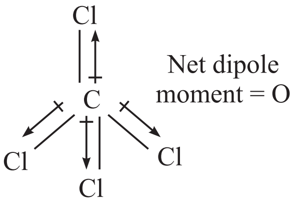
Net bond dipole and orbital dipole

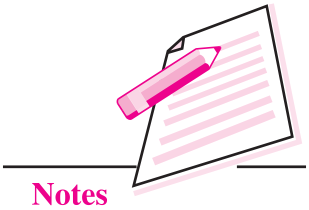
Net dipole of the molecule

The net dipole moment of NH_3 is 1.47D (4.90×10^{-30} Cm).

(v) **Carbon tetrachloride, CCl_4**

It has a net zero dipole moment due to its symmetrical tetrahedral shape





Notes

4.4.6 Covalent Character of Ionic Bond

In the earlier discussion, we have seen that most of the covalent bonds have some ionic character. Similarly, ionic bonds also have some covalent character. The origion of covalent character of an ionic bond lies in the distortion of electron cloud under the influence of an electric charge. This property of an electron cloud to get distorted is called its **polarizability** and the process of distortion of electron cloud is called **polarization.** The power of an electric charge to distort an electron cloud is called its **polarizing power.** In an ionic compound cations and anions are formed as a result of loss and gain of electrons, respectively. Each ion tries to polarize the electron cloud of the other.

Generally, cations have greater polarizing power due to their small size and hence high charge density. Anions are more easily polarized. Due to their large size, the electrons in anions are more loosely bound to the nucleus than in cations. Cation attracts the electron cloud of the anion and this results in its polarization and the electron cloud spreads out towards cation in between the two ions. Thus the electron lost by cation does not fully belong to the anion but partially comes back towards cation and is shared by it. This results in some covalent character in the ionic bond. The more the polarization, the more is the covalent character.

Fajan proposed some empiprical rules that deal with the polarization process. These rules are known as **Fajan's rules** which are given below. The following factors increase the covalent character of an ionic bond

(i) small cation

(ii) large anion

(iii) high positive charge on cation

(iv) cations with electronic configuration $(n–1)d^xns^0$ (typically transition metal cations) as compared to cations with same size and charge but having ns^2np^6 (noble gas) configuration.

4.4.7 Covalent Bond Parameters

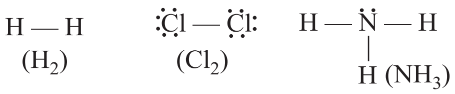
Each covalent bond is characterized by the following parameters which are called covalent bond parameters.

(1) Bond order

Bond order is the number of bonds present between two atoms in a molecule or ion. Generally, bond order has an integral value. For example,

Bond order = 1

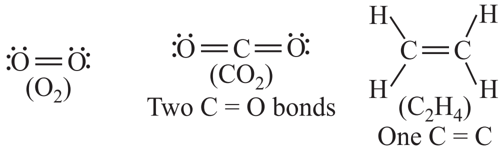
Bond order is 1 (one) when there is only **one covalent bond** (sigma bond) between the two bonded atoms. H_2, Cl_2, NH_3 are some such examples. These are called single bonds.



In NH_3 molecule, there are three single N–H bonds.

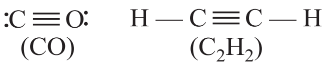
Bond order = 2

Bond order is 2 (two) when there are **two covalent** bonds between the two bonded atoms. Of the two, one is a sigma bond and the other is a pi bond. These are called double bonds. Examples are as follows.



Bond Order = 3

Bond order is 3 (three) when there are three bonds between the two bonded atoms. Out of these, one is a sigma bond and two are pi bonds. These are called triple bonds. Examples are given below.



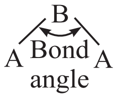
(2) Bond Length

Bond length is the distance between the nuclei of the two bonded atoms. It is expressed in picometer (pm). Bond length depends upon the sizes of the bonded atoms and the bond order of the bond linking them. The greater the bond order, the smaller is the bond length.

Bond	Bond Length/pm	Bond	Bond Length/pm
H–H	74	O=O	121
H–F	92	N≡N	109
H–Cl	127	C–C	154
H–Br	141	C=C	134
H–I	160	C≡C	120
		C=O	122

(3) Bond Angle

It is the angle between the two bonds in a molecule. Since covalent bonds are formed through overlapping of orbitals, it may also be defined as the angle between the two orbitals that contain bonding electrons and overlap with atomic orbitals of other atoms. Bond angle between two bonds or bonding orbitals is shown below



The bond angle between two O–H bonds in H_2O molecule is 104.5°, between N–H bonds in NH_3 molecule is 107.3° and between C–H bonds in CH_4 is 109°28'.

(4) Bond Enthalpy Δ_aH

It is the amount of energy required for breaking one mole of bonds of a particular type in gaseous molecules. It is also called bond dissociation enthalpy, and is applicable to simple molecules, containing only one bond of the particular type. For example, the bond enthalpy of Cl–Cl bond in Cl_2 is 243 kJ mol^{-1}, of O=O in O_2 is 498 kJ mol^{-1} and of N≡N bond in N_2 is 946 kJ mol^{-1}.

A difficulty arises in using this definition in case of molecules that contain more than one bond of the same type. H_2O molecule has two O–H bonds and the two bonds require different amounts of energies to break.

$$H_2O(g) \longrightarrow H(g) + OH(g) \quad \Delta_a H_1^0 = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g) \quad \Delta_a H_2^0 = 427 \text{ kJ mol}^{-1}$$

Likewise, there are three N–H bonds in NH_3 and four C–H bonds in CH_4. Each one of these bonds requires a different amount of energy to break. In such cases, **average bond enthalpy** is considered. It is defined as the average energy per bond required to dissociate one mole of bonds in gaseous atoms.

$$\text{Average bond enthalpy} = \frac{\begin{array}{l}\text{Total energy required to break}\\ \text{all the bonds of a particular type}\\ \text{in one mole of gaseous molecules}\end{array}}{\text{Total no. of moles of bonds broken.}}$$

For example in case of water molecule

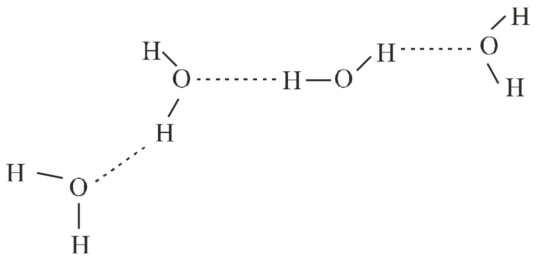
$$\text{Average bond enthalpy of O–H bond} = \frac{502+427}{2} = 464.5 \text{ kJ mol}^{-1}$$

Some bond enthalpy values are given below:

Bond	**Bond Enthalpy/kJ mol^{-1}**	**Bond**	**Bond Enthalpy/kJ mol^{-1}**
H–H	436	N≡N	946
H–C	414	O=O	498
H–N	391	C–C	347
H–O	464	C=C	611
N–N	159	C≡C	837
O–O	138	C≡N	891
F–F	157	C–Cl	330

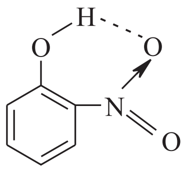
4.5 HYDROGEN BONDING

It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol^{-1}. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol^{-1} of energy to break. However, it is strong enough to be responsible for the high boiling points of H_2O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.

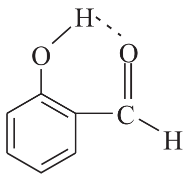


H—F······ H—F ······ H—F ······H—F

Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a partial positive charge while the electronegative atom bears the partial negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bond.** Salicyldehyde ad o-nitrophenol are two common examples of the molecules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.



o-nitrophenol



Salicyldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecules like proteins and nucleic acids.

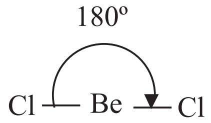
4.6 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

POSTULATE 1

The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples.

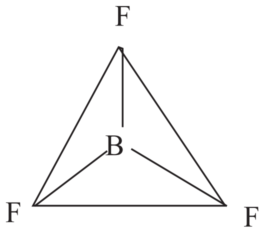
$BeCl_2$ is one of the simple triatomic molecules. In this molecule, the central atom, beryllium has an electronic configuration of $1s^2\ 2s^2$. That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180° which gives the molecule a linear shape.



Cl — Be — Cl
linear molecule

Other molecules of this type would also have a similar shape.

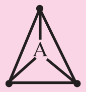
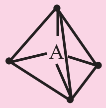
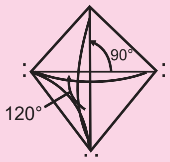
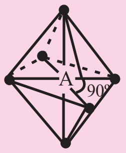
BF_3 : In boron trifluoride, the central atom, boron has an electronic configuration of $1s^2\ 2s^2\ 2p^1$. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.



Planar trigonal shape

Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 4.1.

Table 4.1: Geometric arrangements of electron pairs around central atom.

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX_2	2	Linear		**$HgCl_2$, BeCl**
AX_3	3	Planer trigonal		**BF_3, BCl_3**
AX_4	4	Tetrahedral		**CCl_4, CH_4, $SiCl_4$**
AX_5	5	Trigonal bipyramidal		**PCl_5, PF_5**
AX_6	6	Octahedral		**SF_6, PF_6^-**

POSTULATE 2

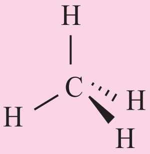
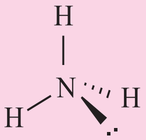
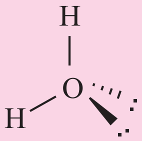
The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than between two bond pairs. The order of repulsive force between different possibilities is as under.

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

The shapes of the molecules given in Table 4.1. correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 4.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs, while one is a lone pair. Similarly, in case of water again there are four pairs of electrons ; two are bond pairs, while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 4.2.

Table 4.2: Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH_4	4	0	tetrahedral		109.5
NH_3	3	1	trigonal pyramidal		107.3
H_2O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons.

The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 2. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

INTEXT QUESTION 4.2

1. What are the basic postulates of VSEPR theory?
2. Predict the shape of methane (CH_4) on the basis of VSEPR theory.
3. It is a molecule the difference between the electro-negativity of two atom is 1.7. How much % will be ionic and covalent character?

4.7 MODERN THEORIES OF CHEMICAL BONDING

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are known as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

4.7.1 Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

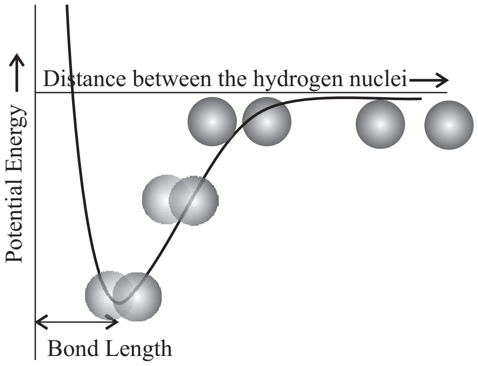


Fig. 4.2 : *Formation of hydrogen molecule from overlapping of two hydrogen atoms*

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1*s* orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead to decrease in energy, Fig. 4.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

This simple approach can be used to explain the bonding in simple diatomic molecules like HF,F_2 etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridisation need to be used.

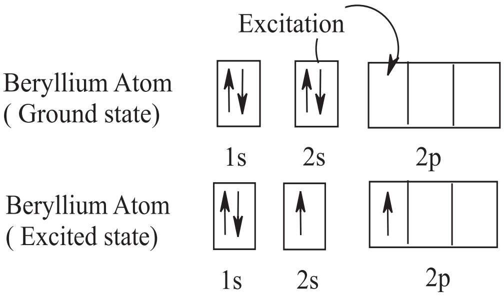
4.7.1.1 Hybridisation

"Hybridisation is the process of forming new orbitals by mixing of atomic orbitals in a particular atom. The new hybrid orbitals that are formed are all equivalent orbitals and have the same energy. The phenomenon is know as hybridisation". Two main characteristics of hybridisation are:

(i) The number of hybrid orbitals formed is the same as the number of atomic orbitals undergoing hybridisation.

(ii) All the new hybrid orbitals that are formed are exactly identical in their shapes and energy.

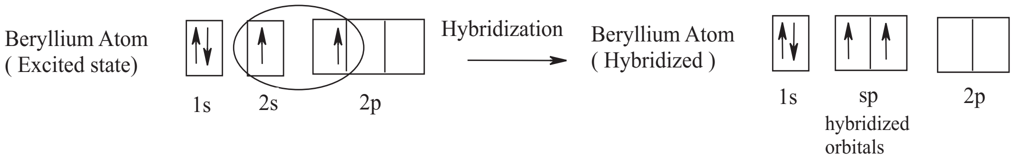
Let us take up the example of bonding in a triatomic molecule; say, beryllium hydride (BeH_2) to understand the concept of hybridisation of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is $1s^2\ 2s^2$. In order to form bonds with two hydrogen atoms the valence electrons ($2s^2$) of beryllium atom must overlap with the 1s electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e., 2s) it cannot overlap with the 3p orbital of hydrogen atoms containing one electron.[You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the 2s orbital of beryllium atom gets momentarily excited to the empty 2p orbital as shown below.



Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of 2*s* orbital of beryllium with 3*p* orbital of chlorine while the other would involve overlapping of 2*p* orbital of beryllium with 2*p* orbital of chlorine. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called **hybridisation** of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of $BeCl_2$ the two singly occupied orbitals (2s and 2p) hybridize to give two sp- hybrid orbitals. This is called **sp hybridisation**. These hybrid orbitals lie along the *z*- direction and point in opposite directions.



These hybrid orbitals can now overlap with the 3p orbitals of chlorine atoms to give the linear molecule of $BeCl_{2.}$ as shown below, Fig. 4.3 .

The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridisation of suitable orbitals. Let us take up some more cases involving hybridisation of *s* and *p* orbitals.

Boron trichloride (sp^2 hybridisation) : In boron there are five electrons and the electronic configuration is $1s^2$, $2s^2$,$2p^1$. There are three electrons in the valence shell of boron atom. In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital.

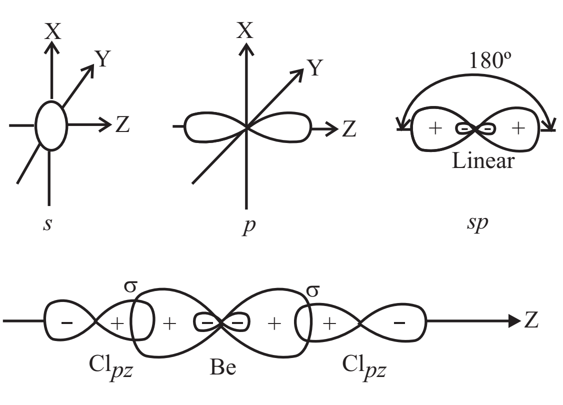
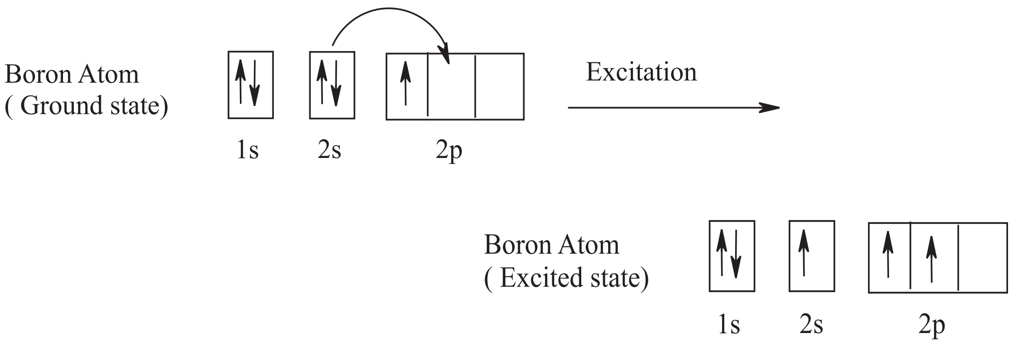
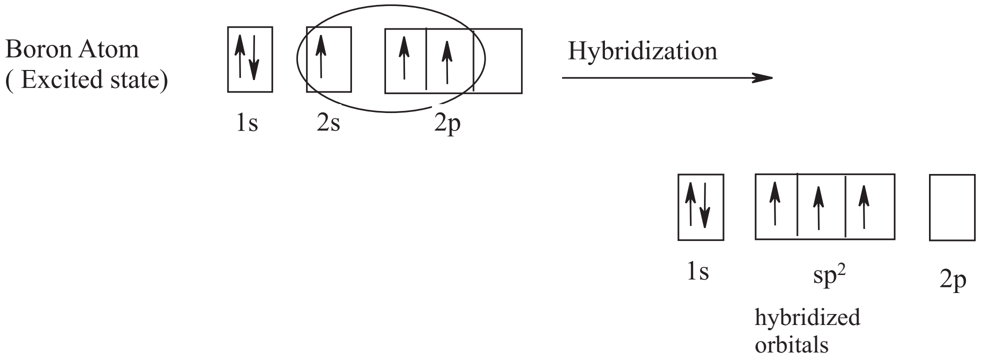


Fig. 4.3 : *Formation of $BeCl_2$; sp hybridisation*



One 2s orbital and two 2p orbitals hybridise to give three sp^2 hybridized orbitals. This is called **sp^2 hybridisation**.



The three hybridized orbitals are coplanar and directed towards the corners of an equilateral triangle. These **hybrid** orbitals then form bonds with the p –orbitals of chlorine atoms as shown below, Fig. 4.4.

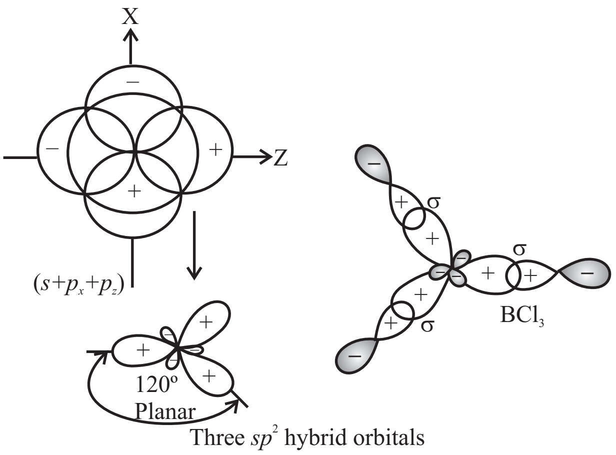
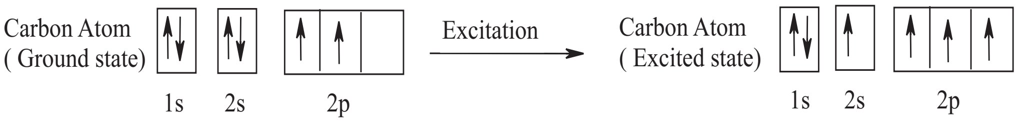
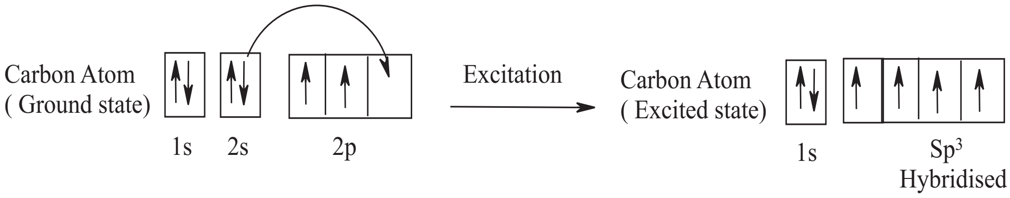


Fig. 4.4 : *Formation of BCl$_3$; sp^2 hybridisation.*

Bonding in Methane (sp^3 hybridisation) : In case of methane the central atom, carbon, has an electronic configuration of 1s^2, 2s^2 ,2p^2. In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital.



One 2s orbital and three 2p orbitals of the carbon atom then hybridise to give four sp^3 hybridised orbitals. This is called **sp^3 hybridisation.**



These four sp^3 hybrid orbitals are directed towards the corners of a regular tetrahedron. These **hybrid** orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 4.5.

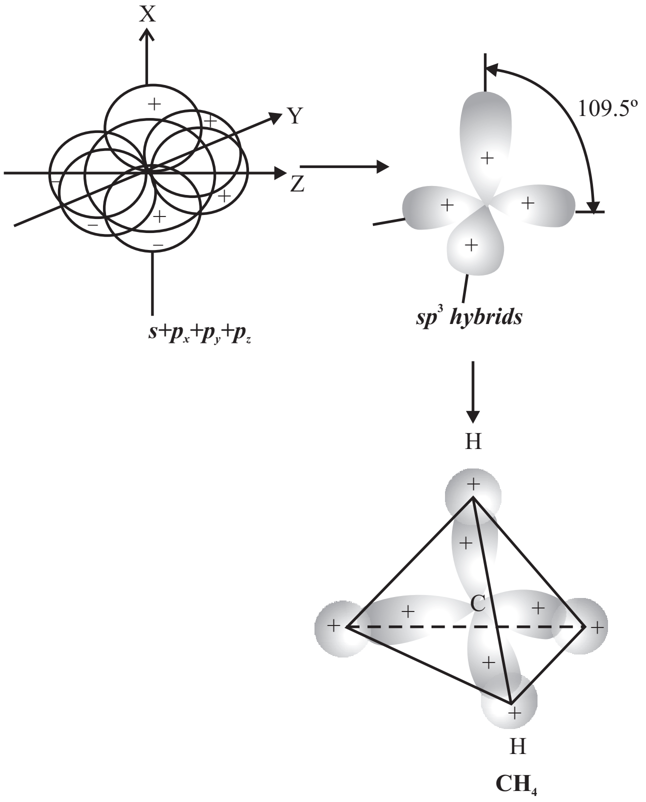
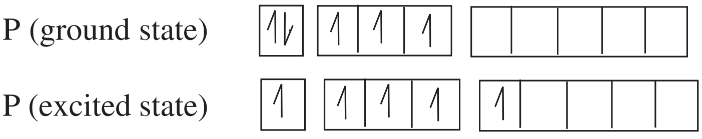


Fig. 4.5 : *Formation of CH_4 ; sp^3 hybridisation.*

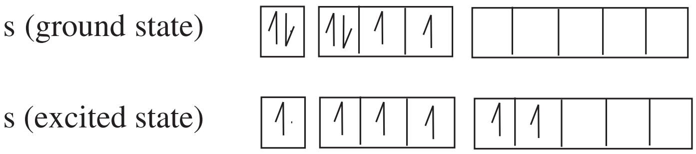
Phosphorus pentachloride (sp^3d hybridisation):



sp^3d hybridisation

Five sp^3d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramid (Fig. 4.5a). These orbitals overlap with singly filled *p*-orbitals of five chlorine atoms and five σ bonds are formed. Thus PCl_5 molecule has a trigonal bipyramidal geometry. Three P–Cl bonds (equatorial) make an angle of 120° with each other and lie in one plane. The other two P–Cl bonds (axial) are at 90° to the equatorial plane, one lying above and the other lying below the plane.

SF_6 (sp^3d^2 hybridisation):



sp^3d^2 hybridisation

Six sp^3d^2 hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form σ bonds giving a regular octahedral geometry (Fig. 4.5 b)

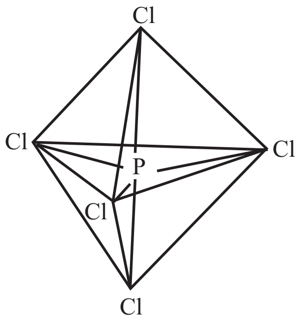


Fig. 4.5 (a) : *Trigonal bipyramidal geometry of PCl_5 molecule.*

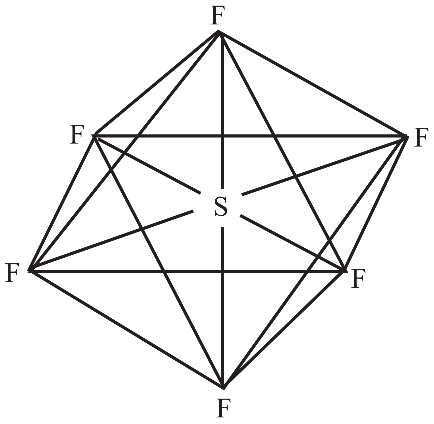


Fig. 4.5 (b) : *Octahedral geometry of SF_6 molecule*

4.7.1.2 Hybridisation and Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo sp^3 hybridisation. In ethane each carbon atom undergoes sp^3 hybridisation to give four sp^3 hybridized orbitals. The two carbon atoms form a carbon – carbon bond by sp^3 - sp^3 overlapping. The remaining six sp^3 *hybridized* orbitals overlap with 1*s* orbitals of hydrogen atoms to give a molecule of *ethane*, C_2H_6 as shown in Fig.

4.6. The C-C bond so formed is along the internuclear axis. Such a bond is called a **ó bond.**

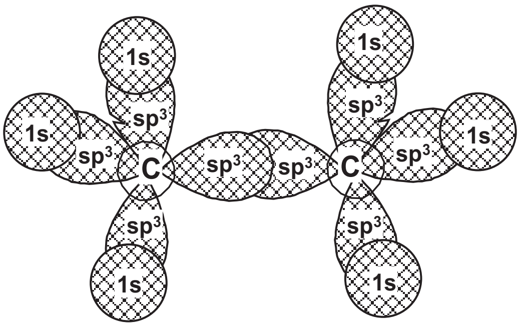


Fig. 4.6 : *Formation of ethane molecule*

Bonding in ethene: In case of ethene, the relevant orbitals of the carbon atoms undergo *sp*^{2} hybridisation. Here, only two of the three *p* orbitals of the carbon atoms hybridize with the *2s* orbital to form three *sp*^{2} hybrid orbitals each. The remaining p-orbitals (one on each carbon atom) do not take part in hybridisation. A carbon – carbon bond is formed by overlapping of *sp*^{2} orbital on the two carbon atoms [Fig. 4.7(a)]. The remaining four *sp*^{2} hybridized orbitals overlap with the 1*s* orbitals of hydrogen atoms to give the basic skeleton of the molecule. This leaves an un-hybridized *p* orbital each on both the carbon atoms[Fig. 4.7(b)]. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plane above and below the molecule [Fig. 4.7(b and c)]. This is called a **π- bond**. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

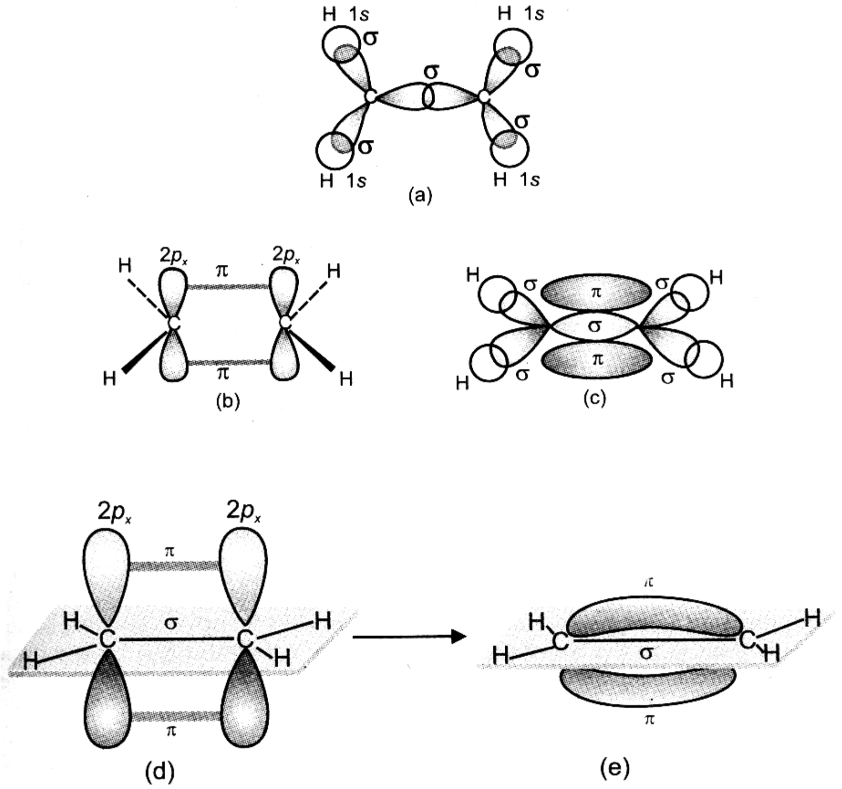


Fig. 4.7 : *Formation of ethylene molecule: (a) formation of the basic skeleton of the molecule (b) sideways overlapping of the unhybridized p orbitals and (c) a π- bond (d) and (e) complete picture of ethylene molecule.*

Bonding in ethyne (acetylene): In case of acetylene the bonding can be explained in terms of sp-hybridisation in carbon atoms. One 2s and one 2p orbitals hybridize to give two sp-hybridized orbitals. This leaves two mutually perpendicular unhybridised *p* orbitals each on both the carbon atoms. The carbon – carbon bond is formed by sp - sp overlapping with each other. The remaining sp orbital on each carbon overlaps with the 1s orbital of hydrogen to give C-H bonds (Fig. 4.8). The unhybridised *p* orbitals each on both the carbon atoms overlap sideways to give two π-bonds.

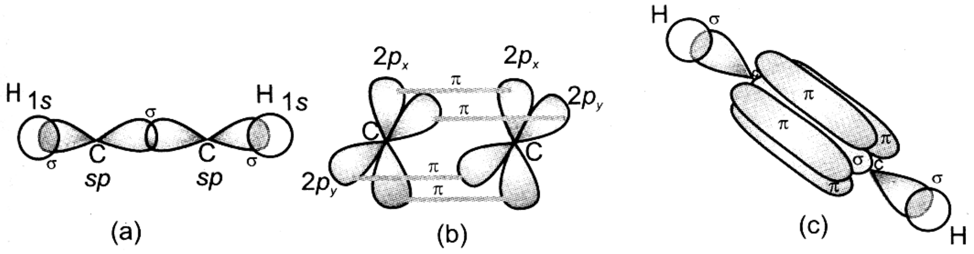
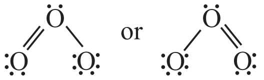


Fig. 4.8 : *Formation of acetylene molecule : (a) formation of the basic skeleton of the molecule (b) sideways overlapping of two pairs of un-hybridized p orbitals and (c) two mutually perpendicular π- bonds.*

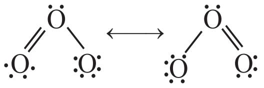
4.7.1.3 Resonance

Some times it is possible to write more than one Lewis structure of a compound that agree with the electronic requirements. For example, we can write two Lewis structures for ozone molecules, O_3.

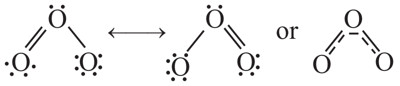


Both of these structures satisfy the octet rule and have a double bond on one side and single bond on the other side of the central oxygen. According to these structures one oxygen-oxygen bond (O=O) would be shorter than the other (O–O). However, this is not the case. Experimentally both the oxygen-oxygen bonds are found to have the same bond length (128 pm) which is in between the bond lengths of a (O=O) double bond (121 pm) and a (O–O) single bond (148 pm).

These experimental observations can be explained with the help of the concept of *resonance*. The alternate Lewis structures are called **canonical structures.** These are separated by a double headed arrow(↔) All canonical structures must have similar positions of nuclei, similar number of bonding and non-bonding electrons and similar energy. The actual structure is the **resonance hybrid** of all the contributing canonical or resonating structures. The structure of O_3 molecule is represented as



Resonance does not mean that the molecule constantly changes from one canonical structure to the other. The structure is stable and the bond lengths and energies have values which are intermediate between those of single and double bonds. The concept of the resonance is necessary because of the limitations in the way *we write* the structures. Some times the structure of a resonance hybrid is shown with help of representation of bonds by broken lines or dashes. The structure of resonance hybrid of O_3 is shown below:

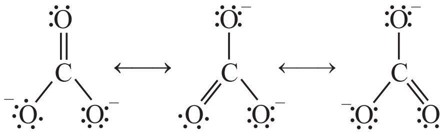


In molecules or ions containing more than two atoms and having double bonds or triple bonds, there are **pi (π) bonds.** The electrons involved in π-bonds are not localized between two atoms, but are spread over the entire structure (or the portion of the structure) which has only sigma-(σ) bonds. This spreading of π-electrons is known as the delocalization of the electrons. Broken lines or dashes depict the region of delocalization of the π-electrons. Delocalization results in stabilizing the structure. Therefore, the resonance hybrid is more stable than the contributing canonical structures.

Some examples of resonance structures:

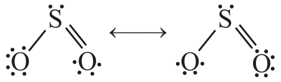
(1) Carbonate ion $\left(CO_3^{2-}\right)$

The three possible canonical structures of carbonate ion are



(2) Sulphur dioxide (SO_2)

The two canonical structures of sulphur dioxide are shown below



(3) Dinitrogen oxide (N_2O)

The three canonical structure of dinitrogen oxide are shown below

$$:\ddot{N}=N=\ddot{O}: \longleftrightarrow :N\equiv N-\ddot{O}: \longleftrightarrow :\ddot{N}-N\equiv O:$$

INTEXT QUESTION 4.3

1. What do you understand by the term, 'hybridisation'?
2. How would you explain the shape of ammonia molecule on the basis of hybridisation?
3. Draw the canonical structures of $CO^{2}{}_{3}$ and SO_2.

4.7.2 Molecular Orbital Theory

You have just learnt about valence bond theory. It describes bond formation as a result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised. Molecular orbital theory (MOT) was developed by F.Hund and R.S.Mulliken in 1932. In contrast to the localized bonding in VBT, the molecular orbital theory visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- **The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals).** These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not "belong" to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals **(LCAO)** approach in which, **the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.**
- The available **electrons then fill these orbitals in the order of increasing energy as in the Aufbau principle** used in the electron configurations of atoms.

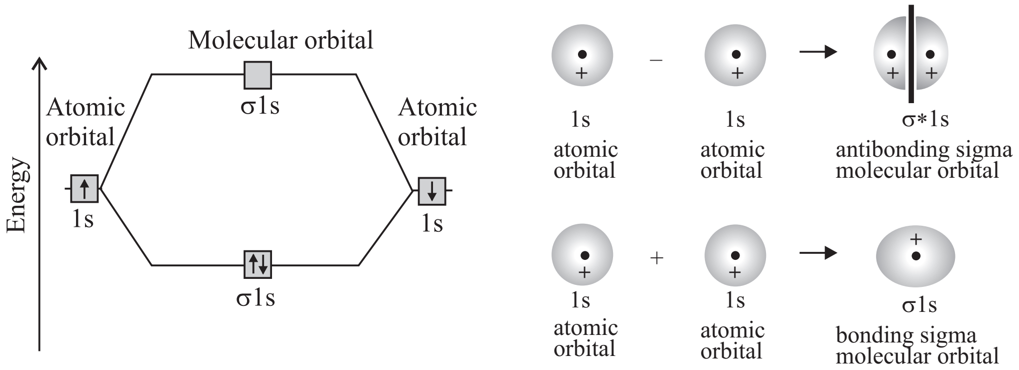
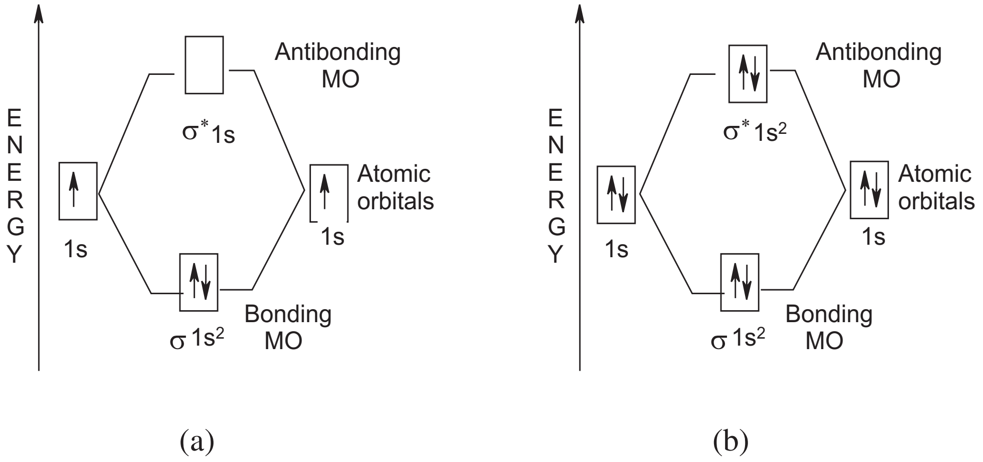


Fig. 4.9 : *Formation of bonding (σ) and anti bonding (σ*) molecular orbitals*

Let us take the example of hydrogen molecule to understand the molecular orbital approach to chemical bonding. The two hydrogen atoms have one electron each in their respective 1s orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wavefunction is obtained by addition of the two atomic wave functions whereas in the other the MO is obtained by subtraction of the wave function. The combination of the 1s orbitals on the two hydrogen atoms are shown in Fig. 4.9.

The molecular orbital obtained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals and is called a **bonding orbital.** On the other hand, the orbital obtained by subtraction of atomic orbitals is of higher energy and is called an **anti-bonding orbital.** You can note here that the molecular orbitals obtained here are symmetric around the bond axis (the line joining the two nuclei). Such molecular orbitals are called **sigma** (σ) molecular orbitals. The bonding orbital obtained above is denoted as σ1s while the anti- bonding orbital is denoted as σ^*1s. Here σ indicates the type of molecular orbital; 1s tells about the atomic orbital involved and * is indicative of the anti-bonding nature of the MO. There are a total of 2 electrons in a hydrogen molecule; according to Aufbau principle these are filled into σ_{1s} orbital. Since the σ_{1s} orbital is a bonding orbital, its getting filled leads to stability or the bond formation.

Like electronic configuration of atoms we write MO electronic configuration for molecules. The MO configuration of hydrogen molecule is given as $(\sigma 1s)^2$. The molecular orbital energy level diagram is given in Fig. 4.10(a).



(a) (b)

Fig. 4.10 : *Molecular orbital energy level diagram for a) H_2 and b) He_2 molecules*

Bond Order: we may define a new parameter called bond order as

Bond order = (b.o.) = $\frac{1}{2}(n_b - n_a)$

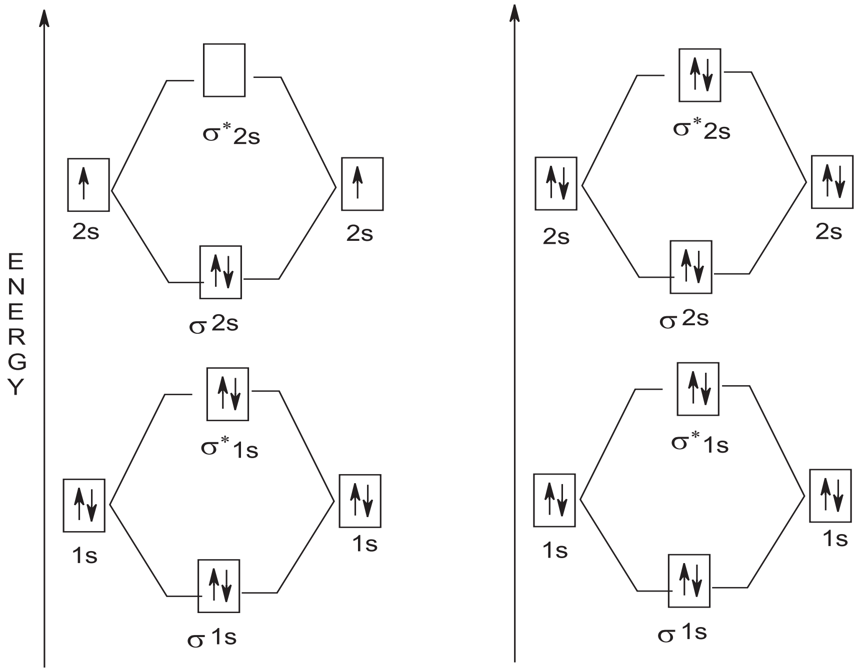
Where, n_b and n_a refer to the number of electrons present in bonding and antibonding molecular orbitals, respectively. For hydrogen molecule the bond order will be ½(2–0) = 1, i.e., there is a single bond between two hydrogen atoms.

Helium (He_2) molecule

In case of He_2 also, there will be linear combination of 1s orbitals leading to the formation of σ1s and σ^*1s orbitals. The four electrons would be distributed as per the MO electronic configuration : $(\sigma 1s)^2\ (\sigma^* 1s)^2$. The molecular orbital energy level diagram is given in Fig. 4.10 (b) .This gives a bond order of ½(2–2) = 0, that is there is no bond between two helium atoms. In other words He_2 molecule does not exist.

Li_2 and Be_2 molecules

The bonding in Li_2 and Be_2 can be explained by combining the 1s and 2s orbitals to give appropriate MO's. The molecular orbital diagrams for Li_2 and Be_2 are given in Fig. 4.11.



(a) **(b)**

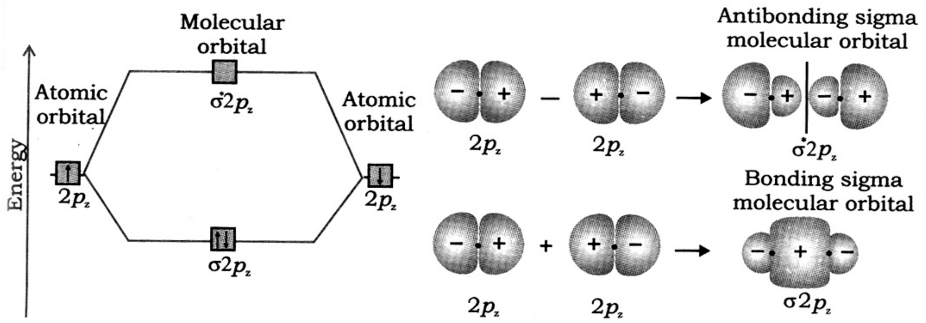
Fig. 4.11: *Molecular orbital energy level diagram for a) Li_2 and b) Be_2 molecules*

4.7.2.1 Molecular Orbital Bonding in Diatomic Molecules of Second Period

So far we have talked about bonding in the elements in which the MO's were obtained from the linear combination of s orbitals. In case of the atoms of second period (beyond Be) elements both *s* and *p* orbitals are involved in the formation of molecular orbitals. In such a case a number of different molecular orbitals are obtained depending on the type and symmetry of the atomic orbitals involved in the process. Let us try to understand the nature of MO's obtained in this case.

Here also the 1s and 2s orbitals of the two atoms would combine to give corresponding bonding and anti-bonding molecular orbital as shown in Fig. 4.11 (b). Let us learn about the formation of MO's from the combination of p orbitals

As mentioned above, in LCAO, the atomic orbitals of **comparable energies** and of **suitable symmetry** combine to give molecular orbitals. A suitable symmetry means that the combining orbitals should have same symmetry about the molecular axis. It is nomally assumed that the bond formation takes place along the z-direction. You have learnt in the first unit that the three *p* orbitals are directed towards three mutually perpendicular directions namely the x, y and z directions. Therefore the p_z orbitals of the two atoms would combine along the bond axis to give two molecular orbitals as shown below Fig. 4.12. Since these molecular orbitals are symmetric around the molecular axis these are called σ orbitals. The designation of the orbitals would be σ_{2pz} and σ^*_{2pz} .



(a) (b)

Fig. 4.12: *Overlapping of two $2p_z$ orbitals to give molecular orbitals*

Combination of a p_z-orbital with either a p_x or a p_y orbital would not lead to any bonding. On the other hand a p_x orbital will combine with a p_x and the p_y with a p_y as shown in Fig. 4.13.

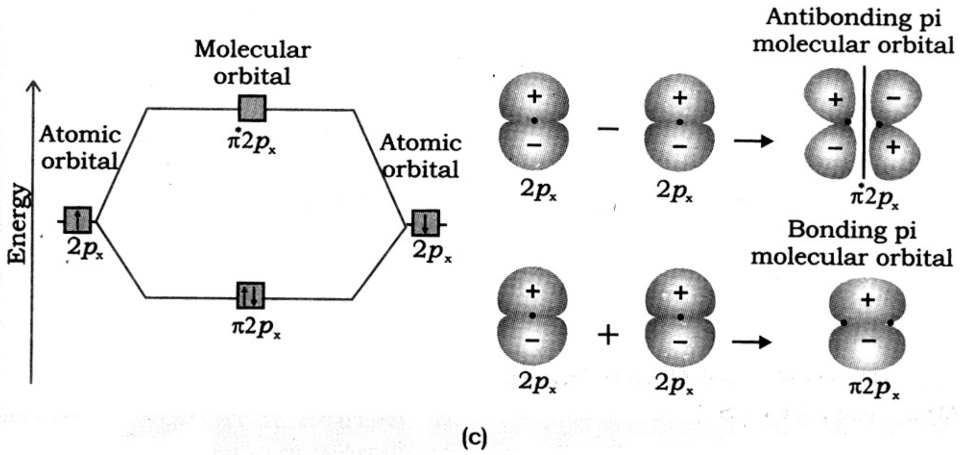


Fig. 4.13 : *Formation of molecular orbitals from two $2p_x$ atomic orbtials.*

You may note here that these orbitals combine in a lateral fashion and the resulting molecular orbitals are not symmetric around the bond axis. These MO's are called π- molecular orbitals. These have large electron density above and below the internuclear axis. The anti-bonding π orbital, $\pi^* 2p_x$ (or $\pi^* 2p_y$) have a node (a region of zero electron density) between the nuclei.

The molecular orbitals obtained as a result of combination of respective AO's of two atoms can be represented in the form of following energy level diagram, Fig. 4.14(a) . The MO's obtained from the combination of 1s orbitals are not shown.(these belong to the inner core and are completely filled) The electrons in these molecular orbitals are filled in accordance with Aufbau principle and Hund's rule.

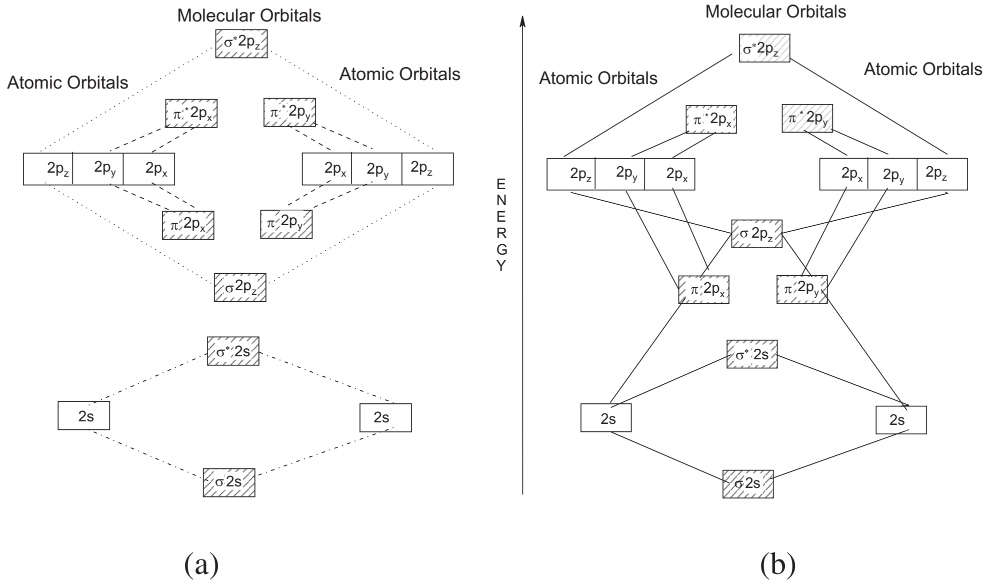


Fig. 4.14: *Molecular orbital energy level diagrams a) for O_2 and F_2 and b) for diatomic molecules of lighter elements Li, Be, B, C and N*

However, this energy level diagram is valid for the diatomic molecules O_2 and F_2 only; For the diatomic molecules of the lighter elements like, B, C and N this energy level diagram is somewhat modified. It is so because in case of lighter elements the difference in the energy of 2s and 2p orbitals is very low and *s* and *p* orbitals on the two atoms get mixed up. In place of normal pure 2*s*-2*s* or 2*p*-2*p* combinations we may have s-p combinations; for example 2*s* orbital of first atom can have a reasonable overlapping with $2p_z$, orbital of the second atom and vice versa. The modified energy level diagram is given in Fig. 4.14 (b).

4.7.2.2 MO Electronic Configuration and Properties of a Molecule

The MO energy level diagram discussed above can be used to find out the MO electronic configuration of a molecule. This in turn provides the information about some properties of the molecule. Let us take the example of nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's. Using Fig. 4.14 , the MO electronic configuration can be written as $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi\, 2p_x^{\,2}$, $\pi\, 2p_y^{\,2}$, $\sigma 2p_z^{\,2}$

Bond order : ½ $[n_b-n_a]$ = ½ [8–2] = ½ [6]= 3 ; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

Magnetic nature: molecules show magnetic behaviour depending on their MO electronic configuration. If all the MO's are **doubly occupied** the substance shows **diamagnetic** behaviour. In case one or more MO's are **singly occupied,** the substance shows **paramagnetic** behaviour. The MO electronic configuration of O_2 (with 12 valence electrons) is $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^{\,2}$, , $\pi\, 2p_x^{\,2}$, $\pi\, 2p_y^{\,2}$, $\pi^*\, 2p_x^{\,1}$, $\pi^*\, 2p_y^{\,1}$ **;** Since it contains unpaired electrons, oxygen shows paramagnetic behaviour. This has been found to be so experimentally also. In fact, the explanation of the paramagnetic behaviour of oxygen is an achievement of MOT.

The bond order and the magnetic behaviour of the diatomic molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +ve charge we subtract an electron. For example, $O_2^{\,2-}$(oxygen molecule dianion) would have a total of 14 valence electrons (12 + 2) while oxygen molecule cation $O_2^{\,+}$ would have 12–1 = 11 valence electrons.

INTEXT QUESTION 4.4

1. What is the basic difference between the valence bond and molecular orbital theories?
2. Calculate the bond orders for Li_2 and Be_2 molecules using the molecular orbital diagrams given in Fig. 4.12.
3. Predict the magnetic behaviour of O_2.

WHAT YOU HAVE LEARNT

- A chemical bond may be visualised as an effect that leads to the decrease in the energy of the combination of two atoms when they come closer.
- The atoms combine in such a way so as to attain stable electronic configuration of noble gases.
- According to Kossel, transfer of an electron from one atom to the other achieves the stable configuration. This leads to formation of ions, which are held together by electrostatic interactions called ionic bond.

- According to Lewis, the stable configuration is achieved by sharing of electron pairs between the bonding atoms. This leads to the formation of a covalent bond.
- Bonding in simple molecules can be conveniently represented in terms of Lewis electron-dot structures.
- In some covalently bound atoms the shared pair of electron is more towards the atom with greater electronegativity and leads to partial ionic character in the molecule.
- Valence shell electron pair repulsion (VSEPR) theory is very helpful in predicting the shapes of simple molecules. It is based on the interactions between the electron pairs around the central atom in the molecule.
- Valence bond theory (VBT) and Molecular orbital theory (MOT) are two modern theories of chemical bonding. These are based on the wave mechanical model of atom.
- According to the valence bond theory the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The overlap increases the electron charge density in the inter-nuclear region.
- In order to explain bonding in molecules containing more than two atoms, Pauling proposed the concept of hybridisation. In hybridisation, the atomic orbitals of the valence shell of the central atom ' hybridise' or merge and give newer orbitals with proper orientations, which explain the shape of the molecule.
- According to the Molecular orbital theory the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals. These molecular orbitals extend over the entire region of the molecule i.e., these are delocalised over the whole molecule.
- When two atomic orbitals combine it gives a pair of molecular orbitals; one is called bonding molecular orbital of lower energy and the other of higher energy is called anti-bonding orbital.
- The electrons present in the molecule are filled in these orbitals in the order of increasing energy (Aufbau principle) to give the MO electronic configuration.
- The number of bonds between the two atoms is called bond order and is defined as Bond order = b.o. = $\frac{1}{2}(n_b - n_a)$
- The MO electronic configuration can be used to predict the magnetic nature of the molecule. If all the MO's are doubly occupied the substance shows diamagnetic behaviour and if one or more MO's are singly occupied the substance shows paramagnetic behaviour.

TERMINAL EXERCISE

1. What do you understand by a chemical bond?
2. Explain the process of bond formation as a decrease in energy.
3. What do you understand by the term, ‘bond length’ ?
4. Describe the two possible ways in which the noble gas electronic configuration is achieved in the process of bond formation.
5. What are Lewis electron dot symbols ? Show the formation of $MgCl_2$ in terms of Lewis symbols.
6. Define a coordinate bond and give some examples.
7. What is VSEPR theory ? predict the shape of SF_6 molecule using this theory.
8. Why do we need the concept of hybridisation ? How does it help in explaining the shape of methane ?
9. Give the salient features of molecular orbital theory.
10. Be_2 molecule does not exist. Explain on the basis of molecular orbital theory.
11. Write down the molecular orbital electronic configuration of the following species and compute their bond orders.

    O_2 ; O_2^+ ; O_2^- ; O_2^{2-}
12. BF3 is a polar molecule but it does not show dipole moment. Why?
13. Atom A and B combine to form AB molecule. If the difference in the electronegativity between A and B is 1.7. What type of bond do you expect in AB molecule?
14. Write down the resonating structures of N_2O, SO_4^{2-}, CO_3^{2-} and BF_3.

ANSWERS TO INTEXT QUESTIONS

4.1

1. An electrovalent bond is formed when one or more electrons are transferred from one atom to another atom or atoms.

2. 

$$:\underset{\cdot}{\dot{N}}\cdot + \cdot\underset{\cdot}{\dot{N}}: \longrightarrow :N\vdots\vdots N: \longrightarrow :N\equiv N:$$

3. In a covalent bond the shared pair of electrons is closer to the more electronegative atom. This leads to charge separation in the molecule and the bond becomes polar

4. A bond in which both the bonding electrons are contributed by one atom only.

4.2

1. The two postulates of VSEPR theory are
   i) The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion
   ii) The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is stronger than that between two bond pairs The order of repulsive force between different possibilities is as under.

   lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

2. In methane the central carbon atom would have four pairs of electrons in its valence shell. According to VSEPR theory these would be placed tetrahedrally around the carbon atom. Hence the methane molecule would have a tetrahedral shape.

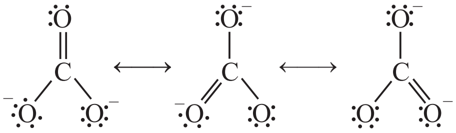
3. 50% ionic and 50% covalent character.

4.3

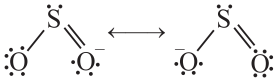
1. Hybridisation is a concept which is quite useful in explaining the shapes of molecules. According to this two or more than two non equivalent orbitals with comparable energies and different shapes mix and give rise to an equal number of equivalent hybrid orbitals in an atom. The hybrid orbitals have identical energies and shapes.

2. In ammonia the 2s and three 2p orbitals hybridize to give four sp^3 hybridized orbitals. Three of these overlap with the 1s orbitals of hydrogen and one remains nonbonding containing a lone pair. The sp^3 hybridized orbitals are directed towards the corners of a regular tetrahedron. But due to the difference in the repulsion between lone pair - bond pair and bond pair - bond pair the ammonia molecule has a distorted tetrahedral shape which is some what like a trigonal pyramid.

3. The Cannonical structure of CO_3^{2-} ion are represented as.



Sulphur dioxide is as–



4.4

1. Valence bond theory visualises the bond formation to be localized whereas according to MOT it is delocalised.

2. Bond order = b.o. = ½(n_b – n_a)
for Li_2 ; Bond order = ½ [4 – 2] = ½ [2] = 1
for Be_2 ; Bond order = ½ [4 – 4] = ½ [0] = 0

3. MO configuration of O_2 is $\sigma\ 2s^2$, $\sigma^*\ 2s^2$, $\sigma 2p_z^2$, $\pi 2p_x^2 = \pi\ 2p_y^2$
$\pi^*\ 2p^1_x = \pi^*\ 2p^1_y$
Due to 2 unpaired electrons O_2 molecule is paramagnetic.

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5

THE GASEOUS AND LIQUID STATE

We know that matter exist in three* different states namely solid, liquid and gas. The most familiar example to show these different states of matter is water. Water exists as a solid (ice), a liquid (water) and a gas (steam) under different conditions of temperture and pressure. The difference between these three states of matter is due to the difference in their intermolecular distances and intermolecular forces. In addition to these, temperture and pressure also play an important role in deciding the states of matter.

In this lesson we shall first discuss the differences in properties of the solid, liquid and gaseous state and the factors due to which these differences arise. We shall also study the effect of pressure and temperature on the volume of the given amount of gas. These are governed by the gas laws namely Boyles' law, Charles' law and Avogadros' law.

You are familiar with gases, liquids and solids in your daily life. You are aware that water can exist as a liquid, a solid (ice) or as a gas (vapour). These are called three *states of matter*. The properties of gaseous state can be explained in terms of large separation of molecules and very weak intermolecular forces. In this lesson, we shall also study about the intermolecular forces in liquids and see how their properties can be explained in terms of these forces.

OBJECTIVES

After reading this lesson, you will be able to:

- differentiate between the three states of matter - solid, liquid and gas;

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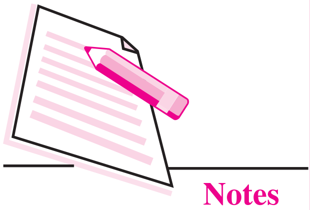
* There is fourth state of matter called Plasma. In this state matter exists as ionised gas. This occur at very high temperature. For example matter in the sun is in the Plasma State.



- describe various intermolecular interactions;
- list the characteristic properties of gases;
- state the gas laws (Boyle's law, Charle's law, Gay Lussac's law and Avogadro's law) and express these mathematically;
- draw the *p-V, p-1/V, p-pV* and *V-T* graphs;
- interpret the effect of temperature and pressure on the volume of a gas from the graph;
- derive the ideal gas equation from the gas laws;
- state the Dalton's law of partial pressure and explain its significance;
- state Graham's law of diffusion;
- explain the role of Gay Lussac's law of combining volumes and Avogtadso's law in developing the concept of molecule;
- state the postulates of Kinetic Molecular Theory of gases;
- explain the Maxwell's distribution of velocities; and effect of temperature and molar mass of gas on it.
- differentiate between u_{rms}, u_{mp} and u_{av};
- explain the deviation of real gases from ideal behaviour in term of compressibility factor;
- state the van der Waal's equation and explain the significance of van der Waals constants and
- explain the liquifaction of gases with the help of Andrews curves.
- explain the properties of liquids in terms of their structure (molecular arrangement and intermolecular forces);
- differentiate between evaporation and boiling;
- define vapour pressure of a liquid and correlate it with its boiling point;
- define surface tension and explain the effect of various factors on it;
- explain the consequences of surface tension and
- define viscosity of a liquid and correlate it with intermolecular forces.

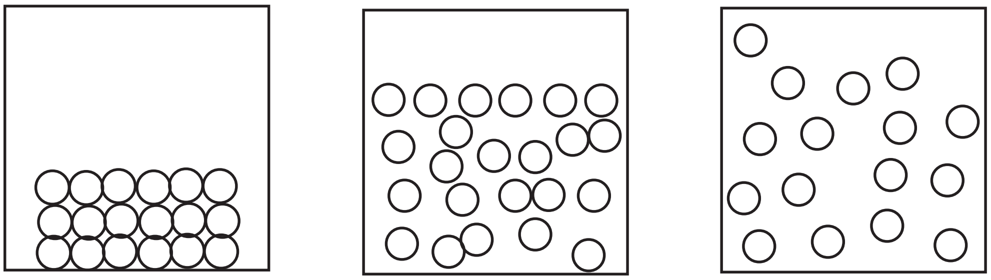
5.1 THE THREE STATES OF MATTER

At any given conditions of temperature and pressure, matter exists in one of the three states namely solid, liquid and gas. The characteristic properties of solid, liquid and gaseous state are listed in Table 5.1.

Table 5.1 : Properties of different states of matter

Property	Solid	Liquid	Gas
Shape	Definite	Indefinite; takes up the shape of the vessel.	Indefinite
Volume	Definite	Definite	Indefinite (fills the container completely)
Density	High	Less than solids but much higher than gases.	Low
Compressibility	Incompressible	largely incompressible	Highly compressible

The different characteristics of the three states of matter as listed above depend upon the relative closeness of particles that make up the substance. In solid state, the particles are held close together in a regular pattern by strong intermolecular forces. In liquid state, intermolecular forces are weak as compared to solid state hence the particles are less tightly held and allow them to move away from each other. In the gaseous state, the molecules are farthest apart as compared to solid and liquid states and the intermolecular forces are negligible so the particles move randomly. A simplified picture of particles in solid, liquid and gaseous states is represented in Fig. 5.1.



Solid (a) Liquid (b) Gas (c)

Fig. 5.1 : *A simplified picture of particles in solid, liquid and gaseous state*

5.2 INTERMOLECULAR INTERACTIONS

Intermolecular interactions are the interactions or forces that operate between the constituent particles of a substance, which may be atoms, molecules or ions. These forces are very weak as compared to intramolecular forces–the forces that operate within a molecule i.e. covalent and ionic bonds. These forces, though weak, are responsible for the existence of condensed phases, namely, liquids and solids.

5.2.1 Types of Intermolecular Interactions

There are four types of intermolecular interactions or forces: (i) London forces; (ii) Dipole – dipole forces; (iii) Dipole – induced dipole forces and (iv) Hydrogen bonding. Out of these four, the first three are collectively called **van der Waals forces**. Hydrogen bonding is a type of strong dipole – dipole forces and is *not* included in van der Waals forces. Let us now learn about these forces.

(i) London forces.

Normally we assume that electrons are evenly distributed around nucleus (Fig. 5.2(a)). However, since electrons constantly move around the nucleus, at a particular instant, the distribution of electrons may become uneven around the nucleus (Fig. 5.2 (b)) and result in generation of a dipole with a slight negative charge on one side and an equal positive charge on the opposite side. Thus, an ordinarily non-polar species like an atom of a noble gas like argon or neon becomes a polar species for an instant. This instantaneous dipole would induce dipoles in its neighbours. (Fig 5.3). These dipoles attract each other as their oppositely charged poles are near each other. The very next instant of time, this dipole disappears as the electronic distribution once again becomes symmetrical in this particular atom or molecule. With this, all the induced dipoles also disappear. However, a new instantaneous dipole appears in some other atom or molecule which induces dipoles in its neighbours.

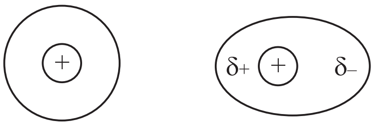
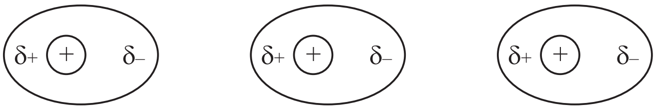


Figure 5.2: Development of instantaneous dipole



Induced depole

Instantaneous dipole

Induced dipole

Fig. 5.3: Induced dipoles in neighbours of an atom or a molecule with instantaneous dipole.

This phenomenon continues for ever. At any given instant, a large number of such atoms or molecules distributed randomly develop instantaneous dipoles which induce dipoles in their neighbours. This results in the presence of weak interactions in the substance.

These forces are named after the Germany born physicist Fritz London. London forces are the weakest of all intermolecular forces and operate at extremely short distances. These are also called **dispersion forces**. These are the only forces that are present in atoms or non-polar molecules and are responsible for the existence of their condensed phases. These forces are present universally in all types of molecules, polar or non-polar and contribute majorly toward intermolecular forces present in them.

(ii) Dipole – Dipole Forces

If molecules of a substance are polar in nature, the positive (δ+) end of one dipole attracts the negative (δ–) end of the other (Fig. 5.4) Magnitude of these forces depends upon the dipole moment of the substance. These interactions are quite strong as compared to London forces and increase the melting and boiling points of polar compounds (such as ethers) as compared to those of similar non-polar compounds (such as hydrocarbons) that have nearly the same molar mass

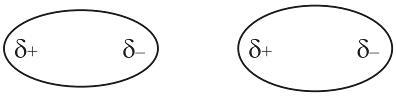


Fig. 5.4: Dipole-dipole forces

	Compound	**Molar Mass /(g mol^{-1})**	**Melting Point/K**	**Boiling point/K**
n-Butane (non-polar)	C_4H_{10}	58	135.2	272.6
Propanone (polar)	$(CH_3)_2C = O$	58	179.4	329.3

In addition to the dipole-dipole forces, London or dispersion forces also operate between polar molecules.

(iii) Dipole – Induced Dipole Forces

This type of forces operate in mixtures (solutions) of two substances, out of which one is polar in nature and the other is non-polar. The polar molecules induce a dipole in the neighbouring non-polar molecules and an electrostatic force of attraction starts operating between them (Fig 5.5). Magnitude of these forces depend upon two factors

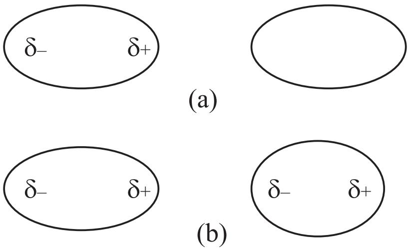


Fig. 5.5 Dipole-induced dipole forces: (a) A pair of polar and a non-polar molecules (b) Induced dipole in the non-polar molecule

(a) Dipole moment of the polar molecule. Greater the dipole moment, stronger is the attractive force.

(b) Polarizability of the non-polar molecule. More polarizable is the non-polar molecule, greater is the dipole moment of the induced dipole and stronger is the attractive force.

Dispersion or London forces also operate between polar and non-polar molecules and they experience the cumulative effect of both types of forces.

(iv) Hydrogen Bonding

Hydrogen boding is responsible for abnormally high melting and boiling points of water, ethanol, ammonia, hydrogen fluoride etc. The following table gives the boiling points of hydrides of group 14, 15, 16, and 17 elements. In each group the boiling point of hydrides is increasing with molar mass from top to bottom. The trend is clearly seen in hydrides of group 14. In other groups, the trend can be seen in all the hydrides, except that of the first element in each group i.e. NH_3 (Group 15), H_2O(Group 16) and HF (Group 17) respectively. Their boiling points are exceptionally high due to the presence of hydrogen bonding in these hydrides.

Boiling Points of some Hydrides

Group 14		**Group 15**		**Group 16**		**Group 17**	
Hydride	B. P./K	Hydride	B.P./K	Hydride	B.P./K	Hydride	B.P./K
CH_4	109	NH_3	240	H_2O	373	HF	293
SiH_4	161	PH_3	183	H_2S	212	HCl	188
GeH_4	183	AsH_3	218	H_2Se	232	HBr	207
SnH_4	221	SbH_3	255	H_2Te	271	HI	238

Hydrogen bonding is responsible for some unusual properties of water, like its existence in liquid state over a wide range of one hundred degrees (273 K to 373 K), high heats of fusion and vaporization and its solid form (ice) being lighter than liquid water. Hydrogen bonding plays a crucial role in the structure of DNA by holding together the two helical nucleic acid chains.

5.3 GENERAL BEHAVIOUR OF GASES: THE GAS LAWS

The volume of a given mass of a gas depends upon the temperature and pressure under which the gas exists. It is, therefore, possible to describe the behaviour of gases in terms of the four variables: temperature, T ; pressure p; volume V and amount (number of moles, n). For a given amount of gas the volume of gas changes with change in variables such as temperture and pressure. The relationship between any two of the variables is studied, keeping the other variable constant by various laws which are described below.

5.3.1 Effect of Pressure on the Volume of the Gas (Boyle's law)

The effects of pressure on the volume of gas for a given amount of gas at constant temperture was studied by Robert Boyle in 1662 for different gases. He observed that if the volume of gas is doubled the pressure is halved and vice versa. Boyle's law states that at constant temperature, the volume of a given amount of a gas is inversely proportional to its pressure.

Mathematically Boyle's law is expressed as shown below:

$$V \propto \frac{1}{p} \qquad \text{(at constant } T \text{ and } n\text{)}$$

or

$$p_1 V_1 = p_2 V_2$$

when the pressure of the gas, p is plotted against volume of the gas, V the exponential curve is obtained (Fig. 5.6). However when the pressure, p of the gas is plotted against $\frac{1}{V}$ a straight line is obtained (Fig. 5.7). If the product of pressure and volume (pV) is plotted against pressure (p) a straight line parellel to x-axis (pressure is axis) is obtained (Fig. 5.8).

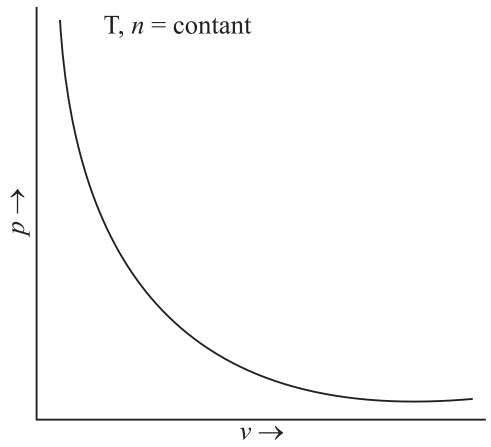


Fig. 5.6 : *A graph of p versues V*

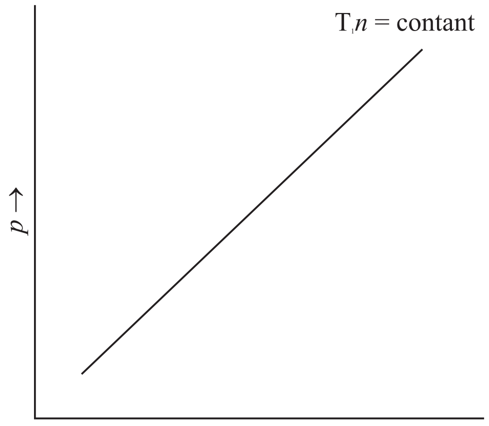


Fig. 5.7 : *A graph of p versues* $\left(\frac{1}{V}\right)$

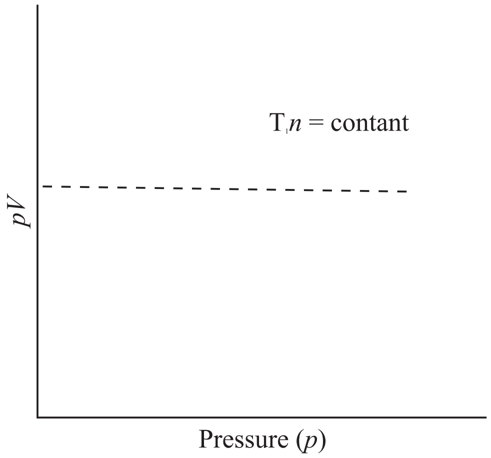


Fig. 5.8 : *A graph of p*V *versues p*

Example 5.1 : The volume occupied by a given mass of a gas at 298 K is 24 mL at 1 atmospheric pressure. Calculate the volume of the gas if the pressure is increased to 1.25 atmosphere keeping temperature constant.

Solution : Given that

$$V_1 = 25 \text{ mL} \qquad p_1 = 1 \text{ atm}$$

$$V_2 = ? \qquad p_2 = 1.25 \text{ atm}$$

According to Boyle's Law, $p_1V_1 = p_2V_2$

substituting the values of p_1, V_1 and p_2 in the above expression we get

$$V_2 = \frac{p_1 V_1}{p_2} = \frac{(1 \text{ atm})\,(25\text{mL})}{(1.25 \text{ atm})} = 20 \text{ mL}$$

The volume occupied by the gas is 20 mL at 298 K and 1.25 atm pressure.

Example 5.2 : The volume of a certain amount of a gas is decreased to one fifth of its initial volume at a constant temperature. What is the final pressure?

Solution : Let

Initial volume = V_1 Initial pressure = p_1

Final volume $V_2 = V_1/5$ Final pressure = p_2

By Boyle's law, we know that at constant temperature

$$p_1V_1 = p_2V_2$$

$$p_2 = \frac{p_1 V_1}{V_2} = \frac{p_1 \times V_1}{\frac{V_1}{5}} = 5p_1$$

Thus when volume is decreased to $\frac{1}{5}$th of its initial volume, the pressure is increased by 5 times of the initial voluem.

5.3.2 Effect of Temperature on the Volume of Gas (Charles' Law)

The effects of temperature on the volume of the gas was studied by Jacques Charles in 1787 and Gay Lussac in 1802 at constant pressure for different gases. Their conclusion can be given as Charles' law which states that at a constant pressure, the volume of a given amount of gas is directly proportional to the absolute temperature.

So, according to Charles' Law, the volume of a gas increases as its absolute temperature is being raised, if its absolute temperature is lowered, its volume will consequently decrease. Mathematically, Charles' Law is expressed as shown below:

$$V \propto t \qquad \text{(at constant } p \text{ and } n\text{)}$$

$$V = k\,.\,t \qquad (k \text{ is a constant})$$

Therefore, $V_1/t_1 = V_2/t_2$

Graphical representation of Charles' Law is a straight line pointing away from the origin of the graph as shown in Fig. 5.9.

Here graph of the volume of a gas (V) plotted against its temperature at constant pressure and amount (in moles). Notice that the graph is a straight line with a positive gradient (slope).

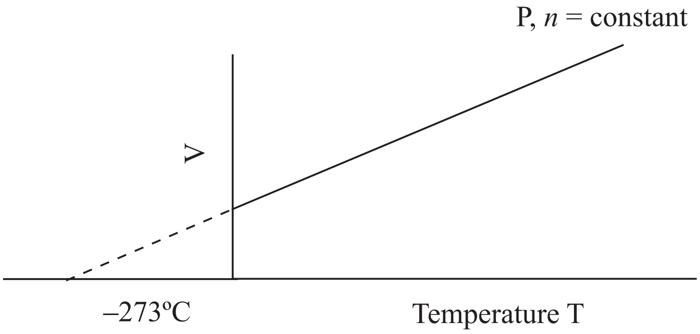


Fig. 5.9 : *A graph of V versues T*

Mathematically volume of a gas at temperature *t* is given as

$$v_t = v_0 + \frac{v_0}{273} \times t = v_0\left(1 + \frac{t}{273}\right) = v_0\left(\frac{273 + t}{273}\right)$$

Thus at $t = -273°C$

$$v_t = v_0\left(\frac{273 - 273}{273}\right) = 0$$

This means that at –273°C, the volume of the gas is reduced to zero i.e., the gas ceases to exist. Thus this temperature (–273°C) at which the gas hypothetically ceases to exist is called **Absolute zero.** It is represented by zero K.

This is the theoretically lowest possible temperature. In actual practice, we cannot reduce the temperature of the gas to zero kelvin.

Kelvin Scale of Temperatue

The scale of temperature which has –273°C as zero is called Kelvin Scale. Degree celsius is converted to Kelvin by adding 273. Thus

$$t/°C + 273 = T/K$$

where T = temperature in Kelvin

t = temperature in celcius

For example 15°C can be converted in K by adding 273 to 15.

Notes

5.3.3 Effect of Temperature on Pressure (Gay-Lussac's Law)

This law states that.

Pressure of given amount of a gas at constant volume is directly proportional to its absolute temperature.

$$p \ \alpha \ T$$

$$p = kT$$

Example 5.3 : A given amount of a gas is maintained at constant pressure and occupies a volume of 2 litres at 1000ºC. What would be volume if gas is cooled to 0ºC keeping pressure constant.

Solution : Given that,

Initial volume $V_1 = 2L$ $\quad T_1 = 1000 + 273 = 1273$ K

Final volume $V_2 = ?$ $\quad T_2 = 0 + 273 = 273$ K

Now using Charle's Law $\quad V_1/T_1 = V_2/T_2$ or $V_2 = (V_1/T_1) \times T_2$

On substituting the values we get

$V_2 = (V_1/T_1) \times T_2 = (2L/1273 \text{ K}) \times 273 \text{ K} = 0.4291$ L

5.3.4 Avogadros' Law

The Italian physicist Amadeo Avogadro was the first to propose, in 1811, a relationship between the volume of a gas and the number of molecules present in it. This, relationship is known as Avogadros' Law. It states that :

Equal volumes of all gases at the same temperature and pressure contain equal number of molecules.

Mathematically, Avogadros' law is expressed as :

$V \ \alpha \ N$ (at constant temperature and pressure)

Where V and N are volume and number of molecules respectively.

At a given temperature and pressure, the number of molecules present in the gas is directly proportional to the number of moles.

therefore, $\quad N \propto n$

Where n is the number of moles

$$\therefore \qquad V \propto n$$

$$\text{or} \qquad \frac{V}{n} = \text{constant}$$

Also $$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

He also found that the number of molecules present in 1 mole of any substance (22.4 litre of any gas at 273 K temperature and 1 atmosphere pressure) is 6.022×10^{23} molecules. This number is known as **Avogadros' number**.

It is the number of molecules (6.022×10^{23}) of any gas present in a volume of 22.4 L (at 273 K and 1 atm) and it is the same for the lightest gas (hydrogen) as for a heavy gas such as carbon dioxide or bromine.

Example 5.4 : 0.965 mol of a gas occupies a volume of 5.0 L at 298 K temperature and 1 atm pressure. What would be the volume of 1.80 mol of the gas at the same temperature and pressure?

Solution :

$$V_1 n_2 = V_2 n_1$$

$$V_2 = \frac{V_1 n_2}{n_1} = \frac{(5.0\ \text{L})\ (1.8\ \text{mol})}{(0.965\ \text{mol})}$$

$$V_2 = 9.33\ \text{L}$$

Example 5.5 : Compare the volumes of 16 g of oxygen and 14 g nitrogen at the same temperature and pressure.

Solution : Number of moles of $O_2 = 16\ \text{g}/32\ \text{g mol}^{-1} = 0.5$ mol

Number of moles of $N_2 = 14\ \text{g}/28\ \text{g mol}^{-1} = 0.5$ mol

Since the two gases are at the same temperature and pressure, and contain equal number of mole, hence according to the Avogadro's Law they should also occupy the same volume.

INTEXT QUESTION 5.1

1. The density of a gas is usually less than that of the liquid. Explain.
2. Calculate the pressure (atm) required to compress 500 mL of gas at 0.20 atm into a volume of 10 mL.
3. Equal volumes of oxygen gas and an unknown gas weigh 2.00 and 1.75 g respectively under the same experimental conditions. What is the molar mass of the unknown gas?
4. What type of intermolecular interactions are present in (a) Ne gas (b) Carbon monoxide.

5.3 THE IDEAL GAS EQUATION

Boyle's Law, Charles' Law and Avogadro's Law can be combined to give a single equation which represents the relation between the pressure, volume and kelvin temperature of a given amount of a gas under different conditions. Thus

$V \propto 1/p$ at constant temperature (Boyles' Law)

$V \propto T$ at constant pressure (Charles' Law)

$V \propto n$ at constant temperature and pressure (Avogadros' Law)

All the three expressions can be combined into a single expression

$$V \propto nT/P \text{ or } pV \propto n\,T$$

$$\text{or } \; pV = \text{constant} \times n\,T$$

The constant in this equation is called **'universal gas constant'** or **'molar gas constant',** represented by R. Thus we can write for 1 mole of a gas

$$pV = RT$$

Correspondingly, for n moles of a gas we have

$$pV = n\,RT$$

This is known as the ideal gas equation because it holds only when gases are behaving as 'ideal' gases.

Since for a given mass of gas we can write

$$pV/T = \text{a constant, we have}$$

$$p_1\,V_1/T_1 = p_2\,V_2/T_2$$

Where p_1, V_1 and T_1 refer to one set of conditions and p_2, V_2 and T_2 refer to a different set of conditions.

The numerical value of R can be found by substituting experimental quantities in the equation. At STP, $T = 273.15$ K, $p = 1$ bar (10^5 Pa) and for 1 mol of gas ($n = 1$), $V = 22.711$ L. Consequently,

$$R = pV/nT = (10^5\ \text{Pa})\ (22.711 \times 10^{-3}\ \text{m}^3)\ /\ (1\ \text{mol})\ (273.15\text{K})$$

$$= 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$$

At STP conditions used earlier (0°C and 1 atom pressure) the volume occupied by 1 mol of gas is 22.414 L

The value of R depends on the units adopted for the quantities in the equation $pV = nRT$. The various values are:

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

$R = 0.082057\ \text{L atm K}^{-1}\ \text{mol}^{-1}$ (for calculation purpose the value is taken as $0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1}$)

$R = 8.314 \times 10^7\ \text{erg K}^{-1}\ \text{mol}^{-1}$

$R = 1.987\ \text{cal K}^{-1}\ \text{mol}^{-1}$

Example 5.6 : At 273 K, 10 mol of a gas is confined in container of volume 224 L. Calculate the pressure of the gas. $R = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}$.

Solution : The ideal gas equation $pV = nRT$ will be used here

$n = 10$ mol, $R = 0.0821\ \text{atm L K}^{-1}\ \text{mol}^{-1}$

$V = 224$ L $T = 273$K $p = ?$

On substituting these values in the above equation we get

$p = n\text{RT/V} = (10\ \text{mol} \times 0.0821\ \text{atm L mol}^{-1}\ \text{K}^{-1} \times 273\text{K}) / 224\text{L} = 0.99998\ \text{atm} = 1\ \text{atm}$

5.4 DALTONS' LAW OF PARTIAL PRESSURE

The behaviour observed when two or more non-reacting gases are placed in the same container is given by Dalton's Law of partial pressures. Dalton's Law states that.

The total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the various gases present in the mixture.

The partial pressure is defined as the pressure the gas would exert if it was alone in the container. Suppose a sample of hydrogen is pumped into a one litre box and its pressure is found to be 0.065 atm. Suppose, further a sample or argon is pumped into a second one litre box and its pressure is found to be 0.027 atm. If both samples are now transferred to a third one litre box, the pressure is observed to be 0.092 atm. For the general case, Daltons' Law can be written as

$$p_{\text{total}} = p_{\text{A}} + p_{\text{B}} + p_{\text{C}} + \ldots.$$

Where p_{A}, p_{B}, p_{C},.... are the partial pressure of gases A, B, C, ... respectively. This gas laws provide a simple way of calculating the partial pressure of each component, given the composition of the mixture and the total pressure. First we introduce the mole fractions X_A and X_B. These are defined as

$$X_A = \frac{n_{\text{A}}}{n} \quad \text{and} \quad X_B = \frac{n_{\text{B}}}{n}$$

Where n_{A} and n_{B} are the number of moles of gas A and B respectively and $n = n_{\text{A}} + n_{\text{B}}$.

Since $p_A = n_A\, RT/V,\ p_B = n_B\, RT/V$ and $p = n\, RT/V$,

it follows that

$$p_A = X_A p \text{ and } p_B = X_B p$$

This is an exceptionally useful (and simple) way of calculating at partial pressures when the composition and total (measured) pressure of a mixture of gas is known.

Example 5.7 : Atmosphere is often considered mainly as a mixture of nitrogen and oxygen: 76.8% by mass of nitrogen and 23.2% by mass of oxygen. Calculate the partial pressure of each gas when the total pressure is 1 atm.

Solution : The number of moles of each component is

$$p_{N_2} = 76.8 \text{ g} / 28 \text{ g mol}^{-1} = 2.74 \text{ mol}$$

$$p_{O_2} = 23.2 \text{ g} / 32 \text{ g mol}^{-1} = 0.725 \text{ mol}$$

The mole fractions of the components are therefore

$$X_{N_2} = \frac{2.74}{2.74 + 0.725} = 0.791\ ;\ X_{O_2} = \frac{0.725}{2.74 + 0.725} = 0.209$$

The partial pressures are therefore given by

$$p_{N_2} = 0.791 \times 1 \text{ atm} = 0.791 \text{ atm}$$

$$p_{O_2} = 0.209 \times 1 \text{ atm} = 0.209 \text{ atm}$$

5.5 GRAHAM'S LAW OF DIFFUSION

If we open a bottle of perfume in one corner of a room or burn an incense stick we can feel the smell of the perfume or the incense stick all over the room also. The smell of perfume or incense stick spreads from one point of the room to the other by mixing with air. This free intermingling of gases when placed in contact with each other is known as **diffusion.**

Diffusion occurs in liquids as well as in gases. **Effusion** is the escape of a gas through a small hole, as in case of a puncture in a tyre.

The experimental observation of the rate of effusion of gases through a small hole in the side led Graham (1829) to formulate the following law:

At constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. Graham's law is applicable to both diffusion and effusion.

If the time for a given volume of gas A to escape is t_A, while the time for the same volume of gas B to escape is t_B, it follows, that,

$t_A/t_B = (\text{rate})_B / (\text{rate})_A = \sqrt{\rho_A/\rho_B}$ where ρ_A and ρ_B are the densities of gases A and B respectively.

The ratio of the densities of the gases is the same as the ratio of the molecular masses of the gases at the same temperature and pressure.

hence, $t_A/t_B = (\text{rate})_B / (\text{rate})_A = \rho_A / \rho_B = \sqrt{M_A/M_B}$ where M_A and M_B are the molecular masses of gases A and B respectively.

INTEXT QUESTIONS 5.2

1. What is the difference between diffusion and effusion.
2. Explain why Daltons' law is not applicable to a system of ammonia and hydrogen chloride gas.
3. The rates of diffusion of CO_2 and O_3 were found to be 0.29 and 0.271. What is the molecular mass of O_3 if the molecular mass of CO_2 is 44.
4. Calculate the pressure exerted by 5.0 mol of carbon dioxide in a 1 litre flask at 47ºC using ideal gas equation.

5.6 GAY LUSSAC'S LAW OF COMBINING VOLUMES

One of the laws of chemical bomination is Gay Lussac's law of combining volumes.

This law states that in any chemical reaction involving gases the volumes of gaseous reactants and products (if any) bear a simple ratio to one another, when measured under similar conditions of pressure and temperature in the reaction

$$\underset{1\ \text{vol}}{N_2(g)} + \underset{3\ \text{vol}}{3H_2(g)} \longrightarrow \underset{2\ \text{vol}}{2NH_3(g)}$$

The ratio of volumes of nitrogen, hydrogen and ammonia is 1 : 3 : 2 when their volumes are measured at the same temperature and pressure. Similarly, in the reaction

$$\underset{2\ \text{vol}}{2H_2(g)} + \underset{1\ \text{vol}}{O_2(g)} \longrightarrow 2H_2O(l)$$

hydrogen and oxygen always react in the ratio 2 : 1 by volume.

This law is nothing but the law of definite proportions stated in terms of volume. Gay Lussac's law when combined with gas laws led to the concept of molecules.

Gay Lussac's Law and the concept of molecule

Prior to the Avogadro's law, a similar hypothesis was put forward by Berzelius. "Equal volumes of all gases, under similar conditions of temperature and pressure contain equal number of **atoms**." This hypothesis, when combined with the Gay-Lussac's law led to conclusions which contradicted Dalton's atomic theory. For example consider the gas phase reaction between hydrogen and chlorine to form hydrogen chloride

$$\underset{1\ \text{vol}}{\text{Hydrogen(g)}} + \underset{1\ \text{vol}}{\text{Chlorine(g)}} \longrightarrow \underset{2\ \text{vol (same } T \text{ and } P)}{\text{Hydrogen chloride(g)}}$$

Gay Lussac's law (experimental result)

Berzelius hypothesised	x number of hydrogen atoms	x number of chlorine atoms	$2x$ number of compound atoms of hydrogen chloride
Divided by x	1 atom of hydrogen	1 atom of chlorine	2 compound atoms of hydrogen chloride
Divided by 2	$\frac{1}{2}$ atom of hydrogen	$\frac{1}{2}$ atom of chlorine	1 compound atom of hydrogen chloride

('Compound atom' was the term used by Dalton for the smallest particle of compounds before of molecule was developed)

Thus, one compound atom of hydrogen chloride contains one-half atom of each of hydrogen and chlorine. This contradicts the Dalton's atomic theory according to which atoms are indivisible. Therefore fractional atoms ($\frac{1}{2}$ atom each of H and Cl) cannot be present in hydrogen chloride. Due to this contradiction Avogadro modified the Berzelius hypothesis by replacing the term 'atom' by 'molecule'. According to Avogadro's law, equal volumes of all gases, under similar conditions of temperature and pressure contain equal number of **molecules**". This law when applied to the same reaction as earlier, modifies the conclusion.

$$\underset{1\ \text{vol}}{\text{Hydrogen (g)}} + \underset{1\ \text{vol}}{\text{Chlorine (g)}} \longrightarrow \underset{2\ \text{vol}}{\text{Hydrogen chloride (g)}}$$

Gay Lussac's Law

Avogadros law	'x' molecules of hydrogen	'x' molecules of chlorine	'$2x$' molecules of hydrogen chloride
Divide by $2x$	$\frac{1}{2}$ molecule of hydrogen	$\frac{1}{2}$ molecule of chlorine	1 molecule of hydrogen chloride

Thus, now, one molecule of hydrogen chloride, is made from one-half molecule each of hydrogen and chlorine. 'Molecule' was accepted as the smallest stable particle of matter (element or compound) which has the same properties as the bulk of the matter. Further, it was suggested that each molecule of an element may contain more than one atom of the element. Later studies showed that both, hydrogen and chlorine molecules are diatomic and contain two atoms each. Their chemical formulae are H_2 and Cl_2 respectively; one-half molecule, now, would mean one atom of H or Cl. Thus one molecule (rather than compound atom) of hydrogen chloride would be formed by one atom each of hydrogen and chlorine and its formula becomes HCl. Now we may write the reaction as

$H_2(g)$	+	$Cl_2(g)$	$\longrightarrow$	$2HCl(g)$
1 vol		1 vol		2 vol
'x' molecules		'x' molecules		'$2x$' molecules
$\frac{1}{2}$ molecule		$\frac{1}{2}$ molecule		1 molecule
1 atom		1 atom		1 molecule

Thus Gay-Lussac's law and Avogadro's Law led to the concept of 'molecule'.

5.7 KINETIC MOLECULAR THEOY OF GASES (ACCOUNTING FOR THE GAS LAWS)

To explain the behaviour of the gases theoretically, Clausius, Maxwell and Boltzmann made the following assumptions:

(1) Gases consist of large number of tiny particles called molecules.

(2) The gas molecules are so small and so far apart that the total volume of the molecules is a negligible fraction of the total volume occupied by the gas.

(3) The molecules are in a state of constant, rapid and random motion colliding with one another and with the walls of the container.

(4) There are no attractive or repulsive forces between the molecules of the gas.

(5) The collisions of the molecules among themselves and with the walls of the containing vessel are perfectly elastic, so that there is no loss of energy during collisions.

(6) The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the containing vessel.

(7) The kinetic energy of a gas is a directly proportional to the absolute temperature of the gas.

On the basis of this model, it is possible to derive the following expression for a gas:

$$pV = \frac{1}{3} m \, \mathrm{N}\overline{\mathrm{C}^2}$$

Where p is pressure, V denotes volume, m is the mass of a gas molecule, N is the total number of molecules, and $\overline{\mathrm{C}}$ is the root mean square velocity of the gas molecules.

5.7.1 Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{\left(C_1^2 + C_2^2 + ...+ C_N^2\right)}/N$$

where C_1, C_2.... C_N the molecular velocities.

5.7.2 Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + ... + u_N}{N}$$

and is given by the expression

$$u_{av} = \sqrt{\frac{8\,RT}{\pi M}}$$

5.8 DISTRIBUTION OF MOLECULAR SPEEDS

According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the resdistribution of the energy takes place. As a result their speed and the kinetic energy changes. Therefore at any instant different molecules have different speed and hence different kinetic energy. At the given temperature even though the speed of the individual molecule constinuously changes, the fraction of the molecules having the same speed remains constant and this is known as **Maxwell–Bolttzmann Distribution Law.**

At the given temperature this fraction is denoted by $\frac{dN}{N}$ where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown as figure 5.10.

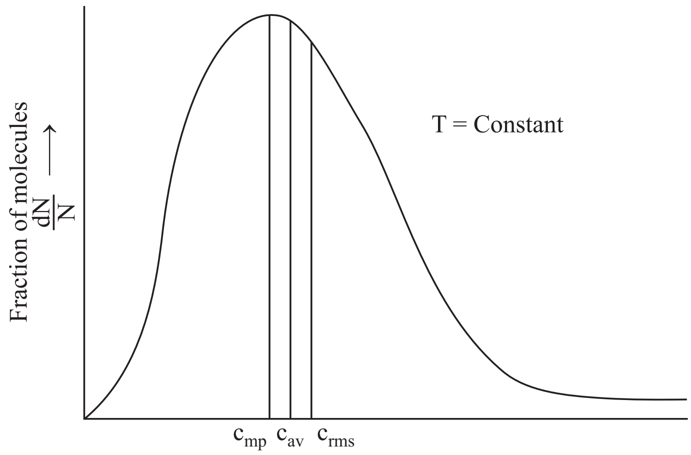


Fig. 5.10: *Maxwells distribution of speeds of molecules at a constant temperature*

In the above Fig. 5.10, the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of molecules. This is known as the **most probable speed c_{mp}**. Also shown in the figure are the **average speed, c_{av}** and the **root mean square (rms) speed c_{rms}** These types of speeds are related to the temperatures, T and the molar mass, M of the gas by the following relations

$$c_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

$$c_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}$$

$$c_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

The relative values of these speeds are

$$c_{\text{mp}} : c_{\text{av}} : c_{\text{rms}}$$

$$1 : 1.13 : 1.22$$

Or $$0.82 : 0.92 : 1$$

From any of the above relations it can be seen that these speeds are related to the temperature and molar mass of the gas.

Dependence of molecular speeds on temperature

The temperature dependence of molecular speeds is shown in Fig. 5.11. On increasing the temperature the fraction of molecules with higher speeds increases and with somes speeds decreases. The maxima shifts to higher velocity side but its height decreases.

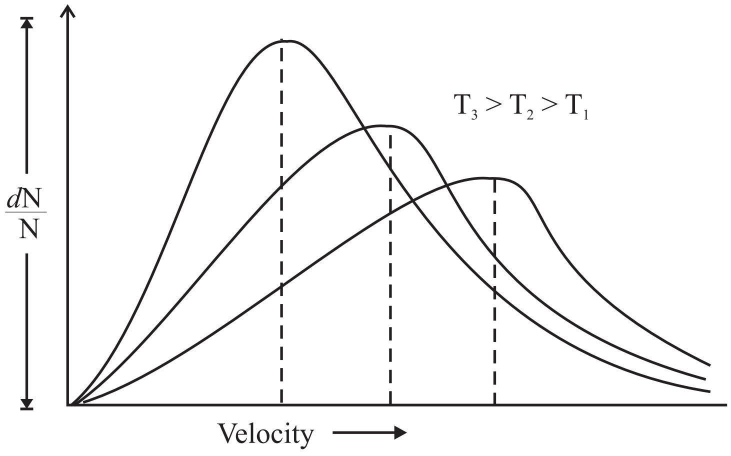


Fig. 5.11: *Effect of temperature on distribution of velocities.*

Dependence of molecular speeds on molar mass of the gas

At a constant temperature any of the three types of speeds is inversely proportional to the square root of the molar mass of the gas, that is,

$$C_{mp} \propto \sqrt{\frac{1}{M}}$$

Hence, at the same temperature, the most probable speed of a lighter gas would be more than that of a heavier gas. Figure 5.12 a shows the distribution curves of H_2 and N_2 gases.

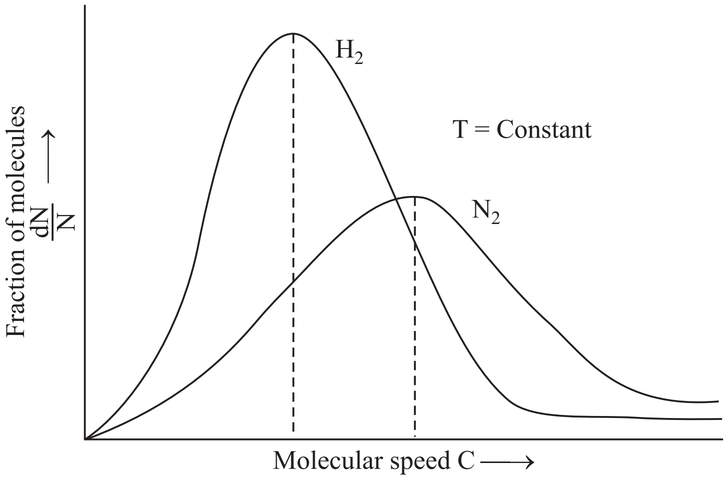


Fig. 5.12 A: Effect of molar mass of the gas on distribution of speeds.

5.9 DEVIATION FROM IDEAL GAS BAHAVIOUR

The gas laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Real gases show deviations from these laws at low temperature and high pressure. These deviations can be shown clearly by plotting $\frac{pV}{nRT}$ as a function of pressure at constant temperature,

$$\frac{pV}{nRT} = \frac{V_{observed}}{V_{ideal}} = Z \text{ (compressibility factor)}$$

Such a plot is shown in Fig. 5.13 for an ideal gas and a few real gases. you may note that for in ideal gas pV = nRT hence $\frac{pV}{nRT} = z = 1$. Thus a straight line obtained for ideal gas in this plot, but for real gases diferent curves are obtained.

Gases deviate from ideal behaviour due to the following faulty assumptions of kinetic theory :

1. Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
2. There is no force of attraction between the molecules of a gas.

Notes

Contrary to assumption(1), the volume occupied by the molecules of a gas becomes significant at high pressures. If *nb* is the volume occupied by the molecules, the actual volume of the gas is ($V - nb$). Assumption (2) too doesn't hold good as at high pressures molecular interactions start operating. Molecules are dragged back by other molecules which affects the pressure exerted by them on the walls of the container.

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

(P_{real} is observed pressure and $\frac{an^2}{V^2}$ is correction term)

In view of the corrections for pressure and volume, ideal gas equation can be rewritten as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

This is known as van der Waals' equation

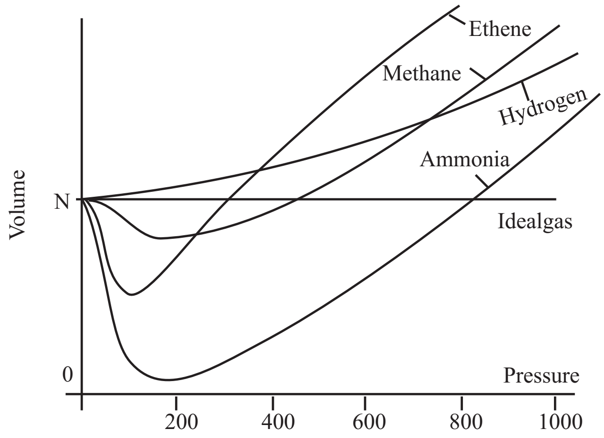


Fig. 5.13 : *The plot volume versus P for real gases*

5.10 LIQUEFACTION OF GAS

Any gas can be liquified at atmospheric pressure if it is cooled sufficiently. Many gases (but not all) can be liquified at ordinary temperature by compressing them.

The conditions of temperature and pressure under which gases liquify were first investigated by Andrews in 1869.

Andrews subjected CO_2 to various pressures at different temperatures and plotted the effect of pressure on volume (Fig. 5.14). The curve obtained at a given temperature is called an *isotherm.* As can be seen in the figure, at 321 K the volume of the gas decreased with the increased pressure approximately in accordance with the Boyle's Law. At 294 K, however, the volume first decreases in accordance with Boyle's Law until the pressure was increased to about 60 atm. At this pressure there was a sudden break in the curve and liquid carbon dioxide appeared. The pressure remained constant until all the gas had been converted into liquid. Subsequent increase of pressure caused practically no change in volume. In accordance with the general rule that extremely high pressures are required to compress liquids appreciably.

Liquefaction of Gases

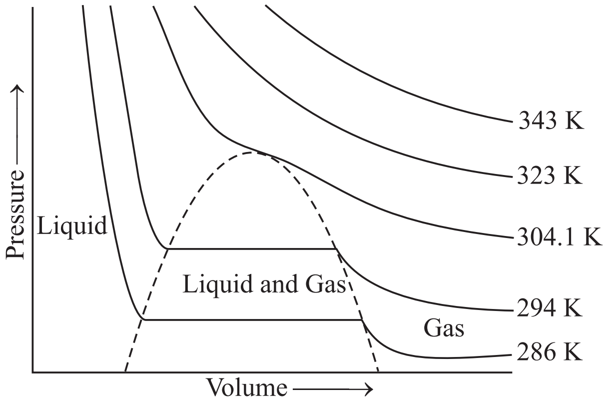


Figure 5.14: *Isotherms of carbon dioxide*

Similar changes took place when the isotherms were constructed for temperatures below 294 K, except that the pressure required to liquify the gas became smaller as the temperature decreased. Andrews found that liquifaction could be brought about at all temperatures below 304.1 K. But above this temperature no liquifaction occured no matter how much pressure was increased. This temperature was therefore called the **critical temperature** for CO_2. The pressure required to liquify the gas at the critical temperature was called **critical pressure,** and the volume of 1 mole of the substance at the critical temperature and pressure, the **critical volume.**

The temperature above which a gas cannot be liquified, however large the pressure may be is known as critical temperature.

Table 5.2 list values of the critical temperature and pressure critical volume for some common substances.

Table 5.2 : Critical temperatures and critical pressures

Substance	Critical Temperature (K)	Critical Pressure (atm)
Water, H_2O	647	217.7
Sulphur dioxide, SO_2	430	77.7
Ammonia, NH_3	406	112.5
Hydrogen Chloride, HCl	324	81.6
Carbon dioxide, CO_2	304	73.0
Oxygen, O_2	154	49.7
Nitrogen, N_2	126	33.5
Hydrogen, H_2	33	12.8

INTEXT QUESTIONS 5.3

1. What are the conditions under which real gases behave as ideal gas.
2. Which term in van der waals equation accounts for the molecular volume.
3. Calculate the root mean square velocity of ozone kept in a closed vessel at 20ºC and 1 atm pressure.
4. What is compressibility factor.

5.11 NATURE OF LIQUIDS

Look at Figure 5.1 in which the molecular arrangement has been shown in the three states of matter. What do you notice?

In figure 5.1a, you would find that the molecules are far apart. A gaseous state can be represented by this arrangement. In liquid state (figure 5.1b), molecules are closer as compared to gaseous state. You would notice that they have very little spaces between them. However, there is no order in arrangement of molecules. Further we say that, these molecules can move about, but with lesser speeds than those in gases. They can still collide with one another as in the gaseous state. You would recall that the molecules in gases have very little attraction between them. But in liquid state the attraction between the molecules is comparatively much stronger as compared to that in the gaseous state. The attractions are strong enough to keep the molecules in aggregation. Contrary to this, in solids (Fig. 5.1a) you notice that the molecules are arranged at the closest possible distance.

Solid state is a well ordered state and has very strong intermolecular forces. You would learn more about solids in lesson 8.

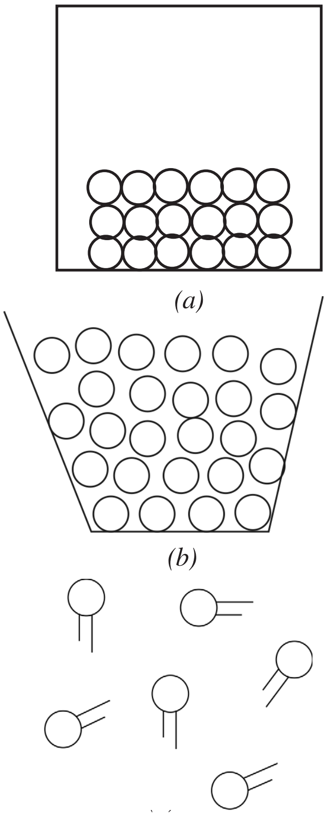


Fig. 5.15 : *Arrangement of molecuels in (a) solids; (b) liquids and (c) gases*

We would say, in a gas there is complete chaos due to very weak intermolecular forces, whereas in solids there is a complete order due to strong forces. Liquids fall between gases and solids. Liquid molecules have some freedom of gases state and some order of solid state. Intermolecular forces in liquids are strong enough to keep the molecules close to one another but not strong enough to keep them in perfect order.

Notes

5.12 PROPERTIES OF LIQUIDS

In this section you would learn how the properties of liquids can be explained in terms of molecular arrangement and intermolecular forces. Let us consider a few properties of liquids as examples.

5.12.1 Volume and Shape

You would recall that the liquids (for example water) take the shape of the container in which they are kept. However, they have a definite volume. How can you explain the properties of definite volume and variable shape? In liquids, the attractive forces are strong enough to keep the molecules moving within a definite boundary. Thus, they maintain a definite volume. These intermolecular forces are not strong enough to keep them in definite positions. The molecules can, therefore, move around and take the shape of the container in which they are kept.

5.12.2 Compressibility

Compressibility of a substance is its ability to be squeezed when a force is applied on it. Let us study the compressibility of liquids with the help of the following activity.

ACTIVITY 5.1

Aim: To study the compressibility of water.

What is required?

A 5 mL syringe and water.

What to do?

(i) Take the syringe and fill it with water by pulling out the plunger.

(ii) Note the volume of water.

(iii) Press the plunger while blocking the nozzle of the syringe with a finger.

What to observe?

Observe the volume of water in the syringe while pressing the plunger. Does the volume of water change by pressing the plunger? You would observe that it does not change.

The above activity clearly shows that liquids are largely incompressible. It is because there is very little empty space between the molecules. In contrast, the gases are highly compressible because of large empty spaces between their molecules.

The large difference in the free space in gaseous and liquid states becomes evident from the fact that the volume occupied by a given amount of a substance in liquid state is *100-1000 times less* than that in the gaseous state.

5.12.3 Diffusion

Diffusion is the process of spreading of a substance from a region of higher concentration to a region of lower concentration. Let us study the phenomenon of diffusion in liquids with the help of the following activity.

ACTIVITY 5.2

Aim : To study the phenomenon of diffusion through water.

What is required?

A glass, water, blue ink and a dropper.

What to do?

(i) Take some water in the glass.

(ii) Add a few drops of blue ink into water with the help of a dropper.

What to observe?

Observe the water and ink in the beaker.
Initially the ink does not mix with water. After some time it starts spreading slowly. After a few hours the whole of water in the glass becomes coloured due to diffusion of ink through water.

The above activity demonstrates that diffusion occurs in liquids. Why does it happen? Because the molecules of both the liquids are moving and help in the diffusion process.

5.12.4 Evaporation

You know that water left in an open pan evaporates slowly until the pan becomes dry. Evaporation is the process by which a liquid changes into vapour. It occurs at all temperatures from freezing point to boiling point of the liquid.

In a liquid, at any temperature, a small fraction of the molecules is moving with relatively high velocity. Such molecules have high kinetic energy. These can overcome the intermolecular attractive forces and escape through the surface of the liquid.

Rate of evaporation of a liquid depends on a number of factors. For example, more is the surface area, faster will be the evaporation. For faster drying, we increase the surface area by spreading the wet clothes. If we supply heat to the liquid, evaporation is faster. The wet clothes dry faster in the sun. The increase in temperature increases the kinetic energy of the molecules of the liquid and the liquid evaporates at a faster rate. We feel cool after the bath. Why do we feel so? It is because during evaporation water takes the heat from our body and we feel cold.

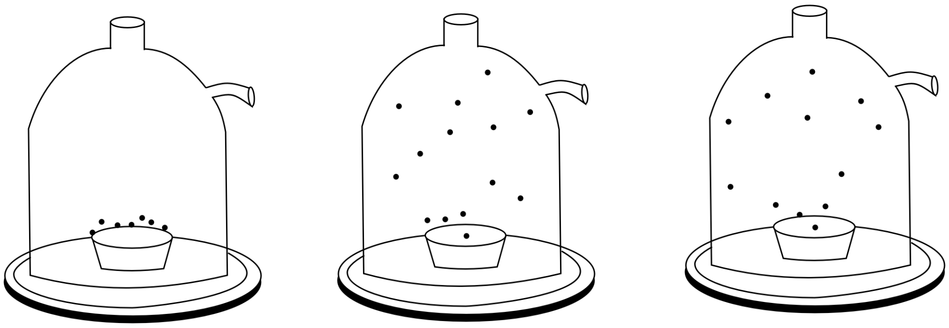
Now let us compare the rate of evaporation of two liquids, for example, water and alcohol. Which of these two liquids evaporates faster? You must have experienced that alcohol evaporates faster. Why does this happen? The number of molecules escaping from a liquid depends upon the attractive forces. When these forces are stronger, fewer molecule escape. In alcohol, these attractive forces are weaker than those in the water. Hence, alcohol evaporates faster than water.

5.13 VAPOUR PRESSURE AND BOILING POINT

In the previous section you have learnt that liquids evaporate when kept in an open vessel. Different liquids evaporate to different extent under similar conditions. The extent of evaporation of a liquid is measured with the help of **vapour pressure** of a liquid. In this section, you will study about it and also about the boiling point of a liquid.

5.13.1 Vapour Pressure of a Liquid

You know that a liquid placed in an open vessel evaporates completely. If, however, the liquid is allowed to evaporate in a closed vessel, say in stoppered bottle or a bell jar, evaporation occurs, but after sometime the level of the liquid does not change any further and becomes constant. Let us understand how does it happen. In the closed vessel, the molecules evaporating from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air and some of them may start moving towards the surface of the liquid and enter into it. This is known as condensation. In the


Initially molecules evaporate

After some time condensation begins

At equilibrium the rates of eavporation and condensation become equal

Fig. 5.16 : *Establishing (vapour liquid) equilibrium under a evacuated jar*

beginning, rate of evaporation is greater than the rate of condensation. But as more and more molecules accumulate in the space above the liquid, rate of condensation gradually increases. After some time, rate of evaporation becomes equal to the rate of condensation and an equilibrium state is reached (Fig. 5.16). The number of molecules in the vapour above the liquid becomes constant. These molecules exert certain pressure over the surface of the liquid. This pressure is known as **equilibrium vapour pressure, saturated vapour pressure** or simply as **vapour pressure.** The vapour pressure of a liquid has a characteristic value at a given temperature. For example, vapour pressure of water is 17.5 Torr and that of benzene is 75.00 Torr at 20º C. The vapour pressure of a liquid increases with increase in temperature. It is so because at a higher temperature more molecules have sufficiently high energy to overcome the forces of attraction and escape to form vapour. A plot of vapour pressure as a function of temperature is called **vapour pressure curve**. Figure 5.17 depicts the vapour pressure curves of some liquids.

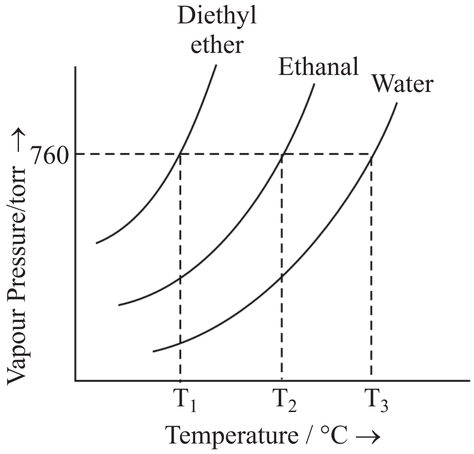


Fig. 5.17 : *Vapour pressure curves of some liquids.*

What would happen if we remove some of the vapour from the closed vessel. Would the vapour pressure of the liquid increase, decrease or remain constant? Vapour pressure of the liquid would remain constant at that temperature. In the beginning, the vapour pressure would decrease after the removal of the vapour, but soon more liquid would evaporate to maintain the equilibrium and the original vapour pressure would be restored. So the vapour pressure of a liquid has a definite value at a particular temperature.

5.13.2 Boiling

You must have seen the formation of bubbles at the base of a vessel, in which a liquid is heated. The rate of formation of bubbles increases with increse in heat supplied. What are the bubbles made up of? The first bubbles that you see are of the air, which is driven out of the liquid by increase in temperature. After some time, bubbles of the liquid are formed throughout vapour. These bubbles rise to the surface and break. When this happens, we say that the liquid is boiling. The bubbles in the liquid the liquid rise and break form only if its vapour pressure is equal to the atmospheric pressure.

The temperature at which boiling occurs is called the **boiling point** of the liquid. At this temperature the vapour pressure of the liquid is equal to the atmospheric pressure. The boiling point, therefore, depends upon the atmospheric pressure. For example, water boils at 100ºC at 760 Torr and at 97.7ºC at 700 Torr.

The normal boiling point of a liquid is defined as the temperature at which the vapour pressure of a liquid is equal to one atmosphere or 760 Torr.

The boiling point of a liquid depends upon its nature. A more volatile liquid would boil at a lower temperature than a less volatile liquid. You can again refer to figure 5.3 and note that diethyl ether boils at a much lower temperature than water, because it is highly volatile liquid. The boiling point of ethanol lies in between those of diethyl ether and water. Vapour pressures or boiling points of liquids give us an idea of the strength of attractive forces between molecules in liquids. Liquids having lower boiling points have weaker attractive forces in comparison to those having higher boiling points.

You can make a liquid boil at temperature other than its normal boiling point. How? Simply alter the pressure above the liquid. If you increase this pressure, you can increase the boiling point and if you can decrease this pressure you decrease the boiling point. On the mountains, the atmospheric pressure decreases and therefore boiling point of water also decreases. People living on hills face problem in cooking their meals. They, therefore, use pressure cooker. How food is cooked faster in it? The lid of pressure cooker does not allow water vapours to escape. On heating the water vapours accumulate and the inside pressure increases. This makes the water boil at a higher temperature and the food is cooked faster.

5.13.3 Evaporation and Boiling

Evaporation and boiling, both involve conversion of a liquid into vapour and appear to be similar. However, they differ from each other in some aspects. Evaporation occurs at all temperatures from freezing point of a liquid to its boiling point, while boiling occurs at a definite temperature only i.e, at its boiling point. Evaporation occurs slowly while boiling is a fast process. Evaporation of a liquid occurs at its surface alone while boiling occurs throughout the liquid. These differences between evaporation and boiling have been summarized in Table 5.3.

Table 5.3 : Differences between evaporation and boiling

S.No.	Evaporation	Boiling
1.	It takes place at all temperatures.	It takes place at a definite temperature.
2.	It is a slow process.	It is a fast process
3.	It occurs only at the surface of the liquid.	It occurs throughout the liquid.

INTEXT QUESTIONS 5.1

1. Match the following.

	Column I		Column II
(i)	Liquids have a definite volume.	(A)	The molecules in a liquid can move about.
(ii)	Liquids acquire the shape of their container.	(B)	The molecules in liquids are close and have very little free space.
(iii)	Liquids are largely incompressible.	(C)	The inter molecular forces liquids strong enough to keep the molecules moving with in a definite space.

2. When a liquid is heated till it starts boiling.
   (i) What are the small bubbles that appears initially at the bottom and sides of the vessel made up of?
   (ii) What are the large bubbles that form in the boiling liquid made up of?

3. Liquids A, B and C boil at 65ºC, 120ºC and 90ºC respectively. Arrange them in the decreasing order of the strength of intermolecular forces.

5.14 SURFACE TENSION

Liquids show the effects of inter molecular forces most dramatically in another property, namely, **surface tension**. Any molecule in the interior of liquid is equally attracted by neighbour molecules from all sides and it does not experience any 'net' force. On the other hand, any molecule at the surface of a liquid is attracted by other molecules at the surface of the liquid or below it. Due to the imbalance of forces, any molecule at the surface experiences a net inward pull (Figure 5.18). As a result, the surface is under tension as if the liquid were covered with a tight skin (or stretched membrane). The phenomenon is called *surface tension*. Quantitatively, the **surface tension** *is defined as the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side* as shown in Figure 5.5. It is represented by the Greek letter *gamma,* γ. Its SI unit is newton per metre (N m^{-1}) and CGS unit is dyne per centimetre (dyne cm^{-1}). The two units are related as : 1 N m^{-1} = 10^3 dyne cm^{-1}

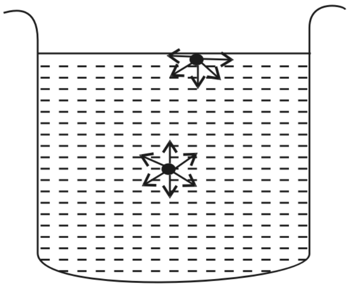


Fig. 5.18 : *Forces acting on molecules, at the surface and in bulk of liquids*

Surface molecules of a liquid experience a constant inward force. Therefore they have a higher energy than the molecules in the bulk of the liquid. Due to this reason liquids tend to have minimum number of molecules at their surface. This is achieved by *minimising the surface area.* In order to increase the *surface area* more molecules must come to the surface. This can happen only if some energy is supplied or work is done. *The energy supplied (or work done) for increasing the surface area of a liquid by a unit amount is known as its* **surface energy.** Its units are joule per square metre J m^{-2} or N m^{-1} (since 1J = 1N m). Thus dimensionally, the surface tension and surface energy are similar quantities and they have the same numerical value.

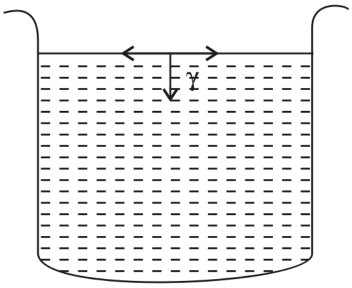


Fig. 5.19 : *Surface tension force acting on the surface of a liquid.*

Effect of Temperature

On raising the temperature surface tension of a liquid decreases. It completely vanishes at the critical temperature. This happens due to the following two factors:

(i) On heating, the liquids expand. This increases the intermolecular distances.

(ii) On heating, the average kinetic energy of molecules and hence their chaotic motion increases.

Due to both of these factors, the intermolcular forces become weak and the surface tension decreases.

Effect of Adding Surface Active Solutes

The solutes which get more concentrated on the surface of the liquid than in the bulk are called **surface active solutes** or **surfactants**. Alcohols are examples of such substances. Their addition to a liquid lowers its surface tension. The cleaning action of soaps and detergents is based on this fact.

Some Effects of Surface Tension

Surface tension results in many interesting and important properties of liquids. Let us now study some of them.

(i) Spherical Shape of liquid drops

You have already learnt that liquids tend to have a minimum surface area. For a given volume, the geometrical shape having minimum surface area is a sphere. Hence, liquids have a natural tendency to form spherical drops, when no external force acts on them. Rain drops are distorted spheres and the distortion is due to the friction of air.

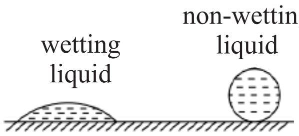


Fig. 5.20 : *Wetting and non-wetting liquids on the surface of a solid.*

(ii) Wetting and Non-wetting properties

When a drop of liquid is placed on a solid surface, the force of gravity should cause it to spread out and form a thin layer (Fig. 5.20). Such a liquid is called a **wetting liquid.** This happens in case of most of the liquids. For example, drops of water or alcohol spread out on the surface of glass. Some liquids behave differently. When a drop of mercury is placed on the surface of glass, it does not spread out (Fig. 5.20). Such liquids are called **non-wetting liquids**.

Wetting or non-wetting nature of a liquid depends upon two types of forces. The intermolecular attractive forces between molecules of a liquid are called **cohesive force** while those between the molecules of the liquid and the solid (whose surface is in contact with the liquid) are called **adhesive forces**. If adhesive forces are stronger than cohesive forces, the liquid would be wetting in nature and when cohesive forces are stronger than adhesive forces it would be non-wetting in nature on the surface of a particular solid.

(iii) Capillary Action

Let us carry out the following activity.

ACTIVITY 5.3

Aim : To study the capillary action.

What is required?

Glass capillary tubes, water, mercury and two petri dishes.

What to do?

(i) Take some water in a petri dish

(ii) Dip one end of a 3-4 cm long capillary in it.

(iii) Take some mercury in another petri dish.

(iv) Dip one end of another 3-4 cm long capillary in it.

What to observe?

Observe the levels of water and mercury in the capillaries. Is it below or above the levels of the liquids in petri dishes?

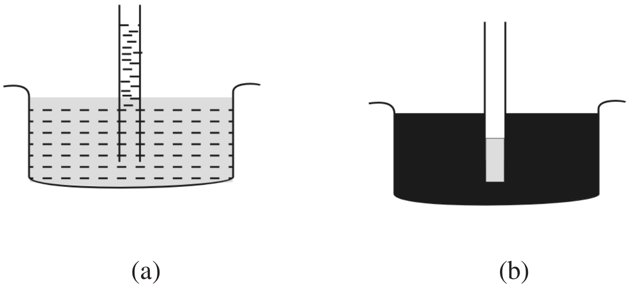

(a) (b)

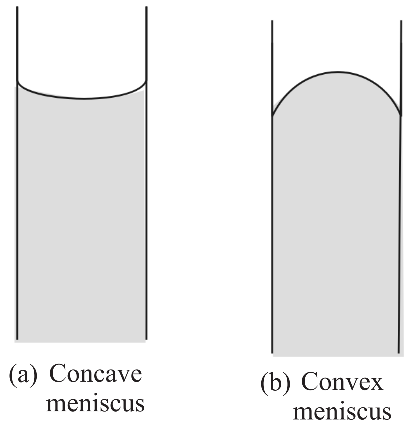
Fig. 5.21 : *Capillary Action*

You would observe that when one end of a capillary tube is dipped in water, it rises in the capillary as shown in Fig. 5.21(a). On the other hand when one end of a capillary tube is dipped in mercury, its level falls in the capillary as in Fig. 5.21(b).

The phenomenon of rise or fall of a liquid in a capillary is known as **capillary action**. The rise of water in the glass capillary is due to its wetting nature as the adhesive forces are stronger than cohesive forces. Water tends to increase the area of contact with glass wall of the capillary by rising in it. Mercury being non-wetting with respect of glass (its cohesive forces are stronger than adhesive forces) tends to minimise the area of contact by depressing inside the capillary

(iv) Curved meniscus

When a wetting liquid such as water is taken in a glass tube, the liquid tends to rise slightly along the walls of the tube for increasing its area of contact with glass. The surface of the liquid (meniscus) becomes curved. It is concave in shape [Fig. 5.22(a)]. When a non-wetting liquid like mercury is taken a glass tube, it tends to decrease its area of contact and depresses along the walls of the glass tube. The meniscus is convex in shape in this case [Fig. 5.22(b)].


(a) Concave meniscus

(b) Convex meniscus

Fig. 5.22 : *Curved meniscus of liquids*

5.15 VISCOSITY

Every liquid has the ability to flow. It is due to the fact that molecules in a liquid move freely, although within a limited space. Water flows down a hill *under gravitational force* or through pipes when forced by a pump. Some external force is always required for a liquid to flow. Some liquids like glycerol or honey flow slowly while others like water and alcohol flow rapidly. This difference is due to the *internal resistance to flow* which is called **viscosity**. The liquids with higher viscosity flow slowly and are more viscous in nature like glycerol or honey. Water and alcohol have lower viscosity and are less viscous in nature.

They flow more rapidly.

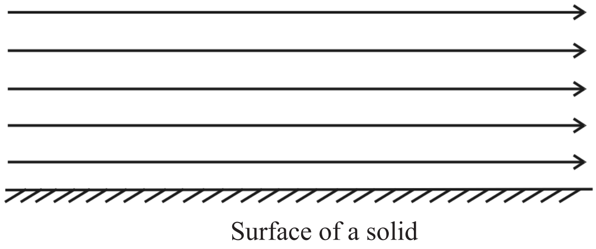


Fig. 5.23 : *Flow of different layers of a liquid*

The viscosity is related to the intermolecular forces. Stronger the intermolecular forces more viscous are the liquids. Let us understand this with the help of Figure 5.9. When a liquid flows steadily, it flows in different layers with one layer sliding over the other. Such a flow is known as **laminar flow**. Consider a liquid flowing steadily on a plane surface. The layer closest to it is almost stationary due to adhesive forces. As the distance of the layer from the surface increases, is velocity increases. Thus different layers move with different velocities. Due to intermolecular forces (cohesive forces) each layer experiences a force of friction from its adjacent layers. This force of friction, f between two layers depends upon:

(i) area of contact between them A.

(ii) distance between the layers, dx.

(iii) difference in velocity between the layers, du.

These quantities are related as

$$f = \eta A \frac{du}{dx}$$

Here η (Greek letter 'eeta') is called the coefficient of viscosity and $\frac{du}{dx}$ is the *velocity gradient* between the layers.

If $A = 1\ \text{cm}^2$, $du = 1\ \text{cm s}^{-1}$ and $dx = 1$ cm, then

$$f = \eta$$

Thus, coefficient of viscosity is the force of friction between two parallel layer of the liquid which have 1cm^2 area of contact, are separated by 1cm and have a velocity difference of 1cm s^{-1}. It may be noted that f is also equal to the **external force** which is required to overcome the force of friction and maintain the steady flow between two parallel layers having A area of contact, and which are dx distance apart and moving with a velocity difference of du.

Units

CGS unit of viscosity is dyne cm^{-2} s. This unit is also known as **poise (P)**. The SI unit of viscosity is N m^{-2}s or Pa s. The two units are related as :

1 Pa s = 10 P

The unit poise is found to be too large and its submultiples **centipoise** (1 cP = 10^{-2} P) and **milli poise** (1 mP = 10^{-3} P) are used for liquids and micropoise (μP = 10^{-6} P) is used for gases.

Effect of Temperature

Viscosity of a liquid decreases on raising the temperature. It is due to decrease in intermolecular forces on heating as discussed in previous section (Section 5.4).

INTEXT QUESTIONS 5.5

1. Fill in the blanks.

   (i) A molecule at the surface of a liquid has .... energy than the one within the liquid.

   (ii) Surface tension of liquid .... on cooling.

   (iii) Meniscus of a non-wetting liquid is .... in shape while that of a wetting liquid is .... in shape.

   (iv) When one end of a glass capillary tube was dipped in a liquid, the level of liquid inside the capillary was observed to fall. The adhesive forces in this liquid are .... than the cohesive forces between the liquid and glass.

   (v) Liquid X is more viscous than liquid Y. The intermolecular forces in Y are .... than in X.

2. What are the SI units of

   (i) Surface tension.

   (ii) Coefficient of viscosity

3. Why do liquids have a tendency to acquire minimum surface area?

WHAT YOU HAVE LEARNT

- Matter exists in three states, namely, solid, liquid and gas.
- The three states of matter differ in the relative closeness of the molecules constituting them.

- Intermolecular interactions present depend upon the nature of the substance. Various types of interactions are London or dispersion forces, dipole-dipole dipode induced dipole forces and hydrogen bonding.
- There exists a definite relationship between the pressure, volume, temperature and number of moles of a gas and they are given by Boyle's law, Charle's law and Avogadro's law.
- The gases obeying gas laws are known as ideal gases.
- Dalton's law give the relationship between partial pressures exerted by the non-reacting gases to the total pressure.
- Gay Lussac's law of combining volume and Avogadre's law led to the concept of molecule.
- Most of the gases deviate from the ideal behaviour. The deviations of gases from ideal behaviour is due to the wrong assumptions of kinetic molecular theory.
- Real gases can be liquified under appropriate conditions.
- In liquids the intermolecular force are quite strong as compared to gases but weak enough to allow the molecules to move within a limited space and the intermolecular distance is short.
- Liquids have definite volume but no definite shape, are almost incompressible and can diffuse.
- Liquids evaporate and exert a definite vapour pressure at specified temperature.
- Boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the external pressure.
- Surface tension is the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side.
- Due to surface tension, liquids tend to have minimum surface area and show the phenomena of capillary rise or fall and curved meniscus.
- Viscosity is the internal force of friction to the flow of liquid.

TERMINAL EXERCISE

1. Draw the graphs of the following :
   a) p vs V at constant T and n
   b) $1/V$ vs p at constant T and n
   c) T vs V at constant p

2. What is the volume occupied by one mole of a gas at STP (0°C, 1 bar pressure)?
3. The volume of a sample of a gas is 500 mL at a pressure of 1.5 atm. If the temperature is kept constant, what will be the volume of that gas at
   (i) 1 atm. (ii) 5.0 atm.
4. List the wrong assumptions of kinetic theory of gases which led to van der Waal's equation.
5. What is the standard temperature and pressure?
6. What is the lowest possible temperature?
7. CO_2 can not be liquefied at 35ºC, however large the pressure may be, Why?
8. A sample of nitrogen gas weighing 9.3 g at a pressure 0.99 atm occupies a volume of 12.4 litres when its temperature is 55K. What will be its volume when the temperature is 220 K? Assume pressure is kept constant.
9. Calculate the volume of one mole of oxygen at 27ºC and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.
10. What is the Maxwell-Boltzmann Law?
11. Explain the following properties of liquids on the basis of their structure:
    (i) Volume (ii) Shape (iii) Compressibility (iv) Ability to flow
12. Why diffusion can occur in liquids. Explain.
13. Define (i) vapour pressure and (ii) boiling point.
14. Differentiate between evaporation and boiling.
15. Explain the effect of temperature on vapour pressure of a liquid.
16. Define surface tension and give its CGS and SI units.
17. What is surface energy?
18. Why is energy required to increase the surface area of a liquid?
19. What is the effect of addition of a surface active substance on the surface tension of a liquid.
20. Why are liquid drops spherical in shape?
21. What are wetting and non-wetting liquids?
22. The cohesive forces acting in liquids A and B are C_1 and C_2 respectively and $C_1 > C_2$ Which of them would have higher surface tension.
23. Liquid A rises in glass capillary tube. If one drop of it is put on a plane glass surface, would it spread out or not. Explain.
24. A liquid forms a convex meniscus in glass tube. Comment on its nature.
25. Define viscosity.
26. What is coefficient of viscosity?

27. Give CGS and SI units of coefficient of viscosity.
28. What is the effect of temperature on (i) vapour pressure (ii) surface tension and (iii) viscosity of a liquid?

ANSWERS TO INTEXT QUESTIONS

5.1

1. Due to more intermolecular distances in gaseous molecule compared to liquid.
2. Boyle Law equation is

$$p_1V_1 = p_2V_2$$

$$(.20\text{ atm})\ (500\text{ mL}) = p_2\ (10\text{ mL})$$

$$p_2 = \frac{(0.20\text{ atm})\ (500\text{ ml})}{10\text{ ml}}$$

$$p_2 = 10\text{ atm.}$$

3. By Avogadro's Law

$$\text{moles of O}_2 = \text{moles of unknown gas}$$

$$\frac{2.00\text{ g}}{32\text{ g mole}^{-1}} = \frac{1.75\text{ g}}{\text{Molecular weight of unknown gas}}$$

$$\text{Molar mass of unknown gas} = \frac{1.75 \times 32}{2.00} = 28\text{ g mol}^{-1}$$

Molar mass of unknown gas is 28.

4. (a) Dispersion or London Forces (b) dipole-dipole interactions and dispersion forces.

5.2

1. Movement of gas molecules through another gas is called diffusion.

   When gas escapes from a container through a very small opening it is called effusion.

2. Ammonia and hydrogen chloride gases are reacting gases and Dalton's Law is applicable to mixture of non-reacting gases.

3. $$\frac{r_{O_3}}{r_{CO_2}} = \left(\frac{M_{CO_2}}{M_{O_3}}\right)^{1/2}$$

$$\frac{0.271}{0.290} = \left(\frac{44}{M_{O_3}}\right)^{1/2}$$

Squaring both sides

$$\frac{(0.271)^2}{(0.290)^2} = \frac{44}{M_{O_3}}$$

$$M_{O_3} = \frac{44 \times 0.29 \times 0.29}{0.271 \times 0.271} = 50.4$$

Molecular mass of $O_3 = 50.4$

4. By ideal gas equation

$$pV = n\text{RT}$$

$$p \times 1.0 = (5.0 \text{ mol})\ (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\ 320 \text{ K}$$

$$p = \frac{(5.0 \text{ mol})\,(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\,320 \text{ K}}{1.0 \text{ L}}$$

$$p = 131.3 \text{ atm.}$$

5.3

1. Low pressure and high temperature.
2. b
3. $$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3\,(8.314 \text{ Jk}^{-1} \text{ mol}^{-1})\,(293 \text{ K})}{(0.048 \text{ kg mol}^{-1})}}$$

$$= \sqrt{\frac{(8.314 \text{ Kg m}^2\text{s}^{-2} \text{ K}^{-1} \text{ mol}^{-1})\,(293 \text{ K})}{0.048 \text{ Kg mol}^{-1}}}$$

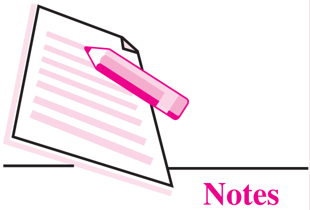
$$= 390.3 \text{ ms}^{-1}$$

4. $Z = \dfrac{pV_m}{RT}$ = where V_m = molar volume

   Z is compressibility factor.

5.4

1. (i) C; (ii) A; (iii) B
2. (i) Air (ii) Liquid.
3. B > C > A



Notes

5.5

1. (i) more

   (ii) increases

   (iii) convex; concave

   (iv) stronger

   (v) weaker

2. (i) $N\ m^{-1}$; (ii) $N\ m^{-2}\ s$

3. Molecules in the surface of a liquid have higher energy due to an inward force on them. Therefore liquids tend to have minimum number of molecules in the surface or have minimum surface area.

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6

THE SOLID STATE

You are aware that the matter exists in three different states viz., solid, liquid and gas. In these, the constituent particles (atoms, molecules or ions) are held together by different forces of attraction between them. However, the nature and magnitude of the forces varies. In the first two lessons of this module you have learnt about the gaseous and the liquid states of matter. In this lesson you would learn about solid state- a compact state of matter. The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them. Here, you would learn about structure, classification and properties of solids.

OBJECTIVES

After reading this lesson, you should be able to:

- explain the nature of solid state;
- explain the properties of solids in terms of packing of particles and intermolecular attractions;
- differentiate between crystalline and amorphous solids;
- explain the melting point of a solid;
- classify the crystalline solids according to the forces operating between the constituent particles;
- define the terms crystal lattice and unit cell;
- describe different types of two dimensional and three dimensional unit cells;
- explain different types of packing in the solids;
- define coordination number;

- calculate the number of particles in simple cubic, face-centrad cubic and body centered cubic unit cells;
- relate the density of a solid to the properties of its unit cell;
- calculate the packing efficiency of simple cubic body central cubic and CCP/HCP lattices;
- define radius ratio;
- correlate the radius ratio with the structure of solids;
- explain the structure of simple ionic compounds;
- explain Frenkel and Schottky defects;
- classify solids on the basis of their electrical and magnetic properties; and
- explain the effect of doping of semiconductors by electron deficit and electron rich impurities.

6.1 NATURE OF SOLID STATE

You have learnt in lesson 6 that according to *Kinetic Molecular Theory*, the gases consist of a large number of molecules, which are in constant random motion in all directions in the available space. These molecules have very weak or negligible forces of attraction between them. A sample of gas can be compressed, as there is a lot of free space between the molecules Fig. 6.1(a) In liquids Fig. 6.1(b) on the other hand the molecules are also in constant motion but this motion is relatively restricted. Since there is very little free space available between the molecules the liquids are relatively incompressible.

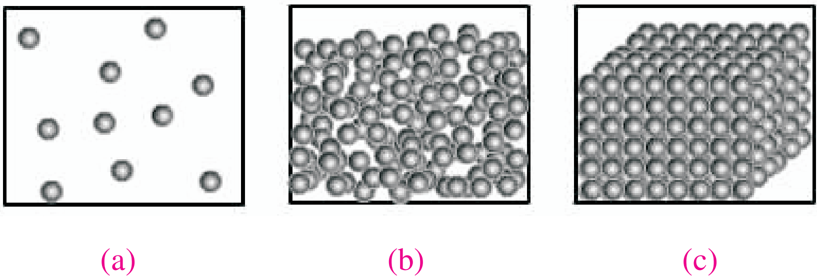

(a) (b) (c)

Fig. 6.1: *A pictorial representation of the three states of matter: (a) gas (b) liquid and (c) solid state.*

In solid state the constituent particles are arranged in a closely packed ordered arrangement Fig. 6.1 (c) with almost no free space. They can just vibrate about their fixed positions. These are in close contact and cannot move around like the molecules of a gas or a liquid. As a consequence, the solids are incompressible, rigid and have a definite shape. Like liquids, the volume of a solid is independent of the size or the shape of the container in which it is kept.

6.2 CLASSIFICATION OF SOLIDS

On the basis of nature of arrangements of the constituent particles the solids are classified into amorphous and crystalline solids.

6.2.1 Amorphous and Crystalline Solids

In **crystalline solids** the constituent particles are arranged in a regular and periodic pattern and give a well defined shape to it. The term 'crystal' comes from the Greek word, *krustallos* meaning ice. The regular pattern extends throughout the solid and such solids are said to have **long range order**. On the other hand, some solids have only a short range of order. This means that the particles are arranged regularly in only some regions of the solid and are relatively disordered in other regions. Such solids are called **amorphous solids**. In Greek, *a* means without and *morph* means form. Thus the word *amorphous* means without form. Sodium chloride and sucrose are common examples of crystalline solids while glass, fused silica, rubber and high molecular mass polymers are some examples of amorphous solids.

An important difference between the amorphous and crystalline solids is that while amorphous solids are **isotropic** in nature (i.e., these exhibit same value of some physical properties in all directions) the crystalline solids are **anisotropic** (i.e., the values of some physical properties are different in different directions). Refractive index and coefficient of thermal expansion are typical physical properties, which have different values when measured along different directions of a given crystal. Another difference between amorphous and crystalline solids is that while crystalline solids have a sharp or definite melting point, whereas the amorphous solids do not have definite melting point, these melt over a range of temperature.

The crystalline solids can be further classified on the basis of nature of interaction between the constituent particles as discussed below.

6.2.2 Classification of Crystalline Solids

In crystalline solids the constituent particles are arranged in an ordered arrangement and are held together by different types of attractive forces. These forces could be coulombic or electrostatic, covalent, metallic bonding or weak intermolecular in nature. The differences in the observed properties of the solids are due to the differences in the type of forces between the constituting particles. The types of forces binding the constituent particles can be used as a basis for classification of crystalline solids. On this basis, the crystalline solids can be classified into four different types- ionic, molecular, covalent and metallic solids. The characteristics and the properties of different types of solids are compiled in Table 6.1.

Notes

Table 6.1: Characteristics and properties of different types of solids.

Type of Solid	Constituent Particles	Nature of interaction between the particles	Appearance	Melting Point	Examples
Ionic	Ions	Coulombic	Hard and brittle	High	Sodium chloride, zinc sulphide, etc
Molecular	Molecules				
Non polar		van der Waals	Soft	low	Iodine, naphthalene
Polar		Dipole-dipole	brittle		water carbon dioxide.
Covalent	Atoms	Covalent bonding	Hard	Very high	Diamond, graphite, silica, etc.
Metallic	Atoms	Metallic bonding	Hard and malleable	Variable	Copper, silver, etc.

Sodium chloride is an example of an ionic solid because in this case the sodium ions and chloride ions are attracted to each other by electrostatic interactions. Iodine on the other hand is an example of a molecular solid because in this the molecules are held together by weak van der Waals forces. Diamond, with strong covalent bonds between the constituent carbon atoms is an example of covalent solids while in metals a large number of positive cores of the atoms are held together by a sea of electrons.

6.3 PROPERTIES OF CRYSTALLINE SOLIDS

You are familiar with the following properties of solids on the basis of handling solids in day to day work.

- Solids are rigid in nature and have well defined shapes
- Solids have a definite volume irrespective of the size and shape of the container in which they are placed
- Solids are almost incompressible.

You are familiar with a number of crystalline solids like sugar, rock salt, alum, gem stones, etc. You must have noticed that such solids have smooth surfaces. These are called ‘faces’ of the crystal. These faces are developed in the process of crystal formation by ordered arrangements of the constituent particles. It is generally observed that the faces of crystals are developed unequally. The internal angle between a pair of faces is called **interfacial angle** and is defined as the angle between the normals to the intersecting faces. An important characteristic of crystalline solids is that irrespective of the size and shape of the crystal of a given substance, the interfacial angle between a pair of faces is always the same.

This fact was stated by Steno as *the law of constancy of interfacial angles* (Fig. 6.2).

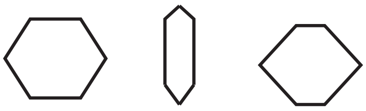


Fig. 6.2 *The constancy of interfacial angles*

6.3.1 Melting Point of a Solid

What is the effect of heat on a solid? You would have observed that when a solid is heated it becomes hot and eventually gets converted into a liquid. This process of conversion of a solid to a liquid on heating is called **melting.** You would also have observed that different solids need to be heated to different extents to convert them to liquids. The temperature at which a solid melts to give a liquid is called its **melting point.** Every solid is characterized by a definite melting point. This in fact is a test of the purity of the solid. The melting point of a solid gives us an idea about the nature of binding forces between constituent particles of the solid. Solids like sodium chloride (m.p = 1077 K) have very high melting points due to strong coulombic forces between the ions constituting it. On the other hand molecular solids like naphthalene (m.p. = 353 K) have low melting points.

The effect of heat on a solid can be understood in terms of energy and motion of the constituent particles. You are aware that in a solid the constituent particles just vibrate about their mean position. As the heat is supplied to the solid, the constituent particles gain energy and start vibrating more vigorously about their equilibrium positions. As more and more heat is supplied, the energy keeps on increasing and eventually it becomes greater than the binding forces between them. As a consequence the solid is converted into a liquid.

INTEXT QUESTIONS 6.1

a) Differentiate between solid, liquid and gaseous state.

b) How are solids classified on the basis of the intermolecular forces.

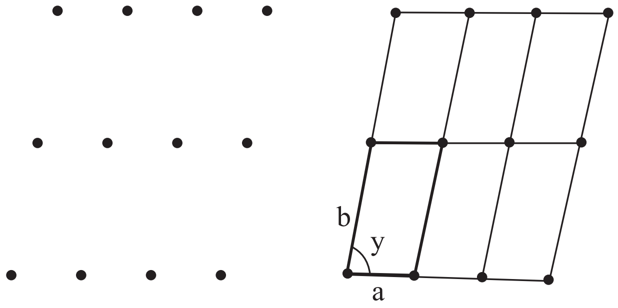
c) What is Steno's law of constancy of interfacial angles?

6.4 CRYSTAL LATTICE AND UNIT CELLS

You know, the crystalline solids have long-range order and the closely packed constituent particles are arranged in an ordered three dimensional pattern. The structure of the crystalline solids can be represented as an ordered three dimensional arrangement of points. Here each point represents the location of a constituent particle and is known as **lattice point** and such an arrangement is called a **crystal lattice** or **space lattice** or simply a **lattice.**

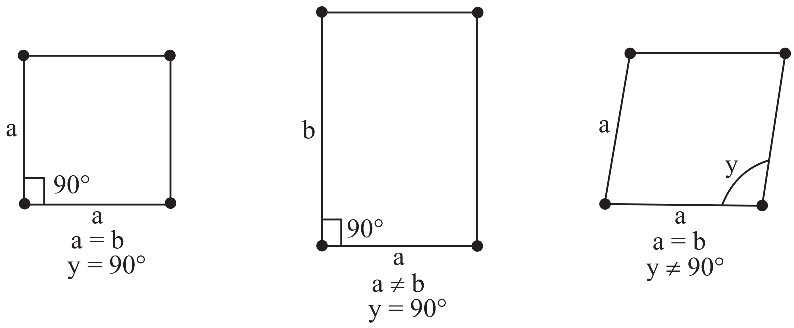
6.4.1 Two Dimensional Lattice and Unit Cells

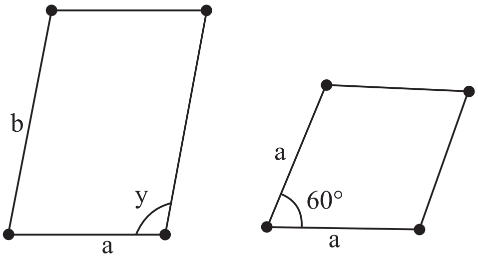
To understand the meaning of the term *lattice*, let us first start with a two dimensional lattice. A two dimensional lattice has a set of points arranged in a regular pattern on a plane or a surface (in two dimensions). One such lattice is shown in Figure 6.4(a). The arrangement of lattice points is as shown in Fig. 6.4(a). When these lattice points are joined, the geometry of the lattice becomes clear (Fig. 6.4(b). The entire pattern can be generated by repeating a set of four points. On joining these points we get a **unit cell** of the lattice (shown in dark). The unit cell of a two dimensional lattice is a parallelogram which is defined in terms of two sides *a* and *b* and the angle between them γ. Only five types of unit cells are possible in two dimensional lattice. These are shown in Fig. 6.4(b).



(a) (b)

Fig. 6.3 (a) A two dimensional lattice (b) and its unit cell





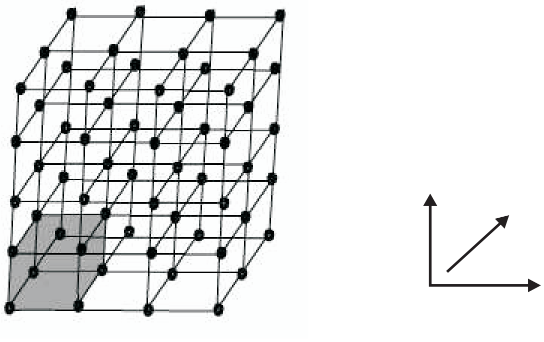
a ≠ b
y ≠ 90°

a = b
y = 60°

Fig. 6.4: Five types of two dimensional unit cells

6.4.2 Three Dimensional Lattice and Unit Cells

In three dimensions, the crystal structure of a solid is represented as a three dimensional array of lattice points. Remember that the lattice points represent the positions of the constituent particles of the solid (Fig. 6.5(a)).



(a) (b)

Fig. 6.5: *Schematic representation of a three dimensional crystal lattice.*

In a crystal lattice we can select a group of points which can be used to generate the whole lattice. Such a group is called **repeat unit** or the **unit cell** of the crystal lattice. The shaded region in the Fig. 6.5(a) represents a unit cell of the crystal lattice. The unit cell is characterized by three distances along the three edges of the lattice (a, b and c) and the angles between them (α, β and γ) as shown in the Fig. 6.5(b). We can generate the whole crystal lattice by repeating the unit cell in the three directions.

On the basis of the external appearance the known crystals can be classified into seven types. These are called **crystal systems**. In terms of the internal structure also the crystal lattices contain only seven types of unit cells. The seven crystal systems and the definition of their unit cells in terms of their unit distances and the angles are compiled in Table 6.2. The seven simple unit cells are given in Fig. 6.6.

Table 6.2: The seven crystal systems and their possible lattice types.

Systems	Axes	Angles	Possible lattice types
Cubic	a = b = c	a = β = γ = 90°	P, F, I
Tetragonal	a = b ≠ c	a = β = γ = 90°	P, I
Orthorhombic	a ≠ b = c	a = β = γ = 90°	P, F, I, C
Rhombohedral	a = b = c	a = β = γ ≠ 90°	P
Hexagonal	a = b ≠ c	a = β = 90°; γ = 120°	P
Monoclinic	a ≠ b = c	a = γ = 90°; β ≠ 90°	P, I
Triclinic	a ≠ b ≠ c	a ≠ β ≠ γ ≠ 90°	P

*** P= primitive, I= body centered, F= face centered and C= side centered**

The unit cell shown in Fig. 6.5 and the ones given in Fig..6.5 have the lattice points at the corners only.

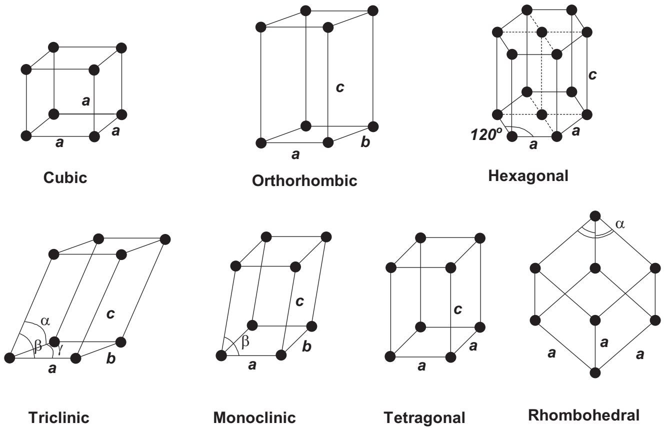


Fig. 6.6 : *The primitive unit cells; the relative dimensions of the three repeat distances (a, b and c) and the angles between them (a, β and γ) are given in Table 6.2.*

Such unit cells are called **primitive** (P) unit cells. Sometimes, the unit cell of a crystal contains lattice point(s) in addition to the ones at the corners. A unit cell containing a lattice point each at the centers of its faces in addition to the lattice points at the corners is called a **face centered** (F) unit cell. On the other hand a unit cell with lattice points at the center of the unit cell and at the corners is called a **body centered** unit cell (I). In some cases, in addition to the lattice points at the corners there are two lattice points located at the centers of any two opposite faces. These are called as **end centered** (C) unit cells. The possible lattice types in different crystal systems are also indicated in Table 6.2. The seven crystal systems when combined with these possibilities give rise to 14 lattice types. These are called **Bravais lattices**.

6.5 NUMBER OF ATOMS IN CUBIC UNIT CELLS

Of the seven crystal systems, let us discuss unit cells belonging to the cubic crystal system in somewhat details. As you can see from Table 6.2 that in the cubic crystal system the three repeat distances are equal and all the three angles are right angles. The unit cells of three possible lattice types viz., primitive or simple cubic, body centered cubic and the face centered cubic, belonging to cubic crystal system are shown in Figure 6.7.

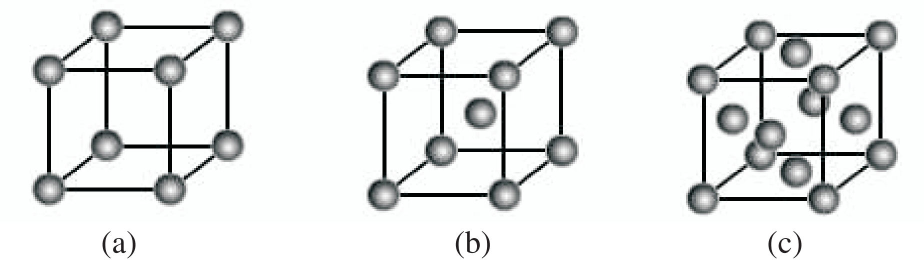


Fig. 6.7: *(a) primitive or simple (b) body centered and (c) face centered cubic unit cells.*

Number of atoms per unit cell

As you know that in unit cells the atoms can be on the corners, in the body center and on face centers. All the atoms do not belong to a single unit cell. These are shared amongst different unit cells. It is important to know the number of atoms per unit cell. Let us learn how to compute these for different cubic unit cells.

(a) Simple Cubic Unit Cell

The simple or primitive unit cell has the atoms at the corners of the cube (Fig. 6.7 (a)). A lattice point at the corner of the unit cell is shared by eight unit cells as you can see from the encircled atom in the Fig. 6.8. Therefore, the contribution of an atom at the corner to the unit cell will be 1/8. The number of atoms per unit cell can be calculated as follows:

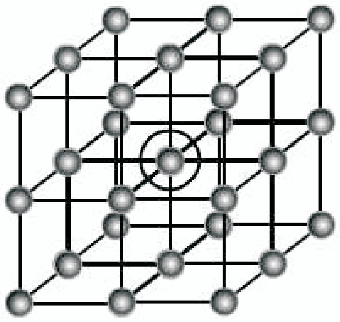


Fig. 6.8: *A corner lattice point is shared by eight unit cells*

Number of corner atoms = 8

Contribution of each corner atom = $\frac{1}{8}$

The number of atoms in a simple cubic unit cell = $8 \times \frac{1}{8} = 1$

(b) Body Centered Cubic Unit Cell

A body centered cubic (*bcc*) unit cell has lattice points not only at the corners but also at the center of the cube(Fig. 6.7 (b)). The atom in the center of the cube belongs entirely to the unit cell, i.e., it is not shared by other unit cells. Each corner atom, on the other hand, as in the case of simple cubic unit cell, is shared by eight unit cells. Thus the number of atoms per unit cell can be calculated as

Number of corner atoms = 8

Contribution of each corner atom = $\frac{1}{8}$

$\therefore$ Contribution of all the corner atoms to the unit cell = $8 \times \frac{1}{8} = 1$

Number of atoms at the center of the cube = 1

Contribution to the unit cell = 1 (as it is not shared)

The number of atoms in a body centered cubic unit cell = 1 + 1 = 2

(c) Face Centered Cubic Unit Cell

A face centered cubic (*fcc*) unit cell has atoms not only at the corners but also at the center of each face. Thus it has eight lattice points at the corners and six at the face centers (Fig. 6.7 (c)). A face centered lattice point is shared by two unit cells, as shown in Fig. 6.9.

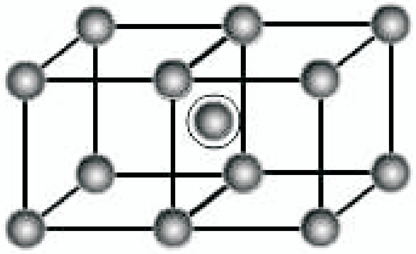


Fig. 6.9: *A face centered lattice point is shared by two unit cells*

Number of corner atoms = 8

Contribution of each corner atom = $\frac{1}{8}$

Contribution of all the corner atoms to the unit cell = $8 \times \frac{1}{8} = 1$

Number of atoms at the face center = 6

Contribution of each atom at the face centre = $\frac{1}{2}$

Contribution of all the face centered atoms to the unit cell = $6 \times \frac{1}{2} = 3$

The number of atoms points in a face centered cubic unit cell = 1 + 3 = 4

Notes

The number of atoms per unit cell in different types of cubic unit cells is given in Table 6.3.

Table. 6.3: Number of atoms per unit cell

S.No.	Type of unit cell	No. of atoms per unit cell
1.	Simple cubic	1
2.	Body centered cubic	2
3.	Face centered cubic	4

6.6 CALCULATION OF DENSITY OF UNIT CELL

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

(i) **Volume of Unit cell**

If the edge length of the cubic unit cell is 'a' its volume is a^3

(ii) **Mass of the Unit cell**

Let the molar mass of substance = M

$$\therefore \quad \text{Mass of one atom or molecule} = \frac{M}{N_A}$$

Where N_A = Avogadro's constant.

Let the number of atoms or molecules of the substance present per unit cell = z

(See table 6.3 for values of z for different type of cubic unit cells)

$$\therefore \quad \text{Mass of unit cell} = (\text{number of atoms/molecules present per unit cell}) \times (\text{mass of one atom/molecule})$$

$$= \frac{z \cdot M}{N_A}$$

(iii) **Density**

$$\text{Density} = \frac{\text{Mass of one unit cell}}{\text{Volume of one unit cell}}$$

$$d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Density of the unit of cell of a substance is the same as the density of the substance. In case of ionic substances, the formula unit is taken as one particle. (For example, formula unit of NaCl = $1Na^+ + 1Cl^-$ ions; of $Na_2SO_4 = 2Na^+ + 1SO_4^{2-}$ ions).

The above relation can be used to calculate z and hence the nature of cubic lattice if d and M are known or M if d and z are known

Example. The unit cell of a metallic element is face centred cubic and the side of the cube is 540.2 pm. Calculate the density of the metal in gcm^{-3} if its relative atomic mass is 202.4.

Solution

$$d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Given:

Side of the cube = a = 540.2 pm = 540.2×10^{-10} cm

Number of atoms per unit cell of a face-centred cubic unit cell = $z = 4$

Molar mass of the element, M = 202.4 g mol^{-1}

Putting these values in the above relation

$$d = \frac{4 \times 202.4 \text{ g mol}^{-1}}{(540.2 \times 10^{-10} \text{cm})^3 \times (6.022 \times 10^{-23} \text{mol}^{-1})}$$

$$= 8.53 \text{ g cm}^{-3}$$

6.7 CLOSE PACKED STRUCTURES OF SOLIDS

In the process of the formation of a crystal the constituent particles get packed quite closely. The crystal structures of the solids can be described in terms of a close packing of identical spheres as shown in Fig. 6.10. These are held together by forces of attraction. Let us learn about the possible close packed structures of solids and their significance.

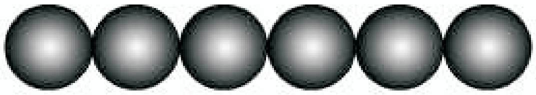
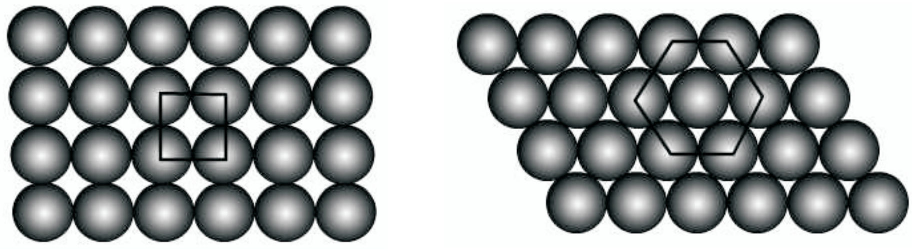


Fig. 6.10 : *Arrangement of identical spheres in one dimension*

A linear horizontal arrangement of identical spheres in one dimension forms a row (Fig. 6.10). A two dimensional close packed structure can be obtained by arranging a number of such rows to form a layer. This can be done in two possible ways. In one of these, we can place these rows in such a way that these are aligned as shown in (Fig. 6.11 (a)). In such an arrangement each sphere is in contact with four other spheres. This arrangement in two dimensions is called **square close packing.**



(a) (b)

Fig. 6.11 : *(a) Square close packing and (b) hexagonal close packing of identical spheres in two dimensions*

In the other way we can place the spheres of the second row in the depressions of the first row and so on and so forth (Fig. 6.11(b)). You may notice that in such an arrangement each sphere is in contact with six other spheres. Such an arrangement in two dimensions is called hexagonal **close packing.** In such a packing, the spheres of the third row are aligned with the first row. You may also have noticed that in the hexagonal close packed the spheres are more efficiently packed. In Fig. 6.11 an equal number of identical spheres are arranged in two different types of packing.

A three dimensional structure can be generated by placing such two dimensional layers on top of each other. Before we move on to the three dimensional packing let us look at the hexagonal close packed layer some what more closely (Fig. 6.12).

You may note from Fig. 6.12 that in a hexagonal close packed layer there are some unoccupied spaces or voids. These are triangular in shape and are called **trigonal voids**. You can further note that there are two types of triangular voids, one with the apex pointing upwards and the other with the apex pointing downwards. Let us call these as X type and Y type voids respectively as marked in the Fig. 6.12.

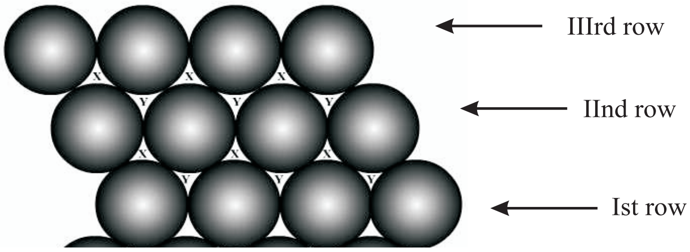


Fig. 6.12 : *A hexagonal Close Packed layer showing two types of triangular voids.*

Close Packed Structures in three dimensions

Let us take a hexagonal close packed layer and call it A layer and place another hexagonal close-packed layer (called the B layer) on it. There are two possibilities.

1. In one, we can place the second layer in such a way that the spheres of the second layer come exactly on top of the first layer.
2. In other, the spheres of the second layer are in such a way that these are on the depressions of the first layer. The first possibility is similar to square close packing discussed above and is accompanied by wastage of space. In the second possibility when we place the second layer into the voids of the first layer, the spheres of the second layer can occupy either the X or Y type trigonal voids but not both. You may verify this by using coins of same denomination. You would observe that when you place a coin on the trigonal void of a given type, the other type of void becomes unavailable for placing the next coin (Fig. 6.13).

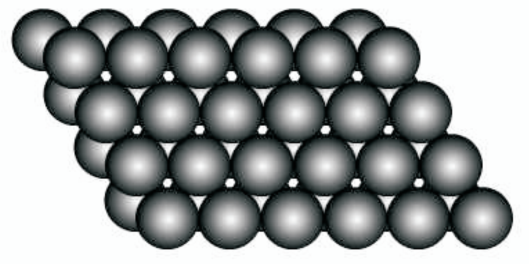
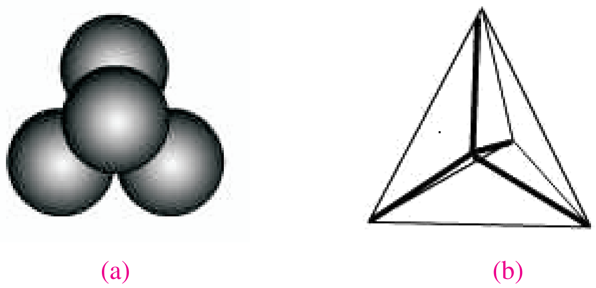


Fig. 6.13 : *Two layers of close packed spheres , the second layer occupies only one type (either X or Y) of triangular voids in the first layer.*

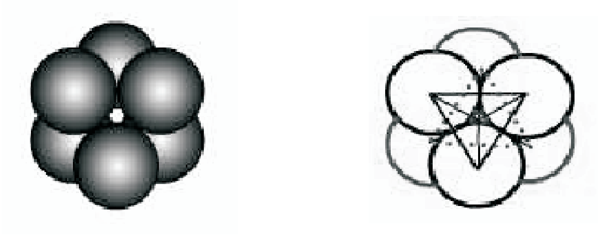
In this process, the sphere of second layer covers the trigonal voids of the first layer. It results into voids with four spheres around it, as shown in Fig. 6.14(a). Such a void is called a **tetrahedral void** since the four spheres surrounding it are arranged on the corners of a regular tetrahedron, Fig. 6.14(b). Similarly, the trigonal voids of the second layer will be placed over the spheres of the first layer and give rise to tetrahedral voids.



(a) (b)

Fig. 6.14 : *A tetrahedral void*

In a yet another possibility, the trigonal voids of the first layer have another trigonal void of the opposite type (X type over Y and Y type over X type) from the second layer over it. This generates a void which is surrounded by six spheres, Fig..6.15 (a). Such a void is called an **octahedral void** because the six spheres surrounding the void lie at the corners of a regular octahedron, Fig..6.15 (b).



(a) (b)

Fig. 6.15 : *An octahedral void*

A closer look at the second layer reveals that it has a series of regularly placed tetrahedral and octahedral voids marked as 't' and 'o' respectively in Fig. 6.16.

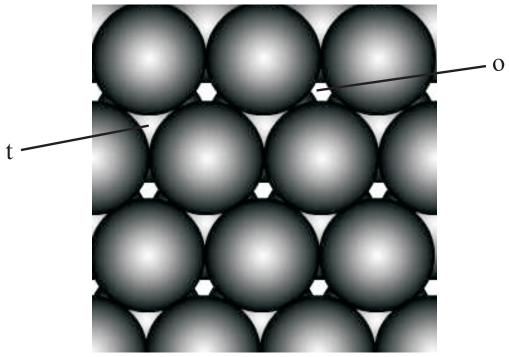
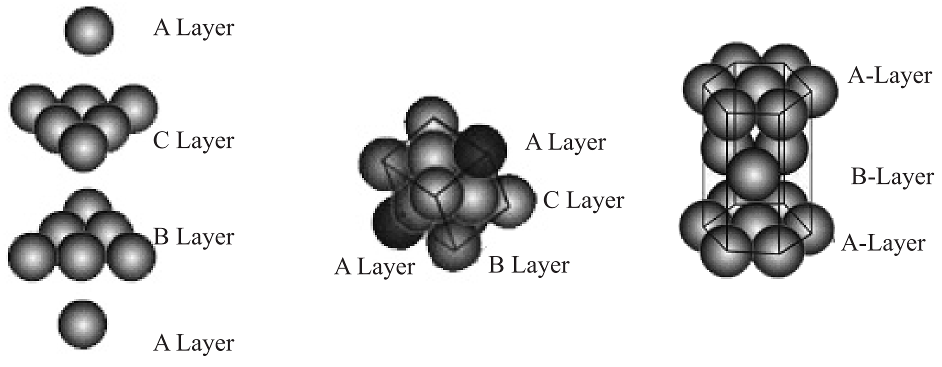


Fig. 6.16 : *The top view of the second layer showing the tetrahedral and octahedral voids.*

Now, when we place the third layer over the second layer, again there are two possibilities i.e., either the tetrahedral or the octahedral voids of the second layer are occupied. Let us take these two possibilities. If the tetrahedral voids of the second layer are occupied then the spheres in the third layer would be exactly on top (i.e., vertically aligned) of the first or A layer The next layer (4th layer) which is then placed would align with the B layer. In other words, every alternate layer will be vertically aligned. This is called AB AB …. pattern or AB AB …. repeat. On the other hand if the octahedral voids of the second layer are occupied, the third layer is different from both the first as well as the second layer. It is called the C layer. In this case the next layer, i.e., the fourth layer, howsoever it is placed will be aligned with the first layer. This is called ABC ABC …. pattern or ABC ABC.. …. repeat. In three dimensional set up the AB AB …. pattern or repeat is called **hexagonal closed packing** (hcp) (Fig. 6.10 (c)) while the ABC ABC …. pattern or repeat is called **cubic closed packing** (ccp) (Fig. 6.17 (a)).



(a) (b) (c)

Fig. 6.17 : *(a) Cubic closed packing (ccp) as a result of ABC pattern of close packed spheres; (b) the layers in (a) tilted and brought closer to show fcc arrangement (c) hexagonal closed packing (hcp) as a result of ABAB pattern of close packed spheres.*

This process continues to generate the overall three dimensional packed structure. These three dimensional structures contain a large number of tetrahedral and octahedral voids. In general there is one octahedral and two tetrahedral voids per atom in the close packed structure. These voids are also called as **interstices.** As mentioned earlier, the identical spheres represent the positions of only one kind of atoms or ions in a crystal structure. Other kind of atoms or ions occupy these interstices or voids.

In the close packed structures (*hcp* and *ccp*) discussed above, each sphere is in contact with six spheres in its own layer (as shown in Fig. 6.12) and is in contact with three spheres each of the layer immediately above and immediately below it. That is, each sphere is in contact with a total of twelve spheres. This number of nearest neighbor is called its **coordination number**. The particles occupying the interstices or the voids will have a coordination number depending on the nature of the void. For example an ion in a tetrahedral void will be in contact with four neighbors i.e., would have a coordination number of four. Similarly the atom or ion in an octahedral void would have a coordination number of six.

INTEXT QUESTIONS 6.2

(a) What is the difference between the square close packed and hexagonal close packed structures?

(b) Which of the above two, is more efficient way of packing?

(c) Clearly differentiate between, trigonal, tetrahedral and octahedral voids.

6.8 PACKING EFFICIENCY

In all closed packed structures there are always some *voids* or empty spaces. The percentage of the total space that is filled by the constituent particles is called the **packing efficiency.** It is calculated from the following relation:

$$\text{Packing efficiency} = \frac{\text{filled space}}{\text{total space}} \times 100\%$$

It depends upon the nature of crystal lattice. For the three types of cubic lattices, the calculations are given below:

(1) **Packing Efficiency of Simple Cubic Lattice**

In simple cubic lattice, the constituent particles occupy only the corner positions of the cubic unit cell. These particles touch one another *along the edge of the cube* as shown in the Figure 6.18. Let a be the edge length of the cube and r the radius of the particle then

$$a = 2r$$

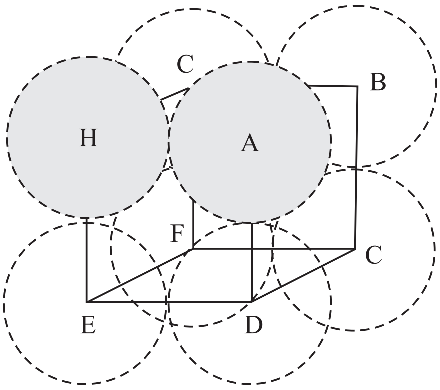


Fig. 6.18: Simple cubic unit cell

The volume of the cube = (edge length/side)^3 = a^3 = $(2r)^3$ = $8r^3$

No. of constituent particles present in each unit cell = 1

The volume of the filled space = volume of 1 particle = $\frac{4}{3}\pi r^3$

$$\text{Packing efficiency} = \frac{\text{filled space}}{\text{total space}} \times 100$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.36\% = 52.4\%$$

(2) Packing Efficiency of Body Centred Cubic Lattice

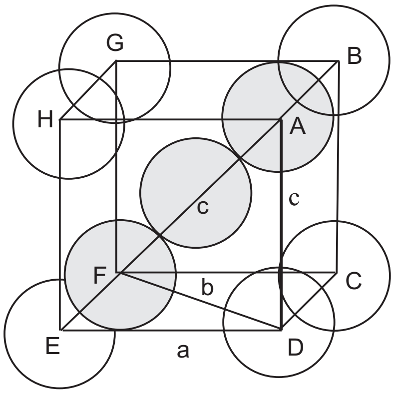


Fig. 6.19. Body centred cubic until cell.

The body centred cubic unit cell has constitutent particles present at all its corners as well as at its body centre. The particle at the body-centre touches the particle at corner positions. Thus, the particles are in contact along the body-diagonal of the cube. Consider the body-diagonal AF along which the contact between the central particles with those at corners A and F has been shown in Fig. 6.19.

$\therefore$ Length of body-diagonal $AF = c = 4\ r$ (6.1)

(Whole of the central particle ($2r$) and one-half of each of the two corner particle ($r + r$) occupy the body-diagonal)

Length of the body-diagonal

In the triangle EFD on the face CDEF, $\mathrm{EF} \perp \mathrm{ED}$.

$$\therefore \qquad \mathrm{FD}^2 = \mathrm{EF}^2 + \mathrm{ED}^2$$

$$b^2 = a^2 + a^2 = 2a^2$$

Where a is the edge-length or side of the cube.

In the triangle AFD, $\mathrm{AD} \perp \mathrm{FD}$

$$\therefore \qquad \mathrm{AF}^2 = \mathrm{AD}^2 + \mathrm{FD}^2$$

$$c^2 = a^2 + b^2 = \mathrm{a}^2 + 2\mathrm{a}^2 = 3\mathrm{a}^2$$

$$\therefore \qquad c = \sqrt{3}a \qquad (6.2)$$

But $c = 4r$

$$\therefore \qquad a = \frac{4r}{\sqrt{3}} \tag{6.3}$$

The number of constituent particles in a body-centred cubic unit cell = 2

$$\therefore \quad \text{Volume of filled space} = 2 \times \frac{4}{3}\pi r^3 \tag{6.4}$$

$$\text{Volume of the cubic unit cell} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 \tag{6.5}$$

$$\text{Packing efficiency} = \frac{\text{filled space}}{\text{total space}} \times 100 = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} \times 100$$

$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}} r^3} \times 100 = \frac{\sqrt{3}\pi}{8} \times 100 = 68.0\%$$

(3) Packing Efficiency of *CCP* and *HCP* Lattices

Cubic close packed or *face centred cubic (FCC)* and *hexagonal close packed* lattices have equal packing efficiency. Packing efficiency of face centred cubic (*FCC*) or cubic close packing (*CCP*) unit cell can be calculated with the help of Figure 6.20. Let the edge length or the side of the cubic unit cell be *a* and its face diagonal AC be *b*. In the triangle ABC, $AB \perp BC$, therefore,

$$AC^2 = AB^2 + BC^2$$

$$b^2 = a^2 + a^2 = 2a^2$$

or

$$b = \sqrt{2}a. \tag{6.6}$$

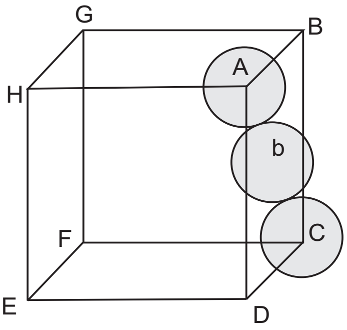


Fig. 6.20: *Face centred cubic or cubic close packing unit cell*

Unit cell of *fcc* (or *ccp*) lattice has constituent particles at all the corners and at the centre of each face.

The particle of face-centre touches the particles occupying the corner positions of the same face.

$$\therefore \quad \text{Length of the face diagonal AC} = b = 4r \qquad (6.7)$$

Where r is the radius of the constitutent particle (whole of central particle, $2r$, and one-half of each of the two corner particles, $r + r$)

From equations 1 and 2

$$b = 4r = \sqrt{2}a$$

or

$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r \qquad (6.8)$$

The number of constituent particles in a face centred cubic unit cell = 4

$$\therefore \quad \text{The Volume of filled space} = 4 \times \frac{4}{3}\pi r^3$$

$$\text{Volume of the cubic unit cell} = (\text{side})^3 = a^3 = (2\sqrt{2}r)^3$$

$$\text{Packing efficiency} = \frac{\text{filled space}}{\text{total space}} \times 100 = \frac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}r)^3} \times 100$$

$$= \frac{\frac{16}{3}\pi}{16\sqrt{2}} \times 100 = \frac{\pi}{3\sqrt{2}} = 74\%$$

Packing efficiencies of the three types of cubic lattices are summarized in the table 6.4.

Table 6.4: Packing efficiency of cubic unit cells

S.No.	Lattice	Packing Efficiency %
1.	Simple Cubic	52.4%
2.	Body Centred Cubic	68.0%
3.	Face Centred Cubic or Cubic close packing	74.0%

6.9 STRUCTURES OF IONIC SOLIDS

In case of ionic solids that consist of ions of different sizes, we need to specify the positions of both the cations as well as the anions in the crystal lattice. Therefore, structure adopted by an ionic solid depends on the relative sizes of the two ions. In fact it depends on the ratios of their radii (r+/r-) called **radius ratio**. Here r+ is the radius of the cation and r- is that of the anion. The radius ratios and the corresponding structures are compiled in Table 6.5.

Table 6.5 : The radius ratios (r + /r–) and the corresponding structures

Radius ratio (r+/r–)	Coordination number	Structure adopted
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 0.91	8	Body centered cubic
>=1.00	12	Cubic Close Packed structure

The common ionic compounds have the general formulae as MX, MX_2, and MX_3, where M represents the metal ion and X denotes the anion. We would discuss the structures of some ionic compounds of MX and MX_2 types.

6.9.1 Structures of the Ionic Compounds of MX Type

For the MX type of ionic compounds three types of structures are commonly observed. These are sodium chloride, zinc sulphide and caesium chloride structures. Let us discuss these in some details.

(a) Caesium Chloride Structure

In CsCl the cation and the anions are of comparable sizes (the radius ratio = 0.93) and has a bcc structure in which each ion is surrounded by 8 ions of opposite type. The Cs^+ ions is in the body center position and eight Cl^- ions are located at the corners (Fig. 6.21) of the cube. Thus it has a coordination number of 8.

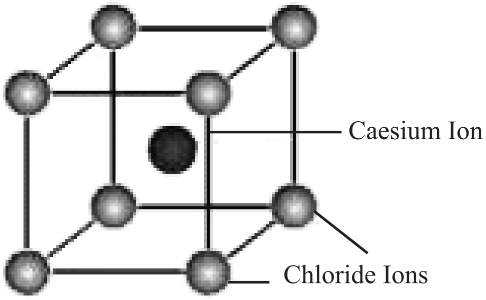


Fig. 6.21: *Caesium chloride structure*

(b) Sodium Chloride Structure

In case of NaCl the anion (Cl^-) is much larger than the cation (Na^+). It has a radius ratio of 0.52. According to Table 3.3 it should have an octahedral arrangement. In sodium chloride the(Cl^-) form a *ccp* (or *fcc*) structure and the sodium ion occupy the octahedral voids. You may visualise the structure having chloride ions at the corners and the face centers and the sodium ions at the edge centers and in the middle of the cube (Fig. 6.22).

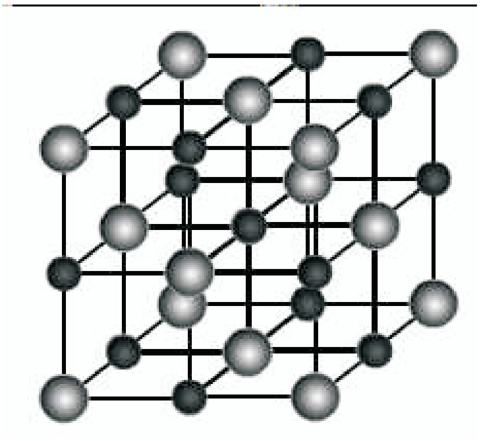


Fig. 6.22 : *Sodium chloride structure.*

(c) Zinc Sulphide Structure

In case of zinc sulphide the radius ratio is just = 0.40. According to Table 3.3 it should have an tetrahedral arrangement. In Zinc sulphide structure, the sulphide ions are arranged in a ccp structure. The zinc ions are located at the corners of a tetrahedron, which lies inside the cube as shown in the Fig. 6.23. These occupy alternate tetrahedral voids.

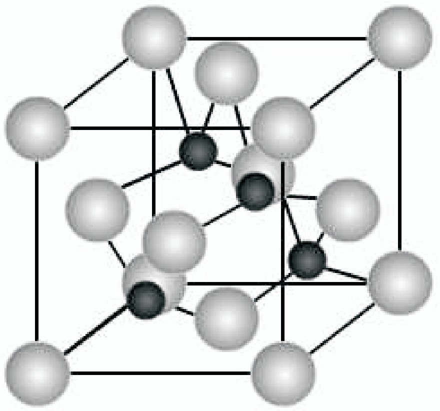


Fig. 6.23 : *Zinc Sulphide structure.*

6.9.2 Structure of Ionic Compounds of MX_2 type

(a) Calcium fluoride or fluorite structure

In this structure the Ca^{2+} ions form a *fcc* arrangement and the fluoride ions are located in the tetrahedral voids (Fig. 6.24).

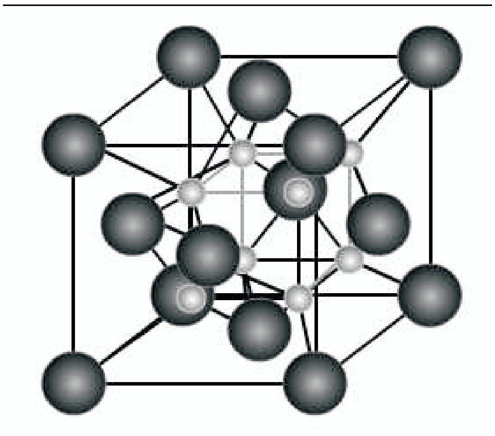


Fig. 6.24 : *Calcium fluoride or Fluorite structure; calcium ions occupy the corners of the cube and face centers The F^- ions are on the corners of the smaller cube which dipict the positions of tetrahedral void.*

(b) Antifluorite Structure

Some of the ionic compounds like Na_2O have antifluorite structure. In this structure the positions of cations and the anions in fluorite structures are interchanged. That is why it is called antifluorite structure. In Na_2O the oxide ions form the ccp and the sodium ions occupy the tetrahedral voids (Fig. 6.25).

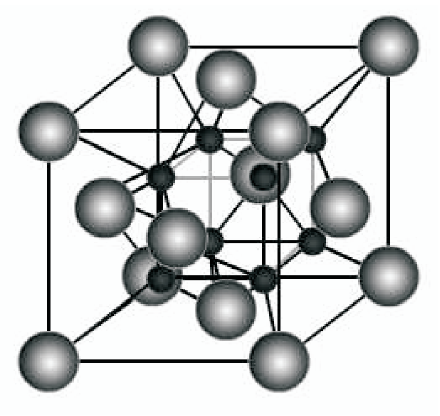


Fig. 6.25: *Antifluorite structure adopted by Na_2O; The oxide ions occupy the corners of the cube and face centers and the Na^+ ions (shown in black) are on the corners of the smaller cube.*

6.10 DEFECTS IN IONIC CRYSTALS

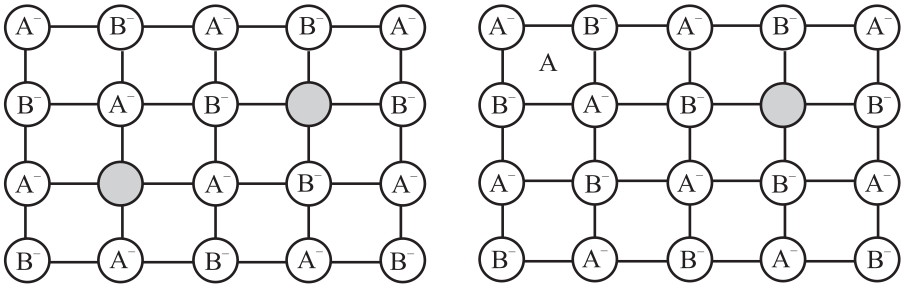
You have learnt that in a crystalline solid the constituent particles are arranged in a ordered three dimensional network. However, in actual crystals such a perfect order is not there. Every crystal has some deviations from the perfect order. These deviations are called imperfections or defects. These defects can be broadly grouped into two types. These are **stoichiometric** and

non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material. Here, we would deal only with stoichiometric defects. In such compounds the number of positive and negative ions are in stoichiometric proportions. There are two kinds of stoichiometric defects, these are

- Schottky defects
- Frenkel defects

(a) Schottky defects : This type of defect are due to the absence of some positive and negative ions from their positions. These unoccupied lattice sites are called holes. Such defects are found in ionic compounds in which the positive and negative ions are of similar size e.g., NaCl and CsCl. The number of missing positive and negative ions is equal. The presence of Schottky defects decreases the density of the crystal [Fig. 6.26(a)].

(b) Frenkel defects : This type of defect arise when some ions move from their lattice positions and occupy interstitial sites. The interstitial sites refer to the positions in between the ions. When the ion leaves its lattice site a hole is created there. ZnS and AgBr are examples of ionic compounds showing Frenkel defects. In these ionic compounds the positive and negative ions are of quite different sizes. Generally the positive ions leave their lattice positions, as these are smaller and can accommodate themselves in the interstitial sites. The Frenkel defects do not change the density of the solids [Fig. 6.26(b)].



(a) (b)

Fig. 6.26: *Stoichiometric defects a) Schottky and b) Frenkel defects*

These defects cause the crystal to conduct electricity to some extent. The conduction is due to the movement of ions into the holes. When an ion moves into a hole it creates a new hole, which in turn is occupied by another ion, and the process continues.

INTEXT QUESTIONS 6.3

(a) What do you understand by crystal lattice?

b) What is a unit cell ?

c) How many atoms are there in a fcc unit cell?

6.11 ELECTRICAL PROPERTIES

Conductance of electricity is an important property of a substance. Solids show a very wide range of conductivities from a high of 10^7 to a low of 10^{-20} sm^{-1}, thus spanning 27 orders of magnitude. Based upon their ability to conduct electricity, solids may be classified into three categories; conductors, insulators and semiconductors.

6.11.1 Conductors' Insulators and Semiconductors

(i) Conductors

These are the solids with conductivities ranging from 10^4 to 10^7 S m^{-1}. Metals conduct electricity through movement of their electrons and are called *electronic conductors.* Ionic solids conduct electricity when in molten state or dissolved in water, through movement of their ions. They are called *electrolytic conductors.*

(ii) Insulators

These are the solids with extremely low conductivities ranging from 10^{-20} to 10^{-10} S m^{-1}. Insulators are used to provide protective covering on conductors.

(iii) Semiconductors

These are the solids with intermediate conductivities ranging from 10^{-6} to 10^4 S m^{-1}. Although semiconductors have low conductivities, they find vide applications in solid state devices like diodes and transistors. Their conductivities can be modified by introduction of a suitable impurity.

6.11.2 Conduction of Electricity in Metals

Metals conduct electricity through movement of their electrons. In unit 5 you have learnt that when two atoms come closer, their atomic orbitals overlap and they form an equal number of molecular orbitals. One-half of these have lower energy while the other half have higher energy than the energy of the atomic orbitals. As the number of molecular orbitals increases, the energy-separation between them decreases.

In a piece of metal, the number of metal atoms is very large and so is the number of their valence orbitals. This results in formation of an equally large number of molecular orbitals which are so close to one-another that they form a continuous *band*. The band in which the valence electrons are present is called **valence band**. Electrons present in this band are strongly bound to the nucleus and cannot conduct electricity. The band formed by vacant molecular orbitals of higher energy is called **conduction band.** When electrons reach conduction band from valence band on excitation, they become loosely bound to the nucleus and can conduct electricity by moving under the influence of an electric field. Such electrons are also called *free electrons.* Conductivity of a solid depends upon how easy or difficult it is for the valence electrons to jump to the conduction band. See figure 6.27.

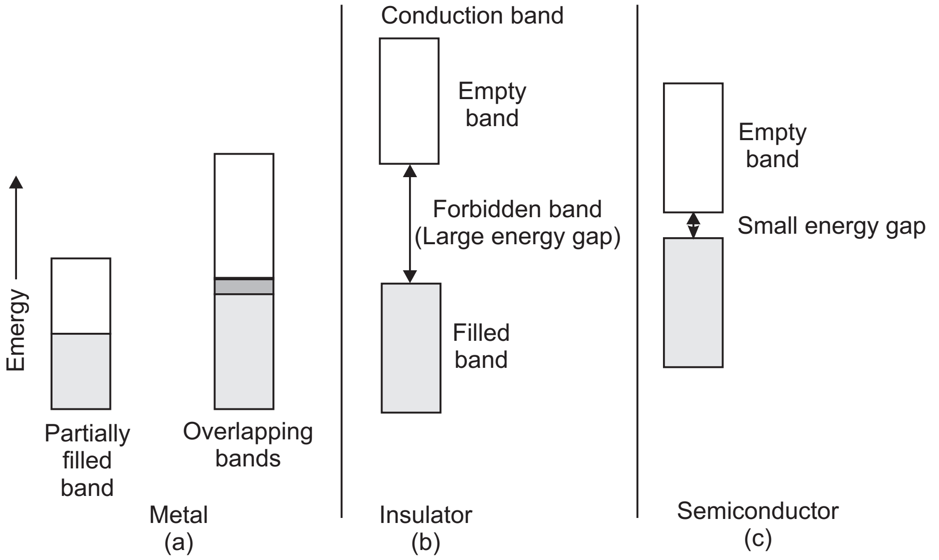


Fig. 6.27: Valence and conduction bands in (a) metals, (b) insulators and (c) semi conductors.

(i) **In conductors** either the valence band is only partially filled or it overlaps a vacant conduction band of slightly higher energy. In both the cases its electrons can easily flow under the influence of electric field and the solid behaves as a conductor (Fig. 6.27(a))

(ii) In **insulators** the gap between the valence band and conduction band is large. Due to this the valence electrons *cannot* jump to the conduction band and conduct electricity (Fig. 6.27(b))

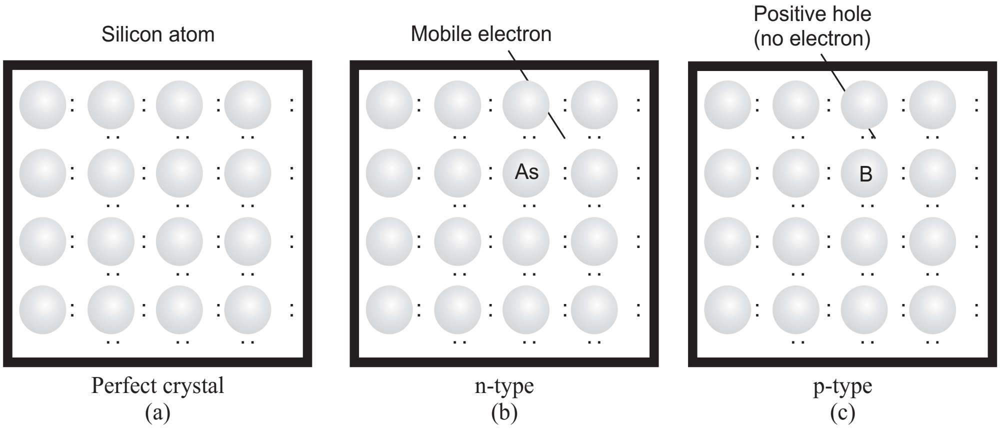
(iii) **In semiconductors** the gap between the valence band and nearest conduction band is small (Fig. 6.27(c)). On applying the electric field, some electrons can jump to the conduction band and provide low conductivity. On increasing the temperature more electrons can jump to the conduction band and the conductivity increases. Silicon and germanium show this type of behaviour. They are called **intrinsic semiconductors.**

6.11.3 Doping of Semiconductors

Conductivities of silicon and germanium are too low to be put to any practical use. Their conductivities can be improved by introduction of controlled quantities of impurities which are either electron-rich or electron-deficit with respect to these elements. This process is known as **doping**.

(a) Doping with electron–rich impurities

Silicon and germanium both belong to group 14 of the periodic table and have 4 valence electrons each. In their crystal lattice each silicon (or germanium) atom forms four covalent bonds with its neighbours (Fig. 6.23(a)) when it is doped with a group 15 element like As or P, whose each atom carries 5 valence electrons which is one more than Si. After sharing its four electrons with four neighbouring Si atoms, it has 9 electrons in its valence shell (Fig. 6.28(b)) which is highly unstable electronic configuration. The ninth electron being highly unstable roams freely in the whole of the crystal lattice randomly. In the presence of an electric field this electron (*mobile electron*) moves from negative to positive terminal and increases the conductivity of Si (or Ge). Since the increased conductivity of Si (or Ge) is due to **negatively charged** mobile electrons, the Si doped with electron rich impurity becomes a ***n*-type semiconductor**.



Perfect crystal
(a)

n-type
(b)

p-type
(c)

Fig. 6.28: Creation of *n*-type and *p*-type semiconductors

(b) Doping with electron-deficit impurities. When Si (or Ge) is doped with a group 13 element like B or Al containing 3 valence electrons (1 electron less than Si/Ge), this results in creation of one-electron vacancy in the structure which is called an **electron hole** (Fig. 6.28(c)). An electron from its neightbouring atom can come and occupy it, leaving a hole at its original position. Electrons can randomly occupy holes and the hole would appear to move randomly. On applying an electric field, the electrons move from negative to positive terminal and the *hole* would appear move in the opposite direction, i.e., from positive to negative terminal and would behave as if it is *positively charged*. Such semiconductors are called ***p*-type semiconductors**. The movement of electrons and the hole increases the conductivity of Si. Semiconductors like Si, doped with electron-deficit or electron-rich impurities are called **extrinsic semiconductors.**

Applications of *n*-type and *p*-type semiconductors

Due to their special properties, *n*-and *p*-type semiconductors find several applications.

(i) *Diodes:* Diode is a combination of a *n*-type and a *p*-type semiconductor. Diodes are used as rectifier to convert an AC signal to a DC signal.

(ii) *Transistors.* Transistors are made by combination of 3 layers of semiconductors. Transistor of *n-p-n* type is made by sandwiching a layer of *p*-type semiconductor between two layers of *n*-type semiconductors and *of p-n-p* type by sandwiching a layer of *n*-type semiconductors between two layers of *p*-type semiconductor. Transistors are used as detectors and amplifiers of radio or audio frequency signals. They are used in circuits of solid state devices.

(iii) *Solar cells.* Solar cells are photo diodes which have a special property of emitting electrons when sunlight falls on them. They are used to convert solar energy into electricity.

6.12 MAGNETIC PROPERTIES

All substances are affected (attracted or repelled) by a magnetic field. Magnetic properties present in any substance are due to the electrons present in it. Each electron in an atom behaves like a tiny magnet. Electrons are negatively charged particles. When an electron *revolves* around nucleus and *spins* about its own axis, two types of magnetic moments are created – *orbital magnetic moment* due to its revolution around the nucleus and *spin magnetic moment* due to its spin. Overall magnetic properties of a substance depend upon the orientation of these tiny magnets.

On the basis of magnetic properties, all substances can be classified into five categories:

(i) paramagnetic, (ii) diamagnetic, (iii) ferromagnetic, (iv) antiferromagnetic and (v) ferrimagnetic

6.12.1 Paramagnetic Substances

On placing these substances in a magnetic field, these are weakly attracted by it. O_2, Cu^{2+}, Fe^{3+} and Cr^{3t} are some examples of paramagnetic substances Paramagnetism is due to the presence of one or more unpaired electrons in an atom, molecule or ion.

6.12.2 Diamagnetic Substances

When placed in a magnetic field, diamagnetic substances are weakly repelled by it. H_2O, NaCl and C_6H_6 are some examples of such substances. Diamagnetism is shown by substances in which all the electrons are paired.

6.12.3 Ferromagnetic Substances

When placed in a magnetic field, ferromagnetic substances are strongly attracted by it. Fe, Ni, Co, Gd, MnAs, $CrBr_3$ and CrO_2 are such substances. These substances can be permanently magnetized. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. In each domain, the individual magnetic moments of the metal ions are directed in the same direction and they add up. As a result, each domain acts as a tiny magnet. Ordinarily, these domains are randomly oriented which cancels out their magnetic moment. When placed in a magnetic field, all the domains get oriented in the direction of the magnetic field. This adds up their magnetic moments and makes them strong magnets (Fig. 6.29(a)). They lose their ferromagnetism on being given mechanical jerks or on heating above a certain temperature, called *Curie temperature* they become paramagnetic.

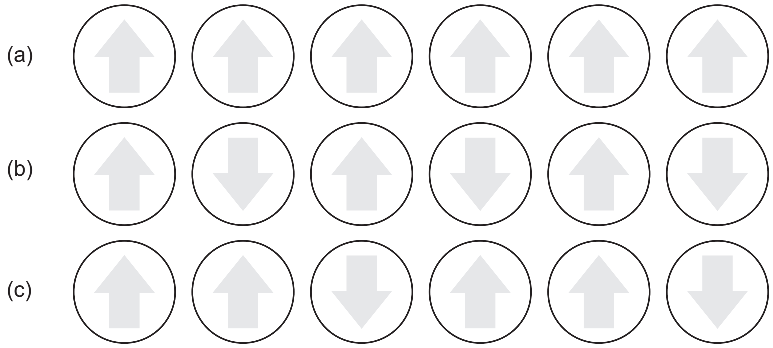


Fig. 6.29 Arrangement of magnetic moments of domains in (a) ferromagnetic, (b) anti ferromagnetic and (c) ferrimagnetic substances

6.12.4 Antiferromagnetic Substances

Some substance that have domains in them like ferromagnetic substances but their domains are oppositely oriented and cancel out the magnetic moments of each other (Fig. 6.29 (b)) are caled antiferro magnetic substances. FeO, $MnCl_2$, MnO, Mn_2O_3 and MnO_2 are examples of antiferromagnetic substances. They also become paramagnetic on heating above a certain temperature.

6.12.5 Ferrimagnetic Substances.

Some substances like Fe_3O_4 (magnetite) and ferrites (MFe_2O_4 where M is a bivalent cation like Cu^{2+}, Zn^{2+}) show an intermediate behavior between that of ferromagnetic and antiferromagnetic substances. These substances are quite strongly attracted by magnetic field as compared to paramagnetic substances but weakly as compared to ferromagnetic substances. Their domains are aligned in parallel and antiparallel directions in unequal numbers (Fig. 6.29(c)). They also become paramagnetic on heating above a certain temperature.

WHAT YOU HAVE LEARNT

- In solid state the constituent particles are arranged in a closely packed ordered arrangement with almost no free space. These are held together by strong forces of attraction and vibrate about their fixed positions. Solids are incompressible and rigid and have definite shapes.
- Solids are classified into amorphous and crystalline solids. The crystalline solids have long range order while amorphous solids have only short range order.
- The crystalline solids can be classified into four different types- ionic, molecular, covalent and metallic solids on the basis of nature of forces of attraction between the constituent particles.
- The temperature at which a solid melts to give a liquid is called its melting point.
- The three dimensional internal structure of a crystalline solid can be represented in terms of a crystal lattice in which the location of each constituent particle is indicated by a point.
- The whole crystal lattice can be generated by moving the unit cell in the three directions.
- The crystal structures of the solids can be described in terms of a close-packing of identical spheres.
- In three dimensions there are two ways of packing identical spheres. These are hexagonal closed packing (hcp) and cubic closed packing (ccp). The hcp arrangement is obtained by ABAB repeat of the two dimensional layers whereas the ccp arrangement is obtained by ABCABC repeat.
- On the basis of the external appearance the known crystals can be classified into seven types called crystal systems.
- The unit cells of cubic crystal system has three possible lattice types. These are simple cubic, body centered cubic and the face centered cubic.
- The atoms at the corner of a cubic unit cell is shared by eight unit cells while a face centered atom is shared by two unit cells. The atom at the body center, on the other hand is exclusive to the unit cell as it is not shared.

- The number of atoms per unit cell for the simple cubic, bcc and fcc unit cells are 1,2 and 4 respectively.
- The structure adopted by an ionic solid depends on the ratios of their radii (r+/r-), called radius ratio.
- The structures of some simple ionic solids can be described in terms of ccp of one type of ions and the other ions occupying the voids.
- Actual crystals have some kind of imperfections in their internal structure. These are called defects.
- There are two types of defects called stoichiometric and non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material.
- There are two kinds of stoichiometric defects, these are called Schottky defects and Frenkel defects.
- Solid can be classified as conductors, insulators and semiconductors on the basis of their electrical conductivities.
- Electrical properties of solids can be explained with the help of band theory.
- On the basis of their interaction with external magnetic field, solids can be classified as paramagnetic, diamagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic substances.

TERMINAL EXERCISES

1. Outline the differences between a crystalline and an amorphous solid.
2. How can you classify solids on the basis of the nature of the forces between the constituent particles?
3. What do you understand by the melting point of a solid ? What information does it provide about the nature of interaction between the constituent particles of the solids?
4. What do you understand by coordination number? What would be the coordination number of an ion occupying an octahedral void.?
5. Explain the following with the help of suitable examples.
   (a) Schottky defect
   (b) Frankel defect
6. Explain why a particular solid behaves as conductor or semiconductor or insulator on the basis of band theory.
7. What are (i) paramagnetic (ii) diamagnetic and (iii) ferromagnetic substances?

ANSWERS TO INTEXT QUESTIONS

6.1

1. Solids have definite shape and definite volume.

Liquids have indefinite shape but define volume.

Gases have indefinite shape and indefinite volume.

2. Coulombic forces, dipole-dipole attractions, covalent bonding and metallic bonding.

3. Irrespective of the size and shape of the crystal of a substance, the interfacial angle between a pair of faces is always the same

6.2

1. Refer to section 6.7.
2. Hexagonal close packed.
3. Refer to sections 6.7.

6.3

1. Ordered three dimensional arrangement of points representing the location of constituent particles.
2. A select group of points which can be used generate the whole lattice. Unit cell is characterised by three edges of the lattice and angles between them.
3. Four.

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7

SOLUTIONS

You know that when sugar or salt is added to water, it dissolves. The resulting mixture is called a solution. Solutions play an important role in our life. In industry, solutions of various substances are used to carry out a large number of chemical reactions.

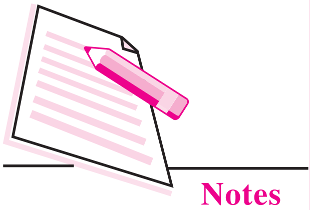
Study of solutions of various substances is very interesting.

In this lesson, let us learn about the various components of a solution and the ways in which concentration of solutions is expressed. We shall also learn about some properties of solutions which are dependent only on the number of solute particles. (you will learn about solute in this lesson)

OBJECTIVES

After reading this lesson, you will be able to:

- identify the components of different types of solution;
- express the concentration of solutions in different ways;
- list different types of solutions;
- state Henry's law;
- define vapour pressure;
- state and explain Raoult's law for solutions;
- define ideal solutions;
- give reasons for non-ideal behaviour of solutions;
- state reasons for positive and negative deviations from ideal behaviour;
- explain the significance of colligative properties;



- state reasons for the elevation of boiling point and depression in freezing point of solutions;
- explain the abnormal colligative properties;
- define osmosis and osmotic pressure;
- define Van't Hoff factor;
- correlate the degree of dissociation of solute and
- solve numerical problems.

7.1 COMPONENTS OF A SOLUTION

When we put sugar into water, it dissolves to form a solution. We do not see any more sugar in it. Like sugar, a large number of other substances such as common salt , urea, potassium chloride etc dissolve in water forming solution . In all such solutions , water is the solvent and substances which dissolve are the solutes .

Thus, solute and solvent are the components of a solution . Whenever a solute mixes homogeneously with a solvent , a solution is formed

$$\text{solute} + \text{solvent} \rightarrow \text{solution}$$

A solution is a homogeneous mixture of two or more substances .

Solvent is that component of a solution that has the same physical state as the solution itself.

Solute is the substance that is dissolved in a solvent to form a solution.

7.1.1 The Concentration of a Solution

Some of the properties of solutions , e.g.. the sweetness of a sugar solution or the colour of a dye solution , depend on the amount of solute compared to that of the solvent in it. This is called the solution concentration . There are several ways for describing concentration of solution . They include molarity, molality, normality, mole fraction and mass percentage.

Molarity: Molarity is defined as the number of moles of solute dissolved per litre of solution and is usually denoted by *M*. It is expressed as :

$$M = \frac{n}{V}$$

Where *n* is the number of moles of solute and V is the volume of the solution in litres. A 2.0 molar solution of sulphuric acid would be labelled as 2.0 *M* H_2SO_4.

It is prepared by adding 2.0 mol of H_2SO_4 to water to make a litre of solution. Molarity of a solution changes with temperature because of expansion or contraction of the solution.

Molality : It is defined as the number of moles of solute dissolved per kilogram of solvent.

It is designated by the symbol m. The label 2.0 m H_2SO_4 is read "2 molal sulphuric acid" and is prepared by adding 2.0 mol of H_2SO_4 to 1 kg of solvent. Molality is expressed as:

$$m = \frac{1000\, n_B}{W_A}$$

where n_B is the number of moles of the solute and W_A is the mass in grams of solvent. The molality of a solution does not change with temperature.

Example 7.1 : Find out the molarity of the solution which contains 32.0 g of methyl alcohol (CH_3OH) in 200 mL solution.

Solution : Molar mass of $CH_3OH = 12 + 1 \times 3 + 16 + 1 = 32\ \text{g mol}^{-1}$

$$\text{Number of moles of } CH_3OH = \frac{32\ \text{g}}{32\ \text{g mol}^{-1}} = 1\ \text{mol}$$

Volume of the solution = 200 mL = 0.2 litre

$$\therefore \qquad \text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}} = \frac{1}{0.2} = 5\ \text{M}$$

Example 7.2 : What is the molality of a sulphuric acid solution of density 1.20 g/cm^3 containing 50% sulphuric acid by mass.

Solution : Mass of 1cm^3 of H_2SO_4 solution = 1.20 g

Mass of 1 litre (1000 cm^3) of H_2SO_4 solution = 1.20 × 1000 = 1200 g

Mass of H_2SO_4 in 100 g solution of H_2SO_4 = 50 g

$$\text{Mass of } H_2SO_4 \text{ in 1200 g solution of } H_2SO_4 = \frac{50}{100} \times 1200 = 600\ \text{g}$$

$\therefore$ Mass of water in the solution = 1200 – 600 = 600 g

Molar mass of $H_2SO_4 = 98\ \text{g mol}^{-1}$

$$\text{No. of moles of } H_2SO_4 = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{600\ \text{g}}{98\ \text{g mol}^{-1}}$$

$$\therefore \quad \text{Molarity} = \frac{\text{No. of moles of } H_2SO_4}{\text{Mass of water in grams}} \times 1000$$

$$= \frac{600}{98} \times \frac{1}{600} \times 1000 = 6.8 \text{ m}$$

Normality : Normality is another concentration unit. It is defined as the number of gram equivalent weights of solute dissolved per litre of the solution.

The number of parts by weight of a substance (element or compound) that will combine with or displace, directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen and 35.5 parts by weight of chlorine is known as equivalent weight. Like atomic weight and molecular weight, equivalent weight is also a number and hence no units are used to express it. However, when equivalent weight is expressed in grams, it is known as gram equivalent weight of the substance.

Equivalent weight $= \dfrac{\text{Atomic or molecular weight}}{\text{Valency}}$

Equivalent weight of an acid $= \dfrac{\text{Molecular weight}}{\text{Basicity}}$

Equivalent weight of a base $= \dfrac{\text{Molecular weight}}{\text{Acidity}}$

Equaivalent weight of a salt $= \dfrac{\text{Molecular weight}}{\text{Total valency of the metal atom}}$

oxidising and reducing agents may have different equivalent weights if they react to give different products under different conditions. Thus, the equivalent weight of such substances can be calculated from the reactions in which they take part.

Normality is denoted by the symbol *N*.

$$\therefore \text{ Normality } (N) = \frac{\text{No. of gram equivalent weights of the solute}}{\text{volume of the solution in litres}}$$

$$= \frac{\text{Mass of the solute in grams}}{\text{Equivalent weight of the solute}} \times \frac{1}{\text{volume of the solution in litres}}$$

$$= \frac{\text{Strength of solution in grams/litre}}{\text{Equivalent weight of the solute}}$$

The label 0.5 N $KMnO_4$ is read “0.5 normal” and represents a solution which contains 0.5 gram equivalent of $KMnO_4$ per litre of solution.

Notes

Mole Fraction : The mole fraction of a component in a solution is the ratio of its number of moles to the total number of moles of all the components in the solution. If a solution contains 2 mol of alcohol and 3 mol of water, the mole fraction of alcohol is $\frac{2}{5}$, and that of water $\frac{3}{5}$. The sum of mole fractions of all the components of a solution is equal to one. The mole fraction (x_A) of a component A in solution with B is :

$$x_A = \frac{n_A}{n_A + n_B}$$

Where n_A and n_B are the number of the moles of A and B respectively.

Mass Percentage : Mass percentage is the mass of solute present in 100 g of solution. Thus 5% solution of $KMnO_4$ in water means that 5 g of $KMnO_4$ is present in 100 g of the aqueous solution of $KMnO_4$.

Example 7.3 : A solution contains 36.0 g water and 46.0 g ethyl alcohol (C_2H_5OH). Determine the mole fraction of each component in the solution.

Solution : Molar mass of water = 18 g mol^{-1}

Molar mass of C_2H_5OH = 46 g mol^{-1}

$$\text{No. of moles of water} = \frac{36 \text{ g}}{18 \text{ g mol}^{-1}} = 2.0 \text{ mol}$$

$$\text{No. of moles of } C_2H_5OH = \frac{46 \text{ g}}{46 \text{ g mol}^{-1}} = 1.0 \text{ mol}$$

Total number of moles in the solution = 2.0 + 1.0 = 3.0

$$\text{Mole fraction of water} = \frac{\text{No. of moles of water}}{\text{Total no. of moles in the solution}} = \frac{2.0}{3.0} = 0.67$$

$$\text{Mole fraction of } C_2H_5OH = \frac{\text{No. of moles of } C_2H_5OH}{\text{Total no. of moles in the solution}} = \frac{1.0}{3.0} = 0.33$$

Example 7.4 : Calculate the normality of a solution of NaOH if 0.4 g of NaOH is dissolved in 100 ml of the solution.

Solution : Mass of NaOH present in 100 mL of the solution = 0.4 g

$$\therefore \text{ Mass of NaOH present in 1000 mL of the solution} = \frac{0.4}{100} \times 1000 = 4.0 \text{ g}$$

Mol. wt. of NaOH = 23 + 16 + 1 = 40 amu

$$\text{Eq. wt. of NaOH} = \frac{\text{Mol. Wt.}}{\text{Acidity}} = \frac{4.0}{1} = 40$$

$$\therefore \text{ Normality} = \frac{\text{Strength in g/litre}}{\text{Eq. wt.}} = \frac{4}{40} = \frac{1}{10}\text{N}$$

Hence, the normality of the solution = $\frac{1}{10}$ N or 0.1 N

INTEXT QUESTIONS 7.1

1. List the various methods of expressing the concentration of a solution?
2. Define the following
   (i) Molarity (ii) Molality (iii) Normality

7.2 TYPES OF SOLUTIONS

Solutions can be solid, liquid or gaseous. Depending upon the physical state of the solute and the solvent, there are nine possible types of solutions consisting of two components (binary solutions) Different types of solutions are given in Table 7.1.

Table 7.1 Different Types of Solutions

SOLUTE	SOLVENT	SOLUTION
Gas	Gas	Air
Gas	Liquid	Soda water
Gas	Solid	Hydrogen in palladium
Liquid	Gas	Humidity in air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in gold
Solid	Gas	Camphor in air
Solid	Liquid	Sugar in water
Solid	Solid	Alloys such as brass (zinc in copper) and bronze (tin in copper)

Generally, we come across only the following three types of solutions:

(a) Liquids in Liquids: In the solution of liquids in liquids such as alcohol in water, the constituent present in smaller amounts is designated as solute and the constituent present in larger amounts is called the solvent. When two liquids are mixed, three different situations may arise:

(i) Both the liquids are completely miscible, i.e., when, two liquids are mixed, they dissolve in each other in all proportions, e.g., alcohol and water, benzene and toluene.

(ii) The liquids are partially miscible, i.e., they dissolve in each other only to a certain extent, e.g., water and phenol.

(iii) The liquids are immiscible, i.e., they do not dissolve in each other, e.g., water and benzene, water and toluene.

The solubility of liquids in liquids generally increases with rise in temperature.

(b) Gases in Liquids: Gases are generally soluble in liquids. Oxygen is sufficiently soluble in water, which allows the survival of aquatic life in ponds, rivers and oceans. Gases like CO_2 and NH_3 are highly soluble in water. The solubility of a gas in a liquid depends on the pressure, temperature and the nature of the gas and the solvent. These factors are discussed below in detail :

(i) Effect of Pressure: The variation of solubility of a gas in a liquid with pressure is governed by *Henry's* law. *Henry's* law states that

The mass or mole fraction, of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.

Henry's law is represented by

$$x = Kp$$

where K is a constant, p is the partial pressure of the gas and x is the mole fraction of the gas in the solution. Let us now see what are the conditions for the validity of Henry's law.

(i) Conditions for validity of Henry's law: It is found that gases obey Henry's law under the following conditions.

(i) the pressure is not too high.

(ii) the temperature is not too low.

(iii) the gas does not dissociate, associate or enter into any chemical reaction with the solvent.

(ii) Effect of temperature: The solubility of a gas in a liquid at constant pressure decreases with rise in temperature. For example, the solubility of CO_2 in water at 20°C is 0.88 cm^3 per cm^3 of water, where as it is 0.53 cm^3 per cm^3 of water at 40°C. This happens because on heating a solution, containing a dissolved gas, some gas is usually expelled from the solution.

(iii) Effect of the nature of the gas and the solvent: Gases like CO_2, HCl and, NH_3 are highly soluble in water where as H_2, O_2 and N_2, are sparingly soluble.

(c) **Solids in liquids:** When a solid is dissolved in a liquid, the solid is referred as the solute and the liquid as the solvent. For example, in a solution of sodium chloride in water, the solute is sodium chloride and water is the solvent. Different substances dissolve to different extent in the same solvent.

7.3 VAPOUR PRESSURE

If we keep an inverted beaker over a small beaker containing a pure liquid, it is found that the molecules of the liquid start evaporating in the form of vapours and fill the empty space above the beaker containing the liquid. A time comes when the number of molecules evaporating per unit time is equal to the number of molecules condensing during that time (Fig. 7.1). An equilibrium is thus established between the vapour and the liquid phase. The pressure exerted by the vapour of the liquid in such a case is called the vapour pressure of the liquid.

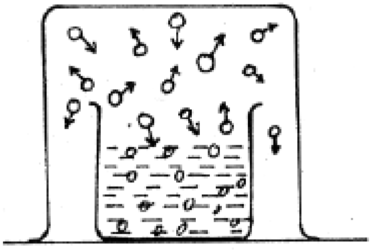


Fig.7.1 : *Vapour pressure of a liquid*

7.4 RAOULT'S LAW FOR SOLUTIONS

Did you ever think that if you mix two miscible volatile liquids A and B, what would be the vapour pressure of the resulting solution? The relationship between vapour pressure of a liquid and its mole fraction is given by Raoult's law.

Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each liquid in the solution is directly proportional to its mole fraction.

Raoult's law is applicable only if the liquids are miscible. The vapour phase now consists of vapours of both the liquids A and B. The partial vapour pressure of each liquid will depend upon its mole fraction in the solution. Let the mole fractions of the liquids A and B be X_A and X_B respectively. Also, if P_A and P_B are the partial vapour pressures of A and B respectively, then

$$P_A \propto X_A \text{ or } P_A = P^0_A X_A$$

Similarly,
$$P_B = p^0_B X_B$$

where p_A^0 and p_B^0 represent the vapour pressures of pure liquids A and B respectively.

If the values of P_A and P_B are plotted against the values of X_A and X_B for a solution, two straight lines are obtained as shown in Fig. 7.2 the total vapour pressure P of the solution is given by the sum of partial vapour pressures P_A and P_B.

Thus,

$$P = P_A + P_B$$

or

$$p = p_A^0 X_A + p_B^0 X_B$$

The total vapour pressure (P) of a solution is represented by the line joining p_A^0 and p^0_B. The solutions which obey Raoult's law are known as **ideal solutions.**

A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.

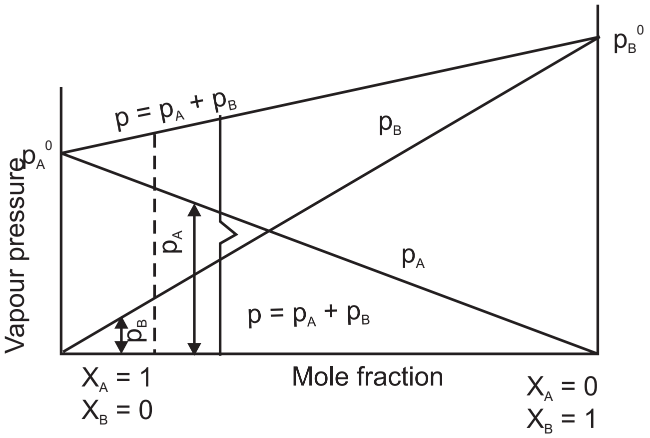


Fig. 7.2 : *Relationship between vapour pressure and mole fraction in a solution*

INTEXT QUESTIONS 7.2

1. State Raoult's law.
2. State Henry's law and list the conditions necessary for the validity of Henry's law

7.5 RAOULT'S LAW FOR SOLUTIONS CONTAINING NON-VOLATILE SOLUTE

If we have an aqueous solution containing a non-volatile solute, such as sugar or salt, what do you think about the vapour pressure exerted by such a solution? The vapour phase of such a solution consists of vapours of solvent (A) only because the solute is non-volatile. Since the mole fraction of the solvent in solution is less than one, therefore according to Raoult's law, the vapour pressure of the solution will be less than the vapour pressure of the pure solvent. If the total vapour pressure of the solution is *P,* then

$$P_A = p_A^0 \; X_A \qquad \text{...(7.1)}$$

for a binary mixture

$$X_A + X_B = 1$$

therefore,

$$X_A = 1 - X_B$$

Substituting the value of X_A in equation (7.1) we get

$$P_A = p^0{}_A(1 - X_B)$$

$$\frac{P_A}{P_A^0} = 1 - X_B$$

therefore, $$\frac{p_A^0 - p_A}{P_A^0} = X_B$$

In the above equation, $(P^0{}_A - P_A)$ represents the lowering of the vapour pressure

and $\frac{p_A^0 - p_A}{P_A^0}$ is called the relative lowering of the vapour pressure of the solution.

An alternative statement of Raoult's law for solutions of non-volatile solute is :

The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.

7.6 IDEAL AND NON-IDEAL SOLUTIONS

Ideal solutions obey Raoults Law and during their formation there is no change in heat and volume.

Non-ideal solutions are those solutions which do not obey Raoult's law and whose formation is accompanied by changes of heat and volume.

Most of the real solutions are non-ideal. They show considerable deviation from the ideal behaviour. Generally deviations are of two types;

(i) Positive deviation: Positive deviations are shown by liquid pairs for which the A-B molecular interactions are weaker than the A-A and or B-B molecular interactions. The total vapour pressure for such solutions is greater than predicted by Raoults law. The total vapour pressure for such a solution will be maximum for a particular intermediate composition (Fig. 7.3)

Examples of non-ideal solutions showing positive deviation from the ideal behaviour are mixtures of liquids such as water-propanol, ethanol-chloroform, acetone- carbon disulfide, ethanol-cyclohexane etc.

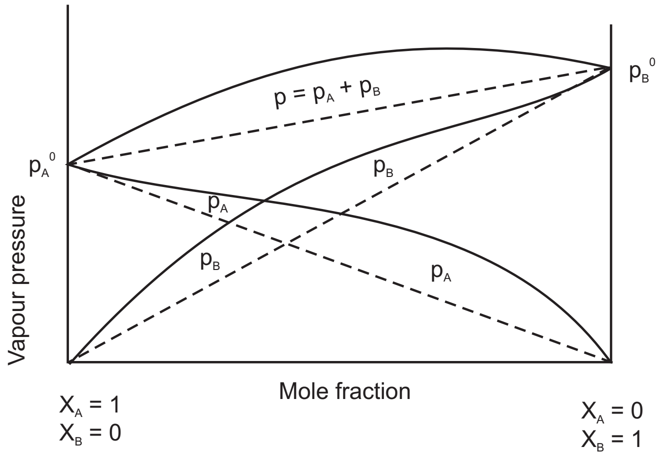


Fig. 7.3 : *Positive deviation for a liquid pair*

(ii) Negative Deviation: Negative deviations are shown by liquid pairs for which the A-B molecular interactions-are stronger than A-A or B-B molecular interactions. The total vapour pressure for such solutions is less than that predicted by Raoult's law. For a particular intermediate composition, the total vapour pressure of such a solution will be minimum (Fig. 7.4). Examples of such liquid pairs are chloroform acetone, water-sulphuric acid, phenol-aniline, water- HCI etc.

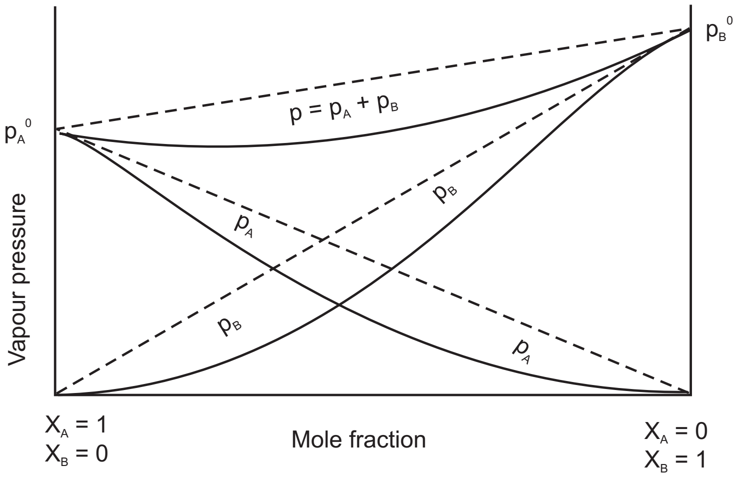


Fig. 7.4 : *Negative deviation for a liquid pair*

7.7 COLLIGATIVE PROPERTIES

Do you know that there are certain properties of dilute solutions which depend only on the number of particles of solute and not on the nature of the solvent and the solute? Such properties are called **colligative properties.** There are four colligative properties : relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure.

We shall discuss these colligative properties in detail in the following sections.

7.7.1 Relative Lowering of Vapour Pressure

According to Raoult's law for solutions containing non- volatile solute

$$\frac{P_A^0 - P_A}{P_A^0} = X_B \text{ (see section 7.5)} \qquad \text{...(i)}$$

Also

$$X_B = \frac{n_B}{n_A + n_B}$$

In a dilute solution $n_B << n_A$ Therefore the term n_B can be neglected in the denominator.

Hence,

$$X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B \,.\, M_A}{W_A \,.\, M_B}$$

Therefore equation (i) can be written as

$$\frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{W_B \,.\, M_A}{W_A \,.\, M_B}$$

The above expression can be used to determine the molecular mass of the solute B, provided the relative lowering of vapour pressure of a solution of known concentration and molecular mass of the solvent are known. However, the determination of molecular mass by this method is often difficult because the accurate determination of lowering of vapour pressure is difficult.

Example 7.5: The relative lowering of vapour pressure produced by dissolving 7.2 g of a substance in 100g water is 0.00715. What is the molecular mass of the substance?

Solution: We know that

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

Substituting the values we get

$$0.00715 = \frac{7.2 \times 18}{M_B \times 100} \quad \text{or} \quad M_B = \frac{7.2 \times 18}{0.00715 \times 100}$$

∴ Molecular mass of the substance = 181.26 amu

7.7.2 Elevation of Boiling Point

Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

As you know, the vapour pressure of a pure solvent is always higher than that of its solution. So, the boiling point of the solution is always higher than that of the pure solvent. If you see the vapour pressure curves for the solvent and the solution (Fig. 7.5), you will find that there is an elevation in the boiling point of the solution.

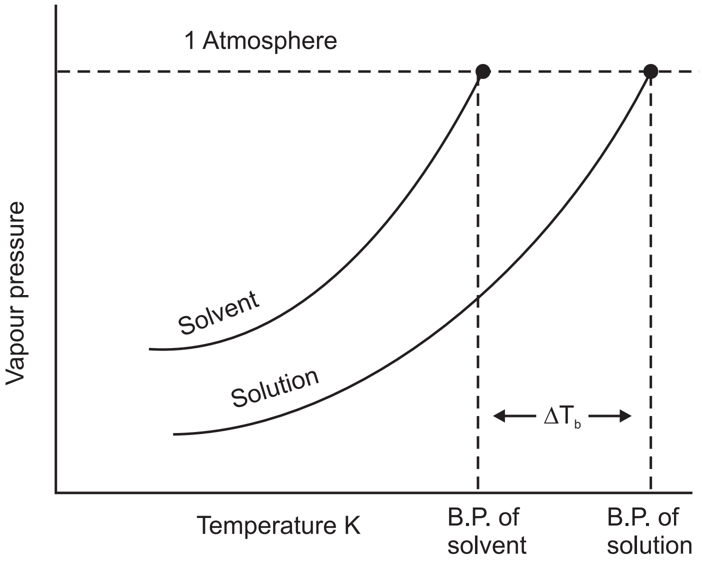


Fig. 7.5 : *Vapour pressure curves for solvent and solution*

Now let ΔT_b be the elevation in boiling point and Δp be the lowering in vapour pressure. Then,

$$\Delta T_b \propto \Delta p \propto X_B \text{ or } \Delta T_b = K\, X_B \qquad \text{(i)}$$

K is the proportionality constant

As you know $$X_B = \frac{n_B}{n_A + n_B}$$

In a dilute solution, $n_B << n_A$ and thus the term n_B is neglected in the denominator.

Thus, $$X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} = n_B \times \frac{M_A}{W_A}$$

Substituting the value of X_B in the equation (i) we get

$$\Delta T_b = K \times n_B \times \frac{M_A}{W_A}$$

If we take the mass of the solvent W_A in kilograms the term $\frac{n_B}{W_A}$ is molality *m. Thus*

$$\Delta T_b = K\ M_A\ .\ \mathrm{m} = K_B\ \mathrm{m}$$

The constant K_b is called the **molal elevation constant** for the solvent. K_b may be defined as **the elevation in boiling point when one mole of a solute is dissolved in one kilogram of the solvent.** K_b is expressed in degree per molality.

7.7.3 Depression in Freezing Point

Freezing point is the temperature at which the solid and the liquid forms have the same vapour pressure

The freezing point of the solution is always less than that of the pure solvent. Thus, there is a depression in the freezing point of the solution This is because the vapour pressure of the solution is always less than that of the pure solvent.

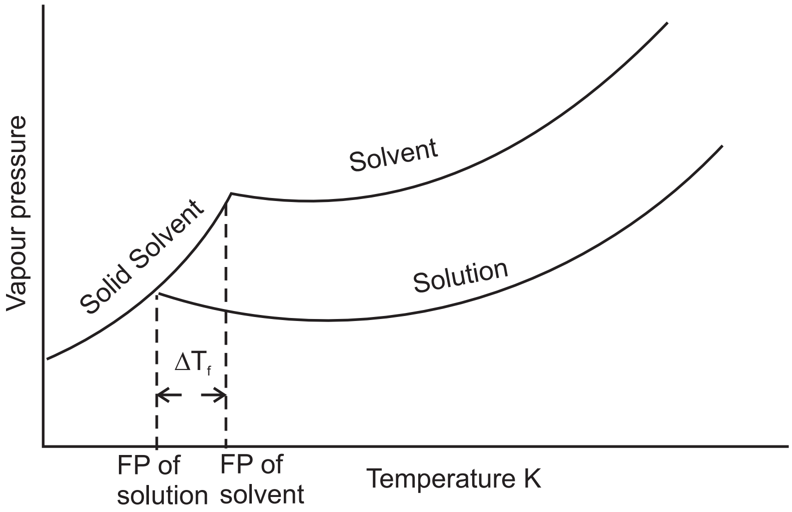


Fig. 7.6 : *Vapour pressure curves for solid, solvent and solution*

Let ΔT_f be the depression in freezing point. Then:

$$\Delta T_f \ \alpha \ X_B$$

or $$\Delta T_f = KX_B \qquad \text{...(ii)}$$

Where *K* the proportionality constant

You know that $$X_B = \frac{n_B}{n_A + n_B}$$

In dilute solutions $n_B << n_A$

Therefore, the term n_B can be neglected from the denominator. Thus,

$$X_B = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} = n_B \times \frac{M_A}{W_A}$$

$$\left(\text{since } n_B = \frac{W_B}{M_B}\right)$$

Substituting the value of X_B in equation (ii) we get

$$\Delta T_f = K \times n_B \times \frac{M_A}{W_A}$$

If the mass of the solvent W_A is taken in kg, then the term $\frac{n_B}{W_A}$ becomes molality m.

Thus, $\Delta T_f = K M_A \,.\, m = K_f \,.\, m$

The constant (K_f) for a solution is known as **molal depression constant or molal cryoscopic constant** for the solvent. K_f may be **defined as the depression in freezing point of a solution when one mole of a solute is dissolved in 1 kilogram of the solvent.**

Example 7.6: Find the (i) boiling point and (ii) freezing point of a solution containing 0.520 g glucose ($C_6H_{12}O_6$) dissolved in 80.2g of water.(K_f = 1.86 K/m, K_b = 0.52 k/m.)

Solution: Molality of glucose $= \frac{\text{Wt. of glucose}}{\text{mol. Wt.}} \times \frac{1000}{\text{Wt. of solvent}}$

$$= \frac{0.52}{180} \times \frac{1000}{80.2} = 0.036$$

$$\Delta T_b = K_b m = 0.52 \times 0.036 = 0.018 \text{ K}$$

∴ Boiling point = 373 + 0.018 = 373.018 = 373.02 K

(ii) $K_f = 1.86$ K/m

$$m = \frac{0.52}{180} \times \frac{1000}{80.2} = 0.036$$

∴ $\Delta T_f = 1.86 \times 0.036 = 0.66$ K

∴ Freezing point = 273 – 0.66 = 272.34 K

7.7.4 Osmosis and Osmotic Pressure

You must have observed that if rasins are soaked in water for some time, they swell. this is due to the flow of water into the rasins through its skin which acts as a semipermeable membrane (permeable only to the solvent molecules). This phenomenon is also observed when two solutions of different concentrations in the same solvent are separated by a semipermeable membrane. In this case the solvent flows from a solution of lower concentration to a solution of higher concentration. The process continues till the concentrations of the solutions on both sides of the membrane become equal.

The spontaneous flow of the solvent from a solution of lower concentration (or pure solvent) to a solution of higher concentration when the two are separated by a semipermeable membrane is known as **osmosis.**

The flow of solvent into the solution of higher concentration from a solution of lower concentration (on pure solvent) can be stopped if some extra pressure is applied to that side of the solution which has a higher concentration. The pressure that just stops the flow of the solvent is called **osmotic pressure.**

Thus, *osmotic pressure may be defined as the excess pressure that must be applied to the solution side to just prevent the passage of pure solvent into it when the two are seprated by a perfect semipermeable membrane.* This is illustrated in Fig. 7.7.

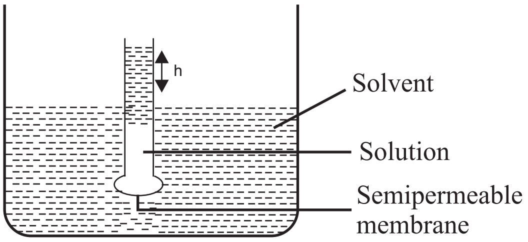


Fig. 7.7 : *Osmosis*

The pressure that must be applied to the solution side to prevent it from rising in the tube is the osmotic pressure. It is also equal to the hydrostatic pressure of the liquid column of height h.

If the two solutions have the same osmotic pressure, they are known as **isotonic** solutions. The osmotic pressure is a colligative proper̃tly. It depends on the number of particles of solute present in the solution and not on their nature. At a given temperature T, the osmotic pressure (π) of a dilute solution is experimentally found to be proportional to the concentration of the solution in moles per litre.

Mathematically, $\pi = \text{CRT}$

where π is the osmotic pressure and R is the gas constant

or $$\pi = \frac{n_B}{V} \text{RT}$$

where n_B is the number of moles of solute present in V litres of the solution

Notes

or $$\pi V = \frac{w}{M_{solute}} RT$$

where w in the mass of solute dissolved in V litres of the solution and M_{solute} is the molar mass of the solute. Thus, knowing π, V and w, the molar mass of the solute can be calculated.

Thus, the molar masses of the solutes can be determined by measuring the osmotic pressure of their solutions. This method has been widely used to determine the molar masses of macromolecules, proteins, etc., which have large molar masses and limited solubility. Therefore their solutions have very low concentrations and the magnitudes of their other colligative properties are too small to measure. yet their osmotic pressures are large enough for measurements. As the osmotic pressure measurements are done at around room temperature, this method is particularly useful for determining the molar masses of biomolecules as they are generally not stable at higher temperature.

Example 7.7 : The osmotic pressure of an aqueous solution of a protein containing 0.63 g of a protein in 100 g of water at 300 K was found to be 2.60×10^{-3} atm. Calculate the molar mass of the protein. R = 0.082 L atm K^{-1} mol^{-1}.

We know that osmotic pressure of a solution in given by the expression

$$\pi V = \frac{w}{M_{solute}} RT$$

or $$M_{solute} = \frac{w}{\pi V} RT$$

Substituting the values, we get

$$\text{Msolute} = \frac{(0.63\text{g}) \times (0.082\ \text{L} - \text{atm K}^{-1}\text{mol}^{-1}) \times (300\ \text{K})}{(2.60 \times 10^{-3}\ \text{atm}) \times (0.100\ \text{L})}$$

$$= 61022\ \text{g mol}^{-1}$$

Thus, molar mass of the protein is 61022 g mol^{-1}.

Reverse Osmosis and Water Purification

If a pressure higher than the osmotic pressure is applied to the solution side, the direction of flow of the solvent can be reversed. As a result, the pure solvent flows out of the solution through the semipermeable membrane. This process is called **reverse osmosis.** It is of great practical application as it is used for desalination of sea water to obtain pure water.

INTEXT QUESTIONS 7.3

1. Define colligative property. List two colligative properties.
2. What type of liquid pairs show (i) positive deviations (ii) negative deviations.
3. Why is the determination of osmotic pressure a better method as compared to other colligative properties for determining the molar masses of biomolecules.

7.8 ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of the solutions depend only upon the number of solute particles present in the solution and not on their nature But sometimes while measuring colligative properties abnormal results are obtained due to the following reasons :

(i) If the solution is very concentrated, the particles of the solute start interacting with each other. Therefore, the solution should not be concentrated.

(ii) In case of **association** two or more solute molecules associate to form a bigger molecule. The number of effective molecules in the solution, therefore decreases. Consequently, the value of the collgative property (relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure) is observed to be less than that calculated on the basis of unassociated molecules. Since, the colligative property is inversely proportional to the molar mass, the molar mass of such solutes calculated on the basis of collgative property will be greater than the true molar mass of the solute.

(iii) **In case of dissociation** of the solute in the solution, the number of effective solute particles increases. In such cases the value of the observed collgative property will be greater than that calculated on the basis of undissociated solute particles. The molar mass of the solute calculated from the measurement of collgative property will be lower than the true molar mass of the solute.

Van’t Hoff factor

In order to account for extent of association or dissociation Van’t Hoff introduced a factor ‘i’.

$$i = \frac{\text{Observed colligative property}}{\text{Normal (calculated or expected) colligative property}}$$

Since the colligative property is proportional to the number of solute particles or the number of moles of solute

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}}$$

Also, since colligative properties vary inversely as the molar mass of the solute, it follows that

$$i = \frac{\text{Normal (calculated or expected) molar mass}}{\text{Observed molar mass}}$$

Here the observed molar mass is the experimentally determined molar mass whereas the normal molar mass is the molar mass calculated on the basis of chemical formula of the solute. In case of association the value of van't Hoff factor, i, is less than unity while for dissociation it is greater than unity. For example, benzoic acid associates in benzene to form a dimer. The value of i is, therefore, close to 1/2. The value of i for aqueous NaCl is close to 2.0 because NaCl dissociates in water to form Na^+ and Cl^- ions.

The inclusion of van't Hoff factor, *i*, modifies the equations for the colligative properties as follows :

$$\frac{P_A^0 - P_A}{P_A^0} = i X_B$$

$$\Delta T_b = i K_b m$$

$$\Delta T_f = i K_f m$$

$$\pi V = i \text{CRT}$$

Degree of Association

Degree of association may be defined as the fraction of the total number of molecules which associate to form a bigger molecule. Let us consider the association of benzoic acid in benzene. In benzene two molecules of benzoic acid associate to form a dimer. It can be represented as

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

If *x* represents the degree of association of benzoic acid in benzene (i.e out of one molecule of benzoic acid, x molecules associate to form a dimer), then at equilibrium.

No. of moles of unassociated benzoic acid = $1 - x$

No of moles of associated benzoic acid = $\frac{x}{2}$

Total number of effective moles of benzoic acid = $1 - x + \frac{x}{2} = 1 - \frac{x}{2}$

According to definition, Van't Hoff factor is given by

$$\underline{i} = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1-\frac{x}{2}}{1}$$

Example 7.8 : Acetic acid (CH_3COOH) associates in benzene to form double molecules 1.60 g of acetic acid when dissolved in 100 g of benzene (C_6H_6) raised the boiling point by 273.35 K. Calculate the van't Hoff factor and the degree of association of benzoic acid. K_b for $C_6H_6 = 2.57 \text{ K kg mol}^{-1}$.

Solution : $$\Delta T_b = i\, k_b\, m = \frac{1000\, i\, K_b\, W_B}{W_A M_B}$$

Normal molar mass (M_B) of $CH_3COOH = 60 \text{ g mol}^{-1}$

$$\text{Van't Hoff factor, } i \text{, is } = \frac{\Delta T_b \times W_A \times M_B}{1000 \times K_b \times W_B}$$

$$= \frac{0.35 \times 100 \times 60}{1000 \times 2.57 \times 1.60}$$

$$= 0.51$$

Since, acetic acid associates in benzene to form double molecules, the following equilibrium exists in the solution.

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

If x represents the degree of association of the solute, then we would have $(1 - x)$ mol of acetic acid left unassociated and $x/2$ moles of acetic acid at equilibrium.

Therefore, total number of particles at equilibrium $= 1 - x + x/2$

$$= 1 - \frac{x}{2}$$

The total number of partilces at equilibrium equal van't Hoff factor. But van't Hoff factor (i) is equal to 0.51.

$$\therefore \qquad 1 - \frac{x}{2} = 0.51$$

$$\text{or} \qquad \frac{x}{2} = 1 - 0.51 = 0.49$$

$$x = 0.49 \times 2 = 0.98$$

Therefore, degree of association of acetic acid in benzene is 98%,.

Degree of dissociation

Degree of dissociation may be defined as the fraction of the total number of particles that dissociate, i.e., break into simpler ions. Consider a solution of KCl in water. When KCl is dissolved in water, it dissociates into K^+ and Cl^- ions.

$$KCl \rightleftharpoons K^+ + Cl^-$$

let x be the degree of dissociation of KCl, then at equilibrium, number of moles of undissociated KCl = 1 – x

According to the dissociation of KCl shown above, when x mol of KCl dissociates, x moles of K^+ ions and x mol of Cl^- ions are produces

Thus, the total number of moles in the solution after dissociation

$$= 1 - x + x + x = 1 + x$$

Hence, $$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1+x}{1}$$

Example 7.9 : A 0.5 percent aqueous solution of potassium chloride was found to freeze at 272.76 K. Calculate the van't Hoff factor and the degree of dissociation of the solute at this concentration. (K_f for H_2O = 1.86 K kg mol^{-1}).

Solution : Normal molecular weight of KCl $= 39 + 35.5 = 74.5$ g mol^{-1}

$$\text{Observed molecular weight, } M_B = \frac{1000 \times W_B \times K_f}{\Delta T_f \times W_A}$$

$$= \frac{1000 \times 0.5\text{g} \times 1.86 \text{ K kg mol}^{-1}}{(0.24 \text{ K}) \times 100 \text{ g}}$$

$$= 38.75 \text{ g mol}^{-1}$$

$$\text{van't Hoff factor (i)} = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

$$= \frac{74.5 \text{ g mol}^{-1}}{38.75 \text{ g mol}^{-1}} = 1.92$$

Potassium chloride in aqueous solution dissociates as follow.

$$KCl \rightleftharpoons K^+ + Cl^-$$

Let x be the degree of dissociation of KCl. Thus at equilibrium,

No. of moles of KCl left undissociated $= (1 - x)$ mol

No. of moles of $K^+ = x$ mol

No. of moles of $Cl^- = x$ mol

Total number of moles at equilibrium $= 1 - x + x + x = 1 + x$

$$\therefore \quad \text{Van't Hoff factor} = \frac{1+x}{1} = 1.92$$

or $$x = 1.92 - 1 = 0.92$$

$\therefore$ Degree of dissociation of KCl = 92%

WHAT YOU HAVE LEARNT

- Solution is a homogeneous mixture of two or more substances.
- Solvent is that component of a solution that has the same physical state as the solution itself.
- Solute is the substance that is dissolved in a solvent to form a solution.
- Molarity is expressed as the number of moles of solute per litre of solution.
- Molality is expressed as the number of moles of solute per kilogram of solvent.
- Normality is a concentration unit which tells the number of gram equivalents of solute per litre of solution.
- Mole fraction is the ratio of the number of moles of one component to the total number of moles in the solution.
- Solutions can be solid, liquid or gaseous.
- Henry's law states that mass or mole fraction of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.
- Raoult's law states that for a solution of volatile liquids, the partial pressure of each liquid in the solution is directly proportional to its mole fraction.
- A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.

- The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.
- Those properties of dilute solutions which depend only on the number of particles of solute and not on their nature are known as colligative properties.
- Molal elevation constant is the elevation in boiling point when one mole of solute is dissolved in one kilogram of the solvent.
- Boiling point of a liquid is the temperatures at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- Freezing point is the temperature at which the solid and the liquid forms of the substance have the same vapour pressure.
- Abnormal result are obtained when the solute associates or dissociates in the solution.
- Van't Hoff factor is defined as the ratio of normal molar mass to experimentally determined molar mass.

TERMINAL EXERCISE

1. What do you understand by ideal and non-ideal solutions?
2. Define freezing point and boiling point.
3. Derive the relationship $\Delta T_b = K_b\ m$
4. A solution containing 7 g of a non-volatile solute in 250 g of water boils at 373.26 K. Find the molecular mass of the solute.
5. 2 g of a substance dissolved in 40 g of water produced a depression of 274.5 K in the freezing point of water. Calculate the molecular mass of the substance. The molal depression constant for water is 274.85 K per molal.
6. Calculate the mole fraction of the solute in a solution obtained by dissolving 10 g of urea (mol wt 60) in 100 g of water.
7. A solution containing 8.6 g of urea (molar mass = 60 per dm^3) was found to be isotonic with a 5 per cent solution of an organic non-valatile solute. Calculate the molar mass of the non-valatile solute.
8. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molar depression constant for benzene in 4.9 K kg mol^{-1}. What is the percentage association of C_6H_5COOH if it forms double molecules in solution.

9. The freezing point depression of 5.0×10^{-3} M solution of Na_2SO_4 in water was found to be 0.0265ºC. Calculate the degree of dissociation of the salt at this concentration. (K_f for H_2O is 1.86 K kg mol^{-1})

ANSWERS TO INTEXT QUESTIONS

7.1

1. Molarity, Molality, Normality, Mole fraction, Mass percentage.
   Molarity is the number of moles of solute dissolved per litre of the solution.
2. Molality is the number of moles of solute dissolved per kg of solvent.
   Normality is the number of gram equivalents of solute dissolved per litre of solution.

7.2

1. For a solution of volatile liquids the partial vapour pressure of each liquid is proportional to its mole fraction.
2. The mass of a gas dissovled in a solvent is directly proportional to its partial pressure. Pressure should not be too high Temperature should not be too low. The gas should not associate or dissociate.

7.3

1. Properties that depend upon the number of particles of solute and not on the nature of solute. e.g. Elevation of boiling point, depression of fruzing point.
2. For which A–B molecular interactions are:
   (i) weaker than A–A and B–B interactions.
   (ii) stronger than A–A and B–B interactions.
3. At low concentration the magnitude of osmotic pressure is large enough for measurement.

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8

COLLOIDS

You are familiar with solutions. They play an important role in our life. A large number of substances such as milk, butter, cheese, cream, coloured gems, boot polish, rubber, ink also play an important role in our daily life. They are mixtures of special type. They are colloidal solutions. The term colloid has been derived from two terms, namely colla and oids. 'Kolla' means glue and 'Oids' means like i.e. glue-like. The size of the particles in colloidal solutions is bigger than the size of particles present in solutions of sugar or salt in water but smaller than the size of particles in suspensions. In this lesson you will learn about the methods of preparation, properties and applications of colloidal solutions.

OBJECTIVES

After reading this lesson you will be able to:

- explain the difference between true solution, colloidal solution and suspension;
- identify phases of colloidal solution;
- classify colloidal solutions;
- describe methods of preparation of colloids;
- explain some properties of colloidal solutions;
- explain Hardy Schultz Rule;
- recognise the difference between gel and emulsion;
- cite examples of the application of colloids in daily life; and
- define nano materials and list some of their properties.

8.1 DISTINCTION BETWEEN A TRUE SOLUTION, COLLOIDAL SOLUTION AND SUSPENSION

You may recall that solution of sugar in water is homogeneous but milk is not. When you closely look at milk you can see oil droplets floating in it. Thus, although it appears to be homogenous it is actually heterogenous in nature. The nature of

Notes

the solution formed depends upon the size of the solute particles. If the size of the solute particles is less than 1 nm it will form ***true solution*** but when the size is between 1 to 100 nm then it will form colloidal solution. When the size of solute particles is greater than 100 nm it will form a suspension. Therefore we may conclude that colloidal solution is an intermediate state between true solution and suspension (Table 8.1).

Table 8.1: Some important properties of true solutions, colloids and suspensions

S.No.	Name of Property	True Solution	Colloids Solution	Suspension
1.	Size	Size of particles is less than 1 nm	Size of particles is between 1nm and 100 nm.	Size of particles is greater than 100 nm.
2.	Filterability	Pass through ordinary filter paper and also through animal membrane.	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper or animal membrane.
3.	Settling	Particles do not settle down on keeping	Particles do not settle down on their own but can be made to settle down by centrifugation.	Particles settle down on their own under gravity.
4.	Visibility	Particles are invisible to the naked eye as well as under a microscope.	Particles are invisible to the naked eye but their scattering effect can be observed with the help of a microscope.	Particles are visible to the naked eye.
5.	Separation	The solute and solvent cannot be separated by ordinary filteration or by ultra filteration.	The solute and solvent cannot be separated by ordinary filteration but can be separated by ultra-filteration.	The solute and solvent can be separated by ordinary filteration.
6.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse

8.2 PHASES OF COLLOIDS SOLUTION

Colloids solutions are heterogenous in nature and always consist of at least two phases : the **dispersed phase** and the **dispersion medium**.

- **Dispersed Phase :** It is the substance present in small proportion and consists of particles of colloids size (1 to 100 nm).

- **Dispersion Medium :** It is the medium in which the colloids particles are dispersed. For example, in a colloidal solution of sulphur in water, sulphur particles constitute the 'dispersed phase' and water is the 'dispersion medium'.

Each of the two phases namely, dispersed phase and dispersion medium can be solid, liquid or gas. Thus, different types of colloidal solutions are possible depending upon the physical state of the two phases. Different types of colloidal solutions and their examples are shown in Table 8.2. You should note that gases cannot form a colloidal solution between themselves, because they form homogenous mixtures.

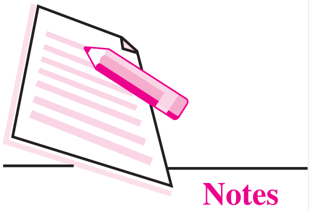
Table 8.2 : Types of Colloidal Solutions

S.No.	Dispersed Phase	Dispersion Medium	Type of Colloidal Solution	Examples
1.	Solid	Solid	Solid sol.	Gemstones,
2.	Solid	Liquid	Sol	Paints, muddy water, gold sol, starch sol, arsenious sulphide sol.
3.	Solid	Gas	Aerosol of solids	Smoke, dust in air
4.	Liquid	Solid	Gel	Jellies, Cheese
5.	Liquid	Liquid	Emulsion	Milk, Cream
6.	Liquid	Gas	Aerosol	Mist, fog, cloud
7.	Gas	Solid	Solid foam	Foam rubber, pumice stone
8.	Gas	Liquid	Foam	Froth, whipped cream

Out of the various types of colloidal solutions listed above, the most common are **sols** (solid in liquid type), **gels** (liquid in solid type) and **emulsions** (liquid in liquid type). If the dispersion medium is water then the 'sol' is called a **hydrosol**; and if the dispersion medium is alcohol then the 'sol' is called an **alcosol**.

INTEXT QUESTIONS 8.1

1. Classify the following into suspension, colloidal solution and true solution.
   milk, sugar in water, clay in water, blood, boot polish, sand in water, face cream, jelly, foam.
2. Give one example each of
   (a) Sol (b) Gel (c) Aerosol (d) Emulsion
3. What is the difference between an alcosol and hydrosol?
4. How does colloidal solution differ from true solution.



Notes

8.3 CLASSIFICATION OF COLLOIDS

Colloidal solutions can be classified in different ways :

(a) on the basis of interaction between the phases.

(b) on the basis of molecular size.

8.3.1 Classification Based Upon Interaction

Depending upon the interaction between dispersed phase and the dispersion medium colloidal solutions have been classified into two categories.

(a) Lyophilic colloids : The word 'Lyophilic' means solvent lover. Lyophilic colloidal solutions are those in which the dispersed phase have a great affinity (or love) for the dispersion medium. Substances like gum, gelatine, starch etc when mixed with suitable dispersion medium, directly pass into colloidal state and form colloidal solution. Therefore, such solutions are easily formed simply by bringing dispersed phase and dispersion medium in direct contact with each other. However, these colloidal solutions have an important property i.e. they are reversible in nature. This means that once lyophilic colloidal solution has been formed then dispersed phase and dispersion medium can be separated easily. Once separated these can again be formed by remixing the two phases. These sols are quite stable.

If water is used as dispersion medium then it is termed as hydrophilic colloid.

(b) Lyophobic Colloids : The word 'Lyophobic' means solvent hating. Lyophobic colloidal solutions are those in which the dispersed phase has no affinity for the dispersion medium. Metals like Au, Ag and their hydroxides or sulphides etc., when simply mixed with dispersion medium do not pass directly into colloidal state. These sols have to be prepared by special methods. These sols can be readily precipitated and once precipitated they have little tendency to go back into the colloidal state. Thus these sols are irreversible in nature. Also they are not very stable and require a stabilizing agent to remain in the colloidal form. In case water is used as dispersion medium it is called as hydrophobic sol.

8.3.2 Classification Based on Molecular Size

Depending upon the molecular size the colloids have been classified as

(a) Macromolecular colloids – In this type of colloids the size of the particles of the dispersed phase are big enough to fall in the colloidal dimension as discussed earlier (i.e. 1–100 nm)

Examples of naturally occurring macromolecular colloids are starch, cellulose, proteins etc.

Notes

(b) Multi molecular colloids – Here individually the atoms are not of colloidal size but they aggregate to join together forming a molecule of colloidal dimension. For example sulphur sol contains aggregates of S_8 molecules which fall in colloidal dimension.

(c) Associated colloids – These are substances which behave as normal electrolyte at low concentration but get associated at higher concentration to form miscelle and behave as colloidal solution. Soap is an example. Soap is sodium salt of long chain fatty acid R COONa. When put in water, soap forms $RCOO^-$ and Na^+. These $RCOO^-$ ions associate themselves around dirt particles as shown below forming a miscelle (Fig. 8.1).

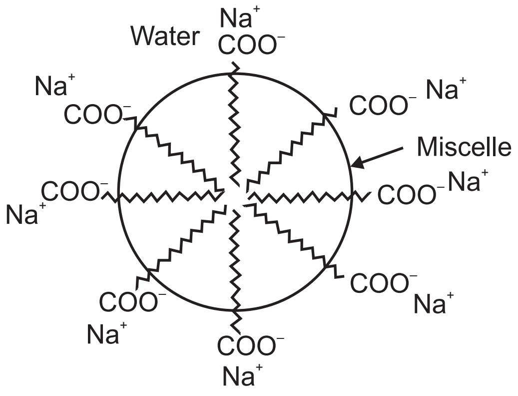


Fig.8.1 : *Aggregation of $RCOO^-$ ions to form a micelle.*

8.4 PREPARATION OF COLLOIDAL SOLUTIONS

As discussed earlier, the lyophilic sols can be prepared directly by mixing the dispersed phase with the dispersion medium. For example, colloidal solutions of starch, gelatin, gum etc. are prepared by simply dissolving these substances in hot water. Similarly, a colloidal sol of cellulose nitrate is obtained by dissolving it in alcohol. The resulting solution is called **collodion**.

However, lyophobic colloids cannot be prepared by **direct method**.

Hence two types of methods are used for preparing lyophobic colloids. These are:

(i) Physical methods

(ii) Chemical methods

(i) Physical methods

These methods are employed for obtaining colloidal solutions of metals like gold, silver, platinum etc. (Fig. 8.2)

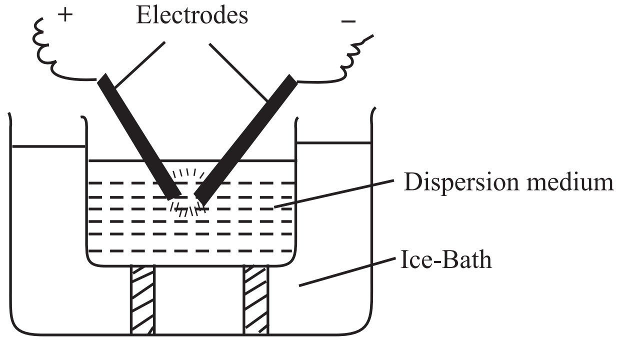


Fig. 8.2 : *Preparation of colloidal solution by Bredig's Arc Method*

An electric arc is struck between the two metallic electrodes placed in a container of water. The intense heat of the arc converts the metal into vapours, which are condensed immediately in the cold water bath. This results in the formation of particles of colloidal size. We call it as metal sol. e.g. gold sol.

Peptisation : Peptisation is the process of converting a freshly prepared precipitate into colloidal form by the addition of a suitable electrolyte. The electrolyte is called peptising agent. For example when ferric chloride is added to a precipitate of ferric hydroxide, ferric hydroxide gets converted into reddish brown coloured colloidal solution. This is due to preferential adsorption of cations of the electrolyte by the precipitate. When $FeCl_3$ is added to $Fe(OH)_3$, Fe^{3+} ions from $FeCl_3$ are adsorbed by $Fe(OH)_3$ particles. Thus the $Fe(OH)_3$ particles acquire + ve charge and they start repelling each other forming a colloidal solution.

(ii) Chemical Methods : By oxidation

Sulphur sol is obtained by bubbling H_2S gas through the solution of an oxidizing agent like HNO_3 or Br_2 water, etc. according to the following equation :

$$Br_2 + H_2S \rightarrow S + 2\,HBr$$

$$2\,HNO_3 + H_2S \rightarrow 2\,H_2O + 2\,NO_2 + S$$

$Fe(OH)_3$ sol, $As_2\,S_3$ sol can also be prepared by chemical methods.

8.5 PURIFICATION OF COLLOIDAL SOLUTION

When a colloidal solution is prepared it contains certain impurities. These impurities are mainly electrolytic in nature and they tend to destabilise the colloidal solutions. Therefore colloidal solutions are purified by the following methods:

(i) Dialysis

(ii) Electrodialysis

Dialysis : The process of dialysis is based on the fact that colloidal particles cannot pass through parchment or cellophane membrane while the ions of the electrolyte can. The colloidal solution is taken in a bag of cellophane which is suspended in a tub full of fresh water. The impurities diffuse out leaving pure coloidal solution in the bag (Fig. 8.3). This process of separating the particles of colloids from impurities by means of diffusion through a suitable membrane is called ***dialysis***.

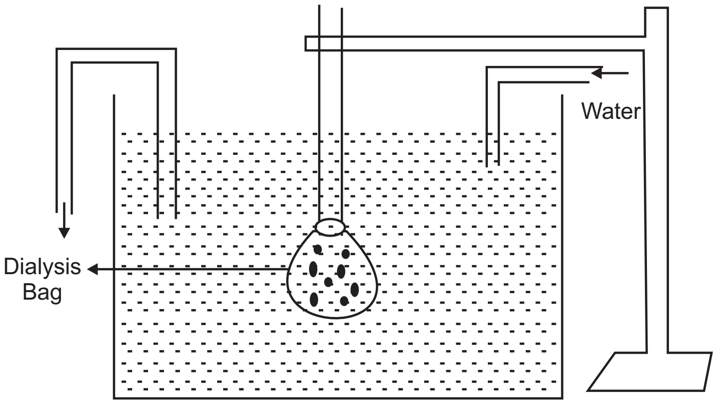


Fig. 8.3 : *A dialyser*

Electrodialysis : The dialysis process is slow and to speed up its rate, it is carried out in the presence of an electrical field. When the electric field is applied through the electrodes, the ions of the electrolyte present as impurity diffuse towards oppositely charged electrodes at a fast rate. The dialysis carried out in the presence of electric field is known as electrodialysis (Fig. 8.4).

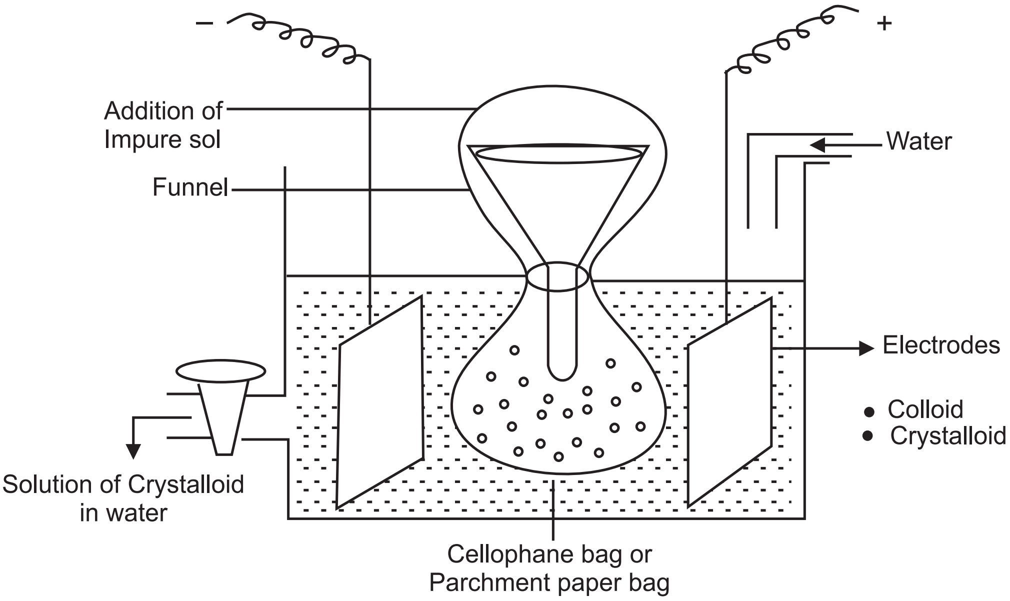


Fig. 8.4 : *Electrodialysis*

The most important use of dialysis is the purification of blood in the artificial kidney machine. The dialysis membrane allows the small particles (ions etc.) to pass through, whereas large size particles like haemoglobin do not pass through the membrane.

INTEXT QUESTIONS 8.2

1. Name two colloids that can be prepared by Bredig's Arc method.
2. Name two colloids that can be prepared by chemical methods.
3. Differentiate between (a) Lyophilic and Lyophobic sol. (b) macromolecular and multimolecular colloids.
4. Explain the formation of miscelle.

8.6 PROPERTIES OF COLLOIDS

The properties of colloids are discussed below :

a) **Heterogeneous character :** Colloidal particles remain within their own boundary surfaces which separates them from the dispersion medium. So a colloidal system is a heterogeneous mixture of two phases. The two phases are dispersed phase and dispersion medium.

b) **Brownian movement :** It is also termed as Brownian motion and is named after its discoverer Robert Brown (a Botanist.)

Brownian Motion is the zig-zag movement of colloidal particles in continuous and random manner (Fig. 8.5). Brownian motion arises because of the impact of the molecules of the dispersion medium on the particles of dispersed phase. The forces are unequal in different directions. Hence it causes the particles to move in a zig-zag way.

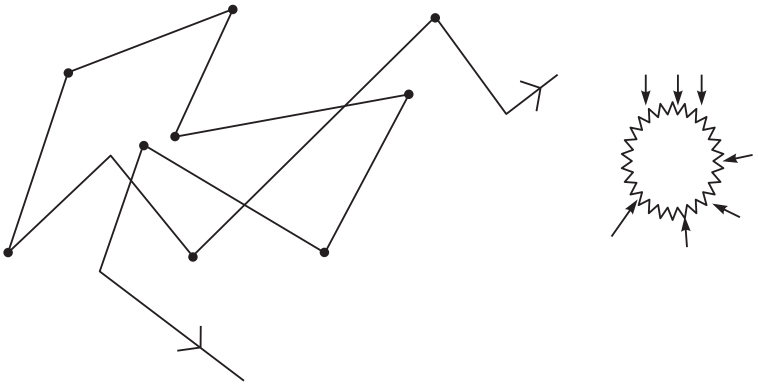


Fig. 8.5 : *Brownian Movement*

c) **Tyndall Effect :** Tyndall in 1869, observed that if a strong beam of light is passed through a colloidal solution then the path of light is illuminated. This phenomenon is called Tyndall Effect. This phenomenon is due to scattering of light by colloidal particles (fig.8.6). The same effect is noticed when a beam of light enters a dark room through a slit and becomes visible. This happens due to the scattering of light by particles of dust in the air.

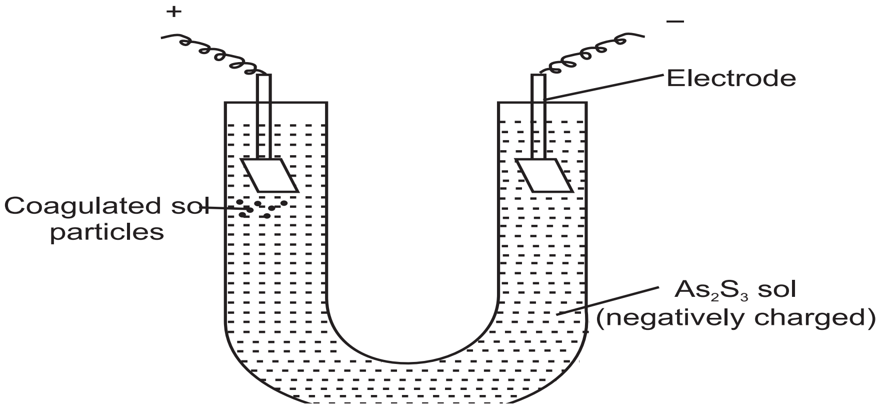


Fig. 8.6 : *The Tyndall Effect*

d) **Electrical Properties :** The colloidal particles are electrically charged and carry the same type of charge, either negative or positive. The dispersion medium has an equal and opposite charge. The colloidal particles therefore repel each other and do not cluster together to settle down. For example, arsenious sulphide sol, gold sol, silver sol, etc. contain negatively charged colloidal particles whereas ferric hydroxide, aluminium hydroxide etc. contain positively charged colloidal particles. Origin of charge on colloidal particles is due to:

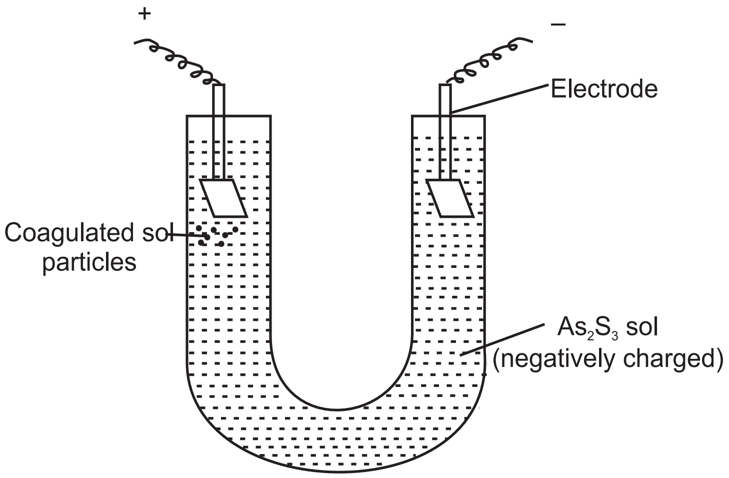


Fig. 8.7 : *A set up for Electrophoresis*

(a) Preferential adsorption of cations or anions by colloidal particles.

(b) Miscelles carry a charge on them due to dissociation.

(c) During the formation of colloids especially by Bredig arc method, colloidal particles capture electrons and get charged. The existence of charge on a colloidal particle is shown by a process called **electrophoresis**.

Electrophoresis is a process which involves the movement of colloidal particles either towards cathode or anode under the influence of electrical field. The apparatns used is as shown in Fig 8.7.

8.7 COAGULATION OR PRECIPITATION

The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity.

The process of settling of colloidal particles is called coagulation or precipitation of the sol.

The coagulation of the lyophobic sols can be carried out in the following ways:

(i) *By electrophoresis*: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.

(ii) *By mixing two oppositely charged sols*: Oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) bring them in the precipitated forms. This type of coagulation is called mutual coagulation.

(iii) *By boiling*: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.

(iv) *By addition of electrolytes*: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation.

The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.

It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

This is known as **Hardy-Schulze rule**. In the coagulation of a negative sol, the flocculating power is in the order:

$$Al^{3+} > Ba^{2+} > Na^{+}$$

Similarly, in the coagulation of a positive sol, the flocculating power is in the order:

$$[Fe(CN)6]^{4-} > PO4^{3-} > SO4^{2-} > Cl^{-}$$

The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.

8.7.1 Coagulation of lyophilic sols

There are mainly two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding an electrolyte and (ii) by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

Protection of colloids

Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

8.8 APPLICATIONS OF COLLOIDAL SOLUTIONS

Colloids play a very important role in our daily life. Some of these applications are discussed below:

(i) **Sewage disposal :** Colloidal particles of dirt, etc. carry electric charge. When sewage is allowed to pass through metallic plates kept at a high potential, the colloidal particles move to the oppositely charged electrode and get precipitated there. Hence sewage water is purified.

(ii) **Purification of Water in Wells :** When alum is added to muddy water, the negatively charged particles of the colloid are neutralized by Al^{3+} ions. Hence the mud particles settle down and the water can be filtered and used.

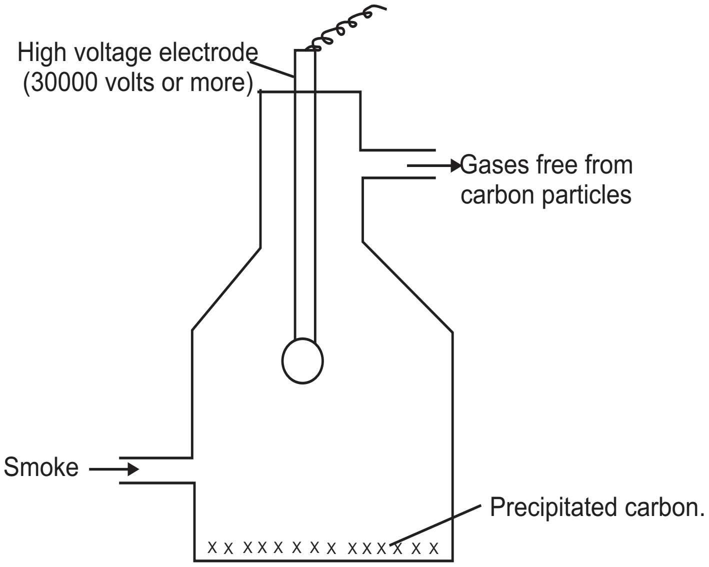


Fig.8.8 : *Cottrell smoke precipitator*

(iii) **Smoke Precipitation :** Smoke particles are actually electrically charged colloidal particles of carbon in air. Precipitation of this carbon is done in a **Cottrell's Precipitator**. Smoke from chimneys is allowed to pass through a chamber having a number of metallic plates connected to a source of high potential as shown in Fig. 8.8. Charged particles of smoke get attracted to the oppositively charged electrode and get precipitated and hot purified air passes out.

Other applications in day to day life are :

(i) **Photography :** A colloidal solution of silver bromide in gelatin is applied on glass plates or celluloid films to form photo-senstive plates in photography.

(ii) **Clotting of Blood :** Blood is a colloidal solution and is negatively charged. On applying a solution of $FeCl_3$ bleeding stops and clotting of the colloidal particles of blood takes place.

(iii) **Rubber Plating :** Latex is a colloidal solution of negatively charged rubber particles. The object to be rubber plated is made the anode in the rubber plating bath. The negatively charged rubber particles move towards the anode and get deposited on it.

(iv) **Blue Colour of Sky :** Have you ever wondered why is the sky blue? It is because the colloidal dust particles floating about in the sky scatter blue light, that makes the sky appear blue. In the absence of these colloidal particles the sky would have appeared dark throughout.

8.8 EMULSION AND GEL

Emulsions are colloidal solutions in which both the dispersed phase and dispersion medium are liquids. However, the two liquids are immiscible, as miscible liquids will form true solution.

Emulsion are of two kinds :

(a) ***Oil-in-water emulsion :*** Here the dispersed phase is oil while the dispersion medium is water. Milk is an example of this kind as in milk liquid fats are dispersed in water. Vanishing cream is another example.

(b) ***Water-in-oil emulsion :*** Here dispersed phase is water and dispersion medium is oil. Butter, cod- liver oil, cold creams are examples of this type.

The liquids forming emulsion i.e. oil and water will separate out on keeping as they are immiscible. Therefore an emulsifying agent or emulsifier is added to stabilise the emulsion. Soap is a common ***emulsifier.*** The preparation of emulsion in the presence of an emulsifier is called emulsification.

How does an emulsifier work? It is believed that an emulsifier gets concentrated at the interface between oil and water i.e. the surface at which oil and water come in contact with each other. It acts as a binder between oil and water.

Applications of Emulsions - Emulsions play very important role in our daily life. Some of the common applications are given below :

1. The cleansing action of soap and synthetic detergents for washing clothes, bathing etc is based upon the formation of oil in water type emulsion.
2. Milk is an emulsion of fat in water. Milk cream and butter are also emulsions.
3. Various cold creams, vanishing creams, body lotions etc. are all emulsions.
4. Various oily drugs such as cod liver oil are administered in the form of emulsion for their better and faster absorption. Some ointments are also in the form of emulsions.
5. The digestion of fats in the intestine occurs by the process of emulsification.
6. Emulsions are used for concentrating the sulphide ores by froth flotation process. Finely powdered ore is treated with an oil emulsion and the mixture is vigorously agitated by compressed air when the ore particles are carried to the surface and removed.

Notes

Gels - Gels are the type of colloids in which the dispersed phase is a liquid and the dispersion medium is a solid. Cheese, jelly, boot polish are common examples of gel. Most of the commonly used gels are hydrophilic colloidal solution in which a dilute solution, under suitable conditions set as elastic semi solid masses. For example 5% aqueous solution of gelatin in water on cooling forms the jelly block.

Gels may shrink on keeping by loosing some of the liquid held by them. This is known as **syneresis** or resetting on standing.

Gels are divided in two categories elastic gels and non elastic gels. Elastic gels are reversible. When partly dehydrated on loosing water, they change back into the original form on addition of water. The non elastic gels are not reversible.

Gels are useful in many ways. Silica, cheese, jelly, boot polish, curd are commonly used gels. Solidified alcohol fuel is a gel of alcohol in calcium acetate.

In recent past nano materials have attracted enormous interest because of their potential for wide ranging applications in number of fields like medicine, electronics and various industries. They can be metals, ceramics, polymeric materials or composite materials.

A material containing particles with dimension in the size range 1 nm – 100 nm in atleast one direction is termed as **nano material.** One nanometre is 10^{-9}m which is extremely small in size. It is about the size of three to five atoms lined up in a row.

Nano materials have been produced and in use for hundreds of years. The beautiful ruby red colour of some types of glass is due to the presence of nano particles of gold in it. The decorative lusture found on some articles of medieval pottery is due to nano particles of some metals in the glaze.

Nano materials fall in two categories (i)fullerenes and (ii) inorganic nano materials.

(i) Fullerenes

Fullerenes are allotropes of carbon which are hollow carbon spheres consisting of large number of carbon atoms bonded chemically like C_{60}.

(ii) Inorganic nano particles

Inorganic nano particles are made of metals, semiconductors or oxides with peculiar electrical, mechanical, optical or chemical properties.

Properties

Nanomaterials are available in great variety and the range of their properties and possible applications is enormous.

(i) They are used for making miniature batteries, super absorbents, extremely tiny electronic devices, parts of automobiles and as packaging films.

(ii) Nanocapsules and nanodevices present new possibilities for drug delivery, gene therapy, and medical diagnostics.

(iii) Nanocomposites are obtained by mixing a small quantity of nano material to polymers. For example, adding such small amounts as 2% by volume of silicate nanoparticles to a polyimide resin increases the latter's strength by 100%. Addition of nanoparticles not only improves the mechanical properties, but has also been shown to improve thermal stability.

(iv) Nano materials generally have high plasticity.

(v) Due to their large surface, nanoparticles made of transition element oxides exhibit catalytic properties

(vi) Magnetic nanoparticles show super paramagnetism and have lead to the discovery of a new class of permanent magnetic materials.

WHAT YOU HAVE LEARNT

- Size of the particles in the colloidal state is intermediate between that of suspension and true solution.
- There are eight different types of colloidal systems.
- Sols are classified on the basis of (a) interaction between dispersed phase and dispersion medium (b) molecular size of dispersed phase.
- Colloidal solutions are prepared by physical and chemical methods.
- The zig zag motion of colloidal particles is called Brownian motion.
- Colloidal size particles scatter light and so the path of light becomes visible in a semi darkened room due to dust particles.
- Colloidal particles may carry electric charge.
- A colloidal dispersion of a liquid in another liquid is called an emulsion.
- A colloidal solution of a liquid dispersed in a solid medium is called a gel.
- Colloids are extremely useful to mankind both in daily life and in industry.
- Nano materials contain particles with dimension of 1–100 mm in atleast in one direction. They have special properties and find many applications.

TERMINAL EXERCISE

1. List three differences between a true solution and a colloidal solution.
2. Describe one method of preparation of
   (a) a lyophilic colloid (b) a lyophobic colloid
3. What are associated colloids?
4. What is Brownian motion? How does it originate?
5. Why bleeding from a fresh cut stops on applying alum?
6. Two beakers A and B contain ferric hydroxide sol and NaCl solution respectively. When a beam of light is allowed to converge on them, (in a darkened room), beam of light is visible in beaker A but not in breaker B. Give the reason. What is this effect called?
7. Define the following terms and give two examples of each
   (i) Gel (ii) Sol
8. Describe two important applications of colloidal solutions.
9. Give two examples of emulsions used in daily life.
10. Explain the role of emulsifier in an emulsion?
11. What are nano materials? Give their three applications.

ANSWERS TO THE INTEXT QUESTIONS

8.1

1. Suspension – Clay in water, Sand in water
   Colloidal – Milk, Blood, Boot polish, Face Cream, Jelly, Foam.
   True Solution – Sugar in water
2. Sol – Starch in water
   Gel – Silica gel
   Aerosol – Fog
   Emulsion – Milk
3. Alcosol – When alcohol is the dispersion medium.
   Hydrosol – When water is the dispersion medium.

4.

True solution	Colloidal solution
1. Size of solute in less than 1 nm.	1. Particle size (1–100) nm.
2. Form transparent solution and allows light to pass through them.	2. Path of light becomes visible.

8.2

1. Gold sol, Platinum sol

2. As_2S_3, $Fe(OH)_3$ (Arsenious sulphide sol, ferric hydroxide sol)

3. (a) **Lyophilic sol :**

   1. easy to prepare

   2. affinity between dispersed phase and dispersion medium.

   3. Reversible

   Lyophobic

   1. special method used for preparation

   2. No affinity between the two phases.

   3. Not reversible

(b) **Macromolecular –** The size of the colloidal particles large enough to fall in the colloidal dimensions.

Multimolecular – Individually the particles are not of colloidal dimensions but they aggregate to join together to form molecules of colloidal size.

4. Refer to section 8.3.2 (c)

MODULE - IV

CHEMICAL ENERGETICS

313en09

9

CHEMICAL THERMODYNAMICS

When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose, $C_6H_{12}O_6$ by the process of photosynthesis requires the absorption of light energy from the sun. Thus, we see that the energy change that accompanies a chemical reaction can take different forms. In this lesson, you shall study the reactions in which heat is either evolved or absorbed.

OBJECTIVES

After reading this lesson, you will be able to:

- define the commonly used terms in thermodynamics;
- differentiate between exothermic and endothermic reactions;
- explain the first law of thermodynamics;
- explain internal energy;
- define enthalpy and enthalpy change;
- state the relationship between enthalpy change and internal energy change;
- define enthalpies of formation, combustion, neutralisation, atomisation, transition, solution and ionisation;
- state the relationship between enthalpy of reaction and enthalpies of formation of reactants and products;

- solve numerical problems based on the enthalpy changes;
- state Lavoisier-Laplace law and Hess's law;
- calculate enthalpy of a reaction using Hess's law;
- define bond enthalpy and bond dissociation enthalpy and
- calculate enthalpy of a reaction using bond enthalpy data.

9.1 SOME COMMONLY USED TERMS

In this lesson you would come across some frequently used terms. Let us understand the meaning of these terms first.

9.1.1 System and Surrounding

If we are studying the reaction of two substances A and B kept in a beaker, the reaction mixture of A and B is a system and the beaker and the room where it is kept are surroundings as shown in figure 9.1

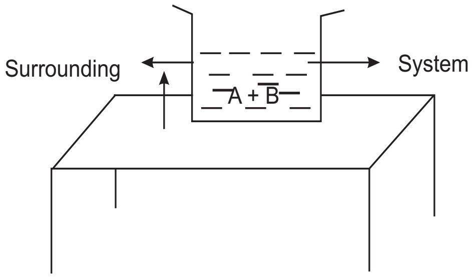


Fig 9.1 : *System and surroundings*

System is the part of the physical universe which is under study, while the rest of the universe is surroundings.

You know that hot tea/milk (let us call it a system) kept in a stoppered thermos flask remains hot for a couple of hours. If this flask is made of perfect insulating material, then there would be no exchange of matter or energy between the system and the surroundings. We call such a system an *isolated system.*

Isolated system is a system which can exchange neither matter nor energy with the surroundings.

If we keep hot tea/milk in a stoppered stainless steel flask, it will not remain hot after some time. Here energy is lost to the surroundings through the steel walls, but due to stopper, the matter will not be lost. We call this system a *closed system.*

Closed system is a system which can exchange energy but not matter with the surroundings.

If we keep stainless steel flask or thermos flask open, some matter will also be lost due to evaporation along with energy. We call such a system an open system. Plants, animals, human beings are all examples of open systems, because they continuously exchange matter (food, etc) and energy with the surroundings.

Open system is a system which can exchange both energy and matter with surroundings.

9.1.2. State of a System

We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system (Fig 9.2).

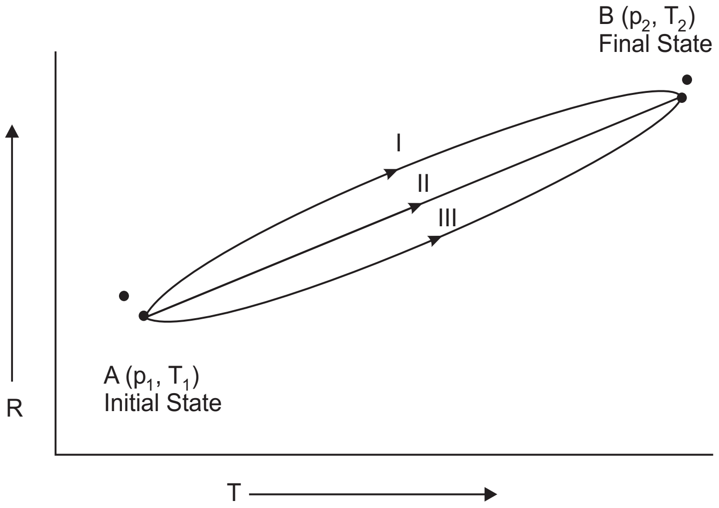


Fig. 9.2 : *Change of state from initial state to final state through three paths I, II and III. The difference $p_2 - p_1$ and $T_2 - T_1$ are independent of the path since pressure and temperature are state functions.*

State functions are those functions which depend only on the state of the system.

Change in state of a system is defined by giving the initial and the final state of the system. We can understand it by considering another example. We travel from one point to another. The distance travelled depends on the path or the route we take. But the separation between these two points on the earth is fixed. Thus, separation is a state function, but not the distance travelled.

9.1.3 Properties of a System

As stated earlier, the measurable properties of a system are called state variables. They may be further divided into two main types.

(i) **Extensive property** (variable) is one whose value depends upon the size of the system. For example, volume, weight, heat, etc.

(ii) **Intensive property** (variable) is one whose value is independent of the size of the system. For example, temperature, pressure, refractive index, viscosity, density, surface tension, etc.

You may note that an extensive property can become an intensive property by specifying a unit amount of the substance concerned. For example, mass and volume are extensive properties, but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

9.1.4 Types of Processes

Let us first understand what do we mean by a process. Suppose we want to raise the temperature of the system. We may do it by *heating* it. Here, heating is the process.

The method of bringing about a change in state is called process.

Processes could be of different types. The different types of processes are explained below.

(i) **Isothermal process**: Ice melts at 273 K and 1 atm pressure. The temperature does not change as long as the process of melting goes on. Such processes are examples of isothermal process. We can define *isothermal process* as followes.

When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.

(ii) **Adiabatic Process**: If an acid is mixed with a base in a closed thermos flask, the heat evolved is retained by the system. Such processes are known as adiabatic processes because the thermos flask does not allow exchange of heat between the system and the surroundings. Adiabatic process can be defined as follows:

In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic processes there is always a change in temperature.

(iii) **Reversible Process:** In a reversible process, the initial and the final states are connected through a succession of equlibrium states. All changes occuring in any part of the process are exactly reversed when it is carried out in the opposite direction. Thus both the systems and its surroundings must be restored exactly to their original state, when the process has been performed and then reversed.

Let us understand it by an example. Imagine a liquid in equlibrium with its vapour in a cylinder closed by a frictionless piston, and placed in a constant temperature bath as shown in figure. 9.3. If the external pressure on the piston is increased by an infinitesimally small amount, the vapours will condense, but the condensation will occur so slowly that the heat evolved will be taken up by the temperature bath. The temperature of the system will not rise, and the pressure above this liquid will remain constant. Although condensation of the vapor is taking place, the system at every instant is in the state of equilibrium. If the external pressure is made just smaller than the vapour pressure, the liquid will vaporize extremely slowly, and again temperature and pressure will remain constant.

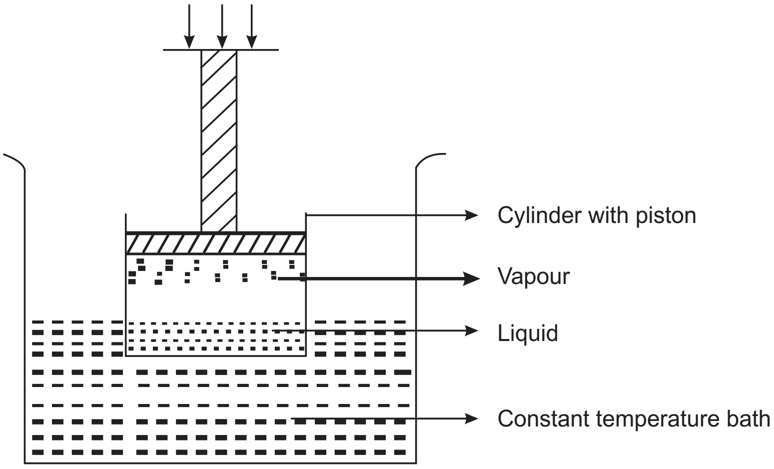


Fig 9.3 : *Reversible process*

Reversible processes are those processes in which the changes are carried out so slowly that the system and surroundings are always in equilibrium.

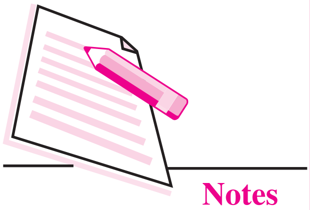
(iv) **Irreversible Processes**: In the above example rapid evaporation or condensation by the sudden decrease or incease of the external pressure, will lead to non-uniformity in temperature and pressure within the system and the equilibrium will be disturbed. Such processes are called as **irreversible processes.**

9.1.5 Standard States

You have seen that a system is described by the state variables. In order to compare the energies for different compounds, a standard set of conditions is chosen. This refers to the condition of 1 bar pressure at any specified temperature, with a substance in its most stable form.

9.2 EXOTHERMIC AND ENDOTHERMIC REACTIONS

(i) Add a few cm^3 of dilute hydrocholoric acid in a test tube containing a few pieces of granulated zinc and observe the evolution of a gas. Feel the test tube. It would be hot.



Notes

(ii) You must have observed that when some water is added to quick lime to prepare white wash, a lot of heat is evolved.

(iii) When a fuel like cooking gas or coal is burnt in air, heat is evolved besides light. Many chemical reactions lead to release of energy (heat) to the surroundings. We call these type of rections as *exothermic reactions.*

Exothermic reactions are those reactions which proceed with the evolution of heat.

Let us now consider the following reactions:

(i) Add a small amount of solid ammonium chloride in a test tube half-filled with water. Shake and feel the test tube. It will feel cold.

(ii) Similarly repeat this experiment with potassium nitrate and feel the test tube, it will feel cold.

(iii) Mix barium hydroxide with ammonium chloride in small quantities in water taken in a test tube. Feel the test tube. It will be cold.

In all the above processes we see that heat is absorbed by the system from the surroundings. Such reactions are called *endothermic reactions.*

Endothermic reactions are those reactions which proceed with the absorption of heat from the surroundings.

9.3 THERMOCHEMICAL EQUATIONS

You are familiar with equations for chemical reactions. Now we shall write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below:

(i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) along side the chemical formulae respectively.

For example, to represent burning of methane in oxygen, we write

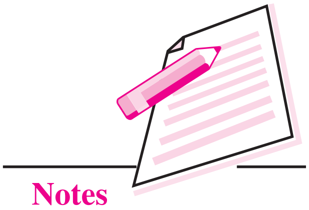
$$CH_4(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + \text{heat}$$

In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol ΔH. The amount of heat evolved or absorbed is written after the equation followed by semicolon. ΔH is negative for exothermic reactions and it is positive for endothermic reactions.

For example:

An exothermic reaction is written as

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)\ ;\ \Delta H = -\,891\ \text{kJ}$$



Notes

Whereas an endothermic reaction is written as

$$H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)\ ;\ \Delta H = 52.2\ kJ$$

(ii) In case of elements which exhibit allotropy, the name of allotropic modification is mentioned. For example,

C (graphite), C (diamond), etc.

(iii) The substances in aqueous solutions are specified using the symbol (aq). For example NaCl (aq) stands for an aqueous solution of sodium chloride.

(iv) Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction and the ΔH values given correspond to these quantities of substances.

(v) In case the coefficients are multipied or divided by a factor, ΔH value must also be multiplied or divided by the same factor. In such cases, the ΔH value will depend upon the coefficients. For example, in equation.

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(g)\ ;\ \Delta H = -\,242\ kJ$$

If coefficients are multiplied by 2, we would write the equation

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)\ ;\ \Delta H = 2\,(-\,242) = -\,484\ kJ$$

9.4 THE FIRST LAW OF THERMODYNAMICS

You have learnt that chemical reactions are accompanied by energy changes. How do we determine these energy changes? You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics. It has been found valid for various situations. We state this law as follows:

Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant.

Mathematically the first law of thermodynamics is stated as:

$$\Delta U = q + w \qquad (9.1)$$

where ΔU = change in internal energy, q = heat absorbed by the system, and w = work done on the system. These terms are explained as:

9.4.1 Internal Energy (U)

Every system has a definite amount of energy. This amount is different for different substances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei.

The internal energy may be defind as the sum of the energies of all the atoms, molecules or ions contained in the system.

It is a state variable. It is not possible to measure the absolute values of internal energy. However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is U_1 and that in the final state is U_2, then change in internal energy ΔU is independent of the path taken from the intial to the final state.

We can write this change as:

$$\Delta U = U_2 - U_1$$

The internal energy of the system can be changed in two ways :

(i) either by allowing heat to flow into the system or out of the system; and

(ii) by work done on the system or by the system

9.4.2 Heat(q) and Work(w)

Heat and work are not state functions. This is because the values of both q and w depend upon the way in which the change is carried out.

Since the law deals with the transfer of heat and work, we assign some signs to these quantities. Any thing which increases the internal energy of a system is given a positive sign.

Heat given to the system (q) and work done on the system (w) are given positive signs. Let us illustrate this with an example.

If a certain change is accompanied by absorption of 50 kJ of heat and expenditure of 30 kJ of work,

$$q = + 50 \text{ kJ}$$

$$w = - 30 \text{ kJ}$$

Change in internal energy $\Delta U = (+ 50 \text{ kJ}) + (- 30 \text{ kJ}) = = + 20 \text{ kJ}$

Thus the system has undergone a net increase in the internal energy of –20 kJ.

Change in the internal energy of the surroundings wll be 20 kJ.

9.4.3 Work of Expansion

Let us assume that pressure p is constant and the volume of the system changes from V_1 to V_2. The work done by a system is given as

$$w = - p\,(V_2 - V_1) = - p\,\Delta V \qquad (9.2)$$

(Here we have taken minus sign, because the work is done by the system). Let us substitute the expression given for w in equation 9.1.

We get

$$\Delta U = q - p\,\Delta V \tag{9.3}$$

If the process is carried ot at constant volume, i.e. $\Delta V = 0$, then

$$\Delta U = q_v \tag{9.4}$$

The subscript v in q_v denotes that volume is constant.

The equation 9.4 shows that we can determine internal energy change if we measure the heat gained or lost by the system at constant volume. However, in chemistry, the chemical reactions are generally carried out at constant pressure (atmospheric presure). What do we do then? Let us define another state function, called, enthalpy.

9.4.4 Enthalpy (*H*)

For measuring heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by

$$H = U + p\,V \tag{9.5}$$

Enthalpy change, ΔH, is given by

$$\Delta H = \Delta U + \Delta(pV) \tag{9.6}$$

$$\text{or } \Delta H = \Delta U + p\,\Delta V + V\,\Delta p$$

If the change is carried out at constant pressure, then $\Delta p = 0$. The equation 9.6 will become

$$\Delta H = \Delta U + p\,\Delta V \text{ (at constant pressure)} \tag{9.7}$$

Substituting the value of ΔU from equation 9.3 in equation 9.7, we get

$$\Delta H = q - p\,\Delta V + p\,\Delta V$$

$$= q \text{ (at constant pressure)}$$

We denote q at constant pressure by q_p hence

$$\Delta H = q_p \tag{9.8}$$

Equation 9.8 shows that by measuring heat lost or gained at constant pressure, we can measure enthalpy change for any process.

9.4.5 Relation between Δ*H* and Δ*U*

For liquids and solids, the difference between $\Delta_r H$ and $\Delta_r U$ is not significant but for gasses, the difference is significant as we will see here.

Let V_A be the total volume of the gaseous reactants,

V_B the total volume of the gaseous products,

n_A the number of moles of gaseous reactants,

and n_B the number of moles of gaseous products, at constant pressure and temperature.

Then, using ideal gas law, we can write

$$p\,V_A = n_A\,RT \tag{9.9}$$

$$p\,V_B = n_B\,RT \tag{9.10}$$

Subtracting equation 9.9 from equation 9.10, we get

$$p\,V_B - pV_A = n_B\,RT - n_A\,RT = (n_B - n_A)\,RT$$

$$p\,(V_B - V_A) = p\,\Delta\,V = \Delta\,n_g RT$$

At constant pressure

$$\Delta\,H = \Delta\,U + p\,\Delta\,V$$

Therefore $\Delta\,H = \Delta\,U + \Delta\,n_g\,RT$

Here $\Delta\,n_g$ = (number of moles of gaseous products) - (number of moles of gaseous reactants)

Thus we can find the value of $\Delta\,H$ from $\Delta\,U$ or vice versa.

For solids and liquids $\Delta\,V$ is very small. We can neglect the term $p\,\Delta\,V$, hence $\Delta\,H$ is nearly the same as $\Delta\,U$.

INTEXT QUESTIONS 9.1

1. Which of the following is false ?

   (a) The reaction

   $H_2(g) + Cl_2(g) \rightarrow 2HCl\ (g) + 185\ kJ$

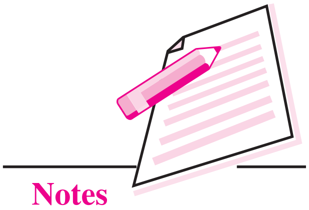
   is endothermic.

   (b) Enthalpy change is a state function.

   (c) Standard state condition for a gaseous system is 1 bar pressure at a specified temperature.

2. For the reaction at 298 K,

   $$\frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2\,(g) \rightarrow NH_3(g)\ ;\ \Delta\,H = -\,46\ kJ$$



(a) What is the value of Δn_g ?

(b) Calculate the value of ΔU at 298 K?

3. Which of the following will increase the internal energy of a system?

   (a) Heat given to the system

   (b) Work done by the system

9.5 STANDARD ENTHALPY OF REACTIONS

Let as denote total enthalpy of reactants as $H_{\text{reactants}}$ and total enthalpy of products as H_{products}. The difference between these enthalpies, ΔH, is the enthalpy of the reaction

$$\Delta_r H = H_{\text{products}} - H_{\text{reactants}}$$

When H_{products} is greater than $H_{\text{reactants}}$ then ΔH is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,

$$H_2(g) + I_2(g) \rightarrow 2HI\ (g);\ \Delta_r H = 52.5 \text{ kJ}$$

When H_{products} is less than $H_{\text{reactants}}$ then ΔH is negative and heat is evolved in the reaction, and the reaction will be exothermic. For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\ (l);\ \Delta_r H = -\,890.4 \text{ kJ}$$

Enthalpy of a reaction changes with pressure and temperature. It is convenient to report enthalpies of the reactions in terms of standard state of substances as we have defined earlier. When substances are in their standard states, we call the enthalpy of reaction as *standard enthalpy of reaction*. It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states. It is donoted by $\Delta_r H^0$.

9.5.1 Enthalpy of formation ($\Delta_f H°$)

The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by $\Delta_f H^0$.

When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by $\Delta_f H^0$. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero.

For example:

$$C_{(\text{Graphite})} + O_2(g) \rightarrow CO_2\ (g)\ ;\ \Delta_f H^0 = -\,393.5 \text{ kJ mol}^{-1}$$

This means that carbon dioxide is formed from its elements in their most stable states. Carbon in the form of graphite and at room temperature and gasesous O_2 and CO_2 being at 1 bar.

9.5.2 Enthalpy of Combustion (Δ_{comb} H°)

Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a substance in oxygen at a given temperature and 1 bar pressure.

For example :

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \; ; \; \Delta_{comb} H^0 = -\,1365.6 \text{ kJ}$$

Enthalpy of combutsion of $C_2H_5OH(l)$ is – 1365.6 kJ mol^{-1}

9.5.3 Enthalpy of Neutralization (Δ_{neut} H^o)

Enthalpy of neutralization is the enthalpy change (heat evolved) when one mole of hydrogen ions (H^+)is neutralized by one mole of hydroxyl ions (OH^-) in dilute aqueous medium to form water.

For example:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O\,(l) \; ; \; \Delta_{neut} H = -57 \text{ kJ/mol}$$

Enthalpy of neutralization of a strong acid with a strong base is always constant having a value of –57 kJ. However, enthalpy of neutralization of strong acid with a weak base or weak acid with a strong base will be different, because of varying degree of ionization of weak acids and bases.

9.5.4 Enthalpy of atomisation ($\Delta_a H^0$)

It is the change in enthalpy when one mole of a substance is converted into its atoms in gaseous state at a given temperature and 1 bar pressure

Examples:

(i) $C(\text{graphite}) \longrightarrow C(g) \qquad \Delta_a H^0 = 716.68 \text{ kJ mol}^{-1}$

In case of *elements in solid state*, it is equal to the enthalpy of sublimation.

(ii) $CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta_a H^0 = 1660 \text{ kJ mol}^{-1}$

(iii) $Hg(l) \longrightarrow Hg(g) \qquad \Delta_a H^0 = 61.32 \text{ kJ mol}^{-1}$

For *elements in liquid state*, it is equal to the enthalpy of vaporization.

9.5.5 Enthalpy of transition (phase transformation) ($\Delta_{trs} H^0$)

It is the change in enthalpy when one mole of substance changes from one phase to another at a constant temperature and under 1 bar pressure. Phase transition/ transformation is a general term that includes the following:

Name of Process	*Process*	*Specific symbol*
(i) Sublimation:	Solid $\longrightarrow$ Gas	$\Delta_{sub}H^0$
(ii) Vaporisation:	Liquid $\longrightarrow$ Gas	$\Delta_{vap}H^0$
(iii) Fusion:	Solid $\longrightarrow$ Liquid	$\Delta_{fus}H^0$
(iv) Transition	Solid (one crystalline form) $\longrightarrow$ Solid (another crystalline form)	$\Delta_{trs}H^0$

Examples:

(i) $Hg(l) \longrightarrow Hg(g)$ $\Delta_{trs}H^0/\Delta_{vap}H^0 = 61.32$ kJ mol^{-1}

(ii) $H_2O(l) \longrightarrow H_2O(g)$ $\Delta_{trs}H^0/\Delta_{vap}H^0 = 4079$ kJ mol^{-1}

(iii) $H_2O(s) \longrightarrow H_2O(g)$ $\Delta_{trs}H^0/\Delta_{sub}H^0 = 6.01$ kJ mol^{-1}

(iv) C(graphite) $\longrightarrow$ C(diamond) $\Delta_{trs}H^0 = 1.90$ kJ mol^{-1}

9.5.6 Enthalpy of Solution ($\Delta_{sol}H^0$)

It is the change in enthalpy when one mole of a solute is dissolved in a specific amount of a solvent at a constant temperature and under 1 bar pressure. It is also known as integral enthalpy of solution. The amount of solvent is mentioned as its of moles in which one mole of solute is dissolved.

Examples

(i) $HCl(g) + 10H_2O(l) \longrightarrow HCl.10\ H_2O$ $\Delta_{sol}H^0 = -69.5$ kJ mol^{-1}

(ii) $HCl(g) + 25H_2O(l) \longrightarrow HCl.25\ H_2O$ $\Delta_{sol}H^0 = -72.2$ kJ mol^{-1}

9.5.7. Enthalpy of ionization ($\Delta_{ion}H^0$)

It is the change in enthalpy when one mole of a weak electrolyte ionizes completely in its solution at a constant temperature and under 1 bar pressure

Example:

$$HCN(aq) \longrightarrow H^+(aq) + CN^-(aq) \quad \Delta_{ion}H^0 = 43.7 \text{ kJ mol}^{-1}$$

9.6 LAWS OF THERMOCHEMISTRY

There are two laws of thermochemistry : The Lavoisiter–Laplace law and the Hess's Law of Constant Heat Summation.

Lavoisier – Laplace Law : When a chemical equation is reversed, the sign of $\Delta_r H$ is changed. For example,

$$N_2\ (g) + O_2\ (g) \rightarrow 2NO\ (g);\ \Delta_r H = 180.5\ \text{kJ}$$

$$2NO\ (g) \rightarrow N_2\ (g) + O_2\ (g);\ \Delta_r H = -180.5\ \text{kJ}$$

Hess's Law of constant heat summation: Hess's law states that the enthalpy of reaction is independent of the number and the nature of the intermediate steps.

You have learnt that standard enthalpy change of the reaction

$$C\ (\text{graphite}) + O_2(g) \rightarrow CO_2(g)$$

is equal to – 393.5 kJ mol^{-1}. This value can be determined with the help of a calorimeter. However, there are some reactions for which the direct measurement of enthalpy in the laboratory is not possible. For example the standard enthalpy change for the reaction,

$$C\ (\text{graphite}) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$$

cannot be to determined with the help of calorimeter because the combustion of carbon is incomplete unless an excess of oxygen is used. If excess of oxygen is used, some of the CO is oxidized to CO_2. How can then we determine the enthalpy change for such reactions when direct measurement is not possible?

Since ΔH is a state function, it is not dependent on the way the reactions are carried out. Let us carry out the reactions as follows.

(1) First carry out the following reaction and let $\Delta_r H_1^0$ be the enthalpy change of the reaction.

$$C\ (\text{graphite}) + O_2\ (g) \rightarrow CO_2\ (g);\ \Delta_r H_1^0 = -393.5\ \text{kJ/mol.}$$

(2) Now let us write the reaction for which we have to determine the enthalpy change of the reaction and let it be $\Delta_r H_2^{\circ}$

$$C\ (\text{graphite}) + \frac{1}{2}\ O_2\ (g) \rightarrow CO(g);\ \Delta_r H_2^0 = ?$$

(3) Let us carry out the following reactions and let $\Delta_r H_3^0$ be the enthalpy change of the reaction

$$CO(g) + \frac{1}{2}\ O_2(g) \rightarrow CO_2(g);\ \Delta_r H_3^0 = -\ 283.0\ \text{kJ}$$

We have obtained the products $CO_2(g)$ from carbon and oxygen through two routes, namely first as in step (1) and second as in step (2) + (3).

According to Hess's Law

$$\Delta_r H_1^0 = \Delta_r H_2^0 + \Delta_r H_3^0$$

or

$$\Delta_r H_2^0 = \Delta_r H_1^0 - \Delta_r H_3^0$$

Fig 9.4 shows alternate paths for the conversion of carbon and oxygen to carbon dioxide.

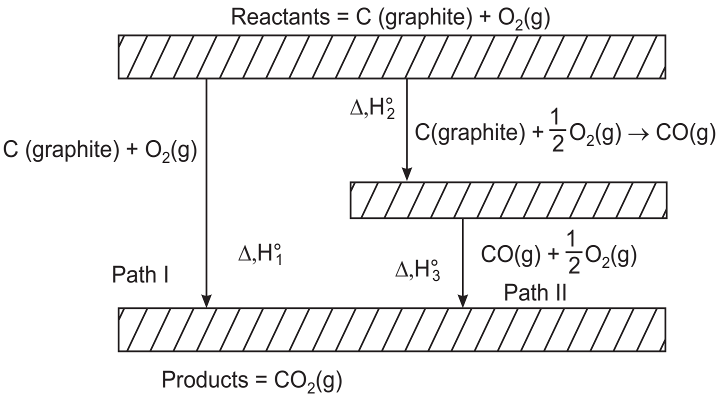


Fig 9.4 : *Alternate paths for the conversion of carbon and oxygen to carbon dioxide*

The result of Hess's law is that thermochemical equations can be added and substracted just like algebraic equations to get the desired reaction. A useful practical application of this law is that we can calculate enthalpy changes for the reactions which cannot be studied directly as in the above case.

To obtain the enthalpy change for the reactions, we algebraically combine the known values of $\Delta_r H^0$ in the same way as the reactions themselves,

Thus

$$\text{C(graphite)} + O_2\,(g) \rightarrow CO_2\,(g)\ ;\ \Delta_r H_1^0 = -393.5 \text{ kJ/mol}$$

$$-\left[\text{CO(graphite)} + \frac{1}{2}\,O_2(g) \rightarrow CO_2\,(g)\right];\ \Delta_r H_3^0 = -\,283.0 \text{ kJ/mol}$$

$$\text{C(graphite)} + \frac{1}{2}\,O_2\,(g) \rightarrow CO(g)\ ;\ \Delta_r H_2^0 = \left[(-393.5) - (-283.0)\right]$$

$$= -110.5 \text{ kJ/mol}$$

Example 9.1 The heat evolved in the combustion of glucose is shown in the following equation:

$$C_6H_{12}O_6\,(s) + 6O_2(g) \rightarrow 6CO_2\,(g) + 6H_2O(l);\ \Delta_{comb}H = -\,2840 \text{ kJ/mol}$$

How much energy will be required for the production of 1.08 g of glucose?

Soluton: Glucose will be prepared by the reverse reaction.

$$6CO_2(g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6CO_2\ (g)\ ;\ \Delta H = 2840\ \text{kJ}.$$

This equation refers to 1 mol of glucose (180 g of glucose).

Production of 180 g of glucose requires 2840 kJ of energy. Therefore, production of 1.08 g will require;

$$\frac{2840\ \text{kJ}}{180\ \text{g}} \times 1.08\ \text{g} = 17.04\ \text{kJ}$$

Example 9.2 Calculate the standard enthalpy of formation of ethane, given that

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2\ (g)\ ;\ \Delta_f H^0 = -\ 394\ \text{kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}\ O_2\ (g) \rightarrow H_2O(\ell);\ \Delta_f H^0 = -\ 286\ \text{kJ mol}^{-1}$$

$$C_2H_6(g) + \frac{7}{2}\ O_2\ (g) \rightarrow 2CO_2(g) + 3H_2O\ (\ell);\ \Delta_r H^0 = -\ 1560\ \text{kJ mol}^{-1}$$

Solution: Given that

$$C_{(\text{graphite})} + O_2(g) \rightarrow CO_2(g)\ ;\ \Delta_r H^0{}_1 = -394\ \text{kJ/mol} \qquad (1)$$

$$H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l)\ ;\ \Delta_r H^0{}_2 = -\ 286\ \text{kJ/mol} \qquad (2)$$

$$C_2H_6(g) + \frac{7}{2}\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)\ ;\ \Delta_r H^0{}_3 = -1560\ \text{kJ/mol} \qquad (3)$$

The required equation is

$$2C_{(\text{graphite})} + 3H_2(g) \rightarrow C_2H_6(g)\ ;\ \Delta_f H^0 = ? \qquad (4)$$

To obtain the above equation, mulitply equations (1) by 2 and equation (2) by 3 and then add both the equations we get

$$2C_{(\text{graphite})} + 3H_2(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)\ ;\ \Delta_r H^0{}_5 = -1656\ \text{kJ/mol} \quad (5)$$

(where $\Delta_r H^0{}_5 = 2\Delta_r H^0{}_1 + 3\Delta_r H^0{}_2 = 2 \times (-394) + 3 \times (-286) = -1656$ kJ/mol)

Subtract equation (3) from equation (5) to get the equation (4)

$$2C_{(\text{graphite})} + 3H_2(g) \rightarrow C_2H_6(g)\ ;$$

where $\Delta_f H^0 = -1656 - (-1560) = -96$ kJ/mol

Thus, standard enthalpy of formation of ethane is –96 kJ/mol

INTEXT QUESTIONS 9.2

1. Which of the following is true?

   (a) Enthalpy of formation is the heat evolved or absorbed when one gram of a substance is formed from its elements in their most stable states.

   (b) When one mole of H+ (aq) and 1 mole of OH^- (aq) react, 57.1 kJ of energy is absorbed.

   (c) In the thermochemical equation,

   $$C(graphite) + O_2\,(g) \rightarrow CO_2(g)\ ;\ \Delta_f H^0 = -394\ kJ\ mol^{-1}$$

   $\Delta_f H^0$ is known as enthalpy of formation of $CO_2(g)$

2. Calculate the enthalpy change for complete combustion of 29.0 g of butane, if

   $$C_4H_{10}(g) + \frac{3}{2}O_2\,(g) \rightarrow 4CO_2\,(g) + 5H_2O\,(l)\ ;\ \Delta_{comb} H^0 = -\ 2658\ kJ$$

3. Calculate the standard enthalpy of the reaction

   $$2H_2S(g) + SO_2(g) \rightarrow 3S\,(s) + 2H_2O\,(l)$$

   given that

   $\Delta_f H^0\ (H_2S) = -\ 20.6\ kJ\ mol^{-1}$

   $\Delta_f H^0\ (SO_2) = -\ 296.9\ kJ\ mol^{-1}$

   $\Delta_f H^0\ (H_2O) = -\ 289.9\ kJ\ mol^{-1}$

9.7 BOND ENTHALPIES

In a chemical reaction, you have seen that energy is either absorbed or evolved. Do you know the origin of this change in energy? You know that bonds are broken and new bonds are formed in chemical reactions. Energy changes take place in breaking some bonds of the reactants and in forming new bonds of the products. So the energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only.

At high temperature, hydrogen molecules dissociate into atoms as

$$H_2(g) \rightarrow H\,(g) + H(g)\ ;\ \Delta_r H = 435\ kJ/mol$$

The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the H_2 molecules. For a diatomic molecule like $H_2(g)$, we define **bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms.**

Now, let us consider a polyatomic molecule like $H_2O(g)$. The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in

$$H_2O\ (g) \rightarrow H\ (g) + OH\ (g)\ ;\ \Delta_r H^0 = 502\ \text{kJ/mol}$$

$$OH(g) \rightarrow O(g) + H\ (g)\ ;\ \Delta_r H^0 = 427\ \text{kJ/mol}$$

In the first reaction, one of the two OH bonds in H_2O (g) dissociates with an enthalpy change of 502 kJ/mol and in the second reaction, second OH bond dissociates with an enthalpy change of 427 kJ/mol. It is clear that the dissociation energy of the O – H bond is sensitive to its environment. However, the difference is not very large. We take the average value (464.5 kJ/mol in this case) in case of polyatomic molecules and call it bond enthalpy.

Bond enthalpy is defined as the average amount of enthalpy change involved in the dissociation of one mole of bonds present in different gaseous compounds.

Now you know the distincton between bond dissociation enthalpy and bond enthalpy. Bond dissociation enthalpy refers to breaking a particular bond in a particular molecule whereas bond enthalpy is the average value of bond dissociation energies for a given type of bond. The bond enthalpies of some bonds are listed in table 9.1.

By using bond enthalpies (B.E.) it is possible to estimate the energy released when a gaseous molecule is formed from its gaseous atoms. For example, the energy released at constant pressure for the reaction ($\Delta_r H$),

$$3H(g) + C(g) + Cl(g) \rightarrow CH_3Cl(g)$$

is the sum of the energies of three C – H bonds, and one C – Cl bond, all taken with a negative sign because energy is released. Using the values of bond enthalpies (B.E.) from table 9.1 we get,

$$\begin{aligned}\Delta_r H &= -\,3 \times \text{B.E. (C – H)} - \text{B.E. (C – Cl)}\\ &= (-3 \times 415 - 335)\ \text{kJ mol}^{-1}\\ &= (-1245 - 335)\ \text{kJ mol}^{-1}\\ &= -\,1574\ \text{kJ mol}^{-1}\end{aligned}$$

We will now show you how to use bond enthalpy data to estimate the enthalpy of a reaction, when direct calorimetric data are not available. Note that in section 9.7 we used enthalpy of formation data to estimate enthalpy of a reaction. In principle, bond enthalpy data can be used to calculate $\Delta_r H$ for a chemical reaction occuring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products.

$$\Delta_r H = \Sigma \text{ B.E. (reactants)} - \Sigma \text{ B.E. (products)} \tag{9.10}$$

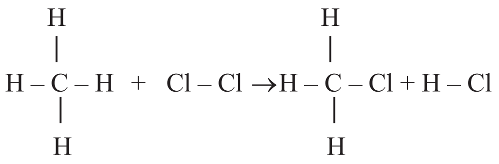
Table 9.1 : Average Bond enthalpies

BOND	BOND ENTHALPY /(kJ mol^{-1})
H – H	435
C – H	415
C – Br	284
C – C	356
C = C	598
Br – Br	193
Cl – Cl	242
C – Cl	339
F – F	155
H – Cl	431
H – O	462
H – N	390
H – F	563
H – Br	366
H – I	296
C – O	355
C = O	723
C – N	391
C = N	619
C ≡ N	878
C ≡ C	832

Example 9.3: Use bond enthalpy data given in table 9.1 to calculate the enthalpy of the reaction.

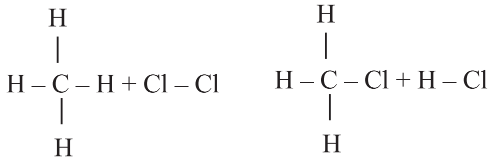
$$CH_3\,(g) + Cl_2\,(g) \rightarrow CH_3Cl\,(g) + HCl\,(g)$$

Solution: 1. Write the equation using structural formula



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H + Cl-Cl \rightarrow H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Cl + H-Cl$$

2. List the bonds broken and bonds formed under the equation as shown



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H + Cl-Cl \qquad H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-Cl + H-Cl}$$

number of bonds broken	number of bonds formed
$C-H = 4$	$C-Cl = 1$
$Cl-Cl = 1$	$H-Cl = 1$
	$C-H = 3$

3. Look up the values of bond enthalpies for the bonds in the reactants and products and list them as shown

Reactants	Products
B.E. $(C-H) = 435$ kJ mol^{-1}	B.E. $(Cl-C) = 339$ kJ mol^{-1}
B.E. $(Cl-Cl) = 242$ kJ mol^{-1}	B.E. $(H-Cl) = 431$ kJ mol^{-1}
	B.E. $(C-H) = 435$ kJ/mol

4. Use equation 9.10,

Enthalpy of the rection $\Delta_r H = \Sigma$ B.E. (reactants) - Σ B.E. (products)

$= 4[\text{B.E. }(C-H) + \text{B.E. }(C-Cl)] - [\text{B.E. }(C-Cl) + \text{B.E. }(H-Cl) + 3\text{ B.E. }(C-H)]$

$= [4 \times 435 + 242] - [339 + 431 + 3 \times 435] = -93$ kJ

Now let us take one example in which we calculate the enthalpy of a reaction using

(i) Enthalpy of formation data

(ii) Bond enthalpy data.

Example 9.4: Calculate $\Delta_r H°$ for the reaction

$$Cl_2\,(g) + 2HF\,(g) \rightarrow 2HCl\,(g) + F_2\,(g)$$

(a) Using enthalpy of formation data

$\Delta_f H°\,(HCl) = -92.5$ kJ

$\Delta_f H°\,(HF) = -269$ kJ

(b) Using bond enthalpy data

B.E. $(H-Cl) = 431$ kJ mol^{-1}

B.E. $(F-F) = 155$ kJ mol^{-1}

B.E. (H – F) = 563 kJ mol^{-1}

B.E. (Cl – Cl) = 242 kJ mol^{-1}

Solution :

(a) Using enthalpy of formation of compounds,

$$\Delta_r H = [2\Delta_f H^0\,(\mathrm{HCl}) + \Delta_f H\,(\mathrm{F_2})] - [2\Delta_f H^0\,(\mathrm{HF}) + \Delta_f H^0(\mathrm{Cl_2})]$$

$$= [2\mathrm{x}\,(-92.5) + 0] - [2\mathrm{x} - (269) + 0]\ \mathrm{kJ}$$

$$= -185\ \mathrm{kJ} + 538\ \mathrm{kJ}$$

$$= +353\ \mathrm{kJ}$$

(b) Using bond enthalpies

$$\Delta_r H^0 = \Sigma\,\mathrm{B.E.\ (reactants\ bonds)} - \Sigma\,\mathrm{B.E.\ (products\ bonds)}$$

$$= [\mathrm{B.E.\ (Cl - Cl)} + 2\mathrm{B.E.\ (H - F)}] - [2\ \mathrm{B.E.\ (H - Cl)} + \mathrm{B.E.\ (F - F)}]$$

$$= [242 + 2\,(563)]\ \mathrm{kJ} - [2 \times 431 + 155]\ \mathrm{kJ}$$

$$= 1368\ \mathrm{kJ} - 1017\ \mathrm{kJ}$$

$$\Delta_r H^0 = 351\ \mathrm{kJ}$$

$\Delta_r H^0$ calculated by these two different methods are nearly the same.

INTEXT QUESTIONS 9.3

1. Write True or false
   - (a) Enthalpy of a reaction is equal to the sum of the enthalpy of formation of products minus the sum of the enthalpy of formation of the reactants.
   - (b) Enthalpy of formation of any elementary substance is equal to zero.
   - (c) If a reaction can be carried out in several steps, the enthalpy change for the overall reaction is equal to enthalpy change in the last step.
   - (d) Bond enthalpy and bond dissociation energy are same for polyatomic molecules.
2. Calculate the bond enthalpy of N – H in NH_3 (g), given

$$\frac{1}{2}\mathrm{N_2\,(g)} + \frac{3}{2}\mathrm{H_2\,(g)} \rightarrow \mathrm{NH_3(g)}\ ; \quad \Delta_f H^0 = -46\ \mathrm{kJ\ mol^{-1}}$$

$\frac{1}{2}$ H_2 (g) $\rightarrow$ H (g); $\Delta_r H^0 = 218$ kJ mol^{-1}

$\frac{1}{2}$ N_2 (g) $\rightarrow$ N(g); $\Delta_r H^0 = 973$ kJ mol^{-1}

3. Calculate the enthalpy of the reaction

H_2 (g) + Cl_2 (g) $\rightarrow$ 2HCl (g)

given;

Bond enthalpy (H - H) = 435 kJ mol^{-1}

Bond enthalpy (Cl - Cl) = 242 kJ mol^{-1}

Bond enthalpy (H - Cl) = 431 kJ mol^{-1}

WHAT YOU HAVE LEARNT

- System is the part of the physical universe which is under study, while the rest of the universe is surroundings.
- Isolated system is a system which can exchange neither matter nor energy with the surroundings.
- Closed system is a system which can exchange energy but not the matter with the surroundings.
- Open system is a system which can exchange both energy and matter with the surroundings.
- State functions are those functions which depend only on the state of the system.
- Extensive properties depend upon the size of the system whereas intensive properties do not depend upon the size of the system.
- When the temperature of the system is kept constant during various operations then the process is said to be isothermal.
- In an adiabatic process there is no exchange of heat between the system and the surroundings.
- Reversible processes are those processes in which the changes are carried out so slowly that the system and surrounding are always in equilibrium.
- Exothermic reactions are those reactions which proceed with the evolution of heat.

- Endothermic reactions are those which proceed with absorption of heat from the surroundings.
- First law of Thermodynamics states that energy can neither be created nor destroyed.
- Internal energy is the sum of the energies of all the atoms, molecules or ions contained in the system.
- The state function enthalpy (H) is given by the relation $H = U + PV$.
- When a chemical equation is reversed, the sign of ΔH is also reversed.
- The enthalpy of reaction is independent of the number and nature of the intermediate steps.
- Bond enthalpy is the average amount of bond dissociation enthalpies for a given type of bond present in different gaseous compounds, when one mole of bonds is broken in the gaseous state.

TERMINAL EXERCISE

1. Enthalpy of combustion of ethyl alcohol, C_2H_5OH, is – 950 kJ mol^{-1}. How much heat is evolved when one gram of ethyl alcohol burns?

2. Given :

$$C_2H_2(g) + \frac{5}{2} O_2(g) \rightarrow 2CO_2(g) + H_2O(l) ; \Delta_{comb}H = -1299 \text{ kJ/mol}$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) ; \Delta_f H = -393 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) ; \Delta_f H = -285.5 \text{ kJ/mol}$$

Calculate enthalpy of formation of $C_2H_2(g)$

3. Calculate the enthalpy of combustion of propane

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

Given the following:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l); \quad \Delta_f H = -285.5 \text{ kJ/mol}$$

$$C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta_f H = -393 \text{ kJ/mol}$$

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g); \quad \Delta_f H = -104 \text{ kJ/mol}$$

4. When two moles of H_2 and one mole of O_2 react to produce two moles of gaseous water at 373 K and 1 bar pressure, a total of 484 kJ are evolved. What are (a) ΔH and (b) ΔU for the production of a single mole of H_2O (g).

5. Calculate enthalpy of the reaction:

   $2Na_2O_2\ (s) + 2H_2O\ (l) \rightarrow 4NaOH\ (s) + O_2\ (g)$

   Enthalpies of formation of NaOH (s), Na_2O_2 (s) and H_2O (l) are - 426.4 kJ mol^{-1}, 504 kJ mol^{-1} and - 285 kJ mol^{-1} respectively.

6. Calculate the heat of formation of gaseous ethyl alcohol,

   $$2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH\ (g)$$

   given that enthalpy of sublimation of graphite is 714 kJ/mol and bond enthalpies of H – H, O = O, C – C, C – H, C – O and O – H are respectively 435 kJ/mol^{-1}, 498 kJ/mol^{-1}, 347 kJ/mol^{-1}, 415 kJ/mol^{-1}, 355 kJ/mol^{-1} and 462 kJ/mol^{-1} respectively.

ANSWERS TO INTEXT QUESTIONS

9.1

1. (a)

2. (a) $\Delta n = 1 - \frac{1}{2} - \frac{3}{2} = -1$

   (b) $\Delta U = \Delta H - \Delta n RT$

   $= 46000\ (J\ mol^{-1}) - (-1)\ (8.314\ Jk^{-1}\ mol^{-1}) \times (298\ K)$

   $= -46000\ (J\ mol^{-1}) + 2247.6\ (J\ mol^{-1})$

   $= -43.5\ kJ\ mol^{-1}$

3. (a)

9.2

1. (c)

2. – 1329 kJ

3. $\Delta_r H^0 = 2\ \Delta_f H^0\ (H_2O) - 2\Delta_f H^0\ (H_2S) - \Delta_f H^0\ (SO_2)$

   $= -241.7\ kJ$

9.3

1. (a) T

   (b) T

   (c) F

   (d) F

2. $\Delta rH^0 = \Sigma$ B.E. (reactant bonds) – Σ B.E. (products bonds)

   or – 46 (kJ mol^{-1}) = 3 × 218 (kJ mol^{-1}) + 973 (kJ mol^{-1}) – B.E. (NH_3(g) Bonds)

   B.E. (NH_3(g) Bonds) = 1673 kJ mol^{-1}

   B.E. (N – H) = 557.7 kJ mol^{-1}

3. $\Delta_r H^0 = -\,185$ kJ mol^{-1}

313en10

10

SPONTANEITY OF CHEMICAL REACTIONS

We have studied about the first law of thermodynamics in lesson 09. According to this law the processes occur in such a way that the total energy of the universe remains constant. But it does not tell us whether a specified change or a process including a chemical reaction can occur spontaneously i.e., whether it is feasible or not. For example, the first law does not deny the possibility that a metal bar having a uniform temperature can spontaneously become warmer at one end and cooler at the other. But it is known from experience that such a change does not occur without expenditure of energy from an external source.

The first law also states that energy can be converted from one form into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work without producing some changes elsewhere. In this lesson you shall learn to predict whether a given process or a chemical reaction can occur spontaneously or not.

OBJECTIVES

After reading this lesson you will be able to :

- define entropy;
- recognise that entropy change in a system is given by

$$\Delta S = \frac{q_{rev}}{T}$$

- state entropy criterion for a spontaneous process $\Delta S_{universe} > 0$ and at equilibrium $\Delta S_{universe} = 0$
- state the second law of thermodynamics.

- state the third law of thermodynamics;
- state the relationship between G, H and S ;
- derive the relation $\Delta G_{system} = T \Delta S_{system}$;
- state Gibbs energy criterion for spontaneous process

  $\Delta G < 0$ for a spontaneous process

  $\Delta G = 0$ at equilibrium

  $\Delta G > 0$ for a non-spontaneous process
- define standard Gibbs energy of formation of a subtance;
- relate the standard Gibbs energy change with the equilibrium constant and
- solve numerical problems.

10.1 SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

We know that hot water kept in a container cools down by losing heat to the surroundings. On the other hand, water at room temperature cannot become hot by gaining heat from the surroundings. It can be made hot by heating it over a gas burner. The cooling down of hot water is an example of a spontanneous process. Heating of water (at room temperature) is an example of a non-spontaneous process because an outside agency (gas burner) has been used.

A spontaneous process is a process that occurs in a system by itself; once started, no action from outside the system (outside agency) is necessary to make the process continue. A **non-spontaneous process** will not take place unless some external action is continuously applied. Let us consider another example, we know that when iron objects are exposed to moist atmosphere, rusting of iron takes place. Although the rusting of iron is a slow process but it always takes place in the same direction. We say that the rusting of iron is a spontaneous process. During rusting of iron, iron is oxidised to iron (III) oxide.

$$4\ Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3\ (s)$$

The reverse of the above reaction is also possible but it is non-spontaneous. An external agency has to be used to reduce iron (III) oxide to iron.

From our discussion it can be concluded that

- if a process is spontaneous, the reverse process is non-spontaneous.
- all the spontaneous processes and most of the non-spontaneous processes are possible.
- spontaneous processes occur naturally whereas non-spontaneous processes require the help of an outside agency to occur.

10.2 ENTROPY

In fig 10.1(a) the bulb 'I' contains 1 mol of an ideal gas 'A' at a pressure of 1 bar and the bulb II contains 1 mol of another ideal gas 'B' at 1 bar. The two bulbs are joined together through a valve.

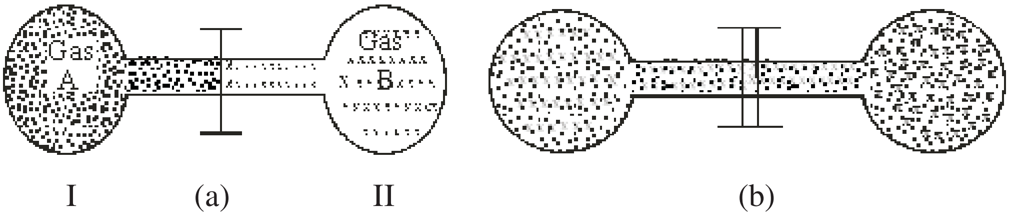


Fig 10.1

When the valve between the two bulbs is opened [Fig 10.1 (b)], the two gases mix spontaneously. The mixing of gases continues until the partial pressure of each gas becomes equal to 0.5 bar in each bulb i.e., the equilibrium is attained. We know from experience that the process cannot be reversed spontaneously - the gases do not unmix on their own. What is the driving force behind this process?

We know that the internal energy (U) and enthalpy (H) of an ideal gas depend only upon the temperature of the gas and not upon its pressure or volume. Since there are no intermolecular forces in ideal gases, $\Delta U = \Delta H = 0$ when ideal gases mix at constant temperature. Thus, energy change is not the driving force behind the spontaneous mixing of ideal gases. The driving force is simply the tendency of the molecules of the two gases to achieve maximum state of mixing, i.e., disorder. The thermodynamic property related to the disorder of the system is called *entropy*. It is denoted by the symbol S.

The entropy is the measure of disorder or randomness in a system. The greater the disorder in a system, the greater is the entropy of the system.

For a given substance,

(i) the crystalline state is the most ordered state, hence its entropy is the lowest.

(ii) the gaseous state is the most disordered state, hence its entropy is the maximum, and

(iii) the disorder in the liquid state is intermediate between the solid and the gaseous state.

Entropy of any substance increases on heating. In a chemical reaction, entropy increases if there is an increase in number of moles of gases during the reaction and *vice-versa.*

When a *system* changes from one state to another, the change of entropy ΔS is given by

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{10.1}$$

where q_{rev} is the heat supplied reversibly at a constant temperature T.

10.3 CRITERIA FOR SPONTANEOUS CHANGE : THE SECOND LAW OF THERMODYNAMICS

So far we have studied about internal energy, enthalpy and entropy. Can we define the spontaneity of a process in terms of these properties? Let us see whether these changes in properties can be used as a criterion for determining the spontaneity of a process or not.

(i) We know that most of the processes which occur spontaneously are exothermic. Water kept in a container at room temperature evaporates spontaneously. It is an endothermic process. Thus enthalpy change cannot be used as a criteria for spontaneous change.

(ii) Can we use the increase of entropy as a criteria for the spontaneous change? Then how do we explain the spontaneous freezing of water at –10°C? We know that crystalline ice is more ordered then the liquid water and therefore the entropy must decrease. The answer to this question is that we must consider simultaneously two entropy changes:

(a) the entropy change of the system itself, and

(b) the entropy change of the surroundings

$$\Delta S_{\text{total}} = \Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \qquad (10.2)$$

The equation is one of the many forms of the second law of thermodynamics.

According to *the second law of thermodynamics* **all spontaneous or natural processes produce an increase in entropy of the universe.**

Thus, for a spontaneous process when a system is at equilibrium, the entropy is maximum, and the change in entropy is zero

$$\Delta S = 0 \text{ (at equilibrium)} \qquad (10.3)$$

10.4 ENTROPY CHANGE IN PHASE TRANSITIONS

When a solid melts and produces liquid, the process occurs at the melting point of the solid. For example, ice melts at 273 K and produces water at the same temperature.

$$H_2O(s) \xrightarrow{273\text{K}} H_2O(l)$$

The heat involved in the process of melting a solid is called enthalpy of fusion ($\Delta_{\text{fus}}H$). Therefore, the entropy of fusion ($\Delta_{\text{fus}}S$) is given by

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} \qquad (\because q_{\text{rev}} \text{ at const } p = \Delta_{\text{fus}}H)$$

where T is the melting point of the solid.

Similarly, for the equilibrium

$$H_2O(l) \xrightarrow{373\,K} H_2O(g)$$

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T}, \text{ (}T\text{ is the boiling point of the liquid.)}$$

Example 10.1: The enthalpy change for the transition of liquid water to steam at 373 K is 40.8 kJ mol^{-1}. Calculate the entropy change for the process

Solution: $H_2O\ (l) \xrightleftharpoons{373\text{ K}} H_2O(g)$

$$\Delta_{\ vap}S = \frac{\Delta_{vap}H}{T}$$

$$\Delta_{\ vap}H = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 10^3 \text{ J mol}^{-1}$$

$$T = 373 \text{ K}$$

$$\Delta_{\ vap}S = \frac{40.8 \times 10^3 \text{ J mol}^{-1}}{373 \text{ K}} = 109 \text{ J K}^{-1} \text{ mol}^{-1}$$

INTEXT QUESTIONS 10.1

1. The enthalpy change for the transition of ice to liquid water at 273 K is 6.02 kJ mol^{-1}. Calculate the entropy change for the process.
2. Arrange the following systems in the order of increasing randomness,
   (i) 1 mol of gas A
   (ii) 1 mol of solid A
   (iii) 1 mol of liquid A
3. Indicate whether you would expect the entropy of the system to increase or decrease
   (a) $2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$
   (b) $N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3\ (g)$
   (c) $O_2\ (g) \rightarrow 2O\ (g)$

10.5 THIRD LAW OF THERMODYNAMICS AND ABSOLUTE ENTROPY

When temperature of a substance is increased, the translational, vibrational and rotational motions become more vigorous. It leads to greater disorder and as a result the entropy of the substance increases. Thus, on increasing the temperature of a substance the entropy of a substance increases. It decreases on decreasing the temperature of a substance.

The entropy of a pure and perfectly crystalline solid at absolute zero temperature is zero. This is known as the **Third law of thermodynamics.** This third law of thermodynamics helps us to calculate the absolute value of molar entropies (S_m) of substances at different temperatures. The standard molar entropies of some substances at 298 K are given in Table 10.1.

Table 10.1 : Standard molar entropies ($S_m{}^0$/J K^{-1} mol^{-1}) at 298 K

Solids	Entropy	Liquids	Entropy	Gases	Entropy
C (graphite)	5.7	H_2O	69.9	H_2	130.7
C (diamond)	2.4	Hg	76.0	O_2	205.1
Fe	27.3	C_2H_5OH	160.7	N_2	191.6
Pb	64.8	C_6H_6	173.3	CO_2	213.7
Cu	33.1	CH_3COOH	159.8	NO_2	240.1
Al	96.2			N_2O_4	304.3
$C_{12}H_{22}O_{11}$	360.8			NH_3	192.3
$CaCO_3$	92.9			CH_4	186.2

Entropy Change for a Reaction

The absolute entropies can be used for calculating standard entropies changes accompanying chemical reaction. It can be determined by subtracting the standard entropies of reactants from those of products. Thus, for a general reaction

$$aA + bB + \ldots\ldots \rightarrow pP + qQ + \ldots$$

$$\Delta S_m{}^0 = [pS_m{}^0\,(P) + qS_m{}^0\,(Q) + \;\ldots.] - [aS_m{}^0\,(A) + bS_m{}^0\,(B) + \ldots]$$

$$\Delta_r S_m{}^0 = \Sigma\, S_m{}^0\ (\text{products}) - \Sigma\, S_m{}^0\ (\text{reactants})$$

Example 10.2 : Calculate the entropy change, $\Delta_r S_m{}^0$ for the following reaction at 298K.

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

Given that the standard molar entropies of Fe(s), O_2(g), and Fe_2O_3(s) at 298 K are 27.3, 205.0 and 87.4 J K^{-1} mol^{-1} respectively.

Solution : $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

$$\Delta_r S^o = \sum \nu_P S^o_m\ (\text{products}) - \sum \nu_R\, S^o{}_m\ (\text{reactants})$$

$$\Delta_r S^o = 2S^o_m\,(Fe_2O_3) - [4S^o_m(Fe) + 3S^o_m(O_2)]$$

$$= [2 \times 87.4 - (4 \times 27.3 + 3 \times 205.0)]\ J\ K^{-1}\ mol^{-1}$$

$$= -\,549.4\ J\ K^{-1}\ mol^{-1}$$

10.6 GIBBS ENERGY AND SPONTANEITY

We can use the expression

$$\Delta S_{univ} = \Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} > 0 \tag{10.4}$$

as our basic criterion for a spontaneous change. But it is very difficult to apply it because we have to evaluate the total entropy change i.e. the entropy change of system plus that of surroundings. This is a tedious process as it is difficult to figure out all the interactions between the system and the surroundings. For a system which is not isolated from its surroundings.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} \tag{10.5}$$

At constant temperature and pressure if q_p is the heat given out by the system to the surroundings, $-q_p$ is the heat gained by the surroundings we can write

$$\Delta S_{surrounding} = \frac{-q_p}{T} = -\frac{\Delta H_{system}}{T} \tag{10.6}$$

(since $q_p = \Delta H$ at constant pressure)

Substituting Eq. 10.6 in Eq. 10.5, we get

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

$$T\Delta S_{total} = T\Delta S_{system} - \Delta H_{system}$$

or
$$-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system} \tag{10.7}$$

Now, let us define another thermodynamic property, Gibbs energy. It is defined by the equation

$$G = H - TS \tag{10.8}$$

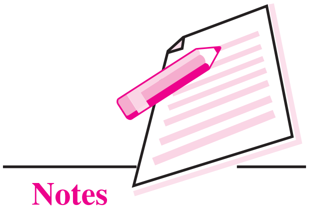
For a change in Gibbs energy, we write

$$\Delta G = \Delta H - \Delta (TS)$$

$$\Delta G = \Delta H - T\Delta S - S\Delta T$$

For a change at constant temperature, $\Delta T = 0$,

Therefore
$$\Delta G = \Delta H - T\Delta S \tag{10.9}$$



Notes

Since H, T and S are state functions, it follows that G is also a state function. Comparing equations 10.7 and 10.9, we find that

$$\Delta G = -T \Delta S_{total} \tag{10.10}$$

We have seen that if ΔS_{total} is positive, the change will be spontaneous. Equations 10.10 can be used to predict the spontaneity of a process based on the value of ΔG.

The use of Gibbs energy has the advantage that it refers to system only. Thus for a process occurring at constant temperature and pressure, if

$\Delta G < 0$ (negative), the process is spontaneous

$\Delta G > 0$ (positive), the process is non-spontaneous

$\Delta G = 0$ (zero), the process is at equilibrium

In deciding the spontaneity of a chemical reaction, the equation $\Delta G = \Delta H - T \Delta S$ takes into account two factors (i) the energy factor ΔH, and (ii) the entropy factor ΔS. Based on the signs of ΔH and ΔS there are four possibilities for ΔG. These possibilities are outlined in table 10.2

Table 10.2 Criterion for spontaneous change : $\Delta G = \Delta H - T\Delta S$

S.No	ΔH	ΔS	ΔG	Result
1	–	+	–	Spontaneous at all temperatures.
2.	–	–	–	Spontaneous at low temperatures.
			+	Non-spontaneous at high temperatures.
3.	+	+	+	Non-spontaneous at low temperatures.
			–	Spontaneous at high temperatures.
4.	+	–	+	Non-spontaneous at all temperatures.

Example 10.3 : For the reaction

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

Calculate $\Delta_r G$ at 700 K when enthalpy and entropy changes ($\Delta_r H$ and $\Delta_r S$) are respectively -113.0 kJ mol^{-1} and -145 JK^{-1} mol^{-1}

Solution : Given that

$$\Delta H = -113.0 \text{ kJ mol}^{-1}$$

$$\Delta S = -145 \text{ JK}^{-1} \text{ mol}^{-1} = -145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 700 \text{ K}$$

Substituting the values in

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = (-113.0 \text{ kJ mol}^{-1}) - (700 \text{ K})(-145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$= (-113.0 \text{ kJ mol}^{-1}) + (101.5 \text{ kJ mol}^{-1})$$

$$= -11.5 \text{ kJ mol}^{-1}$$

INTEXT QUESTIONS 10.2

1. Determine whether the following reaction

   $CCl_4 \text{ (l)} + H_2 \text{ (g)} \rightarrow HCl \text{ (g)} + CHCl_3 \text{ (l)}$

   is spontaneous at 298 K if $\Delta_r H = 91.35$ kJ mol^{-1} and $\Delta_r S = 41.5$ JK^{-1} mol^{-1} for this reaction.

2. Which of the following conditions would predict a process that is always spontaneous?

   (i) $\Delta H > 0, \Delta S > 0$

   (ii) $\Delta H > 0, \Delta S < 0$

   (iii) $\Delta H < 0, \Delta S > 0$

   (iv) $\Delta H < 0, \Delta S < 0$

10.7 STANDARD GIBBS ENERGY CHANGE (ΔG°) AND EQUILIBRIUM CONSTANT (K)

The standard Gibbs energy change is defined as the change in Gibbs energy for the process in which the reactants in their standard states are converted into the products in their standard states. It is denoted by the symbol $\Delta_r G^\circ$.

The value of $\Delta_r G^\circ$ can be found from the standard Gibbs energy of formation of substances.

The standard Gibbs energy of formation of a compound is defined as the change in Gibbs energy when 1 mole of the compound is formed from its constituent elements in their standard states. Like the standard enthalpy of formation of an element, the standard Gibbs energy of formation of an element in its standard state is taken as zero.

Thus for a reaction

$$aA + bB + ... \rightarrow pP + qQ + ...$$

$$\Delta_r G^\circ = (p\, \Delta_f G_P^o + q\, \Delta_f G_Q^o + ...) - (a\, \Delta_f G_A^o + b\, \Delta_f G_B^o + ...)$$

$$\Delta_r G^\circ = \Sigma\, v_R\, \Delta_f G^\circ \text{ (products)} - \Sigma v_R\, \Delta_f\, G^\circ \text{ (reactants)}$$

The standard Gibbs energy change ($\Delta_r G°$) is related to the equilibrium constant (K) of the reaction by the expression

$$\Delta_r G^o = -RT \ln K = -2.303\, RT \log K$$

Example 10.4 : The equilibrium constant of the reaction

$$P(s) + \frac{3}{2}\, Cl_2\,(g) \rightleftharpoons PCl_3\,(g)$$

is 2.00×10^{24} at 500 K. Calculate the value of $\Delta_r G°$.

Solution : Given that

$$K = 2.00 \times 10^{24}$$

$$T = 500\ K$$

$$\Delta_r G° = -2.303\, RT \log K$$

$$= -2.303 \times (8.314\ J\ mol^{-1}\ K^{-1})\ (500\ K) \log 2.0 \times 10^{24}$$

$$= -2.303 \times (8.314\ J\ mol^{-1}\ K^{-1})\ (500\ K)\ 24.30$$

$$= -232.6\ kJ\ mol^{-1}$$

Example 10.5 : Calculate the standard Gibbs energy change for the reaction

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

at 298K. The standard Gibbs energies of formation of CH_4, CO_2 and H_2O at 298K are – 50.8 kJ mol^{-1}, –394.4 kJ mol^{-1}, and –237.2 kJ mol^{-1} respectively.

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

$$\Delta_r G° = \Delta_f G°(CO_2) + 2\,\Delta_f G°\,(H_2O) - \Delta_f G°\,(CH_4) - 2\Delta_f G°\,(O_2)$$

$$= -394.4 + 2 \times (-237.2) - (-50.8) - 2 \times 0$$

$$= -394.4 - 474.4 + 50.8$$

$$= -818\ kJ\ mol^{-1}$$

INTEXT QUESTIONS 10.3

1. What is the relationship between the standard Gibbs energy change and the equilibrium constant of the reaction?
2. The standard Gibbs energy change for the reaction

   $$CO\,(g) + 2H_2\,(g) \longrightarrow CH_3OH\,(l)$$

   at 298 K is – 24.8 kJ mol^{-1}. What is the value of the equilibrium constant at 298 K?

WHAT YOU HAVE LEARNT

- All spontaneous processes lead to an increase in disorder or randomness
- The thermodynamic function related to disorder in a system is called entropy, S.
- According to the second law of thermodynamics for a spontaneous change the total entropy change of the system and the surroundings must increase.
- Absolute entropies of different substances can be calculated with the help of the third law of thermodynamics which states that the entropy of a pure and perfectly cystalline solid is zero at absolute zero temperature.
- Gibbs energy is defined as $G = H - TS$
- At a constant temperature, the change in Gibbs free energy is related to enthalpy and entropy changes by the expression

  $\Delta G = \Delta H - T\,\Delta S$

  For a spontaneous change, there must be a decrease in Gibbs energy, i.e., $\Delta G < 0$.

  At equilibrium $\Delta G = 0$

  The standard Gibbs energy change is related to the equilibrium constant of the reaction by the expression

  $$\Delta_r G^\circ = -2.303\, RT \log K$$
- The standard Gibb's energy change is given by

  $$\Delta_r G^\circ = \sum \nu_P \Delta_f G^0 \text{ (products)} - \sum \nu_R \Delta_f G^0 \text{ (reactants)}$$

TERMINAL EXERCISE

1. What do you call the measure of disorder or randomness in a system?
2. Predict the sign of ΔS for each of the following processes.

   (i) H_2 (g) $\rightarrow$ 2H (g)

   (ii) O_2 (g, 300 K) $\rightarrow$ O_2 (g, 500 K)
3. Define entropy.
4. Explain why entropy is not a good criteria for determining the spontaneity of a process?

5. What is the relationship between the enthalpy and the entropy change for a system at equilibrium?

6. For the reaction

   $O_3\ (g) + O\ (g) \rightarrow 2O_2\ (g)$

   $\Delta_r H$ = - 391.9 kJ mol^{-1} and $\Delta_r S$ = 10.3 J K^{-1} mol^{-1} at 298 K. Calculate $\Delta_r G$ at this temperature and state whether the reaction is spontaneous or not.

7. What happens to $\Delta_r G$ during

   (a) a spontaneous process

   (b) a non-spontaneous process

   (c) a process at equilibrium

8. Calculate $\Delta_r G°$ at 298 K for the reaction

   $2NO_2\ (g) \rightarrow N_2O_4\ (g)$

   Given $\Delta_r H$ = - 57.20 kJ mol^{-1} and $\Delta_r S$ = - 175.8 J K^{-1} mol^{-1}

   Is this reaction spontaneous?

9. The standard Gibbs energies of formation at 298 K are – 202.85 kJ mol^{-1} for NH_4Cl (s), – 16.45 kJ mol^{-1} for NH_3 (g) and – 95.3 kJ mol^{-1} for HCl (g)

   (a) What is $\Delta_r G°$ for the reaction

   $NH_4Cl\ (s) \rightarrow NH_3\ (g) + HCl\ (g)$

   (b) Calculate the equilibrium constant for this decomposition.

10. For the following reaction

    $CCl_4\ (l) + H_2\ (g) \rightarrow HCl\ (g) + CHCl_3\ (l)$

    $\Delta_r G°$ = – 103.7 kJ mol^{-1} at 298 K. Calculate the equilibrium constant for this reaction.

ANSWERS TO INTEXT QUESTIONS

10.1

1. $$\Delta_{fus}S = \frac{\Delta_{fus}H}{T} = \frac{6.02\ \text{kJ mol}^{-1}}{273\ \text{K}} = \frac{6.02\times10^{3}\ \text{J mol}^{-1}}{273\ \text{K}}$$

   $$= 22.0\ \text{J mol}^{-1}\ \text{K}^{-1}$$

2. 1 mol of solid, 1 mol of liquid, 1 mol of gas.
3. Decrease (b) Decrease (c) Increase

10.2

1. $\Delta G = -103.7$ kJ. Therefer the reaction is spontaneous.
2. (iii)

10.3

1. $\Delta G^{o} = -2.303\, RT \log K$
2. 2.2×10^{4}

MODULE - V
CHEMICAL DYNAMICS

11. Chemical Equilibrium
12. Ionic Equilibrium
13. Electrochemistry
14. Chemical Kinetics
15. Adsorption and Catalysis

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11

CHEMICAL EQUILIBRIUM

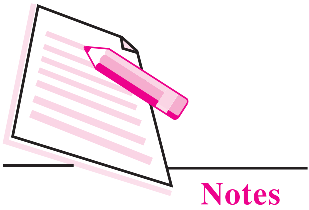
When reactants are mixed in exact stoichiometric proportion to perform a chemical reaction, it is believed that all the reactants would be converted into products with the release or absorption of energy. This is not true in all cases. Many chemical reactions proceed only to a certain extent and stop. When analysed, the resulting mixture contains both the reactants and products. It is because when reactants combine to form products, the products also start combining to give back the reactants.

When such opposing processes take place at equal rates, no reaction appears to take place and it is said that a state of equilibrium has reached. In this lesson, we will examine many aspects of chemical equilibrium. We shall also discuss how can we control the extent to which a reaction can proceed by changing the various conditions of the equilibrium.

OBJECTIVES

After reading this lesson you will able to :

- differentiate between static and dynamic equilibrium;
- identify and differentiate between reversible and irreversible reactions;
- list and explain characteristics of equilibrium state;
- explain the equilibria involving physical changes and their characterstics;
- differentiate between equilibrium in homogeneous and tieterogeneous symbols;
- state and explain the law of mass action;
- apply the law of equilibrium and write expression of equilibrium constant for different types of chemical reactions namely, homogeneous and heterogenous;



- state and derive the relation between K_c and K_p and carry out some calculations involving them and
- list the factors which affect the state of equilibrium and state and apply Le-Chatelier principle.

11.1 STATIC AND DYNAMIC EQUILIBRIUM

The state of equilibrium can be observed in physical and chemical systems. Also, equilibrium can be static or dynamic in nature. A book lying on the table is an example of static equilibrium. The forces of action and reaction cancel each other and no change takes place. Thus it is a case of static equilibrium. On the other hand, when an escalator is coming down and a passenger is going up at the same speed it is a case of dynamic equilibrium. Here, because both are moving in opposite directions and at the same speed, no net change takes place. The equilibrium established in the above examples are in physical systems.

11.2 REVERSIBLE AND IRREVERSIBLE REACTIONS

Chemical reactions can be classified as : **Reversible and Irreversible reactions.**

11.2.1 Reversible reactions

Consider the reaction between ethanol and acetic acid. When mixed in the presence of dilute sulphuric acid they react and form ethyl acetate and water.

$$C_2H_5OH(l) + CH_3COOH\ (l) \xrightarrow{H^+} CH_3COO\ C_2H_5(l) + H_2O(l)$$

On the other hand, when ethyl acetate and water are mixed in the presence of dilute sulphuric acid the reverse reaction occurs.

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{H^+} CH_3COOH(l) + C_2H_5OH(l)$$

It may be noted here that the second reaction is reverse of the first one and under the same conditions, the two reactions occur simultaneously. Such reactions which occur simultaneously in opposite directions are called reversible reactions.

A reaction is said to be reversible if under certain conditions of temperature and pressure, the forward and reverse reactions occur simultaneously.

Reversible reactions are indicated by placing two half arrows pointing in opposite directions ($\rightleftharpoons$) between the reactants and products. Thus the above reaction is more appropriately written as

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O(l)$$

When ethyl acetate and water are formed in the forward reaction the reverse reaction also starts in which ethanol and acetic acid are formed. After some time the concentrations of all the reactants and products become constant. This happens when the rates of forward and reverse reactions become equal; and all the properties of the system become constant. It is said that the system has attained *state of equilibration*. However it may be noted that the state of equilibrium is reached only if the reaction is carried out in a closed system. At the time of equilibrium, forward and reverse reactions are taking place and it is in a state of dynamic equilibrium because no change is taking place.

A reversible reaction is said to be in the equilibrium state when the forward and backward reaction occur simultaneously at the same rate in a closed system and the concentrations of reactants and products do not change with time

A common example of reversible reactions of the type $A + B \rightleftharpoons C + D$

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOH + H_2O$$

The following graphs Fig. 11.1 shows the equilibrium state in a reversible reaction.

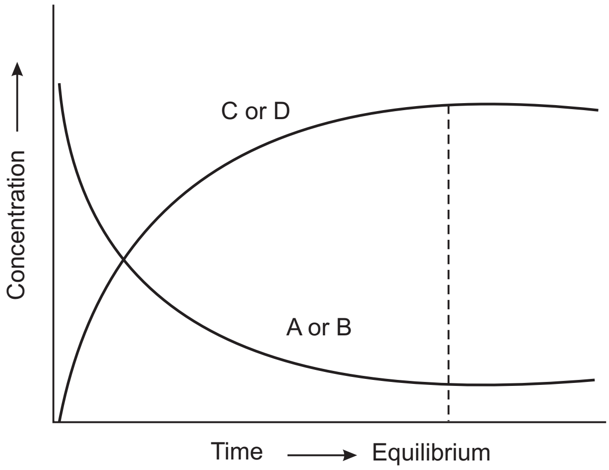


Fig. 11.1 : *Equilibrium in reversible reaction*

The graph depicts that the rate of forward reaction gradually decreases while the rate of backward reaction increase till they become constant and equal to each other.

11.2.2 Irreversible Reactions

Most of the reactions occur only in one direction. They are called *irreversible reactions*. For example when carbon is burnt in air to form carbon dioxide the reaction goes only in one direction i.e. in the direction of formation of carbon dioxide

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$$

Strictly speaking all reactions are considered to be reversible. But the rate of reaction in one particular direction is extremely small compared to the other. Thus the reaction proceeds practically in one direction to near completion, leaving a negligibly small amount of reactant at the end.

When hydrochloric acid is mixed with sodium hydroxide, a base, in equimolar quantities, a neutralisation reaction takes place; with the formation of salt and water.

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

This reaction proceeds to completion in the forward direction. Similarly when a solution of silver nitrate is added to a solution of sodium chloride silver chloride is precipitated immediately.

$$NaCl\,(aq) + AgNO_3\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)$$

11.3 CHARACTERISTICS OF EQUILIBRIUM STATE

1. The state of chemical equilibrium is reached in a reversible reaction when;
   - (i) the temperature of the system attains a constant value.
   - (ii) the pressure of the system attains a constant value.
   - (iii) the concentrations of all the reactants and products attain constant values.

The state of equilibrium has following characteristics properties :

(i) Chemical Equilibrium is dynamic in nature

The chemical equalibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no “net” change occurring in the system.

(ii) Equilibrium can be attained from either side

The same state of equilibrium (characterized by its equilibrium constant which is discussed later can be reached whether the reaction is started from the reactants or products side. For example, the same equilibrium

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

is established whether we start the reaction with N_2O_4 or NO_2.

(iii) Equilibrium can be attained only in a closed system

Equilibrium can be attained only if no substance among, reactants or products, is allowed to escape i.e. the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container, e.g.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape, e.g.

$$FeCl_3(aq) + 3\,NH_4SCN(aq) \rightleftharpoons Fe\,(SCN)_3\,(s) + 3\,NH_4Cl(aq)$$

(iv) A catalyst can not change the equilibrium state

Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

11.4 EQUILIBRIUM IN PHYSICAL PROCESSES; PHASE EQUILIBRIUM

State of equilibrium can also be reached in physical processes.

11.4.1 Liquid – Vapour Equilibrium

Let us take some quantity of a liquid in an empty container and close it. Initially the vapour pressure above the liquid will be zero. The liquid will evaporate and its vapour will fill the empty space above it.

$$\text{Liquid} \rightarrow \text{Vapour}$$

The rate of evaporation is maximum in beginning. As vapours build up, its pressure increases and the rate of evaporation slows down. Also the reverse process of condensation begins (Fig. 11.2).

$$\text{Vapour} \rightarrow \text{Liquid}$$

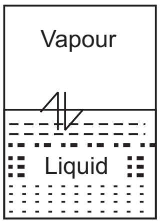


Fig. 11.2 : *Liquid Vapour equilibrium*

and its rate gradually increases with the increase in the vapour pressure. After some time the two rates (of evaporation and condensation) become equal and the following equilibrium is established.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

At equilibrium the vapour pressure reaches its maximum value and is known as the **saturated vapour pressure** or simply the vapour pressure. At a fixed temperature, each liquid has its own characteristic vapour pressure. The vapour pressure of a liquid increases with rise in temprature.

11.4.2 Solid – Vapour Equilibrium

Volatile solids sublime to form vapour. The situation is just similar to the liquid vapour system. When kept in a closed container at a constant temperature the following equilibrium is established.

$$\text{Solid} \rightleftharpoons \text{Vapour}$$

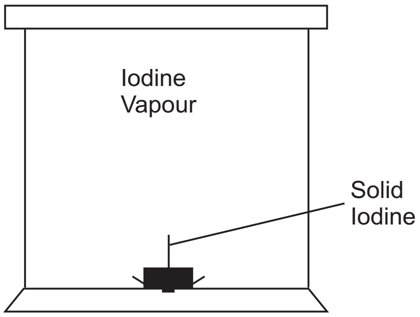


Fig. 11.3 : *Solid vapour equilibrium*

Such an equilibrium can be established by keeping some solid iodine in a gas jar covered with a lid. (Fig. 11.3). Gradually the purple coloured iodine vapours fill the jar and the following equilibrium is established.

$$I_2(s) \rightleftharpoons I_2(g)$$

11.4.3 Solid – Liquid Equilibrium

Below its freezing point a liquid freezes spontaneously

Liquid → Solid

When heated above its melting point the solid melts spontaneously :

Solid → Liquid

At the melting point, the two phases are in equilibrium

Solid $\rightleftharpoons$ Liquid

because the above two processes occur simultaneously and at the same rate. Such an equilibrium is characterized by its temperature i.e. the melting point of the solid.

11.4.4 Solute – Solution Equilibria

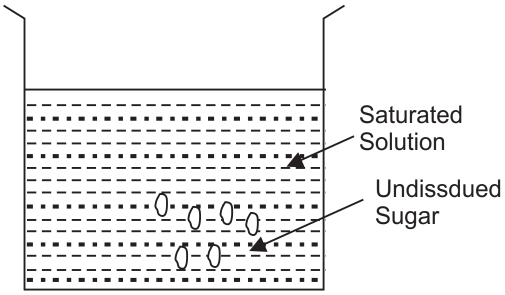


Fig. 11.4 : *Solute - Solution Equilibrium*

When sugar crystals are put in a saturated solution of sugar in water; it will appear that no change is taking place and sugar appears to remain undissolved. Actually, the undissolved sugar does dissolve in the saturated sugar solution; and an equal amount of sugar seperates out from the solution. The solid sugar and the sugar solution form an equilibrium system which is dynamic in nature.

$$\text{sugar (s)} \rightleftharpoons \text{sugar solution (saturated)}$$

The equilibrium is established when the rate of dissolution of sugar becomes equal to the rate of crystallisation. In general such equilibrium can be represented as

$$\text{solute (s)} \rightleftharpoons \text{solution (saturated)}$$

This equilibrium is known as **Solubility Equilibrium.**

11.4.5 Phase and Phase Equilibrium

You must have noticed in each of the above equilibria the system consists of two distinct parts; solid, liquid, solution or vapour. Each of these parts is called a phase.

A phase is defined as a homogenous part of a system which has uniform composition and properties throughout.

A phase is not the same as physical state. A mixture of two solids, even when powdered finely is a two phase system. This is because particles of the two solids have different chemical compositions and physical properties. Completely miscible liquids, solutions and all gaseous mixture constitute only one phase each.

All the cases of physical equilibrium are in fact the systems in which different phases are in equilibrium; only if they contain, at least one common component. A dynamic exchange of the common component between two phases takes place. When the rates of exchange becomes equal the equilibrium is established. In solid solute and solution equilbrium the example given earlier, sugar is the common component.

11.5 EQUILIBRIUM IN HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

11.5.1 Homogeneous and Heterogeneous Systems

Homogeneous system is one which has one phase. It has the same chemical composition and uniform properties throughout. It is formed by particles of molecular size only. Pure solids, liquids, gases and solutions are the examples of homogeneous systems.

A system consisting of only one phase is called a homogeneous system

Heterogeneous system, on the other hand has at least two phases – a mixture of solids or immiscible liquids constitutes a heterogeneous system.

Any system consisting of two or more phases is called heterogeneous system

11.5.2 Homogeneous and Heterogeneous Equilibrium Systems

Equilibrium can be established in either type of systems. Since all physical equilibria involve at least two phases, therefore these are all examples of heterogeneous equilibrium. But chemical equilibrium can be homogeneous or heterogeneous in nature. It is homogeneous if both the reactants and products are present only in one phase gas or liquid and heterogeneous if present in more than one phase. In the following sections we shall study such systems.

11.5.3 Homogeneous Chemical Equilibrium System

(a) Gas – Phase homogeneous systems

Such systems contain only gaseous reactants and products. Since all gaseous mixtures are homogeneous in nature they constitute only one phase. Following are examples of this type of equilibrium:

(i) $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

(ii) $2N_2O_5\ (g) \rightleftharpoons 4NO_2\ (g) + O_2\ (g)$

(b) Liquid – Phase homogeneous systems

These are the systems in which both the reactants and products are present in only one liquid phase (as a solution) for example :

(i) $CH_3\ COOH\ (l) + C_2H_5OH\ (l) \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5(l) + H_2O\ (l)$

(ii) $KCN\ (aq) + H_2O\ (l) \rightleftharpoons HCN\ (aq) + KOH\ (aq)$

11.5.4 Heterogeneous Chemical Equilibrium Systems

The systems in which reactants and products are present in more than one phase belong to this type. For example :

(i) $Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

(ii) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

INTEXT QUESTIONS 11.1

1. What is a reversible reaction? Give two examples.
2. When does a reaction reach equilibrium state?
3. How would you know whether a system has reached the equilibrium state or not?
4. Give two examples of physical equilibrium.
5. Give two example each of chemical homogeneous and heterogeneous equilibria.

11.6 LAW OF MASS ACTION

Equilibrium state of a reversible reaction is characterized by its equilibrium constant, which is related to the equilibrium concentrations of all the reactants and products. The method of writing the expression for equilibrium constant was given for the first time by Guldberg and Wage in 1863 in the form of the **law of mass action** which states:

The rate at which a substance reacts is proportional to its active mass (molar concentration) and the overall rate of the reaction is proportional to the product of active masses (molar concentrations) of all the reacting substances.

For a reaction

$$A + B \longrightarrow \text{Products}$$

Rate of reaction $\propto [A][B]$

and $= k[A][B]$

where $[A]$ = molar concentration (active mass) of A

$[B]$ = molar concentration of B.

k = constant of proportionality and is called the specific rate constant of the reaction.

Consider a reaction

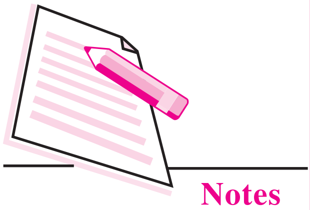
$$2A \longrightarrow \text{Products}$$

It may be written as

$$A + A \longrightarrow \text{Products.}$$

According to the law of mass action state

$$\begin{aligned} \text{rate} &\propto [A]\ [A] \\ &\propto [A]^2 \\ &= k[A]^2 \end{aligned}$$



For the reaction

$$aA \longrightarrow \text{Products}$$

$$\text{rate} \propto [A]^a$$

$$= k[A]^a$$

For a more general reaction

$$aA + bB \longrightarrow \text{Products}$$

$$\text{Rate} = k[A]^a\,[B]^b$$

On applying the law of mass action to the reversible reaction

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

the rate of the forward reaction r_f is

$$r_f = k_f[A]^a[B]^b$$

and the rate of the reverse or backward reaction, r_b is

$$r_b = k_b[C]^c[D]^d$$

where k_f and k_b are the rate constants of the forward and backward reactions reversibly.

At equilibrium

Rate of forward reaction = rate of backward reaction

$$r_f = r_b$$

or $$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

Rearranging these

$$K_{eqm} = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Here $\mathbf{K_{eqm}}$ = equilibrium constant of the reaction. It is also called the concentration equilibrium constant and the symbol given is K_c.

It may be noted here that the powers of concentration terms in the expressions for rates r_f and r_b are each *equal to* the stoichiometric coefficient of the respective reactant *which is not correct* in all the cases as you will learn later in unit 16. Therefore, this derivation of equilibrium constant is not correct. We can obtain the same relation from thermodynamics or we simply accept the relation as the law of equilibrium as explained in the next section.

11.7 QUANTITATIVE ASPECT OF EQUILIBRIUM STATE

11.7.1 Law of Equilibrium and Concentration Equilibrium Constant

Consider the following equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$$

At equilibrium the concentrations of H_2, I_2 and HI become constant. Also, it has been found experimentally that irrespective of the starting concentrations of H_2 and I_2 the following ratio of concentration terms always remains constant.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Here $[H_2]$, $[I_2]$ and [HI] represent the equilibrium molar concentrations of H_2, I_2 and HI respectively and K_e is called the *concentration equilibrium constant* (some times it is written simply as *K*). In general, for reversible reaction

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

at equilibrium, the following ratio of concentration terms always remains constant at a given temperature.

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

The above relation is known as the **law of equilibrium.** It may be noted here that all the concentrations values in the law of equilibrium are the equilibrium concentrations of reactants and products. The numerator of the law of equilibrium is the product of equilibrium molar concentrations of products, each term being raised to the power equal to its stoichiometric coefficient in the chemical equation and the denominator contains products of similar concentration terms of reactants.

11.7.2 Pressure Equilibrium Constant K_p

In case of gases their partial pressures can also be used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, $\boldsymbol{K_p}$**,** is called the pressure equilibrium constant. For the reaction between H_2 and I_2, K_p is given by

$$K_p = \frac{p^2{}_{HI}}{p_{H_2} \times p_{I_2}}$$

Here p_{H_2}, p_{I_2} and p_{HI} are the **equilibrium partial pressures** of H_2, I_2 and HI respectively. For the general gas phase reaction :

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$

it is given by :

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

11.7.3 Relation between K_p and K_c

For a general gas phase reaction at equilibrium

$$aA\ (g) + b\ B\ (g) \rightleftharpoons c\ C\ (g) + d\ D\ (g)$$

The pressure and concentration equilibrium constants Kp and Kc are

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \text{ and } K_C = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

For a gaseous substance i, the ideal gas equation is

$$p_i V = n_i RT$$

where p_i and n_i are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as

$$p_i = \frac{n_i}{V} RT = c_i\ RT$$

Where c_i is the molar concentration or molarity of 'i' expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for K_p.

$$K_p = \frac{(c_C RT)^c\ (c_D RT)^d}{(c_A RT)^a\ (c_B RT)^b}$$

$$= \frac{c_C^c\ c_D^d}{c_A^a\ c_B^b}\ (RT)^{(c+d)-(a+b)}$$

Using the square bracket notation for molar concentration the relation can be written as

$$K_p = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}\ (RT)^{(n_P - n_R)}$$

$$= K_c (RT)^{\Delta n_g}$$

where Δn_g is the change in the moles of gaseous substances in the reaction and is equal to the difference in the moles of gaseous products n_P and the moles of gaseous reactants, n_R. Δn_g may be zero positive or negative.

(i) In the reaction

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

Here n_P = moles of the gaseous product is equal to 2

n_R = moles of gaseous reactant H_2 and I_2 is equal to 2 (as 1 + 1).

Hence $\Delta n_g = n_P - n_R = 2 - 2 = 0$

$\Delta n_g = 0$

(ii) In the reaction

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

$n_P = 2,\ n_R = 1 + 3 = 4$

and $\Delta n_g = 2 - 4 = -2$

(iii) In the reaction involving solids and gases

$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

$\Delta n_g = 1$

11.7.4 Expressions of Equilibrium Constant for Some Reactions

The law of equilibrium can be applied to write down expressions of K_c and K_p for some reactions

11.8 HOMOGENEOUS EQUILIBRIA

(i) Decomposition of N_2O_4

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}\ ;\ K_p = K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$

(ii) Oxidation of sulphur dioxide

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}\ ;\ K_p = \frac{p^2_{SO_3}}{p^2_{SO_2}\cdot p_{O_2}}$$

(iii) Esterification of acetic acid with ethanol

$$CH_3COOH\,(I) + C_2H_5OH\,(I) \rightleftharpoons CH_3COOC_2H_5\,(I) + H_2O(l)$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

In this reaction no gas is involved, therefore expression for K_p is meaningless.

11.8.1 Heterogeneous Equilibrium

Consider the following equilibrium

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

According to the law of equilibrium

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

Here $CaCO_3$ and CaO are pure solids. The concentration of any solid is constant at a fixed temperature therefore these are not written in expression for equilibrium constant for hetrogenous reactions. Equilibrium constants for the reaction can be written as

$$K_c = [CO_2] \text{ and } K_p = Pco_2$$

Following are some more examples of heterogenous equilibrium

(i) Reaction between iron and steam

$$3\,Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$$

$$K_c = \frac{[H_2]^4}{[H_2O]^4}\,;\ K_p = \frac{p_{H_2}^4}{p_{H_2O}^4}$$

(ii) Liquid – Vapour Equilibrium

$$H_2O(I) \rightleftharpoons H_2O\,(g)$$

$$K_c = [H_2O;\,g]\ ;\ K_p = p_{H_2O}\,.$$

11.9 CHARACTERISTICS OF EQUILIBRIUM CONSTANT

11.9.1 Equilibrium Constant and Chemical Equation

The expression of equilibrium constant depends upon the manner in which the chemical equation representing it is written. For the reaction

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

The equilibrium constant K is given by $K = \frac{[HI]^2}{[H_2][I_2]}$

When the same reaction is written as

(a) $\frac{1}{2}\,H_2\,(g) + \frac{1}{2}\,I_2\,(g) \rightleftharpoons HI\,(g)$

the corresponding equilibrium constant K_1 is given by

$$K_1 = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$$

It may be noted that equilibrium constants K and K_1 are related as $K_1 = \sqrt{K}$

(b) When the reaction is written as reverse

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

$$K_2 = \frac{[H_2][I_2]}{[HI]^2}$$

Here it can be seen that

$$K_2 = \frac{1}{K}$$

Similar relationship is also observed in the pressure equilibrium constant K_p. Thus the expression of equilibrium constant depends on how the reaction is expressed in the form of a chemical equation.

11.9.2 Units of Equilibrium Constant

Units of equilibrium constant K_c or K_p depend upon the fact whether during the reactions there is any change in the moles of substance or not.

(a) **The reactions in which there is no change** in moles of substance i.e.

$$\Delta n = 0.$$

The equilibrium constant for such reaction has no units. For example in the reaction between H_2 and I_2

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad K_p = \frac{p_{HI}^2}{p_{H_2} \cdot p_{I_2}}$$

$$K_c = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})(\text{mol L}^{-1})} \qquad K_p = \frac{\text{bar}^2}{(\text{bar})(\text{bar})}$$

∴ Hence K_p and K_c have no units in such cases.

(b) The reaction where there is change in the moles of substance i.e. $\Delta n \neq 0$.

The equilibrium constant for such reactions has units which depend upon the change in moles of substances.

For example :

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

$$\Delta n = \Delta n_P - \Delta n_R$$

$$= 2 - 4 = -2$$

The units of K_c for this reaction would be $(\text{mol L}^{-1})^{-2}$ or $L^2\,\text{mol}^{-2}$ and those of K_p would be bar^{-2} as shown below :

The equilibrium constant for such reactions are

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}}$$

$$K_c = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})(\text{mol L}^{-1})^3}$$

$$= (\text{mol L}^{-1})^{-2}$$

$$= L^2\,\text{mol}^{-2}$$

$$K_p = \frac{\text{pressure}^2}{\text{pressure. pressure}^3}$$

$$= \text{pressure}^{-2}$$

$$= \text{bar}^{-2}$$

For the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

$\Delta n = 2 - 1 = 1$. Therefore,

The units for K_c and K_p are

$K_c = \text{mol L}^{-1}$ and $K_p = \text{bar}$

11.9.3 Significance of the Magnitude of *K*

The equilibrium constant of a reaction has a constant and characteristic value at a given temperature. The changes in starting concentration, pressure and the presence of a catalyst do not change the value of the equilibrium constant. However if the temperature is changed. The value of the equilibrium constant also changes.

The magnitude of the equilibrium constant is a measure of the extent upto which a reaction proceeds before the equilibrium is reached. The magnitude of K is large when the products are present in larger amounts than the reactants in the equilibrium mixture. For the reaction

Notes

$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ $\qquad K_c = 90$ at 298 K

and for $2CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$ $\quad K_c = 2.2 \times 10^{22}$ at 1000 K.

A large value of K_c for the second reaction indicates that amount of products is much more than the reactants present at the time of equilibrium. Thus the magnitude of equilibrium constant tells us about the position of the equilibrium.

11.9.4 Calculation of Equilibrium Constants

Equilibrium constants K_c and K_p can be calculated if the equilibrium concentrations or partial pressures are known or can be obtained from the given data. The following examples illustrate the calculations.

Example 11.1 : Calculate the equilibrium constant for the reaction

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

If at equilibrium 1 mol of A, 0.5 mole of B, 3.0 mole of C and 10 mol of D are present in a one litre vessel.

Solution : From the law of equilibrium

$$K_c = \frac{[C][D]}{[A][B]}$$

Since the volume of the vessel is one litre, the number of moles of A, B, C and D are equal to their concentrations. Thus

[A] = 1 mol L^{-1}, [B] = 0.5 mol L^{-1}, [C] = 3.0 mol L^{-1} and [D] = 10 mol L^{-1} and

$$K_c = \frac{(3.0\text{ mol L}^{-1})(10\text{ mol L}^{-1})}{(1\text{ mol L}^{-1})(0.5\text{ mol L}^{-1})}$$

$$= \frac{3.0 \times 10}{1 \times 0.5} = 60$$

Example 11.2 In an experiment carried out at 298 K, 4.0 mol of NOCl were placed in a 2 litre flask and after the equilibrium was reached 1.32 mol of NO were formed. Calculate K_c at 298 K for the reaction

$$2NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$$

Solution Calculation of equilibrium concentrations

$$\text{(i)}\quad [NO] = \frac{\text{No. of moles of NO}}{\text{Volume}} = \frac{1.32\text{ mol}}{2L} = 0.66\text{ mol L}^{-1}$$

$$\text{(ii)}\quad [Cl_2] = \frac{\text{No. of moles of } Cl_2}{\text{Volume}} = \frac{\frac{1}{2}(\text{No. of moles of NO})}{\text{Volume}}$$

$$= \frac{1.32\ \text{mol}}{2 \times 2\text{L}} = 0.33\ \text{mol L}^{-1}$$

(iii) $$[\text{NOCl}] = \frac{\text{No. of moles of NOCl}}{\text{Volume}} = \frac{\text{(Initial moles - moles decomposed)}}{\text{Volume}}$$

$$= \frac{(4.0 - 1.32)\ \text{mol}}{2\ \text{L}} = \frac{2.68\ \text{mol}}{2\ \text{L}} = 1.34\ \text{mol L}^{-1}$$

For the reaction

$$2\text{NOCl (g)} \rightleftharpoons 2\text{NO (g)} + \text{Cl}_2\text{ (g)}$$

$$K_c = \frac{[\text{NO}]^2\,[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.66\ \text{mol L}^{-1})^2\ (0.33\ \text{mol L}^{-1})}{(1.34\ \text{mol L}^{-1})^2} = \frac{(0.66)^2 \times 0.33}{(1.34)^2}$$

$$= 0.080\ \text{mol L}^{-1}$$

$$K_c = 0.080\ \text{mol L}^{-1}$$

Example 11.3 : 2 moles of HI were heated in a vessel of one litre capacity at 713 K till the equilibrium was reached. At equilibrium HI was found to be 25% dissociated. Calculated K_c and K_p for the reaction.

Solution Initial moles of HI = 2

$$\text{Moles of HI dissociated} = \frac{25 \times 2}{100} = 0.5\ \text{mol}$$

Moles of HI at equilibrium = 2.0 – 0.5 = 1.5 mol

The dissociation of HI occurs as

	2HI (g)	$\rightleftharpoons$	$\text{H}_2\text{ (g)}$	+	$\text{I}_2\text{ (g)}$
Initial moles	2		0		0
Equilibrium moles	(2 – 0.5)		0.25		0.25
	1.5 mol		0.25 mol		0.25 mol
Volume of reaction vessel	1L		1L		1L
Equilibrium concentration	1.5 mol L^{-1}		0.25 mol L^{-1}		0.25 mol L^{-1}

For the reaction

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.25\ \text{mol L}^{-1})\,(0.25\ \text{mol L}^{-1})}{(1.5\ \text{mol L}^{-1})^2}$$

$$= \frac{(0.25)^2}{(1.5)^2} = 0.028$$

Also $K_p = K_c\ (RT)^{\Delta n_g}$

For this reaction $\Delta n_g = n_p - n_R = 2 - 2 = 0$

$\therefore K_p = K_c = 0.028$

Example 11.4 : Calculate K_p for the reaction $COCl_2 \rightleftharpoons CO + Cl_2$ in atm and Nm^{-2}. The equilibrium partial pressures of $COCl_2$, CO and Cl_2 are 0.20, 0.16 and 0.26 atm respectively.

(1 atm = 101300 Nm^{-2})

Solution : (i) K_p in atmospheres

$COCl_2(g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$

$$K_p = \frac{p_{co} \times p_{Cl_2}}{p_{COCl_2}} = \frac{(0.16\ \text{atm})(0.26\ \text{atm})}{(0.20\ \text{atm})} = \frac{0.16 \times 0.26}{0.20}\ \text{atm}$$

$= 0.21$ atm.

(ii) K_p in Nm^{-2}

$K_p = 0.21$ atm and 1 atm = 101300 Nm^{-2}

$\therefore K_p = (0.21\ \text{atm})\ (101300\ Nm^{-2}\ atm^{-1}) = 21273\ Nm^{-2}$

Example 11.5 : When equal number of moles of ethanol and acetic acid were mixed at 300 K, two-third of each had reacted when the equilibrium was reached. What is the equilibrium constant for the reaction?

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

Solution : Let n moles each of acetic acid and ethanol be mixed initially. Then the number of moles each reacted = $\frac{2}{3}\ n$.

Let V be the volume of the reaction mixture in litres.

	$CH_3COOH\ (l)$ +	$C_2H_5OH\ (l)$ $\rightleftharpoons$	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$
Initial mole	n	n	0	0
Equilibrium concentration in moles	$(n - \frac{2}{3}n)$	$(n - \frac{2}{3}n)$	$\frac{2}{3}n$	$\frac{2}{3}n$
	$\frac{1}{3}n$	$\frac{1}{3}n$	$\frac{2}{3}n$	$\frac{2}{3}n$
Equilibrium concentration	$\frac{n}{3V}$	$\frac{n}{3V}$	$\frac{2n}{3V}$	$\frac{2n}{3V}$

Notes

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{\left(\frac{2n}{3V}\right)\left(\frac{2n}{3V}\right)}{\left(\frac{n}{3V}\right)\left(\frac{n}{3V}\right)} = 2 \times 2 = 4$$

$$K_c = 4$$

INTEXT QUESTIONS 11.2

1. For a reversible rection

   $2A + B \rightleftharpoons 3C + 3D$

   Write the expression for the equilibrium constant

2. What is the relation between K_p and K_c.

3. (i) Apply the law of equilibrium to the following and write the expression for K_p and K_c.

   (a) $CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$

   (b) $I_2\ (s) \rightleftharpoons I_2\ (g)$

   (ii) For the above reaction write equation for K_p and K_c.

4. The equilibrium constant for the reactions
   (i) $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

   (ii) $\frac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \frac{2}{3}NH_3$

   are K_1 and K_2 respectively. What is the relation between them.

5. What is the significance of the magnitude of equilibrium constant?

11.10 FACTORS AFFECTING EQUILIBRIUM STATE

Supposing a reaction has reached the equilibrium state and then some conditions like concentrations, temperature, pressure etc. are changed, would it be affecting the equilibrium state. If yes how?

In this section, we shall discuss these questions.

The state of equilibrium is in a dynamic balance between forward and backward reaction. This balance can be disturbed by changing concentration, temperature or pressure. If done so a certain net change occurs in the system. The direction of change can be predicted with the help of Le-Chatelier's principle.

11.10.1 Le Chatelier's Principles

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor.

The prinicple can be applied to various situations.

11.10.2 Change in Concentration

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad \Delta H = -92.4 \text{ kJ/mol}$$

The concentration of nitrogen, hydrogen and ammonia become constant at the point of equilibrium. Now if any amount of reactants or ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

(i) **Increase concentration of reactant :** When the concentration of either nitrogen or hydrogen is increased; a net forward reaction will take place which consumes the added reactant.

(ii) Increase in the concentration of any product : If the concentration of product ammonia is increased, a net backward reaction would take place to utilise the added ammonia.

11.10.3 Change in Pressure

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or hetrogeneons system.

Le Chatelier's prinicple for systems involving gases can be studied as follows :

(i) When the number of moles of products is more than the total number of moles of reactants as in the following system

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decrease i.e. backward direction.

(ii) When the number of moles of products is less than reactants. As in the following case

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

According to Le Chatelier's principle increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing i.e. to the product side as $\Delta n_g = 2$. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing i.e. backward direction.

(iii) When there is no change in the total number of moles of reactant and product as in the following state of equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI$$

There is no net change in equilibrium state when pressure is changed.

11.10.4 Change of Temperature

According to Le Chatelier's prinicple when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

(i) Exothermic equilibrium : For the following system of equilibrium of exothermic nature :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H = -92.4 \text{ kJ/mol}$$

according to Le Chatelier's prinicple increase in temperature brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the backward direction and some ammonia will decompose producing nitrogen and hydrogen. Similarly if the temperature is decreased the equilibrium shifts to the forward direction.

(ii) **Endohermic equilibrium**

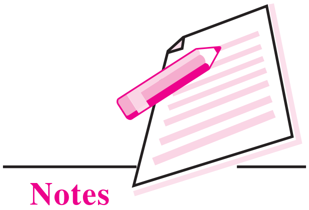
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \quad \Delta H = +180.7 \text{ kJ/mol}^{-1}$$

If the temperature is increased the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the forward direction. If the temperature in decreased it will bring a 'net' change to equilibrium in the backward direction i.e. direction in which it is exothermic.

Addition of a Catalyst : It does not affect the equilibrium. However it helps to achieve the equilibrium faster.

11.10.5 Applications of Le Chatelier's Principle

It can be applied to physical as well as chemical equilibria



Notes

(A) Physical Equilibria

(1) Melting of Ice

$$\text{Ice} \rightleftharpoons \text{Water}; \qquad \Delta H = +\,6\ \text{kJ/mol}^{-1}$$

The change of ice to water is endothermic process. According to Le Chatelier's principle if the temperature is increased the net change will take place in the forward direction some ice will melt into water.

When the pressure is increased on the equilibrium system, then the volume should decrease; according to Le Chatelier's principle the net change in equilibrium takes place in the forward direction and ice melts. Therefore, ice melts on increasing the pressure.

(2) Vaporization of Water

$$\text{Water(l)} \rightleftharpoons \text{Water vapour}; \quad \Delta H = +\ \text{ve}$$

This process occurs with a large increase in volume since $\Delta n_g = 1 - 0 = +1$, and it occurs with absorption of heat.

Increasing the temperature results in more vapour formation (endothermic process). Since $\Delta n_g = +1$, increase in pressure results in a net change in equilibrium in the backward direction as the volume of water vapours is more than that of liquid water for a given mass of water.

(3) Solubility Equilibrium

The equilibrium is

$$\text{Solute (s)} \rightleftharpoons \text{Solute (solution)}$$

The process of dissolution can be endothermic or exothermic. In case of solutes like KCl, KNO_3 and NH_4Cl, ΔH is positive (endothermic) and more solute will dissolve on heating. Thus, the solubility increases with rise in temperature. In case of solutes like KOH and NaOH the ΔH is negative (exothermic) and their solubility decreases on heating.

(B) Chemical Equilibra

(1) Favourable Conditions for Synthesis of Ammonia : This reaction is of great industrial importance. During the synthesis of ammonia such conditions are maintained which favour the ‘net’ forward reaction namely low temperature and high pressure. Addition of catalyst makes the reaction occur fast. Besides, nitrogen and hydrogen gases are continuously fed into the reaction chamber and ammonia is continuously removed. All this keeps the system under stress and equilibrium is never permitted to be attained, so that the synthesis of ammonia continues to occur.

In industry the reaction is carried out at 450 ^{0}C and 200 atm pressure in the presence of finely divided iron (catalyst) and molybdenum (promotor)

(2) Formation of SO_3

The reaction

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)\ ;\ \Delta H = -\ \text{ve}$$

is extothermic and $\Delta n_g = 2 - 3 = -1$. Formation of SO_3 will be favoured by high pressure and low temperature in the presence of a catalyst.

(3) Formation of NO

The reaction

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)\ ; \qquad \Delta H = +\ \text{ve}$$

is endothermic and $\Delta n_g = 2 - 2 = 0$. The reaction is not affected by pressure changes and is favoured at high temperature. Presence of a suitable catalyst would be helpful.

INTEXT QUESTIONS 11.3

1. What is Le Chatelier's principle?
2. What are the factors that can affect a system at equilibrium?
3. What will happen to solid-vapour equilibrium when the temperature and pressure are decreased.
4. (a) Which of the following will result in 'net' forward reaction in case of

   $$A\,(g) + 2B\,(g) \rightleftharpoons C\,(s) + D\,(g)\ ;\ \Delta H = +\ \text{ve}$$

   (i) addition of C

   (ii) addition of A

   (iii) decrease in pressure

   (iv) increase in temperature

   (b) What are the most favourable conditions for the formation of C and D?

WHAT YOU HAVE LEARNT

- A chemical reaction is said to be reversible under certain conditions, if along with the reactants forming the products, the products also react and form back the reactants simultaneously.

- Reversible reactions do not reach completion stage and result in a state of equilibrium which is reached when two opposite processes occur at the same rate.
- The macroscopic properties of the system do not change once the equilibrium has been established.
- Irreversible reactions are in fact the reversible reactions in which the equilibrium is reached only when a negligible amount of the reactants is left unreacted.
- Chemical equilibrium is dynamic in nature. It can be attained by starting the reaction from any side and only in a closed system.
- When equilibrium is reached as a result of two opposite physical changes, it is called physical equilibrium and when as a result of two opposite chemical changes it is called chemical equilibrium.
- A phase is a homogeneous system or a part of a system which has same composition and uniform properties throughout. It is not same as physical state.
- A system with only one phase is called a homogeneous system and the one with more than one phases is called heterogeneous system.
- Chemical equilibrium can be homogeneous or heterogeneous while physical equilibrium is always heterogeneous.
- For a general reaction aA + bB $\rightleftharpoons$ cC + dD according to the law of equilibrium, the equilibrium constant K is given by the expression

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

- Concentration equilibrium constant K_c is obtained when molar concentration are used for calculating K. Concentrations of pure solids and liquids are constant and are not included in the expression of K_c.
- In case of gaseous systems, the concentration of gases are expressed in terms of their partial pressures. The equilibrium constant thus obtained is called the pressure equilibrium constant, K_p.
- The relation between K_p and K_c is = $K_c\,(RT)^{\Delta n_g}$ where Δn_g is the change in the number of moles of gaseous substances during the reaction.
- Expression of equilibrium constant depends upon how the chemical equation is written for the reaction.

- Magnitude of the equilibrium constant is a measure of how close the reaction is to the completion stage.
- Units of *K* depends upon the change in the number of moles of the substances during the reaction.
- Concentration, pressure and temperature can affect the equilibrium systems and the affect can be qualitatively predicted by Le Chatelier's principle which states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in the direction that tends to neutralize the effect of the disturbing factor.
- Changes in concentration and pressure do result in some chemical reaction, but the value of the equilibrium constant is not changed.
- A catalyst does not change the equilibrium constant. It only helps in reaching the equilibrium state quicker.
- A change in temperature change the value of the equilibrium constant.

TERMINAL EXERCISE

1. What do you understand by reversible and irreversible reactions? Give one example of each.
2. What is physical equilibrium? Give one example?
3. Give characteristics of equilibrium state.
4. Is the phase same as physical state? Illustrate your answer with one example of each.
5. How do homogeneous and heterogeneous systems differ from each other? Which of the following are homogeneous systems?
   (a) Liquid $\rightleftharpoons$ Vapour
   (b) $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$
   (c) $NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$
   (d) $CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$
6. What are K_p and K_c? Derive a relation between them.
7. Write down the expression of K_c for the following. Also give units in each case.

   (a) $N_2O_5\ (g) \rightleftharpoons 2NO_2\ (g) + \frac{1}{2}\ O_2\ (g)$

(b) $CH_4\ (g) + H_2O\ (l) \rightleftharpoons CO\ (g) + 3H_2\ (g)$

(c) $FeCl_3\ (aq) + 3NH_4SCN\ (aq) \rightleftharpoons Fe\ (SCN)_3(aq) + 3NH_4Cl\ (aq)$

8. Write down the expression of K_p for the following and give its units (in terms of atmosphere) in each case

(a) $CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (l)$

(b) $3Fe(s) + 4H_2O(l) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

(c) $2SO_3\ (g) \rightleftharpoons 2SO_2\ (g) + O_2\ (g)$

9. Give the relation between K_c and K_p for the reaction.

$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

10. Using the relaction between K_p and K_c write the expression of

(i) K_p for the reactions given in Q. No.7

(ii) K_c for the reactions given in Q. No.8

11. List the factors that can affect

(i) a system at equilibrium and

(ii) equilibrium constant of a system

12. State the Le Chatelier's Principle.

13. What will be the effect of the following factors on the following systems at equilibrium?

$$2\ X\ (g) \rightleftharpoons 2Y\ (s) + Z\ (g);\ \Delta H = +\ ve$$

(i) Addition of X,

(ii) removal of Z

(iii) addition of a catalyst

(iv) increasing the pressure and

(v) increasing the temperature.

14. 5 moles of HI were produced by the reaction between 7.5 moles of H_2 and 2.6 moles of I_2 vapours at 444^{0}C. What is the equilibrium constant of the reaction

$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

15. The equilibrium constant K_p for the reaction

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

at 333 K is found to be 1.33 atm under a total pressure of 1 atm. Calculate K_p for the reaction

$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$

at 333 K and under 1 atm pressure.

16. At 444 ^{0}C, 0.30 mole of H_2 and 0.30 mole of I_2 were taken in a one litre flask. After some time the equilibrium H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g) was established and it was found that the concentration of I_2 decreased to 0.06 mol L^{-1}. Calculate the value of K_c for the reaction at this temperature.

17. The equilibrium constant for the reaction.

    $CH_3COOH(l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ is 4.0.

    What will be the composition of the equilibrium mixture if 1 mole of acetic acid is taken with 8 moles of ethanol?

18. K_c for the reaction

    $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

    at 400^{0}C was found to be 0.5 L^2 mol^{-2}. Calculate K_p of this reaction in atm.

ANSWERS TO INTEXT QUESTIONS

11.1

1. A chemical reaction is said to be reversible, if under certain conditions its products also react and form back the reactants.

   Examples :

   $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

   $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$

2. A reaction reaches an equilibrium state when two opposing reactions occur at the same rate and balance each other at a particular temperature.

3. When a system reaches the equilibrium state, its temperature, pressure and concentrations of all the reactants and products do not change any further with time.

4. (i) Water-vapour system in a closed container at a constant temperature.

   (ii) A saturated solution containing some undissolved solute at a constant temperature.

5. (i) Homogeneous systems :

   $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

   $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$

(ii) Heterogeneous systems :

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2(g)$$

$$Zn\,(s) + CuSO_4\,(aq) \rightleftharpoons Cu\,(s) + ZnSO_4\,(aq)$$

11.2

1. $K = \dfrac{[C]^3\,[D]^3}{[A]^2\,[B]}$

2. $K_p = K_c\,(RT)^{\Delta n_g}$

3. (i) (a) $K_c = \dfrac{[CO][H_2O]}{[CO_2][H_2]}$; $K_p = \dfrac{p_{CO} \times p_{H_2O}}{p_{CO_2} \times p_{H_2}}$

   (b) $K_c = [I_2]$; $K_p = P_{I_2}$

   (ii) For the first reaction $\Delta n_g = (1 + 1) - (1 - 1) = 0$, hence $K_c = K_p$ while for the second reaction $\Delta n_g = 1 - 0 = +1$

   $\therefore \quad K_p = K_c\,(RT)$ or $K_c = \dfrac{K_p}{RT}$ or $K_c < K_p$.

4. $K_1 = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ and $K_2 = \dfrac{[NH_3]^{2/3}}{[N_2]^{1/3}\,[H_2]}$

   $\therefore \quad K_1 = [K_2]^3$.

5. It is a measure of the extent up to which a reaction proceeds before the equilibrium is reached.

11.3

1. Le Chatelier's principle states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in a direction that tends to neutralize the effect of the disturbing factor.
2. Changes in pressure, temperature and concentrations of reactants or products.
3. When the temperature is decreased some vapour will condense and when the pressure is decreased some solid will sublime.
4. (a) (ii) and (iv)

   (b) High temperature, increase in pressure, presence of a catalyst and continuous removal of D.

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12

IONIC EQUILIBRIUM

In the first lesson of this module you learnt about chemical equilibrium, its types and the factors affecting the state of equilibrium. In this the lesson you will learn about the equilibria involving ionic species. The equilibria involving acids and bases are critically important for a wide variety of reactions. The use of buffer solutions for *p*H control is of significance in living systems, agriculture and industrial processes. Similarly, the solubility equilibrium established in the solutions of sparingly soluble salts is also very important. For example, our bones and teeth are mostly calcium phosphate, $Ca_3(PO_4)_2$, a slightly soluble salt. We would focus our attention primarily on the acid- base and the solubility equilibria and some interrelated aspects concerning these equilibria such as *p*H, buffer solutions and common ion effect. In this process you would apply the concepts learnt in the first lesson.

OBJECTIVES

After reading this lesson, you will be able to:

- Differentiate between strong and meak electrolyte ;
- Correlate the degree of dissociation and dissociation constant of a weak electrolyte
- define and explain various concepts of acids and bases;
- define conjugate acid-base pairs and identify them in an acid-base equilibrium;
- derive the expressions for the ionisation constants of weak acids and bases;
- correlate the ionisation constants and the strength of acids and bases;
- explain self ionisation of water and derive an expression for its ionic product;
- define pH and correlate it with the nature of aqueous solutions- neutral, acidic or basic;

- define and explain common ion effect in ionisation of weak acids and bases;
- define buffer solutions;
- apply Henderson equation to calculate the pH of acidic and basic buffers;
- explain hydrolysis of salts with the help of chemical equations;
- express solubility equilibrium with the help of an equation;
- identify the relationship between solubility and solubility product for salts of AB, AB$_2$ A$_2$B and A$_2$B$_3$ types;
- illustrate and explain the common ion effect on solubility equilibrium and
- recall some applications of common ion effect .

12.1 STRONG AND WEAK ELECTROLYTIES

Electrolytes are the compounds which when dissolved in water produce ions in their solutions. These ions are free to move about and can carry electric charge through the solution when an electric field is applied. Such solutions are therefore good conductors of electricity. Thus, electrolytes are the compounds whose solutions can conduct electricity.

Many electrolytes, when dissolved in water, are almost completely converted into ions. Such electrolytes are called **strong electrolytes.** All ionic compounds like NaCl, KCl, KNO_3, NH_4Cl and some colvent compounds like HCl. etc are strong electrolytes. In their case, the process of formation of ions (ionization or dissociation) is represented with the help of a single arrow.

$$\mathrm{NaCl(aq)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

$$\mathrm{HCl(g)} + \mathrm{H_2O(l)} \rightarrow \mathrm{H_3O^+(aq)} + \mathrm{Cl^-(aq)}$$

On the other hand, many electrolytes ionize only partially. Such electrolytes are called **weak electrolytes**. Many covalent compounds like CH_3COOH, NH_4OH, $C_6H_5NH_2$ are weak electrolytes. In its solution, such a compound is present partly in the unionized molecular form and partly in the form of ions. A dynamic equilibrium is established between the two forms when the rate of ionization of molecules to form ions and the rate of combination of ions to form molecules become equal. An equilibrium involving ions is called **ionic equilibrium**. This equilibrium between unionized molecules and the ions is represented by 'reversible arrows'. For example:

$$\mathrm{CH_3COOH(l)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{CH_3COO^-(aq)}$$

The extent to which a weak electrolyte ionizes is expressed with the help of its **degree of ionization**, α. It is defined as the fraction or percentage of the total amount (or concentration) of the electrolyte that is present in the form of ions.

Ionization of Weak Electrolytes

Ionization of a weak electrolyte, AB, is represented as:

$$AB(aq) + H_2O(l) \rightleftharpoons A^{n+}(aq) + B^{n-}(aq)$$

For this equilibrium, the law of equilibrium can be written as:

$$K = \frac{[A^{n+}_{(aq)}][B^{n-}_{(aq)}]}{[AB(aq)]} \qquad (1)$$

K is called **ionization constant or dissociation constant** *of* the electrolyte. It is a characteristic property of the electrolyte. It depends upon temperature.

Since AB is a weak electrolyte, its ionization is not complete. Let α be its degree of ionization. If the initial concentration of the electrolyte is c mol dm^{-3}, the amount of AB ionized at equilibrium would be $c\alpha$ mol dm^{-3}. Hence, the concentrations of A^{n+}(aq) and B^{n-}(aq) would be $c\alpha$ mol dm^{-3} each. The concentration of unionized AB will be $c - c\alpha$ or $c(1-\alpha)$. These equilibrium concentrations are generally represented along with the equilibrium, as shown below.

	$AB(aq) + H_2O(l) \rightleftharpoons$	$A^{n+}_{(aq)}$	$+ B^{n-}_{(aq)}$ (3)
Initial concentrations (mol dm^{-3})	c	O	O
Equilibrium concentrations/(mol dm^{-3})	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Putting these concentrations in the expression for equilibrium constant (1)

$$K = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \qquad (2)$$

For weak electrolytes, generally α is very small and it can be neglected in comparison to 1, i.e.

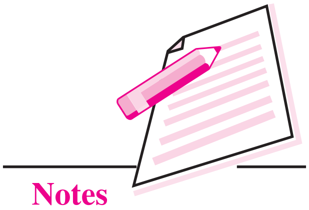
$$(1-\alpha) \simeq 1$$

With this *approximation*, the expression of *K* simplifies to

$$K = c\alpha^2$$

and

$$\alpha = \sqrt{\frac{K}{c}} \qquad (3)$$



This expression for α is known as *Ostwald's Dilution Law*. According to it α, the degree of ionization of a weak electrolyte depends upon:

(i) temperature (since K depends upon T)

(ii) concentration of the electrolyte, c.

At a constant temperature, α is inversely proportion to the square root of the concentration. Qualitatively, α increases with the dilution of the solution.

Example: Calculate the degree of ionization of NH_4OH in 0.001 M solution at 25°C. The ionisation constant of NH_4OH is 1.8×10^{-5} mol dm^{-3} at 25°C.

Solution:

According to the Ostwald's dilution law

$$\alpha = \sqrt{\frac{K}{c}}$$

$$= \sqrt{\frac{1.8\times10^{-5}}{0.001}}$$

$$= 0.134$$

12.2 GENERAL CONCEPTS OF ACIDS AND BASES

You are quite familiar with the terms acid, base, acidic and acidity etc. But how do we define an acid or a base? There is no general definition of acids and bases. There are three different concepts of acids and bases (proposed by Arrhenius, Brønsted and Lowry and Lewis respectively) which are well known. Each of these emphasize a different aspect of acid - base chemistry. Let us try to understand these concepts.

12.2.1 Arrhenius Concept

The most commonly used concept of acids and bases was developed by Svante Arrhenius (1884). According to this concept an acid is a substance that is capable of producing hydrogen ion (H^+) by dissociating in aqueous solution. The reaction can be represented as

$$HA\,(aq) \longrightarrow H^+(aq) + A^-(aq) \qquad (12.1)$$

Where HA represents the acid and A^- refers to the acid molecule (ion) without the hydrogen ion. Hydrochloric acid, HCl is an example of an Arrhenius acid whose ionisation can be represented as

$$HCl\,(aq) \longrightarrow H^+(aq) + Cl^-(aq) \qquad (12.2)$$

The proton or hydrogen ion binds itself to a water molecule and form H_3O^+ ion which is called **hydronium ion.**

$$H^+ + H_2O \longrightarrow H_3O^+$$

The hydronium ion is also known as **oxonium ion** or the **hydroxonium ion**.

In the light of this fact the equation 12.1 can be rewritten as

$$HA\,(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq) \qquad (12.3)$$

A base on the other hand is defined as a substance capable of providing a hydroxyl ion OH^- on dissociation in aqueous solutions.

$$MOH\,(aq) \longrightarrow M^+(aq) + OH^-(aq) \qquad (12.4)$$

Where M^+ refers to the base molecule (ion) without the hydroxyl ion. Sodium hydroxide is an example of a Arrhenius base, dissociating as,

$$NaOH\,(aq) \longrightarrow Na^+(aq) + OH^-\,(aq) \qquad (12.5)$$

Arrhenius concept is quite useful and explains the acid- base behaviour to a good extent. However it has certain drawbacks like,

- It is limited to only aqueous solutions and require dissociation of the substance.
- It does not explain the acidic behaviour of some substances which do not contain hydrogen. for example, $AlCl_3$. Similarly it does not explain the basic character of substances like NH_3 and Na_2CO_3 which do not have a hydroxide groups.

12.2.2 Brønsted and Lowry Concept

In 1923, Brønsted and Lowry pointed out independently that acid-base reactions can be interpreted as proton-transfer reactions. According to them, *an acid is defined as a proton (H^+) donor, and a base is defined as a proton acceptor*. The definition is sufficiently broad and removes the first limitation of Arrhenius concept. Any hydrogen-containing molecule or ion capable of donating or transferring a proton is an acid, while any molecule or ion that can accept a proton is a base.

For example, in a reaction between ammonia (NH_3) and hydrogen fluoride (HF); ammonia acts as a base (accepts a proton) while HF behaves as an acid (donates a proton).

$$NH_3 + HF \longrightarrow NH_4^+ + F^- \qquad (12.6)$$

According to Bronsted-theory an acid is a substance that can donate a proton whereas a base is a substance that can accept a proton.

You may note in this example that there is no role of a solvent. Let us consider the reaction of hydrochloric acid with ammonia in a solvent like water. We can write ionic equation as

$$H_3O^+(aq) + Cl^-(aq) + NH_3(aq) \longrightarrow H_2O(l) + NH_4^+(aq) + Cl^-$$

The hydronium and chloride ions are obtained from the ionisation of HCl . After cancelling Cl^- on both sides, we get the following ionic equation as

$$NH_3\ (g) + H_3O^+(aq) \longrightarrow H_2O(l) + NH_4^+(aq) \qquad (12.7)$$

Here, in aqueous solution, a proton is transferred from the hydronium ion, H_3O^+, to the NH_3 molecule, giving H_2O and NH_4^+. In this case H_3O^+ acts as proton donor or an acid and NH_3 as proton acceptor or a base. We may visualise water (the solvent) playing the role of mediator in the transfer of proton from hydrochloric acid to ammonia. It should be noted that in the **Brønsted- Lowry concept, acids and bases can be either ions or molecular substances.**

In any acid-base equilibrium both forward and reverse reactions involve proton transfers. Let us consider the reaction of NH_3 with H_2O.

$$\underset{acid_1}{H_2O(l)} + \underset{base_2}{NH_3(aq)} \rightleftharpoons \underset{acid_2}{NH_4^+(aq)} + \underset{base_1}{OH^-\ (aq)} \qquad (12.8)$$

In the forward reaction, NH_3 accepts a proton from H_2O. Thus, NH_3 is a base and H_2O is an acid. In the reverse reaction, NH_4^+ donates a proton to OH^-. Thus NH_4^+ ion acts as an acid and OH^- as a base. Here you find that NH_3 and NH_4^+ differ by a proton. That is, NH_3 becomes NH_4^+ ion by gaining a proton, whereas NH_4^+ ion becomes NH_3 molecule by losing a proton. The species NH_4^+ and NH_3 are called **conjugate acid-base pair**. A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the gain or loss of a proton. It can be represented as NH_4^+/NH_3 . The acid in such a pair is called conjugate acid of the base, where as the base is the conjugate base of acid. Thus, NH_4^+ is the conjugate acid of NH_3, and NH_3 is the conjugate base of NH_4^+. The members of each conjugate pair are designated by the same numerical subscript e.g., NH_4^+/NH_3 pair is marked as 2 while the H_2O/OH^- pair is marked as 1.

Let us take another example say of ionization of hydrogen fluoride in water. It can be represented as

$$\underset{acid_1}{HF\ (g)} + \underset{base_2}{H_2O} \rightleftharpoons \underset{acid_2}{H_3O^+(aq)} + \underset{base_1}{F^-(aq)} \qquad (12.9)$$

The equilibrium sign indicates that the reaction does not go to completion. The H^+ ions obtained from the ionisation of HF molecule can be accepted by either of the two bases, F^- and H_2O. The fact that the equilibrium is only slightly towards right tells us that it is the F^- that accepts the proton and make the reaction go to the left i.e., **F^- is a stronger** base than H_2O.

Similarly when HCI is dissolved in water, the HCI molecules give up H^+ ions that can be accepted by either of two bases, Cl^- and H_2O.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^- \qquad (12.10)$$

The fact that HCI is completely ionized in dilute aqueous solution (indicated by a single arrow) tells us that Cl^- is a weaker base than H_2O. We can conclude from these two examples that, a stronger acid (HCl) has a weaker conjugate base, Cl^- and the weaker acid, (HF) has a stronger conjugate base, F^-. We can generalize that in a conjugate acid-base pair the **weaker an acid is, stronger is its conjugate base. Likewise, the weaker a base is, the stronger is its conjugate acid**.

Here you should understand that the terms 'strong' and 'weak' like many other adjectives are used in a relative sense. Consider the following reaction

$$F^- + H_2O \rightleftharpoons HF + OH^- \qquad (12.11)$$

In this case **F^- is a weaker base** as compared to OH^-.

Let us write a few reactions involving conjugate acid-base pairs.

$$\underset{acid_1}{HF\,(aq)} + \underset{base_2}{HCO_3^-(aq)} \rightleftharpoons \underset{acid_2}{H_2CO_3(aq)} + \underset{base_1}{F^-(aq)}$$

$$\underset{acid_1}{HCO_3^-(aq)} + \underset{base_2}{OH^-(aq)} \rightleftharpoons \underset{base_1}{CO_3^{2-}(aq)} + \underset{acid_2}{H_2O(l)}$$

$$\underset{acid_1}{H_2CO_3(aq)} + \underset{base_2}{CN^-(aq)} \rightleftharpoons \underset{base_1}{HCO_3^-(aq)} + \underset{acid_2}{HCN(aq)} \qquad (12.12)$$

If you examine the above reactions closely, you would find that some species can act both as an acid and as a base. Such species are called **amphiprotic** species. In the above reactions $HCO_3^-(aq)$ acts as a base in presence of HF but an acid in presence of CN^-. Similarly H_2O behaves as an acid and a base.

- Thus, we have seen that the Brønsted- Lowry concept of acids and bases has greater scope than the Arrhenius concept.

12.2.3 Lewis Concept

As discussed above the Brønsted- Lowry concept does not depend on the nature of the solvent (a short coming of the Arrhenius concept removed). However, like Arrhenius concept it does not explain the acidity of the substances which do not have a hydrogen atom (e.g., $AlCl_3$) and the basicity of the substances devoid of a OH group (e.g., Na_2CO_3). G.N.Lewis proposed (1923) a yet another concept of acids and bases that includes such substances also. According to him, an acid may be defined as, ‘ any atom, molecule or ion that can accept an electron pair from any other atom , molecule or ion, A lewis base on the other hand can be defined as, ‘ any atom , molecule or ion that can donate a pair of electrons, Let us take an example

$$AlCl_3 + NH_3 \longrightarrow Cl_3Al \longleftarrow NH_3 \qquad (12.13)$$

In the above example $AlCl_3$ is an electron deficient species. It accepts an electron pair from a molecule of NH_3 which has a lone pair of electrons on N atom. Thus, $AlCl_3$ is a Lewis acid and NH_3 is a Lewis base.

INTEXT QUESTIONS 12.1

1. Define Arrhenius acid and give two examples.
2. What are the limitations of Arrhenius definition?
3. How does a Brønsted- Lowry base differ from an Arrhenius base?
4. Classify the following into Brønsted- Lowry acid or Brønsted- Lowry base.

   $HCl,\ NH_3,\ H_3O^+,\ CN^-$
5. The degree of dissociation of two electrolytes X and Y are 1.0×10^{-4} and 0.96. Comment on the nature of these electrolytes.

12.3 RELATIVE STRENGTH OF ACIDS AND BASES

Different acids and bases have different strength depending on their nature. Since there are different ways of defining acids and bases, there are different ways of comparing their relative strengths also.

12.3.1 Relative strength according to Arrhenius concept

According to Arrhenius concept strong electrolytes (like HCl) which dissociate completely in aqueous solutions and produce H^+ (or H_3O^+) ions are called strong acids.

$$HCl\,(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq) \qquad (12.14)$$

Other examples of strong acids are H_2SO_4, HBr, HI, HNO_3 and $HClO_4$. On the other hand weak electrolytes like CH_3COOH whose ionisation is not complete, (because the process is reversible) and produce H^+ (or H_3O^+) ions are called weak acids.

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \qquad (12.15)$$

Similarly strong bases may be defined as the electrolytes with complete ionisation and weak bases as the electrolytes with incomplete ionisation. NaOH and NH_3 are typical examples of strong and weak bases respectively. Their ionisation can be represented as

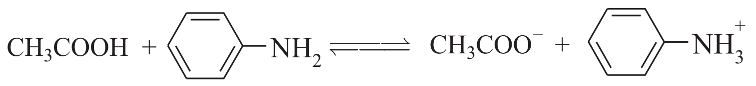
$$NaOH\,(aq) \longrightarrow Na^{+}(aq) + OH^{-}(aq) \qquad (12.16)$$

$$NH_3\,(aq) + H_2O \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq) \qquad (12.17)$$

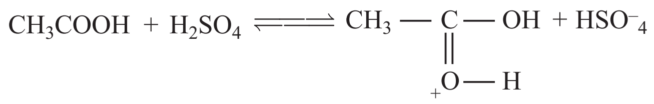
The principal strong bases are hydroxides of Groups 1 and 2 elements (except Be). Most of the other acids and bases we come across are weak bases.

12.3.2 Relative strength according to Brønsted- Lowry concept

You have learnt that according to **Brønsted- Lowry concept** an acid is a species that donates a protons while a base is a species that accepts a protons. The tendency of a substance to donate a proton also depends on the species accepting the proton. A given acid may have different strengths in different solvents (of varying basic strength or proton accepting tendencies) e.g.,



(12.18)



$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3-\underset{\overset{\|}{\overset{+}{O}-H}}{C}-OH + HSO_4^{-}$$

(12.19)

Acetic acid loses a proton to a basic solvent aniline but in sulphuric acid it infact accepts a proton and acts as a base. Therefore the relative strengths of different acids and bases are compared in the same solvent which normally is water. Therefore, in Brønsted- Lowry concept, we may define the relative strength of an acid as its relative tendency to lose (or donate) a proton to water. According to the Brønsted- Lowry concept strong acid are those which lose their protons almost entirely to water. The reaction,

$$\underset{\textbf{acid}}{HCl\,(aq)} + \underset{\textbf{base}}{H_2O\,(aq)} \longrightarrow \underset{\textbf{acid}}{H_3O^{+}(aq)} + \underset{\textbf{base}}{Cl^{-}(aq)} \qquad (12.20)$$

goes completely to the right indicating that HCl is a strong acid. Acetic acid donates its proton to water to the extent of only about 3% and the following equilibrium exists.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^{+} + CH_3COO^{-} \qquad (12.21)$$

Acetic acid is, therefore, termed as a weak acid.

12.4 QUANTITATIVE ASPECTS OF STRENGTHS OF ACIDS AND BASES

We have so far discussed the relative strengths of acids and bases only qualitatively i.e., which is strong and which one is weak. Many a times we need to know the quantitative aspects also i.e., how much?. That is if a acid is stronger than the other we would like to know how many times stronger. Let us learn how do we quantify it ?

12.4.1 Ionisation of weak acids

The dissociation or ionisation of a weak acid, HA, can be represented as

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)} \qquad (12.22)$$

As you know that in case of strong acids the ionisation is almost complete or close to 100% or we may say that the equilibrium lies far to the right. In such cases the sign of equilibrium may be replaced by a single arrow (→)

$$\mathrm{HA\,(aq) \longrightarrow H^+(aq) + A^-(aq)}$$

or

$$\mathrm{HA\,(aq) + H_2O\,(\mathit{l}) \longrightarrow H_3O^+(aq) + A^-(aq)} \qquad ...12.23$$

The reaction given above (eq 12.22) is referred to as ionisation equilibrium and is characterized by an equilibrium constant

$$K_{eq} = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \qquad ...12.24$$

Since the concentration of a pure liquid or a solid is taken as 1, we can rewrite the above expression can as

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA]} = K_a \qquad ...12.25$$

where K_a is a new constant called acid dissociation constant or ionisation constant of the acid.

The magnitude of the equilibrium constant is a measure of the strength of the acid. Higher the value of the equilibrium constant the stronger is the acid. For all strong acids the values of the equilibrium constants is quite high and does not help much in suggesting their relative strengths. However, for a weak acid , this constant is quite useful.

Example 12.1 : Write down the expression for the dissociation constant for acetic acid- a weak acid that ionizes as

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Solution : Applying the law of chemical equilibrium, we can write equilibrium constant K as

$$K = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

Rearranging, we can write .

$$K[H_2O] = K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Dissociation constant of other weak acids also can be written in the same way.

The values of K_a show the extent to which the acids are dissociated in water. Relative strength of acids is judged on the basis of dissociation constant. Like other equilibrium constants the dissociated constant, K_a also depends on the temperature. Therefore, the ionisation constants or dissociation constants are compared at the same temperature. For example

$$CH_3COOH\,(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \quad K_a = 1.8 \times 10^{-5} \qquad (12.26)$$

$$HCN\,(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad Ka = 4.9 \times 10^{-10} \qquad (12.27)$$

On the basis of K_a values we can say that acetic acid is much more ionized than hydrocyanic acid. In other words acetic acid is stronger acid than hydrocyanic acid although both are weak; neither is completely ionized.

12.4.2 Ionisation of weak bases

The ionisation of weak bases (BOH) can be expressed as :

$$BOH\,(aq) \rightleftharpoons B^+(aq) + OH^-(aq) \qquad (12.28)$$

(The equilibrium sign may be replaced by → in case of a strong base.)

The solution contains the base, B the protonated base, BH^+, hydroxide ion OH^-, and water in equilibrium. The equilibrium constant expression for the reaction is

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad (12.29)$$

For example, the dissociation of NH_4OH is represented as

$$NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

and is characterized by

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \tag{12.30}$$

The constant K_b is called dissociation constant of the base. Similar to values of K_a, K_b values also give us the idea about the relative strengths of weak bases. Higher the value of K_b the stronger is the base.

12.4.3 Polyprotic Acids

Many acids have more than one ionizable protons. These are called polyprotic acids. The acids are called diprotic if there are two ionizable protons per molecule. (e.g. H_2SO_3, H_2CO_3), and triprotic if there are three ionizable protons (e.g. H_3PO_4, etc). Such acids dissociate in more than one steps or stages, each with its own ionization constant. In the case of sulphurous acid, H_2SO_3, these steps are

$$H_2SO_3 + H_2O \rightleftharpoons HSO_3^- + H_3O^+ \tag{12.31}$$

$$K_1 = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} = 1.3 \times 10^{-2}$$

$$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+ \tag{12.32}$$

$$K_2 = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]} = 6.3 \times 10^{-8}$$

The values of the two ionisation constants (K_1 and K_2) are quite different ; K_1 being twenty million times K_2. It suggests that the first ionisation of sulphurous acid is much more than the second one. In other words the sulphurous acid behaves as a much stronger acid than the bisulphite ion.

12.4.4 Degree of Ionisation or Degree of Dissociation

As you know that the weak acids / bases do not ionize completely and an equilibrium exists between the ionized and unionized species. The degree of ionisation may be defined as the fraction of total amount of a weak acid or a base that exists in the ionized form. It is denoted by a Greek letter ‘á ‘. The equilibrium constant can be used to calculate the degree of ionisation of a weak acid or a base. An expression relating á and K_a or K_b can be derived as follows.

Consider a weak acid HA which partially dissociates in its aqueous solutions and the following equilibrium is established

	$HA\ (aq)$	$+\ H_2O(l)$	$\rightleftharpoons H_3O^+(aq)$	$+\ A^-(aq)$
Initial concentrations (in moles)	c	~ 55	0	0
Equilibrium concentrations	$c(1-\alpha)$	~ 55	$c\alpha$	$c\alpha$

The equilibrium constant expression can be written as

$$K_a = \frac{[H_3O^+][A^-]}{[H_2O][HA]} = \frac{[c\alpha][c\alpha]}{c(1-\alpha)\,55}$$

rearranging we get,

$$\Rightarrow \qquad 55K = K_a = \frac{[c\alpha][c\alpha]}{c[1-\alpha]} = \frac{c^2\alpha^2}{c\,[1-\alpha]} = \frac{c\alpha^2}{(1-\alpha)} \qquad (12.33)$$

Since the acid HA is very weak, $\alpha << 1$; we can neglect á in comparison to 1 in the denominator to get

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_a}{c} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} \qquad (12.34)$$

So if we know the value of the dissociation constant of the acid and the concentration of the weak acids we can find its degree of dissociation or ionisation. Let us take up an example to see the application of this relationship.

Example 12.2: Compute the degree of dissociation and percent dissociation of acetic acid in its 0.1 M solution. Given $K_a = 1.8 \times 10^{-5}$.

Solution: Using the formula $\alpha = \sqrt{\frac{K_a}{c}}$ and substituting the values of K_a and c, we get,

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = \sqrt{1.8 \times 10^{-4}} = 1.34 \times 10^{-2} = 0.0134$$

The percent dissociation of a weak acid is defined as

$$\text{Percent dissociation} = \frac{\text{The number of moles of acid in the dissocia}}{\text{Total number of moles of the acid}} \qquad (12.35)$$

$$= \text{Degree of dissociation} \times 100\%$$

$$\Rightarrow \qquad = \alpha \times 100\% = 0.0134 \times 100 = 1.34\%$$

Thus acetic acid is dissociated to the extent of only 1.34 % in a 0.1 M aqueous solution.

A similar expression can be obtained for the degree of dissociation of a weak base. The desired expression is

$$\alpha = \sqrt{\frac{K_b}{c}} \tag{12.36}$$

12.5 THE AUTO-IONISATION OR SELF-IONISATION OF WATER

We have seen that water can act as a very weak acid and also as a very weak base. In a sample of water a small number of water molecules undergo auto ionisation. Half of them acting as an acid while the other half acting as a base. As a consequence small concentration of H_3O^+ and OH^- are formed in water. The self ionisation of water can be represented as

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \tag{12.37}$$

The corresponding equilibrium constant expression can be written as

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \tag{12.38}$$

Since the concentration of H_2O is constant we can rearrange the expression and define a new constant K_w , as

$$[H_3O^+]\ [OH^-] = K_{eq} \times [H_2O]^2 = K_w \text{ (a new constant)} \tag{12.39}$$

This constant, K_w, is called the dissociation constant or **ionic product constant of water**. The value of K_w at 298 K has been determined from the measurement of electrical conductivity of carefully purified water and has been found to be 1.0×10^{-14} mol² dm⁻⁶.

Since the concentrations of H_3O^+ and OH^- ions is equal we may write

$$K_w = [H_3O^+]\ [OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_w = [H_3O^+]^2 = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$\Rightarrow \qquad [H_3O^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

and similarly, $[OH^-] = 1.0 \times 10^{-7}$ mol dm^{-3}

Thus in pure water and in neutral solutions

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ at 298 K} \tag{12.40}$$

12.5.1 Acidic, Basic and Neutral Solutions

An acidic solution is defined as one in which the hydrogen ion (or hydronium ion) concentration is greater than the hydroxide ion concentration. A basic solution is one in which the reverse is true, that is, one in which $[OH^-]$ exceeds $[H_3O^+]$ and a neutral solution is one in which $[OH^-]$ equals $[H_3O^+]$.

Neutral solution	$[H_3O^+] = [OH^-]$
Acidic solution	$[H_3O^+] > [OH^-]$
Basic solution	$[H_3O^+] < [OH^-]$ (12.41)

Since the product $[H_3O^+]\,[OH^-]$ is constant, if the concentration of either of these increases, the other one would decrease. In other words the concentrations of $[H_3O^+]$ and $[OH^-]$ are not independent but are linked by the relationship

$$[H_3O^+]\;[OH^-] = K_w \qquad (12.42)$$

This provides an easy way to calculate concentration of one of these if we know that of the other.

You must note that the self ionisation equilibrium discussed above applies not only to pure water but also to the self-ionization of water in any aqueous solution. Hydronium ions and hydroxide ions are present in every aqueous solution, and they are always in equilibrium with water molecules. Let us try to calculate the concentration of these ions in some simple solutions.

Example 12.3 : Calculate the concentrations of OH^- and H_3O^+ ions in 0.01 M solution of HCl.

Solution: In an aqueous solution of HCl, the following two processes would occur simultaneously

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The ionisation of HCl goes to completion and that of water to a very limited extent. In addition according to Le- Chatlier principle, the H_3O^+ from the ionization of HCl will shift the position of the equilibrium of the self-ionization reaction to the left. As a consequence the concentration of the OH^- ions would reduce further. Suppose concentration of OH^- is 'x' mol dm^{-3}, then concentration of H_3O^+ from the self-ionization of water must also be x mol dm^{-3}. The concentration of H_3O^+ from ionization of HCl is 0.010 mol dm^{-3}. Therefore, total concentration of H_3O^+ (aq) = $(0.010 + x)$ mol dm^{-3}.

Thus Equilibrium Concentrations of H_3O^+ and OH^- ions would be $(0.01 + x)$ and x mol dm^{-3} respectively.

Substituting these values into the equilibrium constant for the self-ionization of water, we get

$$K_w = [H_3O^+]\,[OH^-] = (0.01 \times x)\,(x)\,\text{mol}^2\,\text{dm}^{-6} = 1.0 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$$

Since x must be very small, we can assume that $x << 0.01$ and therefore we may assume that the equilibrium concentration of H_3O^+ is equal to 0.01 M

$$(0.01 + x) \cong 0.01, \text{ so}$$

$$0.01x = 1.0 \times 10^{-14}$$

or $$x = 1.0 \times 10^{-14} / 0.01$$

$$x = 1.0 \times 10^{-12}$$

$$[OH^-] = 1.0 \times 10^{-12}\ \text{mol dm}^{-3} \text{ and}$$

$$[H_3O^+] = 0.01 + 1.0 \times 10^{-12}\ \text{mol dm}^{-3} = 0.01\ \text{mol dm}^{-3}$$

Since the value of x (1.0×10^{-12}) the hydronium ions obtained from the self ionisation of water) is far smaller than 0.01, our assumption is justified. Thus you may note that in case of aqueous solutions of strong acids it is reasonable to assume that the concentration of H_3O^+ ions equals the concentration of the acid itself.

12.5.2 *p*H Scale

In aqueous solutions of acids and bases the concentration of H_3O^+ and OH^- ions may vary from about 10 M to 10^{-14} M. It is quite inconvenient to express these concentrations by using powers of 10. in 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called *p*H scale) for expressing the concentrations of H^+ ions. He defined *p*H as the negative logarithm of the molar concentration of hydrogen ions. That is,

$$pH = -\log_{10}[H^+] \qquad (12.43)$$

We now a days it is represented as

$$pH = -\log_{10}[H_3O^+] \qquad (12.44)$$

For neutral solutions (or pure water)

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$$

$$\Rightarrow \quad pH = -\log 1 \times 10^{-7} = 7.0$$

For acidic solutions

$$[H_3O^+] > [OH^-]$$

$$\Rightarrow \quad [H_3O^+] > 1 \times 10^{-7}$$

$\Rightarrow \quad pH = -\log (>1 \times 10^{-7}) = < 7.0$

For basic solutions

$[H_3O^+] < [OH^-]$

$\Rightarrow \quad [H_3O^+] < 1 \times 10^{-7}$

$\Rightarrow \quad pH = -\log (< 1 \times 10^{-7})$

$\Rightarrow \quad > 7.0$

A strongly acidic solution can have a pH of less than zero (i.e., negative) and a strongly alkaline solution can have a pH value greater than 14. However the *p*H range normally observed is between 0 to 14.

The notation p is used in a number of places. It carries the meaning, 'the negative logarithm of'. It has been extended to OH^-(aq) and equilibrium constants like, K_a, K_b and K_w, etc.

$$pOH = -\log_{10}[OH^-]$$
$$pK_a = -\log_{10} K_a$$
$$pK_b = -\log_{10} K_b$$
$$pK_w = -\log_{10} K_w \qquad (12.45)$$

This gives us an important relation. You would recall (eq 12.42)

$K_w = [H_3O^+] [OH^-]$

Taking logs on both sides, we get

$\log K_w = \log [H_3O^+] + \log [OH^-]$

Multiplying through out by –1

$-\log K_w = -\log [H_3O^+] - \log [OH^-]$

$pK_w = pH + pOH$

Since the value of $K_w = 1.0 \times 10^{-14}$ $pK_w = 14$

i.e., $pH + pOH = 14$ (12.46)

If we know the value of pH of a given solution we can find its pOH and vice versa.

Let us take up some examples to understand the application of these important formulae.

Example 12.4: What is the pH of a 0.01 M aqueous solution of HCl?

Solution: Since HCl is a strong acid it would ionize completely.

Therefore, $[H_3O^+]$ in 0.01 M HCl = 0.01 M

$$pH = -\log_{10}[H_3O^+] = -\log 10^{-2}$$
$$= -(-2.0) = 2.0.$$

Example 12.5 : Calculate the pH of 0.010 M aqueous solution of NaOH.

Solution: Since NaOH is a strong base, it is fully ionized to give Na^+ and OH^-

$$[OH^-] = 1.0 \times 10^{-2} \text{ mol L}^{-1}$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

So, $$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{1.00 \times 10^{-2} \text{ mol dm}^{-3}}$$

$$= 1.00 \times 10^{-12} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} (1.0 \times 10^{-12}) = 12$$

Example 12.6 : The pH of a sample of rain water at 25 °C is 5. What is the concentration of hydronium ions ?

Solution: $pH = -\log [H_3O^+]$

or $5 = -\log [H_3O^+] \Rightarrow \log [H_3O^+] = -5$

Taking antilogs, we get

$$[H_3O^+] = 10^{-5} \text{ mol dm}^{-3}.$$

Example 12.7: Calculate the pH of 0.1 M aqueous solution of acetic acid. The dissociation constant, $K_a = 1.85 \text{ x } 10^{-5}$, $\alpha = 0.0134$.

Solution: The following equilibrium exists in this solution

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

If α be the degree of dissociation of acetic acid in this solution, the equilibrium concentrations of various species would be

$$CH_3COOH(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$c(1- á) \qquad\qquad c á \qquad\qquad c á$$

Since c = 0.1 M

$$0.1(1- á) \qquad\qquad 0.1 á \qquad\qquad 0.1 á$$

$$[H_3O^+] = c\, á$$

$$\Rightarrow [H_3O^+] = 0.1 \times 0.0134 = 0.00134$$

$$pH = -\log[H_3O^+] = -\log [0.00134] = -\log [1.34 \times 10^{-3}] = -(-2.87) = 2.87$$

12.5.3 Effect of Common-Ions on the Dissociation of Weak Acids and Bases

In the previous lesson you have learnt about Le Chatelier's principle. According to this principle the presence of common ions in a solution of a weak acid or a base will affect its dissociation. This in fact would suppress the dissociation of the acid or base.

In a solution containing a weak acid HA and its salt NaA, the following equilibria exists:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$NaA(aq) \rightleftharpoons Na^+(aq) + A^-(aq)$$

Here A^-(aq)is the common-ion

and in case of a weak base BOH and its salt BX the equilibria are

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

$$BX(aq) \rightleftharpoons B^+(aq) + X^-(aq)$$

Here, B^+ is the common-ion. According to Le- Chatlier principle, the presence of common ions would make the equilibrium to go to the left. It is said that the common ions suppress the equilibrium.

Let us take an example to understand the effect of common ions on such equilibria.

Example 12.8 : Calculate the pH, degree of dissociation and concentration of various species in a solution of 0.1 M acetic acid which also contains 0.1 M sodium acetate (K_a (for acetic acid) = 1.85×10^{-5} mol dm^{-3}).

Solution : In the given solution the following two equilibria exist simultaneously.

$$CH_3COOH(aq) + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-(aq)$$

$$CH_3COONa\ (aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$

Let α be the degree of dissociation of acetic acid in this solution, the equilibrium concentrations of various species would be

$$CH_3COOH(aq) \longrightarrow H_3O^+(aq) + CH_3COO^-(aq)$$

$$c(1-\text{á}) \qquad\qquad c\text{á} \qquad\qquad c\text{á}$$

Since c = 0.1 M

$$0.1(1-\text{á}) \qquad\qquad 0.1\text{á} \qquad\qquad 0.1\text{á}$$

$$\underset{0}{CH_3COONa(aq)} \longrightarrow \underset{0.1}{Na^+(aq)} + \underset{0.1}{CH_3COO^-(aq)}$$

$$CH_3COOH = 0.1(1-\text{á})$$

CH_3COO^- = 0.1 + 0.1á = 0.1 (1 + á)

H_3O^+ = 0.1á

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COO^-]}$$

rearranging the expression we get,

$$[H_3O^+] = K_a = \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Substituting the values, we get

$$[H_3O^+] = 1.85 \times 10^{-5} \times \frac{0.1(1-\alpha)}{0.1(1+\alpha)}$$

Since acetic acid is a weak acid, its degree of dissociation further decreases in presence of acetate (ions the common ion). Therefore it is reasonable to assume that

$\alpha << 1$; and $(1 - \alpha) \sim 1$; also $(1 + \alpha) \sim 1$

This gives

$[H_3O^+] = 1.85 \times 10^{-5} \times 0.1 / 0.1 = 1.85 \times 10^{-5}$

and $pH = -\log (1.85 \times 10^{-5}) = 4.73$

Also since $[H_3O^+] = 0.1\ \alpha$

$\therefore \alpha = 1.85 \times 10^{-5} / 0.1 = 1.85 \times 10^{-4} = 0.000185$

The concentration of different species at equilibrium will be

$CH_3COOH = 0.1 (1 - 0.000185) = 0.1$

$CH_3COO^- = 0.1 (1 + 0.000185) = 0.1$

H_3O^+ = 0.1 × á = 0.1 × 0.000185 = 1.85×10^{-5}

$\Rightarrow$ the concentration of acid = initial concentration of acid

$\Rightarrow$ the concentration of CH_3COO^- ions = initial concentration of the salt

INTEXT QUESTIONS 12.2

1. HF is a weak acid in water. Write down the expression for K_a for the dissociation of HF.
2. Consider a weak base BOH which partially dissociates in its aqueous solutions as per the following equilibrium

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

3. A sample of lime juice has a hydronium ion concentration of 6.3×10^{-2} M. Calculate its *p*H.
4. Calculate the pH of 1.0 M aqueous solution of amino acid glycine – a weak acid. The $K_a = 1.67 \times 10^{-10}$.

12.6 BUFFER SOLUTIONS

The example discussed above leads us to a very important conclusion that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids / bases and a salt of common ion are important in a yet another way. These act as **buffer solutions**.

Buffer solutions are the ones that resist a change in its pH on adding a small amount of an acid or a base.

In laboratory reactions, in industrial processes and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids and bases. The oxygen carrying capacity of haemglobin in our blood and activity of the enzymes in our cells depends very strongly on the *p*H of our body fluids. *p*H of the blood is very close to 7.4 and *p*H of saliva is close to 6.8. Fortunately, animals and plants are protected against sharp changes in *p*H by the presence of buffers.

There are two kinds of commonly used buffer-solutions

(i) A weak acid and a soluble ionic salt of the weak acid e.g. acetic acid and sodium acetate; $CH_3COOH + CH_3COONa$ and,

(ii) A weak base and a soluble ionic salt of the weak base e.g. ammonium hydroxide and ammonium chloride ; $NH_4OH + NH_4Cl$.

The buffers with pH less than 7 are called *acidic buffers* and those with pH above 7 are called *basic buffers*. Acetic acid - sodium acetate buffer is an example of *acidic buffer* while Ammonium hydroxide - ammonium chloride is a basic buffer.

12.6.1 Buffer Action

A buffer system contains a conjugate acid- base pair and the concentrations of these two are quite high as compared to that of the hydronium ions. These are called as the acid reserve and the base reserve respectively. The added acid or base reacts with these reserves and gets consumed without significantly altering the hydronium ion concentration and therefore the pH does not change significantly. Let us consider a buffer solution containing acetic acid, CH_3COOH and sodium acetate CH_3COONa to understand the buffer action.

In acetic acid - sodium acetate buffer CH_3COOH is the acid reserve while CH_3COONa (or CH_3COO– ions) is the base reserve. In the solution mixture the added components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation.

$$CH_3COOH\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$CH_3COONa\,(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$

If we add a strong acid such as HCI to this solution, it produces H_3O^+. These added H_3O^+ (acid) react with an equivalent amount of the base reserve $[CH_3COO^-]$ to generate undissociated acetic acid. The reaction being

$$H_3O^+(aq) + CH_3COO^-(aq) \longrightarrow CH_3COOH(aq) + H_2O(l)$$

The net effect of this reaction is that there is a slight increase in the concentration of the acid reserve and an equivalent decrease in the concentration of the base reserve. The effective reaction being

$$HCl(aq) + CH_3COONa(aq) \longrightarrow CH_3COOH(aq) + NaCl(aq)$$

Similarly, when small amounts of a strong base like NaOH is added , it generates OH^- ions. These additional OH^- neutralize some of the H_3O^+ ions present in the solution,

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of CH_3COOH to re-establish the equilibrium.

$$CH_3COOH(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

The net result is the neutralization of OH^- by CH_3COOH. In other words we can say that the added OH– ions (base) react with the acid reserve to produce CH_3COO^- ions

$$OH^-(aq) + CH_3COOH(aq) \longrightarrow CH_3COONa^- + H_2O(l)$$

The effective reaction being the reaction of the added base with acid reserve.

$$NaOH(aq) + CH_3COOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

The net effect of this reaction is that there is a slight increase in the concentration of the base reserve and an equivalent decrease in the concentration of the acid reserve.

You may note here that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the

Notes

hydronium ions and thereby the pH does not change significantly. Let us derive a mathematical expression for determining the pH of a buffer solution.

12.6.2 Henderson-Hasselbalch Equation

This equation relates the pH of a given buffer solution to the concentrations of its components viz. weak acid / salt or weak base / salt. Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid – sodium acetate buffer the central equilibrium is

$$CH_3COOH(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

which is characterized by the acid dissociation constant,

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

rearranging, we get

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

The concentration of undissociated acetic acid can be taken as total acid concentration [Acid] and that of sodium acetate as the total salt concentration [Salt]. In the light of this the above equation may be re written as

$$[H_3O^+] = K_a \frac{[Acid]}{[Salt]}$$

Taking logarithm and multiplying through out by (-1) we get

$$-\log [H^+] = -\log K_a - \log \frac{[Acid]}{[Salt]}$$

Recall that pH = $-\log [H_3O^+]$ and $pK_a = -\log K_a$. This gives the desired equation.

$$pH = pK_a - \log \frac{[Acid]}{[Salt]} = pK_a + \log \frac{[Salt]}{[Acid]}$$

This equation is known as **Henderson-Hasselbalch equation**. A similar expression can be derived for a basic buffer (e.g., ammonium hydroxide and ammonium chloride) . The expression is

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Let us take up some examples to see the application of this equation.

Example 12.9 : Calculate the pH of acetic acid – sodium acetate buffer containing 0.1 M acetic acid and 0.1 M sodium acetate. ($K_a = 1.85 \times 10^{-5}$ mol dm^{-3}).

Solution: Here, [Acid] = 0.1 M and [Salt] = 0.1 M

Since $K_a = 1.85 \times 10^{-5}$ mol dm^{-3} ;

$$pK_a = -\log K_a = -\log\ 1.85 \times 10^{-5}$$

$$\Rightarrow \quad pK_a = 4.73$$

According to Henderson equation, $pH = pK_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

Substituting the values in Handerson equation, we get

$$pH = 4.73 + \log(0.1 / 0.1) = 4.73 + \log 1 = 4.73.$$

Example 12.10 : Calculate the pH of ammonium hydroxide – ammonium chloride buffer solution that is 0.1 M in ammonium hydroxide and 0.01 M in ammonium chloride. (pK_b of $NH_4OH = 9.25$).

Solution: Here, [Base] = 0.1 M and [Salt} = 0.01 M

Since $\mathbf{p}K_b = 9.25$;

According to Henderson equation, $pOH = pK_b + \log \dfrac{[\text{Salt}]}{[\text{Base}]}$

Substituting the values in Handerson eqation, we get

$$pOH = 9.25 + \log(0.01 / 0.1) = 9.25 + \log 0.1 = 9.25 - 1.0 = 8.25$$

12.7 SALT HYDROLYSIS

The aqueous solutions of certain salts also behave as acids or bases. They do so because of the hydrolysis of the cation or anion or both. As you know, hydrolysis is a reaction with water. Depending on the behaviour towards hydrolysis there are four different types of salts.

Salt of strong acid + strong base (eg. HCl + NaOH)	NaCl
Salt of strong acid + weak base (e.g. HCl + NH_4OH)	NH_4Cl
Salt of weak acid + strong base (e.g. CH_3COOH + NaOH)	CH_3COONa
Salt of weak Acid + weak Base (e.g. CH_3COOH + NH_4OH)	CH_3COONH_4

Let us learn about the acid- base behaviour of the different types of salts.

Salt of strong acid + strong base : the cations of the strong bases and the anions of the strong acids do not get hydrolysed. Therefore the salts of this category do not show any acid-base behaviour and are neutral.

Salt of strong acid + weak base: the salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid . For example, NH_4Cl dissociates as :

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

As mentioned above, the anion does not get hydrolysed but the cation does get hydrolysed as per the following equation.

$$NH_4^+(aq) + H_2O(l) \longrightarrow NH_4OH + H^+(aq)$$

since it generates $H^+(aq)$ ions, the solution is acidic in nature.

Salt of weak acid and strong base: the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. for example, CH_3COONa dissociates as :

$$CH_3COONa(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$

in this case the cation does not get hydrolysed but the anion does get hydrolysed as per the following equation.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH\ (aq) + OH^-(aq)$$

Since it generates hydroxyl ions the solution is basic in nature.

Salt of weak Acid and weak Base : the salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to a weak base. for example, ammonium acetate, CH_3COONH_4 dissociates as :

$$CH_3COONH_4(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$$

In this case both the cation as well as the anion would undergo hydrolysis and the nature of the solution, whether acidic, basic or neutral would depend on the relative strength of the weak acid and the weak base.

12.8 THE SOLUBILITY EQUILIBRIUM

When we try to dissolve a solid into water, if it dissolves, there are three possibilities:

1. The solid is a non-electrolyte and it dissolves as neutral molecules.
2. The solid is a highly soluble electrolyte; it dissolves almost completely.
3. The solid is a sparingly soluble electrolyte; it dissolves to a limited extent.

It is the third possibility that interests us here. Let us take the example of dissolution of AgCl to understand the equilibria in such cases. When silver chloride is added to water, the following equilibrium is established.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

This is an example of a heterogeneous equilibrium because it involves both a solid and a solution. This equilibrium is known as the ***solubility equilibrium*** for which the equilibrium constant expression is

$$K = \frac{[Ag^+][Cl^-]}{[AgCl(s)]}$$

As a matter of convention the concentration of the undissolved solid is taken as one. We can rewrite the equilibrium as

$$K_{sp} = [Ag^+][Cl^-]$$

The equilibrium constant now is the product of the concentrations of the ions. It is called ***solubility product constant*** or simply ***solubility product***. A new symbol, K_{sp}, has been assigned to this constant. The mass expression on the right , is called, ion product or ionic product. The solubility product constant of a given salt is constant at a given temperature.

12.8.1 Relationship between Solubility and Solubility Product Constant

The ***solubility product constant*** for a substance is related to its solubility. The nature of relationship depends on the nature of the salt.

Salt of AB type: (For example AgCl, $CaSO_4$). In such cases the solubility equilibrium can be represented as

$$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$$

and $K_{sp} = [A^+]\,[B^-]$

If the solubility of salt is 's' mol dm^{-3} then the concentrations of the cations and the anions would be 's' mol dm^{-3} each. Substituting the values in the expression of K_{sp} we get,

$$K_{sp} = [\text{'s' mol dm}^{-3}] \times [\text{'s' mol dm}^{-3}] = s^2\ \text{mol}^2\ \text{dm}^{-6}$$

Salt of AB_2 type: (For example CaF_2). In such cases the solubility equilibrium can be represented as

$$AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq)$$

and $K_{sp} = [A^{2+}]\,[B^-]^2$

If the solubility of salt is 's' mol dm^{-3} then the concentration of the cations and the anions would be 's' mol dm^{-3} and '2s' mol dm^{-3} respectively. Substituting the values in the expression of K_{sp} we get,

$$K_{sp} = [\text{'s' mol dm}^{-3}] \times [\text{'2s' mol dm}^{-3}]^2 = 4s^3\ \text{mol}^3\ \text{dm}^{-9}$$

Salt of A_2B type: (For example Ag_2CrO_4). In such cases the solubility equilibrium can be represented as

$$A_2B(s) \rightleftharpoons 2A^+(aq) + B^{2-}(aq)$$

and $$K_{sp} = [A^+]^2\,[B^{2-}]$$

If the solubility of salt is 's' mol dm^{-3} then the concentrations of the cations and the anions would be '2s' mol dm^{-3} and 's' mol dm^{-3} respectively. Substituting the values in the expression of K_{sp} we get,

$$K_{sp} = [\text{'2s' mol dm}^{-3}]^2 \times [\text{'s' mol dm}^{-3}] = 4s^3\ \text{mol}^3\ \text{dm}^{-9}$$

Salt of A_3B_2 type: (For example $Ca_3(PO_4)_2$. In such cases the solubility equilibrium can be represented as

$$A_3B_2(s) \rightleftharpoons 3A^{2+}(aq) + 2B^{3-}(aq)$$

and $$K_{sp} = [A^{2+}]^3\,[B^{3-}]^2$$

If the solubility of salt is 's' mol dm^{-3} then the concentrations of the cations and the anions would be '3s' mol dm^{-3} and '2s' mol dm^{-3} respectively. Substituting the values in the expression of K_{sp} we get,

$$K_{sp} = [\text{'3s' mol dm}^{-3}]^3 \times [\text{'2s' mol dm}^{-3}]^2 = 108\ s^5\ \text{mol}^5\ \text{dm}^{-15}$$

In general for a salt with the formula A_xB_y and a solubility of s mol dm–^{3} the relationship between the solubility and K_{sp} can be given as

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y = (xs)^x\,(ys)^y = \boldsymbol{x^x\,y^y\,s^{x+y}}$$

Example 12.11: The solubility of calcium sulphate in water is 4.9×10^{-3} mol dm^{-3} at 298K. Calculate the value of K_{sp} for $CaSO_4$ at this temperature.

Solution: The following equilibrium would exist in this case

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

For this reaction; $K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]$

From the equation we see that when 4.9×10^{-3} mol of $CaSO_4$ dissolves to make 1 dm^{-3} of a saturated solution, the ionic concentration are

$$[Ca^{2+}] = 4.9 \times 10^{-3}\ \text{mol dm}^{-3}\ ;\quad [SO_4^{2-}] = 4.9 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}] = [4.9 \times 10^{-3}\ \text{mol dm}^{-3} \times 4.9 \times 10^{-3}\ \text{mol dm}^{-3}\ ]$$

$$= 2.4 \times 10^{-5}\ \text{mol}^2\ \text{dm}^{-6}$$

Example 12.12: Solubility product of silver iodide, Agl is 8.5×10^{-17} at 25°C. What is the molar solubility of AgI in water at this temperature?

Solution: Silver iodide dissolves according to the equation

$$\text{Agl(s)} \rightleftharpoons \text{Ag}^{+}\text{(aq)} + \text{I}^{-}\text{(aq)}$$

Let the solubility of AgI be is 's' mol dm^{-3} the concentrations of silver and iodide ions would be is 's' mol dm^{-3} each.

At equilibrium, $K_{sp} = [Ag^{+}][I^{-}]$; Substituting the values, we get

$[\text{'s' mol dm}^{-3}]\,[\text{'s' mol dm}^{-3}] = s^2 \text{ mol}^2 \text{ dm}^{-6} = 8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$

This gives , solubility (s) = $[8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}]^{1/2}$

$= 9.2 \times 10^{-9} \text{ mol dm}^{-3}$.

The solubility of AgI in water is therefore **9.2×10^{-9} mol dm^{-3}** at 298 K.

12.8.2 Effect of Common Ion on Solubility Equilibria

What will happen if we add a soluble salt containing a common-ion to a solution of a sparingly soluble salt ? You may reason out that according to Le Chatelier's principle, the common-ion will shift the equilibrium in backward direction which would reduce its solubility still further. This actually is the case. Let us understand it with the help of an example.

Example 12.13: Calculate the molar solubility of AgI in a solution containing 0.1 mol dm^{-3} $AgNO_3$. The solubility product of silver iodide, Agl is 8.5×10^{-17} mol^2 dm^{-6} at 298 K.

Solution: Silver nitrate is a strong electrolyte ionsing as

$$AgNO_3(s) \longrightarrow Ag^{+}(aq) + NO_3^{-}(aq)$$

and for AgI the solubility equilibrium is

$$\text{Agl(s)} \rightleftharpoons \text{Ag}^{+}\text{(aq)} + \text{I}^{-}\text{(aq)}$$

If we take the solubility of AgI to be 's' mol dm^{-3}, then the total concentration of Ag^{+} ions in the solution would be [0.1 + s] mol dm^{-3} ~ [0.1] mol dm^{-3} because the value of 's' is very small. And the concentration of I^{-} ions would be 's' mol dm^{-3}.

Substituting in the expression for $K_{sp} = [Ag^{+}][I^{-}]$; we get

$[0.1] \text{ mol dm}^{-3}\,]\,[\text{'s' mol dm}^{-3}] = 0.1 \text{ s mol}^2 \text{ dm}^{-6} = 8.5 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$

This gives , solubility (s) = $[8.5 \times 10^{-17}] / [0.1]$ mol dm^{-3}

$$= 8.5 \times 10^{-16} \text{ mol dm}^{-3}.$$

(The value of ‘s’ is clearly negligible in comparison with 0.10 and thus justifies our assumption)

The solubility of AgI in 0.1M $AgNO_3$ is therefore 8.5×10^{-16} mol dm^{-3} at 298 K. Compare this value with the solubility of AgI in water as determined in the previous example

Solvent	Water	0.1M $AgNO_3$
Solubility	**9.2×10^{-9} mol dm^{-3}**	**8.5×10^{-16} mol dm^{-3}.**

Thus we see that the solubility of a sparingly soluble salt is decreased in the presence of another salt that has common ion. This decrease in solubility is an example of the **Common Ion Effect**.

INTEXT QUESTIONS 12.3

1. Calculate the pH of a solution containing 0.05 M benzoic acid and 0.025 M sodium benzoate. Benzoic acid has a pK_a of 4.2.
2. Calculate the solubility product for Ag_2SO_4 if $[SO_4^{2-}] = 2.5$ ´ 10^{-2} M.

12.8.3 Application of Solubility Product in Qualitative Analysis

The qualitative analysis of cations is carried out by dividing them into several groups. This group separation of cations is based upon **selective precipitation** of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the K_{sp} of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of H_2S. The dissociation of H_2S can be written as

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions.

You are aware, that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the S^{2-} ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out.

WHAT YOU HAVE LEARNT

- Electrolytes are compounds, which, when dissolved in water, produce ions.
- Strong electrolytes are almost completely dissociated while weak electrolytes are only partially dissociated in their solutions.
- There are three different concepts of acids and bases proposed by Arrhenius, Brønsted and Lowry and Lewis respectively.
- According to Arrhenius Concept an acid is a substance capable of producing hydrogen ions by dissociating in aqueous solution while a base is a substance capable of providing a hydroxyl ion. The neutralization reaction is basically the reaction between a proton and a hydroxyl ion to give a molecule of water.
- Since a hydrogen ion H^+ is very small with high charge density it does not exist free in a polar solvent like water. It binds itself to a water molecule and form a hydronium ion (H_3O^+).
- According to Brønsted and Lowry, an acid is defined as a proton (H^+) donor, and a base is defined as a proton acceptor. An acid-base reactions can be thought of as a proton-transfer from an acid to a base. In this concept, acids and bases can be either ions or molecular substances.
- According to Brønsted and Lowry definition the species in either side of the acid-base equilibrium, differ by the gain or loss of a proton. These are called a conjugate acid-base pair. In such a pair a strong acid has a weak conjugate base while a weak acid has a strong conjugate base.
- Lewis definition is quite broad, according to him, an acid is defined as,'any atom, molecule or ion that can accept an electron pair from any other atom, molecule or ion, while a base is 'any atom, molecule or ion that can donate a pair of electron'. The product of a reaction between an acid and a base is called an adduct.
- Strong Arrhenius acids and bases dissociate completely in aqueous solutions where as the weak acids and bases undergo partial ionisation. Higher the extent of ionisation stronger the acid or the base.
- In Brønsted- Lowry concept, the relative strength of an acid is defined as its relative tendency to lose/donate a proton to water.
- The ionisation equilibria of weak acids and bases are characterized by equilibrium constants called ionisation constants. The values of these constants is a measure of their relative strength.
- Water can act both as a weak acid as well a weak base. In a sample of water a small number of water molecules undergo autoionisation, in which half the ions act as an acid while the other half acts as a base.

- In aqueous solutions the concentration of H_3O^+ can be expressed in terms of a logarithmic scale called pH scale. The pH of a solution is defined as pH $= -\log_{10}[H^+]$ or pH $= -\log_{10}[H_3O^+]$.
- A neutral solution has a pH of 7 ; any solution with a pH less than 7 is acidic while the ones with a pH of greater than 7 are basic in nature.
- The presence of common ions in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their pH on addition of small amount of an acid or a base. The pH of buffer solutions depend on their composition and can be found by using a simple equation called **Henderson Hasselbalch equation.**
- The aqueous solutions of certain salts also behave as acids or bases due to the hydrolysis of their cation or anion or both.
- In an aqueous solution of a sparingly soluble salt an equilibrium exists between the undissolved salt and the ions obtained from the dissolved salt. This is called **solubility equilibrium.**
- The product of the concentration of the ions in the solubility equilibrium is a constant called **solubility product** (K_{sp}) and is proportional to the solubility of the sparingly soluble salt.
- The presence common ions decreases the solubility of a sparingly soluble salt. This is called common ion effect and has widespread applications in qualitative analysis.

TERMINAL EXERCISE

1. What is degree of dissociation? What are factors upon which it depends.
2. Write the equilibrium constant expression for the following reaction.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

3. Explain why does a strong Bronsted – Lowry acid has a weak conjugate base?
4. What do you understand by the term 'amphoteric'? Show with the help of equations that water is amphoteric in nature.
5. Calculate the pH of 1×10^{-3} M solution of NH_4OH. The dissociation constant of NH_4OH is 1.85×10^{-5} mol dm^{-3}.
6. The pH of an aqueous solution of HCl is 2.301. Find out the concentration of hydrogen ions in this solution.
7. What is a buffer solution? What are its main constituents?
8. Solubility of lead iodide PbI_2 is 1.20×10^{-3} mol dm^{-3} at 298K. Calculate its solubility product constant.

9. Calculate the solubility of Bi_2S_3 in water at 298K if its $K_{sp} = 1.0 \times 10^{-97}$ mol^5 dm^{-15}.
10. Calculate the solubility of AgI in 0.10M NaI at 298 K. K_{sp} for AgI is 8.5×10^{-7} at this temperature.

ANSWERS TO INTEXT QUESTIONS

12.1

1. According to Arrhenius concept an acid is defined as a substance that is capable of producing hydrogen ion (H^+) by ionisation in aqueous solution. For example, HCl and CH_3COOH.
2. Arrhenius definition has the following drawbacks:
   - It is limited to only aqueous solutions and requires ionisation of the substance.
   - It does not explain the acidic or basic behaviour of some substances which lack a hydrogen (or a hydroxide) ion. For example, $AlCl_3$ and Na_2CO_3 which lack a hydroxide.
3. In the Brnsted-Lowry concept, any molecule or ion that can accept a proton is a base whereas in Arrhenius concept a base is the one which provides hydroxide ions in solution.
4. Acids HCl, H_3O^+

   Bases NH^3, CN^-
5. X is a weak electrolyte and Y is a strong electrolyte.

12.2

1. The ionisation of weak acid, HF, can be represented as

$$HF(aq) + H_2O \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

The expression for K_a would be, $K_a = \dfrac{[H_3O^+][F^-]}{[HF]}$

2. For a weak base BOH which partially dissociates in aqueous solutions, and has a degree of dissociation as α we can write

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Initial concentrations	c	~55	0	0
Equilibrium concentrations	$c(1-\alpha)$	~55	$c\alpha$	$c\alpha$

The equilibrium constant expression or base dissociation constant can be written as

$$K = \frac{[BH^+][OH^-]}{[H_2O][B]} = \frac{[c\alpha][c\alpha]}{c[1-\alpha]55}$$

rearranging we get,

$$\Rightarrow \qquad 55K = K_b = \frac{[c\alpha][c\alpha]}{c[1-\alpha]} = \frac{c^2\alpha^2}{c[1-\alpha]} = \frac{c\alpha^2}{(1-\alpha)}$$

Since the acid B is very weak, α <<1; we can neglected in comparison to 1 in the denominator to get

$$K_b \approx c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_b}{c} \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{c}}$$

3. Given hydronium ion concentration, $[H_3O^+] = 6.3 \times 10^{-2}$M

   As per definition pH $= -\log [H_3O^+]$

   $\Rightarrow$ pH $= -\log 6.3 \times 10^{-2}$

   $\Rightarrow$ pH $= -(0.7993 - 2.0000)$

   $\Rightarrow$ pH $= -(-1.2007) =$ **1.2007**

4. Given: Concentration of glycine = 1.0M

   $K_a = 1.67 \times 10^{-10}$.

   For a weak acid $\alpha = \sqrt{\frac{K_a}{c}} = \alpha = \sqrt{1.67 \times 10^{-10}} = 1.29 \times 10^{-5}$

   $\Rightarrow \qquad [H_3O^+] = 1 \times 1.29 \times 10^{-5} = 1.29 \times 10^{-5}$M

   pH $= -\log [H_3O^+] = -\log [1.29 \times 10^{-5}] = -(-4.8894) =$ **4.8894**

12.3

1. Here, [Acid] = 0.05M and [Salt] = 0.025M; and pK_a = **4.2**

   Substituting the values in Handerson equation, we get

   pH = 4.2 + log (0.05/0.025) = 4.2 + log 2 = 4.2 + 0.3010 = **4.5010**

2. Let the solubility of Ag_2SO_4 be ‘s’ mol dm^{-3}

   The concentrations of the **Ag^+** and the **SO_4^{-2}** would be **‘2s’** mol dm^{-3} and **‘s’** mol dm^{-3} respectively, and Ksp = **$[Ag^+]^2$ $[SO_4^{-2}]$**

   Given **$[SO_4^-] = 2.5 \times 10^{-2}$M $\Rightarrow$ [Ag+] $= 2 \times 2.5 \times 10^{-2}$M $= 5 \times 10^{-2}$M**

   Substituting the values in the expression of K_{sp} we get,

   Ksp $= [5 \times 10^{-2}]^2 \times [2.5 \times 10^{-2}] =$ **6.25×10^{-5} mol^3 dm^{-9}**

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13

ELECTROCHEMISTRY

Electrochemistry deals with the conversion of electrical energy into chemical energy and vice versa. When electric current is passed through an aqueous solution of certain substances or through molten salts, it causes a chemical reaction to occur. On the other hand, in dry cells, button cells or lead acid batteries chemical reactions occur which produce electrical energy. In this lesson you will study some aspects of these processes.

OBJECTIVES

After reading this lesson you will be able to:

- understand oxidation and reduction in terms of electron transfer concept;
- calculate oxidation number (ON) of an atom in a molecule or ion;
- balance the chemical equation for redox reaction;
- explain electrolytic conduction, conductance and molar conductivity;
- describe the effect of dilution on conductivity and molar conductivity of an electrolyte;
- differentiate between electrolytic and Galvanic cell;
- state Faraday's laws of electrolysis;
- predict and justify the products of electrolysis of some common electrolytes;
- state standard electrode potential and use it for calculation of standard electrode potential of a cell;
- explain standard Hydrogen electrode;
- describe electrochemical series and its application;
- state effect of concentration on electrode potential (Nernst equation);
- solve numericals based on Nernst equation and
- find relationship between emf and Gibbs energy change.

13.1 OXIDATION AND REDUCTION AS ELECTRON TRANSFER PROCESS

Oxidation and reduction reactions constitute a very important class of chemical reaction. The electronic concept looks at oxidation and reduction in terms of electron transfer : process in which an atom or ion looses one or more electron to the other is called oxidation and the process in which an atom or ion gains one or more electron is termed as reduction. In the formation of NaCl from Na and Cl

$\mathrm{Na} \rightarrow \mathrm{Na}^+ + e^-$ (loss of e^- by Na; oxidation)

$\mathrm{Cl} + e^- \rightarrow \mathrm{Cl}^-$ (gain of e^- by Cl; reduction)

Sodium undergoes oxidation and chlorine undergoes reduction. Here, sodium helps chlorine to undergo reduction and therefore it is called a reducing agent or reductant.

A reductant is a species in a chemical reaction which looses its electron to another reactant. Chlorine, on the other hand accepts electron, therefore it is an oxidising agent or oxidant. An oxidant is a species which accepts electrons in a chemical reaction.

It may be noted that oxidation and reduction processes do not take place independently but occur simultaneously and are thus called **oxidation-reduction** reaction or **redox** reactions. A redox reaction is a sum of oxidation and reduction half reactions in a chemical reaction.

13.2 OXIDATION NUMBER

It is easy to identify species undergoing oxidation or reduction in simple molecules. However, in polyatomic molecules, it is difficult to do the same. In the example of NaCl taken earlier it was easy to identify as sodium undergoing oxidation and chlorine undergoing reduction but in the reaction involving ferrous sulphate with potassium permanganate ($KMnO_4$) it is difficult. Therefore, a new term called **Oxidation number** has been introduced, **Oxidation number** is the apparent charge which an atom appears to have when each pair of electrons is counted with more elecronegative atom. Oxidation number is always assigned to an atom. It is a number written with +ve or – ve sign. The number indicates the number of electrons that has been shifted from an atom towards a more electro-negative atom, in a hetronuclear covalent bond. The +ve sign for the atom shifting its electron away from itself and –ve is given to more electro –ve atom. The concept of Oxidation Number is based on the assumption that in a polyatomic covalent bonding, shared pair of electrons belongs to more electro–ve atom. Oxidation state (OS) is also used for Oxidation Number.

13.2.1 Rules for Assigning Oxidation Number

There are certain rules that are followed for computing the oxidation number of an atom in a molecule or ion.

1. Oxidation number is taken as zero if atoms are present in elemental form. For example, O_2, Na, P_4 are elemental forms. They have oxidation number zero.
2. The oxidation number of a monatomic ion is the same as the charge present on it. For example, Na^+, Mg^{2+}, Al^{3+}, Cl^-, S^{2-} will have oxidation no +1, +2, +3, –1, –2 respectively.
3. The oxidation number of oxygen is –2 in almost all the compounds except (a) in peroxides e.g. Na_2O_2, H_2O_2 where oxidation number is –1 and (b) super oxides (KO_2) where it is $-\frac{1}{2}$.
4. The oxidation number of H is +1 when combined with non-metal and is –1 when combined with metal e.g. in HCl the O.N. of H is +1 but in Ca H_2 it is –1.
5. The Oxidation Number of alkali metal is +1 in its compounds.
6. In a compound made up of different elements the more electro negative element will have negative oxidation number and less electro negative atoms will have positive oxidation number e.g. in N Cl_3, N has +3 oxidation number and Cl has –1 oxidation number.
7. The sum of the oxidation numbers of all the atoms in a neutral compound is zero.
8. In a polyatomic ion, the sum of the oxidation numbers of all the atoms is equal to the charge on the ion. e.g. in CO_3^{2-}, the sum of oxidation Number of carbon and oxygen is –2.

Let us illustrate the above rules taking few examples. The oxidation number of S, N and Cl atoms in : (a) H_2SO_4 (b)NO^-_3 (c) ClO^-_4 respectively will be calculated as

(a)
1. Let the oxidation number of sulphur be x.
2. Since the oxidation number of O is –2. Therefore the sum of four O atoms is equal to –8.
3. The oxidation number of each H is +1 as bonded to a non-metal so two H atoms have total oxidation number of +2.
4. H_2SO_4 is a neutral molecule. Therefore the sum of all the oxidation numbers is equal to zero. Thus

   $+2 + x - 8 = 0$

   $x = +6$

   Therefore oxidation number of sulphur in H_2SO_4 is + 6.

(b) NO_3^- first assign –2 oxidation number to each O atom. Here the sum of the oxidation number of all the atoms will equal to charge present on the ion.

$\therefore$ $x - 6 = -1$

$x = +5$

oxidation number of N is +5.

(c) In ClO_4^- $x - 8 = -1$

$x = +7$

13.3 BALANCING REDOX REACTION

The redox reaction can be balanced by any of the following methods :

(a) Oxidation number method.

(b) Ion electron method.

13.3.1 Balancing by Oxidation Number method

The steps involved in balancing redox reactions by this method are as follows:

1. Write the skeletal equation of reaction i.e. chemical equation without the stoichiometric coefficient.
2. Write the oxidation number of each atom above its symbol in the equation.
3. Identify the atoms undergoing change in oxidation number.
4. Calculate the increase or decrease in oxidation number per atom for the atom undergoing a change in oxidation number. If more than one atom is involved, multiply the increase or decrease in number with the number of atoms undergoing the change to determine the total change in oxidation number.
5. Equate the increase and decrease in oxidation number on the reactant side by multiplying the formulae of the oxidising and reducing agents suitably.
6. Balance the equation with respect to all the atoms except hydrogen and oxygen.
7. Finally balance H and O also.
8. If the reaction is taking place in acidic medium balance the O atoms by adding required number of H_2O molecule on the side where O atoms are less in number. Balance the H atoms by adding H^+ to the side deficient in H atoms.

9. In the basic medium by add required number of negative charges by adding required number of OH^- ions to the side deficient in the magnitude of charges, then add H_2O molecules to balance OH^- ions.

For example : When Phosphorus is treated with nitric acid, nitric oxide is formed.

1. The skeletal equation is

$$P + HNO_3 \longrightarrow HPO_3 + NO + H_2O$$

2. Write the oxidation number of each atom on the given skeletal equation

$$\overset{0}{P} + \overset{+1\,+5\,-2}{HNO_3} \longrightarrow \overset{+1\,+5\,-2}{HPO_3} + \overset{+2\,-2}{NO} + \overset{+1\,-2}{H_2O}$$

3. P and N are undergoing change in Oxidation Number.

$$\overset{0}{P} + \overset{+5}{HNO_3} \xrightarrow[\text{decrease in ON = 3}]{\text{increase in ON = 5}} \overset{+5}{HPO_3} + \overset{+2}{NO} + H_2O$$

4. Equating the increase and decrease in Oxidation Number of P and N on the reactant side

$$3P + 5HNO_3 \longrightarrow HPO_3 + NO + H_2O$$

5. Balance the P and N atoms on both sides of the equation

$$3P + 5HNO_3 \longrightarrow 3HPO_3 + 5NO + H_2O$$

6. O and H are already balanced in the equation.

13.3.2 Balancing by Ion Electron Method

This method is based on the principle that electrons lost during oxidation half reaction is equal to the electrons gained in the reduction half reaction. The steps involved are

1. Write the skeleton equation.
2. Write the oxidation number of all the atoms above their symbols in the skeletal equation.
3. Find the atoms undergoing change in Oxidation Number. Thus find out the species getting oxidised and reduced respectively.
4. Split the whole (net) equation into two half reactions i.e. oxidation half reaction and reduction half reaction.

5. Balance the atoms, undergoing change in oxidation number in each half reaction.

6. Calculate the total change in oxidation number in each half reaction which is equal to total number of electron transfer.

7. Add total number of electron transfer as calculated above on the reactant side in reduction half and on the right hand side on the oxidation half reaction.

8. Balance the charges by adding H^+ (for reactions in acidic medium) or OH^- (reactions basic medium) either on left or right of equation.

9. Finally balance H and O by adding H_2O on the required side of the reaction.

10. Add the two half reactions such that total number of electrons cancel out on both sides. To do so half reactions may be required to multiplied by some numbers to make the number of electrons equal on both sides.

13.3.3 Example of Balancing

Example 13.1 : Balance the following skeletal reaction by ion electron method

$$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} \quad \text{in acid medium}$$

Refering to the rules given :

Step I and II

Write the oxidation number of the atoms above their symbol in the skeletal equation

$$\overset{+6}{Cr_2}\,O_7^{2-} + \overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{+3}{Fe^{3+}}$$

Step III : Oxidation number of Fe^{2+} is increasing; therefore it is undergoing oxidation and oxidation number of Cr is decreasing so it is undergoing reduction.

Step IV : Split the reactions in two half reactions

(a) Reduction half reaction

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

(b) Oxidation half reaction

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Balance the first reduction half reaction

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Step V : Balance the atoms undergoing change in Oxidation Number.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Step VI & VII : Write the total number of electron transfer taking place. Here each atom undergoes change in ON by 3 therefore two Cr atoms undergoes change in Oxidation Number by 6.

$$Cr_2O_7^{2-} + 6e \longrightarrow 2Cr^{3+}$$

Step VIII : Balance the charge by adding H^+ on the left side

$$Cr_2O_7^{2-} + 6e + 14H^+ \longrightarrow 2Cr^{3+}$$

Step IX : Balance the H and O by adding H_2O on either side

$$Cr_2O_7^{2-} + 6e + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Balancing the oxidation half reaction

According the steps as followed for reduction half reaction

$$Fe^{2+} \longrightarrow Fe^{3+}$$

(i) Atoms are balanced on both side so we go to next step, that is number of electron transfer taking place

$$Fe^{2+} \longrightarrow Fe^{3+} + e.$$

(ii) Balance the charge and it is balanced.

Step X : Add the two half reactions

$$\begin{array}{l} Fe^{2+} \longrightarrow [Fe^{3+} + e] \times 6 \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Ca^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

INTEXT QUESTIONS 13.1

1. Determine the Oxidation number of element in the bold letter in the following:

SiH_4	**B**H_3	**B**F_3	**S**$_2O_4^2$
BrO_4	H**P**O_4^2	**S**$H_{12}O$	H**N**O_3

2. How does oxidation number change in oxidation and reduction?

3. Mention the oxidising agent and reducing agent in the following.

$$H_2S + HNO_3 \longrightarrow NO + S + H_2O$$

4. Write the half reaction for the following

$$2I^{-}_{(aq)} + 2Fe^{3+}_{(aq)} \longrightarrow I_2(s) + 2Fe^{2+}(aq)$$

$$Mg(s) + CI_2(g) \longrightarrow MgCI_2(s)$$

$$I_2 + HNO_3 \longrightarrow HIO_3 + NO_2 + H_2O$$

5. Balance the equation by oxidation number method

$$CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$$

$$MnO_4 + HCl \longrightarrow MnCl_2 + C_2 + H_2O$$

6. Balance the following by ion eelctro half reaction method

$NO_3^- + Bi \longrightarrow Bi^{3+} + NO_2$ acidic medium

$M_nO_4 + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$ acidic medium

$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Fe^{3} + Cr^{3+}$ acidic medium

$Al + NO_3^- \longrightarrow Al(OH)_4^- + NH_3$ basic medium

13.4 ELECTROLYTIC CONDUCTION

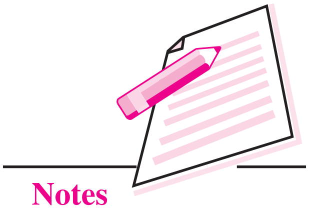
When electricity is passed through an aqueous solution, it may or may not conduct current. The chemical substances whose aqueous solutions conduct electricity are called electrolytes and those which do not conduct current are called as non-electrolytes. This phenomenon of conduction of current through a solution is called electrolytic conduction.

Electrolytic conduction takes place due to the movement of cations and anions in a solution. The electrical conductance of a solution, depends upon (a) nature of solute (b) valency of its ion, (c) the concentration in solution and (d) the temperature. In this section we will learn about various ways of expressing the conductance of electrolytes and the factors affecting them.

13.4.1 Conductance and Conductivity

Like solid conductors, electrolytic solutions also obey Ohm's Law. When a current of *I* amperes flows through a solution which offers a resistance of R ohms and a potential difference of V volts is applied, then according to ohm's law

$$V = I \,.\, R$$



If the solution is taken in a conductivity cell which has two parallel electrodes l cm apart and each having an area of cross section A cm^2, the resistance R of the electrolyte is found to be directly proportional to l and inversely proportional to A i.e.

$$R \propto \frac{l}{A}$$

or

$$R = \rho \, . \, \frac{l}{A} \qquad \text{....(i)}$$

Where ρ "rho" is a constant of proportionality and is called *specific resistance* or *resistivity*. It is characteristic of the nature of electrolyte, its concentration and temperature.

In case of solutions, it is preferred to discuss their *conductance* and *conductivity* rather than their resistance and specific resistance. **The conductance is reciprocal of resistance and the conductivity is reciprocal of specific resistance.**

Conductance is denoted by L and is measured in the unit of ohm^{-1} which has now been named as *siemens, S*. The conductivity is denoted by k "kappa". Thus by definition

$$L = \frac{1}{R} \quad \text{and} \quad k = \frac{1}{\rho} \qquad \text{...(ii)}$$

The units of k can be worked out from relation (i) as under :

The inverse of (i) is,

$$\frac{1}{R} = \frac{1}{\rho} \, . \, \frac{A}{l}$$

or

$$L = k \, \frac{A}{l}$$

and

$$k = L \frac{l}{A}$$

$$= S \, \frac{\text{cm}}{\text{cm}^2}$$

$$= S \, \text{cm}^{-1}$$

The conductivity (K) is expressed in $S \text{ cm}^{-1}$ or 100 S m^{-1}.

13.4.2 Measurement of Conductance

The conductance of an electolyte is measured with the help of a conductivity cell. Conductivity cell is a device which has two parallel platinum electrodes coated with platinum black.

The SI unit of length is metre, hence SI unit of conductivity (K) is Sm^{-1}, but the commonly used unit is Scm^{-1}. In the expression for conductivity, $\frac{\ell}{A}$ is a constant. Here *l* represents the distance between the two parallel electrodes and A represents the area of cross section of the electrodes. Thus for a given conductivity cell, $\frac{\ell}{A}$ is a constant called cell constant.

$$K \text{ (conductivity)} = \text{conductance} \times \text{cell constant}$$

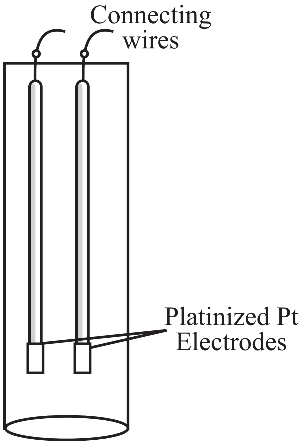


Fig. 13.1 : *Condivity Cell*

The conductivities of some substances are given in the table.

Table 13.1 : The values of conductivity of some selected substances at 298 K

Substance	$k/S\ cm^{-1}$	Substance	$k/S\ cm^{-1}$
Pure water	6.0×10^{-8}	Silver metal	6.1×10^{5}
0.1 M HCl	3.5×10^{-2}	Mercury metal	1.0×10^{4}
0.1M NaCl	9.2×10^{-3}	Glass	1.0×10^{-14}
0.1M CH_3COOH	4.7×10^{-4}		
0.1M NH_4OH	3.4×10^{-4}		

We find from the table that the conductivities of metals are very high and that of pure water and glass very low.

13.4.3 Molar Conductivity

The electrolytic conductivity of a solution depends on the concentration of the electrolyte in the solution. Therefore, the conductivity of an electrolyte is normally expressed as molar conductivity.

Molar conductivity is the conducting power of all the ions furnished by one mole of an electrolyte in a solution of specified concentration.

It is denoted by λ_m and is related to K by the relation.

$$\lambda_m = \frac{1000\,K}{M} \qquad \text{.....(vi)}$$

Where M is the molarity of the solution. Its units are $S\ cm^2\ mol^{-1}$.

13.5 FACTORS AFFECTING CONDUCTIVITY

As mentioned the conductivity of an electrolyte depends upon the following aspects of the electrolyte.

(a) **Nature of Electrolyte :** Conductivity of an electrolyte depends upon the nature of electrolyte on the following points :

  (i) **Weak or strong electrolyte :** A weak electrolyte furnishes fewer ions therefore it has lower conductivity than a strong electrolyte of same concentration.

  (ii) **Valency of the ions :** The ions with higher valency carry more charge and therefore they conduct more charge than the ion of lower valency. Thus higher the valency of the ion greater is the conducting power.

  (iii) **Speed of the ion :** The ion which can move faster will carry the charge also faster and therefore has more conducting power.

(b) **Temperature :** Conductivity of an electrolyte generally increases by 2–3 percent for each degree rise in temperature. With increase in temperature the viscosity of the solvent decreases and thus ion can move faster. In case of weak electrolyte, when the temperature is increased its degree of dissociation increases, thus conductivity increases.

(c) **Concentration :**

  (i) **Variation of conductvity (*k*) with concentration.** When the solution is diluted its conductivity also decreases. It is because *k* is the conducting power of all the ions present per cm^3 of the solution. When the solution is diluted the number of ions per cm^3 also decreases, hence *k* decreases.

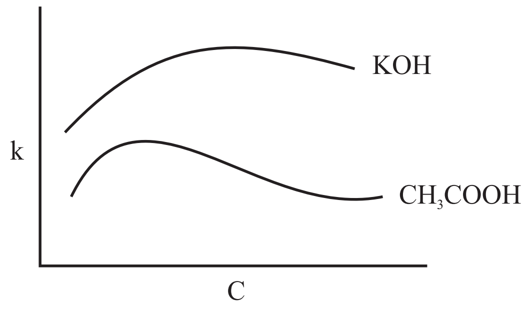


Fig. 13.2 : *Variation of conductivity with concentration*

  (ii) **Variation of Molar and Equivalent conductivity with concentration:** As the solution is diluted its molar conductivity increases. Λm is given as

$$\lambda m = \frac{1000k}{M}$$

where *k* is conductivity and M is molar concentration.

This increase in λm is a resultant of two factors. On decreasing the concentration both k and M decreases. Of the two (*k*) tries to decrease λm while the other factor (M) tries to increase it. Since the decrease in M is much more, the net result is that λm increases. However, strong and weak electrolyte as show different type of behaviour on dilution (Fig. 13.3)

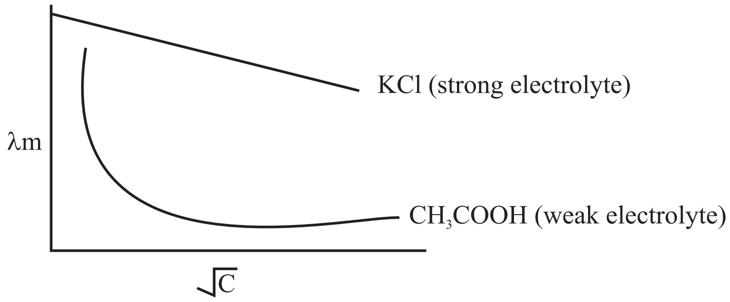


Fig. 13.3 : *Variation of molar conductivity with concentration*

From the Fig. 13.3 we find that the increase in molar conductivity for a strong electrolyte like KCl is very gradual on dilution and also the value is high at all concentrations. Whereas for a weak electrolyte like CH_3COOH, there is a gradual increase in λm on dilution which is followed by a sharper increase on further dilution. These observations can be explained as : since KCl is a strong electrolyte, it is fully dissociated at all concentrations. In concentrated solution, attraction between opposite ions is large and their conducting ability is less. On dilution inter-ionic forces decrease and ions can move faster leading to the increase in molar conductivity.

On the other hand, in weak electrolytes, molar conductivity is low in concentrated solution. This is due to partial dissociation (ionisation) of weak electrolytes. On diluting the solution the degree of ionisation increases, which increases the number of ions. This leads to a sharp increase in molar conductivity in weak electrolytes.

13.5.1 Kohlrausch's Law

Kohlrausch determined the molar conductivity at infinite dilution for a large number of strong electrolytes. On the basis of his observations he concluded that at infinite dilution, each ion makes a definite contribution to the total molar conductivity of an electrolyte. This individual contribution is called ***molar ionic conductivity***. He generalised his observations as

"At infinite dilution each ion of the electrolyte makes a definite contribution towards conductivity of the electrolyte and it is independent of the presence of other ions of the electrolyte." This is called Kohlrausch's Law of independent migration of ions.

For a salt like KCl, molar conductivity at infinite dilution can be written as

$$\lambda_m^\infty \text{ KCl} = \lambda_m^\infty \text{K}^+ + \lambda_m^\infty \text{Cl}^-$$

In general for a salt of formula A_xB_y the molar conductivity at infinite dilution is written as

$$\lambda_m^\infty \ (A_xB_y) = x \ \lambda_m^\infty \ (A^{y+}) + y \ \lambda_m^\infty \ (B^{x-})$$

where λ_m^∞ indicates molar conductivity at infinite dilution. This law is used to calculate the molar conductivity at infinite dilution for weak electrolytes whose λ_m^∞ can not be obtained graphically.

Example 13.2 : Λ^0 for NaCl, HCl and CH_3COONa are 126.0, 426.0 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ^0 for CH_3COOH.

Solution $\Lambda^0 CH_3COOH = \lambda^0(H^+) + \lambda^0(CH_3COO^-)$

$$= \lambda^0(H^+) + \lambda^0(Cl^-) + \lambda^0(Na^+) + \lambda^0(CH_3COO^-) - \lambda^0(Na^+) - \lambda^0$$

$$= 426.0 + 91.0 - 126.0 = 391.0 \text{ S cm}^2 \text{ mol}^{-1}.$$

INTEXT QUESTION 13.2

1. How does the solution of electrolytes conduct electricity?
2. Define conductivity and molar conductivity.
3. Give the units of conductance and conductivity.
4. List factors affecting the conductance of an electrolyte.
5. Draw a graph showing variation in molar conductivity of weak and strong electrolytes.
6. Write the expression for molar conductivity at infinite dilution for $Al_2(SO_4)_3$.

13.6 ELECTRO CHEMICAL CELLS

An electrochemical cell is a device used for the interconversion of electrical and chemical energy. An electrochemical cell contains two electrodes (cathode and anode) and an electrolyte.

These are of two types; based on the nature of conversion of energies

(a) Electrolytic cell (Faradaic cell)

In electrochemical cells, a battery is used to carry out redox reactions on the electrodes of the cell. Thus, these cells convert electrical energy into chemical energy.

(b) Galvanic cell (Voltaic cell)

In galvanic cells an emf is developed as a result of radox reaction occuring on the electrodes. These cells convert chemical energy into electrical energy.

13.7 ELECTROLYTIC CELLS OR RARADAIC CELLS

An electrolytic cell consists of two electrodes connected to a battery as shown in Fig 13.4.

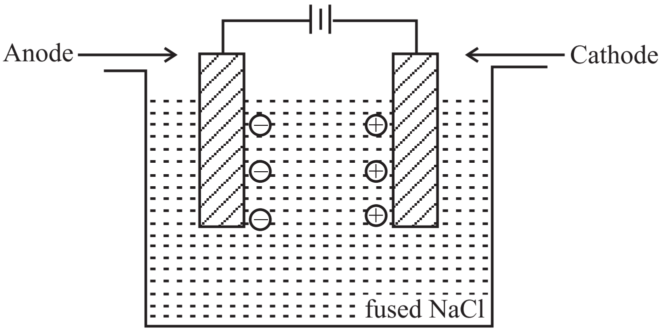


Fig. 13.4 : *Electrolytic cell*

In an electrolytic cell electrical energy is converted into chemical energy. The process of decomposition of an electrolyte into its ions when an electric current is passed through it, is called **electrolysis**.

When electricity is passed through an electrolyte, a chemical change i.e. decomposition of the electrolyte into ions takes place at the electrode. Oxidation and reduction reactions occur in the cell.

In the electrical field Cl^- ions migrate to the +ve electrode (anode) and undergo oxidation by loosing electrons. Na+ ions will go to –ve electrode (cathode) and undergo reduction.

The process can be represented as :

oxidation at anode $Cl^- \longrightarrow Cl + e^-$

$Cl + Cl \longrightarrow Cl_2(g)$

and reduction at cathode, $Na^+ + e^- \longrightarrow Na.$

13.7.1 Faraday's Laws of Electrolysis

Michael Faraday studied the quantitative aspects of electrolysis and expressed the results of his study in the form of the following two laws which are known as the Faraday's laws of electrolysis.

(I) Faraday's First Law of Electrolysis

It states that the mass of a substance liberated during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte taken as a solution or as melt.

Mathematically, if w is the mass of a substance liberated or discharged on passing Q coulomb of electricity

$$w \propto Q$$

and
$$w = zQ \qquad (1)$$

where z, the constant of proportionality is called **electrochemical equivalent** of the substance

The quantity of electricity passed, Q, is related to the strength of the current passed in amperes I, and the time in seconds, t.

$$Q = I.t$$

$$\therefore \qquad w = zIt \qquad (2)$$

Electrochemical equivalent, z, of a substance is its mass liberated or deposited on passing 1 coulomb ($Q = 1$) charge or one ampere ($I = 1$) current for one second ($t = 1$).

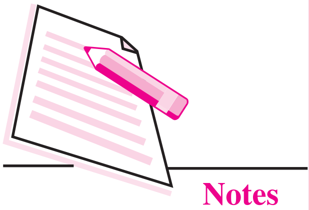
(II) Faraday's Second Law of Electrolysis

This law relates the masses of different substances liberated or discharged by passing the same amount of electricity. It states that when the same quantity of electricity is passed through different electrolytes (taken in different electrolytic cells which are connected in series) the masses of different substances liberated are proportional to their chemical equivalent masses. Equivalent mass of any substance undergoing a redox reaction (oxidation or reduction) is related to its molar mass as.

$$\text{Equivalent mass} = \frac{\text{Molar mass}}{\text{Number of electrons last or gained}}$$

Let w_A and w_B be the masses of two substances liberated in two electrolytic cells connected in series, then:

$$\frac{w_A}{w_B} = \frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}}.$$



Example 13.3: What is the mass of silver deposited when 500 coulomb electricity is passed through a solution of $AgNO_3$? (Atomic mass of Ag = 108 u)

Solution:

Silver is deposited on cathode according the reaction

$$\begin{array}{ccc} Ag^+(aq) + & e^- \rightarrow & Ag(s) \\ 1 \text{ mol} & 1 \text{ F} & 1 \text{ mol} \\ & 96500 \text{ C} & 108 \text{ g} \end{array}$$

Thus, 1 mole of electrons (1 Faraday) or 96500 coulombs of electricity are required to produce 108 g of silver

96500 C produce 108 g of Ag

500 C would produce $\frac{108 \times 500}{96500} = 0.56\text{g of Ag}$

Example 13.4: On passing electric current for some time, it was found that 32.4 g Ag had deposited on cathode in a cell filled with $AgNO_3$. How much would a copper cathode of another electrolytic cell containg $CuSO_4$ solution weigh after the electrolysis if it was connected in series to the $AgNO_3$ cell? The mass of the copper cathode before electrolysis was 27.33 g, Equivalent masses:

Ag = 108 g; Cu = 31.75 g

Solution:

According to the Faraday's second law of electrolysis

$$\frac{\text{Mass of copper deposited}}{\text{Mass of silver deposited}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}.$$

$$\frac{\text{Mass of copper deposited}}{32.4 \text{ g}} = \frac{31.75 \text{ g}}{108 \text{ g}}$$

$$\text{Mass of copper deposited} = \frac{31.75 \text{ g} \times 32.4 \text{ g}}{108 \text{ g}} = 9.53 \text{ g}$$

Mass of copper cathode before electrolysis = 27.33g

Mass of copper cathode after electrolysis = 27.33 + 9.53

= 36.86 g

Notes

13.7.2 Products of Electrolysis

During electrolysis, cations are reduced at cathode and anions are oxidized at anode and a chemical reaction occurs in a non-spontaneous direction. The minimum potential required for any electrode process to occur is called its **discharge potential** or **decomposition potential**. Discharge potential is *equal to* the electrode potential for cathodic (*reduction*) process and *equal in magnitude but opposite in sign* to the electrode potential for anodic (*oxidation*) process. At any electrode that process (oxidation or reduction) would occur which is the easiest. The reduction of that ion would occur which has highest reduction potential and the oxidation of that ion would occur which has the smallest reduction potential in highest oxidation potential.

In many cases, the actual discharge potential exceeds the expected value. The difference between the two is known as **over potential**. Over potential is commonly observed when gaseous products are formed and depends upon the nature of cathode. Over potential for the discharge of H_2 gas is zero on a platinum cathode but it is 1.5 V on mercury cathode. Due to over potential the process which occur may not be the one which otherwise is the easiest. Let us take some, examples now.

1. Electrolysis of molten NaCl (Pt electrodes).

Molten NaCl furnishes its own cations and anions

$$NaCl(l) \rightarrow Na^+ + Cl^-$$

So only one process is possible at anode and cathode

Anodic process (oxidation): $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathodic process (reduction): $2Na^+ + 2e^- \rightarrow 2Na(l)$

2. Electrolysis of aqueous NaCl (Pt electrodes)

Dissolved NaCl ionizes in its solution as

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$

At Cathode

At cathode it is not only Na^+ ions that can be reduced, but H_2O also can be reduced. The two possible reduction processes are:

(i) $Na^+ + e^- \rightarrow Na \quad E° = -2.71$ V

(ii) $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad E° = -0.83$ V

Out of these, the reduction potential of water is much greater than that of Na^+. Therefore only H_2 gas is evolved at cathode. (However, if **mercury cathode** is used, due to large over potential of discharge of H_2, Na^+ ions are reduced and Na is produced which reacts with water to produce NaOH and H_2. It is used for manufacture of NaOH)

At anode

At anode, Cl^- ions and H_2O both can get oxidized:

(iii) $2Cl^- \rightarrow Cl_2(g) + 2e^-$ $\qquad E° = -1.36$ V

(iv) $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ $\qquad E° = -1.23$ V

Oxidation potential of water is slightly greater than that of Cl^- so its oxidation should be easier. But due to *over potential* for discharge of O_2, it becomes more difficult and Cl_2 gas is evolved at anode. Thus the electrolysis of aqueous NaCl occurs as:

Anodic process (*oxidation*): $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathodic process (reduction): $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

H_2 is evolved at cathode and Cl_2 at anode.

3. Electrolysis of aqueous $CuSO_4$ (Pt electrodes)

$CuSO_4$ ionizes in its aqueous solution as

$$CuSO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

At cathode, copper is deposited because reduction of Cu^{2+} is easier than that of water and at anode O_2 is evolved as oxidation of water is easier than that of SO_4^{2-} ions.

Anodic Process (*oxidation*): $2H_2O \rightarrow O_2(g) + 4H^+_{(aq)} + 4e^-$

Cathodic process (*reduction*): $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Thus copper is discharged at cathode and O_2(g) at anode.

4. Electrolysis of aqueous $CuSO_4$ (Cu electrodes)

When copper electrodes are used, oxidation of Cu (from electrode) is easier than oxidation of H_2O or SO_4^{2-} ions. However at cathode, reduction of Cu^{2+} ions occurs as the reduction of water is more difficult even on copper electrode

Anodic process (*oxidation*): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathodic process (*reduction*): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

This process is used for electrolytic refining of copper in its metallurgy.

13.8 GALVANIC CELLS OR VOLTAIC CELLS

In such a cell chemical energy is converted into electrical energy. Dry cells, car batteries and button cells used in wrist watches are all examples of this type of cell. They are energy producing devices.

13.8.1 Redox Reaction and Galvanic Cell

You have already learnt that when electricity is passed through a solution, redox reaction takes place. Now we shall learn how redox reaction can be used to produce electricity.

When a Zinc rod is dipped in $CuSO_4$ solution, a reaction starts in the solution.

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

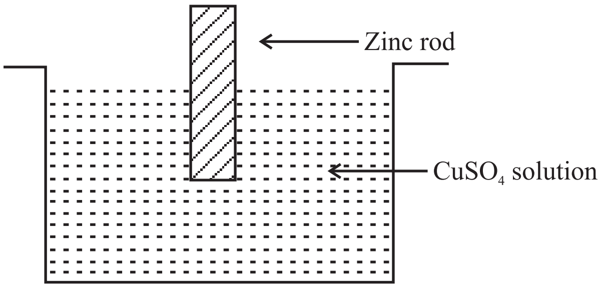


Fig. 13.5 : *Redox reaction*

It is an example of redox reaction. The two ***half reactions*** are

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad \text{oxidation}$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad \text{reduction}$$

In this ***redox reaction*** the electrons given by zinc rod have been directly consumed by Cu^{2+} ion. But, if somehow we make the electrons given by Zinc rod to flow through a wire to reach Cu^{2+} ions, we shall be producing electric current. To do so, the reaction is carried out in the electrochemical cell as shown Fig. 13.6 :

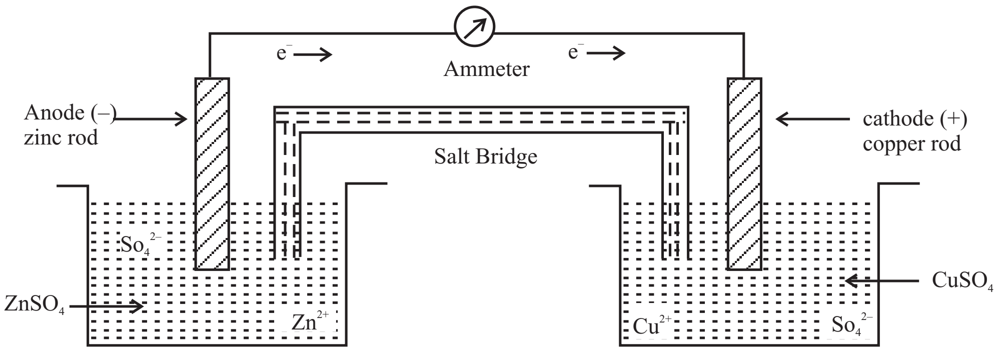


Fig. 13.6 : *Daniell cell having zinc and copper electrodes*

The redox reaction in the electro chemical cell has been modified Zinc rod is dipped in zinc sulphate solution in one beaker while copper rod is dipped in another beaker containing $CuSO_4$ solution. The two solutions are connected through a ***salt bridge*** and the two metals are connected to an ammeter with the help of wire. We find electrons move through the wire from zinc to copper rod.

A metal dipped in its own salt solution is called as ***half cell***. Zinc rod dipped in-zinc sulphate solution is oxidation half cell because oxidation takes place.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation)}$$

The released electrons are taken up by zinc rod and it becomes negatively charged.

Copper in copper sulphate is reduction half cell. Copper acts as cathode and reduction take place here. Copper rod becomes positively charged. Copper gains electrons and in this process, beomes positively charged.

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$

Here the electrons will move from negatively charged electrode to positively charged copper electrode.

Flow of electrons in the external circuit

The electrons released at the anode during oxidation flow through the external circuit and reach the cathode where they are taken up for reduction. Thus in a galvanic cell the electrons always flow from anode to cathode while the conventional positive current flows in the opposite direction i.e. from cathode to anode. Since the electric current always move in a closed circuit salt bridge is used to makeelectrical contact between the two half cells.

13.8.2 Salt Bridge

A salt bridge is a inverted U tube filled with a concentrated solution of an inert electrolyte like KCl or NH_4NO_3 which does not take part in the cell reaction. The electrolyte is taken in the form of solution and mixed with agar-agar. The mixture is heated and filled in the U tube when hot. On cooling it sets into a jelly like mass and does not flow out, during its use. Salt bridge has two functions.

(i) It completes the inner circuit. It acts as a contact between the two half cells without any mixing of electrolytes.

(ii) It prevents accumulation of charges in two half cells and maintains electrical neutrality.

Cations and anions of the salt bridge move into two half cells and neutralise the excess charge. The anions move into oxidation half cell and neutralise the excess charge. The cations move into the reduction half cell and neutralise the charge.

In a Daniell cell a salt bridge is replaced by a porous pot, to make the cell more handy to use.

13.8.3 Symbolic Representation of Galvanic Cells

In the previous section the cell was a Zn-Cu cell. But any two suitable metals can be used to make the cell and everytime we do not always draw the diagrams showing the cell. It is represented in the symbolic form with the help of standard notation. The rules of notations are as follows :

1. Anode is written on the left hand side and cathode on the right hand side.
2. The metal electrode in the anode half cell is written by its symbol and this is followed by the cation (metal ion) along with its concentration in a small bracket. The metal and cations are separated by vertical line or a semicolon (:)

$$Zn_{(s)} \mid Zn^{2+}_{(aq)}\ (1M)$$

3. In the reduction half cell the anion along with its concentration is written first, then vertical line and then the metal

$$Cu^{2+}_{(aq)}\ (1M) \mid Cu_{(s)}$$

4. A salt bridge is represented by two vertical lines.

Thus the Galvanic cell described above is written as

$$Zn_{(s)} \mid Zn^{2+}_{(aq)}(1M) \parallel Cu^{2+}_{(aq)}(IM) \mid Cu_{(s)}$$

or

$$Zn \mid Zn^{2+}_{(1M)} \parallel Cu^{2+}_{(1M)} \mid Cu$$

13.9 ELECTRODE POTENTIAL

Metal atoms have tendency to lose electrons and go into solution as metal ions. Electrode potential is a measure of the tendency of metal atoms to gain or loose electrons when in contact with a solution of its own ions.

When a metal strip M is immersed in a solution of its salt containing ions (M^{n+}), one of the processes as showin in Fig. 13.7 (a) or (b) can occur.

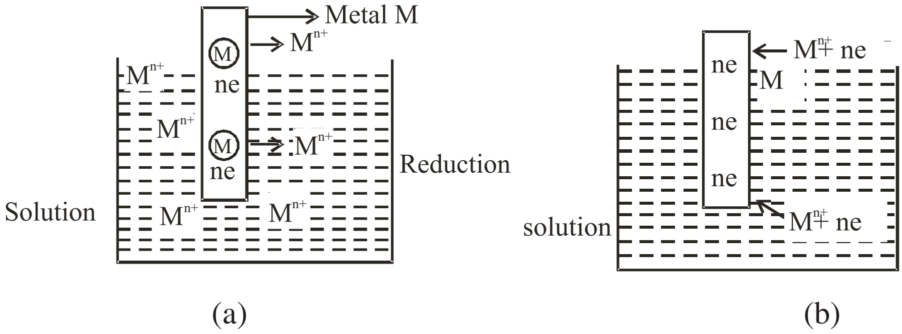


Fig. 13.7 : *Metal placed in a solution of its ions*

(i) The dissolution process where atoms of metal electrode M may loose some electrons to the electrode and enter the solution as M^{n+}

$$M \rightarrow M^{n+} + ne \text{ (metal is oxidised)}$$

The metal electrode gets negative charge and the solution gets extra positive charge.

(ii) The deposition process where metal cations M^{n+} from the solution may come in contact with the metal strip, gain some electrons and get converted into metal atoms M, which get deposited on the surfance of metal strip. Seperation of charges take place and a potential is developed called electrode potential.

$$M^{n+} + ne^{-} \rightarrow M \text{ (the ion is reduced)}$$

The electrode reaction reaches an equilibrium as represented below

$$M(S) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^{-}$$

Electrode potential is the potential developed at the interface between metal and its salt solution; when a metal is dipped in its own salt solution.

13.9.1 Standard Electrode Potential

An electrode is said to be in the standard state if the concentration of the electrolyte is one molar and the temperature is 298K. Then its electrode potential is called standard electrode potential and denoted by E°. If any gas is used to make the electrode then the pressure of the gas should be 1 bar.

13.10 MEASUREMENT OF ELECTRODE POTENTIAL

It is not possible to measure single electrode potential. It is because the reaction taking place at the electrodes is oxidation or reduction and these reactions do not take place in isolation. It can be measured with respect to a reference electrode. The electrode used as reference electrode is standard hydrogen electrode (SHE).

13.10.1 Standard Hydrogen Electode

Standard Hydrogen Electrode (SHE) consists of a container, containing 1M HCl solution kept at 298K. A wire containing Platinum electrode coated with platinum black is immersed in the solution. Pure hydrogen gas is bubbled in the solution at 1bar pressure.

The potential of SHE (E°) is taken as zero volt at all temperatures.

Standard hydrogen electrode may act as anode or cathode depending upon the nature of the other electrode. If its acts as anode, the oxidation reaction taking place is

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$$

If it acts as cathode then the reduction half reaction occuring is

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

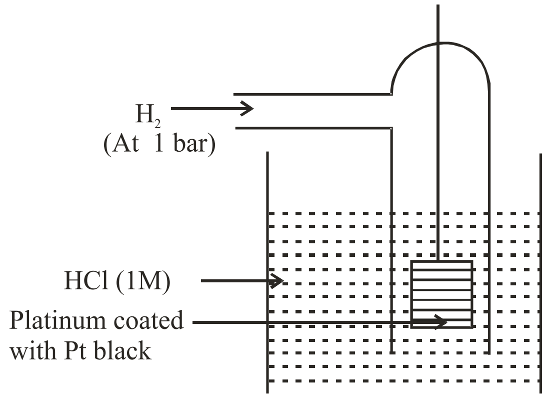


Fig. 13.8 : *Standard Hydrogen electrode*

13.10.2 Measurement of Standard Electrode Potential

(i) **Determination of magnitude :** The standard electrode potential of an electrode can be measured by combining it with standard hydrogen electrode. To illustrate, let us take the example for the measurement of standard electrode potential of zinc electrode. A zinc strip is dipped in 1M $ZnSO_4$ solution and it is connected to Standard Hydrogen electrode. The cell emf is found to be 0.76 V.

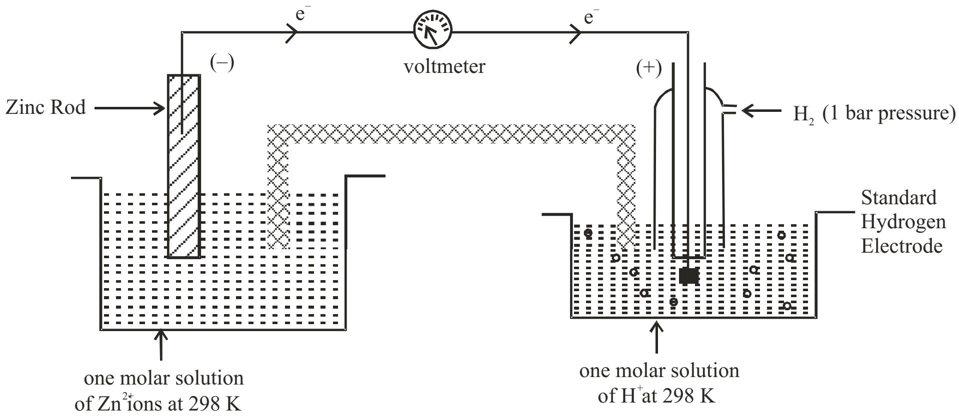


Fig. 13.9 : *Measurement of standard electrode potential of Zn/Zn^{2+} electrode*

When copper electrode i.e. copper dipped in 1M $CuSO_4$ solution is connected to standard hydrogen electrode then the cell emf is 0.34 .

(ii) **Sign of electrode potential**

The galvanic cell formed by the combination of SHE and electrode under study, the polarity of the electrode is determined with the help of a voltmeter. In case the given electrode is found to be positive electrode, its electrode potential is given the positive sign and if it is negative then it is given the negative sign. In the case of zinc connected to SHE the polarity is negative but in case of copper it is positive.

13.11 ELECTROCHEMICAL SERIES AND ITS APPLICATIONS

13.11.1 Cell emf and Potential difference

The difference in potential of the two electrodes (or half cells) of a galvanic cell, when measured in the open circuit is called the cell electromotive force or cell emf. When it is measured in a closed circuit with some external load it is called potential difference.

Cell emf can be measured by using a potentiometer. It depends on the nature of electrodes, concentration of electrolyte and the temperature.

13.11.2 Standard cell emf

The emf of a cell has a standard value if both its half cells are in their standard states. It is denoted by E° cell.

13.11.3 Cell emf and electrode potential

The standard cell emf is related to the standard electrode potentials of its anode and cathode.

$$E^0 \text{ cell} = E^0 \text{ cathode} - E^0 \text{ anode.}$$

$$= E^o_{\text{Right}} - E^o_{\text{left}}$$

Cell emf is related to the electrode potentials of its anode and cathode

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= E_{\text{right}} - E_{\text{left}}$$

13.11.4 Electrochemical Series

Standard potential of a large number of electrodes have been measured and they have been listed in the increasing order of electrode potential in a series called electro chemical series. The table 13.2 gives the standard reduction potentials of some electrodes.

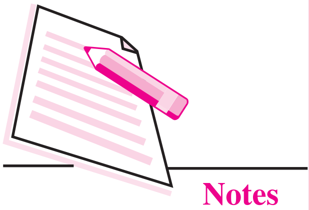
Table 13.2 : Standared Electrode Potentials and Electrochemical Series

Element	*Electrode rection*	*E°(V)*
Li	$Li + e^- \rightarrow Li$	– 3.045
K	$K^+ + e^- \rightarrow K$	– 2.925
Cs	$Cs^+ + e^- \rightarrow Cs$	– 2.923
Ba	$Ba^{2+} + 2e^- \rightarrow Ba$	– 2.906
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	– 2.866
Na	$Na^+ + e^- \rightarrow Na$	– 2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	– 2.363
Al	$Al^{3+} + 3e^- \rightarrow Al$	– 1.662
H_2	$H_2O + 2e^- \rightarrow H_2 + 2OH^-$	– 0.829
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	– 0.763
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	– 0.440
Cd	$Cd^2 + 2e^- \rightarrow Cd$	– 0.403
Pb	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	– 0.310
Co	$Co^{2+} + 2e^- \rightarrow Co$	– 0.280
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	– 0.250
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	– 0.136
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	– 0.126
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	– 0.036
H_2	$2H^+ + 2e^- \rightarrow H_2(SHE)$	0
Cu	$Cu^{2+} + e^- \rightarrow Cu^+$	+ 0.153
S	$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	+ 0.170
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+ 0.337
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+ 0.534
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.799
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+ 0.854
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.066
O_2	$O_2 + 4H^+ + 2e^- \rightarrow 2H_2O$	+ 1.230
Cr	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+ 1.330
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.359
Au	$Au^{3+} + 3e^- \rightarrow Au$	+ 1.498
Mn	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^2 + 4H_2O$	+ 1.510
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.870

The most active metal lithium is placed at the top and the most active non metal fluorine at the bottom. Thus we find that lithium is the most powerful reducing agent and flourine is most powerful oxidising agent.

13.11.5 Applications of Electrochemical Series

(i) **It helps to predict a redox reaction.** A given ion will oxidise all the metals below it and a given metal will reduce ions of any metal placed above it in the series.



Example 13.5 : Predict the redox reaction between zinc and iron. Given E^0 of Zn^{2+} / Zn is – 0.763 and E^0 for Fe^{2+} / Fe is –0.44 V.

The E^0 value of Zn^{2+}/Zn is lower than Fe^{2+}/Fe. It means Zn has a greater reducing power than Fe or zinc can undergo oxidation more quickly than Fe. Zinc will reduce Fe^{2+} ions and itself undergoes oxidation. The given reaction between Zn and Fe will take place as shown.

$$Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$$

(ii) **It helps to calculate the emf of a galvanic cell.**

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}.$$

E^0 cell should always be positive. If E^0 cell comes as –ve it means the cell cannot work and electrodes should be interchanged.

Example : Predict the E° for the cell

$$Mg \,|\, Mg^{2+}(1M) \,||\, Ag^{+}(1M) \,|\, Ag$$

From the table

$$\begin{aligned} E^0_{cell} &= E^0_{cathode} - E^0_{anode} \\ E^0_{Mg^{2+}/Mg} &= -2.365\text{V and} \\ E^0_{Ag^{+}/Ag} &= 0.80\text{V} \\ E^0_{cell} &= 0.80 - (-2.365)\text{V} \\ &= 0.80 + 2.365 \\ &= 3.165\text{ V} \end{aligned}$$

(iii) **It helps to predict the feasibility of a redox reaction**

The feasibility of a redox reaction can be predicted by calculating E^0 cell for the redox reaction. The redox reaction is broken in two half reactions : oxidation half reaction acts as anode and reduction half acts as cathode. The positive E^0 cell indicates the redox reaction is possible.

Example 13.3 : Predict whether the following reaction is feasible or not?

$$Cu^{2+}(aq) + 2Ag(s) \longrightarrow Cu(s) + 2Ag^{+}(aq)$$

Given $E^0_{Ag^{+}/Ag} = 0.80\text{V}$ and $E^0_{Cu^{2+}/cu} = 0.34\text{V}$

The given redox reaction can be written as two half reactions

Anode (Oxidation) $2Ag(s) \longrightarrow 2Ag^{+}(aq) + 2e^{-}.$

Cathode (Reduction) $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

$$\begin{aligned} E^0\text{cell} &= E^0 \text{ cathode} — E^0 \text{ anode} \\ &= E^0\ Cu^{2+}/Cu — E^0 Ag^{+}/Ag \\ &= 0.34\ V - 0.80\ V \\ &= -0.46 V \end{aligned}$$

The –ve E^0 value indicates that the above reaction will never take place and silver cannot displace Copper from a solution of Cu^{2+} ion. Instead the reverse reaction would be feasible.

(iv) **It helps to predict whether a metal can liberate hydrogen from acids.** Any metal which is above hydrogen in the electro chemical series can liberate hydrogen from acid since it is a better reducing agent than hydrogen. Thus metals like, Zinc, Magnesium, Calcium etc can displace hydrogen from HCl or H_2SO_4 but metals like Copper, silver etc cannot displace hydrogen from acid.

13.12 NERNST EQUATION FOR ELECTRODE POTENTIAL

Nernst equation relates electrode potential to the concentration of ions in the electrolyle. An electrode reaction is always written as reduction reaction. Let us take a general example for a metal M.

$$M^{n+}(aq) + ne \longrightarrow M(s)$$

The Nernst equation for its electrode potentials is :

$$E = E^0 - \frac{2.303\ RT}{nF} \log \frac{[M]}{[M^{n+}]} \qquad (i)$$

where E = Electrode potential

E^0 = Standard electrode Potential (Reduction)

R = gas constant in $JK^{-1}\ mol^{-1}$

T = Temperature in Kelvin

F = Faraday constant

n = number of electrons involved in the electrode reaction

$[M^{n+}]$ = molar concentration of M^{n+} ion

[M] = concentration of pure solid metal taken as unity

Therefore,

$$E = E^0 - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

If we put the values of R, T and F in equation (i)

$$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \qquad F = 96500\ \text{Coulomb}$$

$$T = 298\ \text{K}$$

we have $$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \qquad (ii)$$

For example : For copper electrode as half cell

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$

here $n = 2$. $$E^0_{Cu^{2+}/Cu} = +0.34V$$

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

Since $E^0_{Cu^{2+}/Cu}$ is 0.34 V the equation beccomes

$$= 0.34 - 0.0295 \log \frac{1}{[Cu^{2+}]}$$

Example 13.7 : Calculate the reduction potential for the following half cell at 298 K

$$Ag^{+}\ (0.1M) + e^{-} \longrightarrow Ag(s)$$

$$E^0 = 0.80V$$

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[Ag^{+}]}$$

$$= 0.80 - \frac{0.0591}{1} \log \frac{1}{0.1}$$

$$= 0.80 - 0.0591 \log 10$$

$$= 0.80 - 0.0591 = 0.741V$$

13.12.1 Nernst Equation for Cell emf

For a general cell reaction :

$$aA + bB \longrightarrow xX + yY$$

$$E\ cell = E^0\ cell - \frac{2.303\ RT}{nF} \log \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Thus, for the cell reaction :

$$\mathrm{Ni(s)} + 2\mathrm{Ag}^{+}(aq) \xrightarrow{\quad\quad} \mathrm{Ni}^{2+}(aq) + 2\mathrm{Ag}$$

$$\mathrm{E\ cell} = \mathrm{E^{0}cell} - \frac{2.303\ \mathrm{RT}}{n\mathrm{F}} \log \frac{[\mathrm{N}i^{2+}]}{[\mathrm{Ag}^{+}]^{2}}$$

Note: Only the ions are written in the fraction as concentration of pure solid or liquid is taken as unity.

To determine the value of *n* the reaction is written in two half reactions.

Anode reaction (oxidation)

$$\mathrm{Ni(s)} \xrightarrow{\quad\quad} \mathrm{Ni}^{2+}(aq) + 2\mathrm{e}^{-}$$

Cathode reaction (reduction)

$$2\mathrm{Ag}^{+}(aq) + 2\mathrm{e}^{-} \xrightarrow{\quad\quad} 2\mathrm{Ag(s)}$$

This can be represented in the form of a cell as

$$\mathrm{Ni}\,|\,\mathrm{Ni}^{2+}\,\|\,\mathrm{Ag}^{+}\,|\,\mathrm{Ag}$$

The value of $n = 2$ as $2e^{-}$ are exchange between anode and cathode

Example 13.8 : Calculate the EMF of the following cell at 298 K

$$\mathrm{Ni(s)}|\mathrm{Ni}^{2+}\ (0.001\mathrm{M})\ \|\ \mathrm{Ag}^{+}\ (0.1\mathrm{M})\ |\ \mathrm{Ag(s)}$$

$$\mathrm{E}^{0}_{\mathrm{Ni}^{2+}|\mathrm{Ni}} = 0.25\mathrm{V} \qquad \mathrm{E}^{0}_{\mathrm{Ag}^{+}|\mathrm{Ag}} = 0.80\mathrm{V}$$

From the given values first find

$$\mathrm{E^{0}\ cell} = \mathrm{E^{0}\ cathode} - \mathrm{E^{0}\ anode} = 0.80 - (-0.25)\ \mathrm{V} = 1.05\mathrm{V}$$

$$\mathrm{E\ cell} = \mathrm{E^{0}cell} - \frac{0.0591}{2} \log \frac{[\mathrm{N}i^{2+}]}{[\mathrm{Ag}^{+}]^{2}}$$

$$= 1.05 - \frac{0.0591}{2} \log \frac{0.001}{(0.1)^{2}} = 1.05 - 0.0295 \log \frac{10^{-3}}{10^{-2}}$$

$$= 1.05 + 0.0295\ \log 10^{-1} = 1.0795\ \mathrm{V}$$

INTEXT QUESTION 13.2

1. What type of process-spontaneous or non-spontaneous, occurs in (i) electrolytz cell (ii) halvanic cell.
2. Atomic mass of setner is 108 u. What is its electrochemical equivalent?
3. Why is salt bridge used for setting up of galvanic cells.
4. A galvanic cell is made in which the following reactioin occurs.

   $$\mathrm{Fe(s)} + \mathrm{CuSOu(aq)} \rightarrow \mathrm{FeSou(aq)} + \mathrm{Cu(s)}$$

   Write down the cell notation, for this cell.

5. Prodict whether the following reaction is feasible or not?

$$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + 2n(s)$$

Given $E^\circ_{Cu^{2+}|Cu} = +0.34$ V and $E^\circ_{2n^{2+}|Zn} = -0.76$ V

13.13 BATTERIES AND FUEL CELLS

The cells and batteries (combination of 2 or more cells) that we use for various purposes from torch lights, cameras, watches to cars and bikes, are basically of three types: dry cells or primary cells, storage cells or secondary cells and fuel cells. A primary cell is the one that is consumed chemically when current is drawn from it. A secondary cell is the one which after discharge can be recharged by passing electricity through it and carrying out electrolysis. In fuel cells the oxidizing and reducing agents are fed continuously to the cell from outside.

(i) **Dry cell (Primary cell)**

It is the cell commonly used in torches transistor radios, portable music players, clock etc. It is also known as Leclanche cell after the name of its inventer. It consists of a zinc container which also acts as the anode and a carbon (graphite) rod which acts as the cathode. Around carbon rod, a moist paste of graphite, ammonium chloride and manganese dioxide is placed which acts as the electrolyte (Fig 13.10). The electrode reactions that occur are complex but can be written in simplified way as:

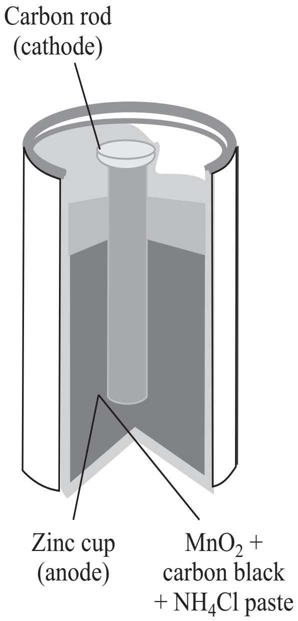


Fig. 13.10: Dry cell

Anodic process (*oxidation*): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cathodic process (reduction):

$$2MnO_2(s) + NH_4^+(aq)\ e^- \rightarrow MnO(OH)(aq) + NH_3(g)$$

The ammonia gas evolved at cathode combines with Zn^{2+} ions produced at anode to give complex ion $[Zn(NH_3)_4]^{2+}$. A single dry cell has a potential of nearly 1.5V. It can be used only once and cannot be recharged.

(ii) Lead Storage Battery (Secondary cell)

Lead storage batteries are used in automobiles (cars, bikes, trucks, buses etc) and in inverters.

A lead storage battery consists of alternate plates of anodes and cathodes. The anode consists of lead plate and the cathode of a grid of lead packed with lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulphuric acid which is 38% or 3.7 M. (See Fig. 13.11) The reactions that occur at the electrodes during the discharge of the battery when it is used to draw current are:

Anodic process (*oxidation*): $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathodic process (*reduction*):

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

Net reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

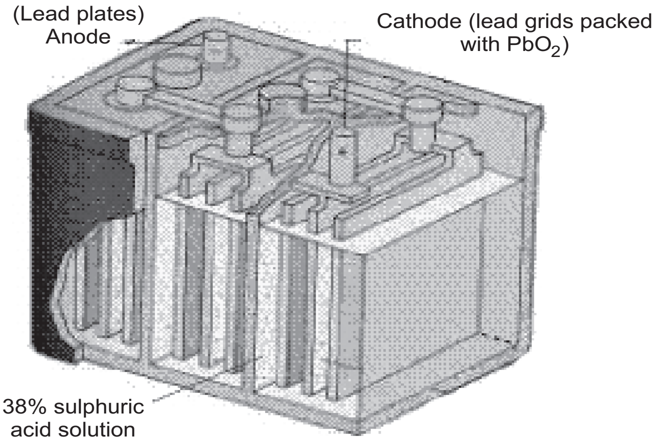


Fig. 13.11: Lead storage battery

The battery can be recharged by passing current through it. Now it acts like an electrolytic cell and the electrode reactions are reversed and the original reactants are regenerated. The battery can be charged and discharged a large number of times.

(iii) Fuel Cells

The maximum amount of electricity is produced by thermal power plants which use fossil fuel like coal or natural gas. Their efficiency is very low but these plants can be run continuously by constant feeding of the fuel. Galvanic cells have high efficiency but can be used only once and then have to be discarded, because reactants can not be fed into them continuously. Fuel cells combine the advantages of the two. They are efficient and can be used continuously. Most of the fuel cells are based on combustion reactions of fuels like hydrogen, methane, methanol etc which are fed continuously into fuel cells. One of the most successful fuel cells uses the combustion reaction of hydrogen (Fig. 13.12).

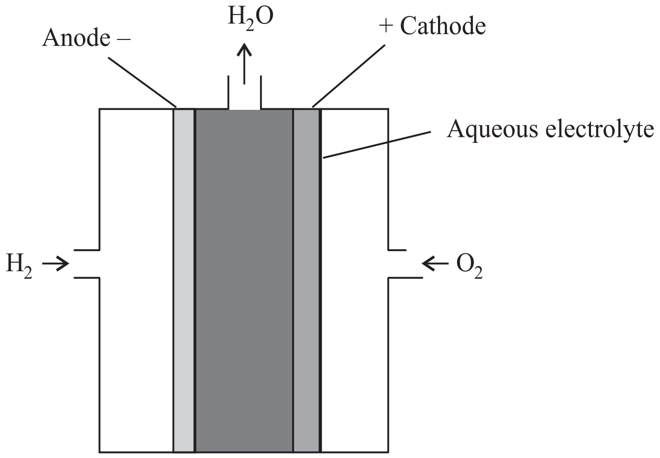


Figure 13.12: Hydrogen-oxygen fuel cell

The electrodes used in it are made of porus carbon impregnated with catalyst (finely divided Pt or Pd). The electrolyte used is an aqueous solution of KOH. Hydrogen gas is bubbled around the anode and oxygen gas around the cathode. The electrode process are:

Anodic process (*oxidation*): $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O + 4e^-$

Cathodic process (*reduction*): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall process: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The cell potential of this cell is 0.9V. It was used as a power source in Apollo space programme and water produced was used for drinking purpose by the crew of the spacecraft.

13.14 CELL EMF AND GIBBS ENERGY

The maximum amount of work that a cell in its standard state can perform is given by

$$W_{max} = -n\,FE^0$$

The significance of –ve sign is that the ***work is done*** by the cell. Since the maximum amount of useful work which a system can perform is equal to decrease in Gibbs energy thus

$$W_{max} = \Delta G^0 = -nFE^0$$

If ΔG^0 calculated is negative, then the cell reaction is spontaneons otherwise not.

Example 13.9 : Calculate the standard Gibb's energy ΔG^0 for the reaction occurring in Daniell cell

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}}(aq) \longrightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{Cu(s)}$$

at 298 K. The E^0 cell at this temperature is 1.1V. Is the reaction spontaneous.

For Daniell cell, $n = 2$.

Solution :

$$\Delta G^0 = -nFE^0$$

$$\Delta G^0 = -2 \times 96500 \times 1.1$$

$$= -212{,}300\text{J}$$

$$= -212.3\text{kJ}$$

Since ΔE^0 is –ve, the cell reaction is spontaneous

INTEXT QUESTIONS 13.4

1. Differentiate between electrolytic cell and galvanic cell.
2. What is a salt bridge? What is the role of the salt bridge?
3. What is electrochemical series? List any two applications of the series.
4. With reference to the electrochemical series arrange the following metals in the order in which they displace each other from their salt solutions.

   Al, Cu, Ge, Mg, Zn, Ag

13.15 CORROSION

Corrosion is the process of deterioration of metals due to their exposure to environment. It slowly forms a layer of oxides, basic carbonates or other salts on the surface of metals. Rusting of iron and tarnishing of silver objects are common examples of corrosion. Corrosion results in huge material loss resulting in damage to buildings, ships, bridges, machinery etc.

Corrosion is essentially an electrochemical process involving anodic oxidation of metals resulting in the formation of their ions and a cathodic process that consumes the electrons. Though rusting is a complex process. The following reactions can be considered to be taking place. One spot on the surface of iron becomes anode and undergoes *oxidation*.

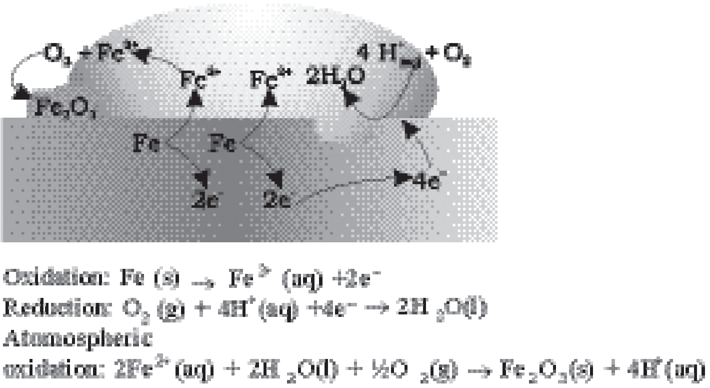


Fig. 13.13: Corrosion of iron

Anodic process: $2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^-$ $\quad E° = -0.44V$

The electrons released here move through the metal to another place which acts like a cathode. Here the *reduction* of oxygen takes place in presence of H^+ ions.

Cathodic proess: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$ $\quad E° = +1.23$ V

The overall process is

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O \quad E^{\circ}_{cell} = 1.6$$

The positive sign of E°_{cell} indicates that this reaction occurs spontaneously. Fe^{2+} ions formed heroe are further oxidized to Fe^{3+} ions by atmospheric oxygen to form rust

$$4Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \rightarrow 2Fe_2O_3(s) + 8H^+(aq)$$

$$Fe_2O_3(s) + xH_2O(l) \rightarrow Fe_2O_3 \cdot xH_2O(s) \text{ (rust)}$$

Rusting requires the combined effect of oxygen and water. It is accelerated by CO_2 and SO_2 (acidic conditions) and retarded by alkalis. It has been observed that completely homogeneous iron does not rust.

Protection against corrosion

There are two general methods used for protection of metallic objects against corrosion.

(a) application of protective layer to inhibit anodic process

(b) cathodic protection

(a) Use of Protective Layer

Many substances are used for applying a protective layer to prevent or limit corrosion:

(i) Machinery, tools and automobile engine parts are often protected by a thin film of oil or grease.

(ii) Metalic doors, windows, coolers are painted with a suitable paint to prevent corrosion.

(iii) In automobile industry, the chassis of vehicles is painted with phosphoric acid which reacts with iron to form an insoluble film of iron (III) phosphate.

(iv) Iron containers are made from tin plated sheets. Tin is less reactive than iron and forms a protective layer. However, if tin layer is broken, rusting starts because iron is more electropositive than tin $(E^{\circ}_{Fe^{2+}/Fe} = -0.44\text{V}$ and $E^{\circ}_{Sn^{2+}/Sn} = -0.14\text{V})$. In contact with each other and with atmosphere, iron becomes anode and tin becomes cathode and rusting of iron begins.

(b) Cathodic Protection

Cathodic protection of a metal can be done by coating it with a more reactive or more electropositive metal with smaller electrode potential.

(i) *Galvanisation:*

Iron sheets or other objects are coated with a layer of zinc by dipping them in molten zinc or using electrolysis. Zinc layer is protected against corrosion by a firmly sticking layer of ZnO. Even when the zinc layer is broken, zinc being more electropestive than iron becomes the anode and iron $(E^{\circ}_{Zn^{2+}/Zn} = -0.76\text{ V};\ E^{\circ}_{Fe^{2+}/Fe} = -0.44\text{ V})$ becomes the cathode, the cell reaction that occurs is

$$Zn(s) + Fe^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Fe(s)$$

Thus, any Fe^{2+} irons formed as a result of atmospheric oxidation are reduced back to iron at the cost of zinc. Therefore, zinc coating becomes **sacrificial anode.**

(ii) Chromium plating (electroplating) is not only decorative, but also protects iron against rusting. Like zinc, chromium is also more electropositive than iron $(E^{\circ}_{Cr^{3+}/Cr} = -0.74\text{ V};\ E^{\circ}_{Fe^{2+}/Fe} = -0.44\text{ V})$. Chromium itself is not affected by atmospheric oxygen. Its layer protects iron. Once this layer is broken, chromium becomes the anode and iron the cathode and the following reaction occurs:

$$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s)$$

(iii) Cathodic protection can also be provided by attaching, rather than coating, a piece of more reactive metal to the object to be protected. Ships, water pipes, iron tanks etc. are often protected against corrosion by connecting a piece of magnesium either directly or through a wire. Magnesium being more electropositive than iron $(E^{\circ}_{Mg^{2+}/Mg} = -2.36V;\ E^{\circ}_{Fe^{2+}/Fe} = -0.44V)$ becomes sacrificial anode. The following reaction occurs in the cell formed.

$$Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(a) + Fe(s)$$

WHAT YOU HAVE LEARNT

- Oxidation is a process in which electrons are lost by an atom or ion.
- Reduction is a process in which electrons are gained by an atom or ion.
- Atoms or ions undergoing oxidation are reducing agents and atoms or ions undergoing reduction are oxidising agents.
- Oxidation number is the state of oxidation of an element in a compound, which is calculated by a set of rules. It is based on the concept that electrons in a covalent bond belong to the more electro negative element.
- Oxidation number of an atom in elemental form is zero. Otherwise the number is always written with positive or negative sign.
- A substance, if in its molten state or aqueous solution conducts current is called electrolyte and if it doesnot conduct electric current then it is called non-electrolyte.
- Ions carry charge in an electrolyte from one point to other. The conduction of electricity follows Ohm's law.
- Reciprocal of resistance and resistivity are called conductance and conductivity respectively.
- On dilution of a solution, its conductivity decreases while molar conductivity increases.
- Electrolysis is a process in which electrical energy is used to decompose an electrolyte into its ions and it is done in an electrolytic cell
- Electrochemical cell or Galvanic cell produce electricity due to oxidation and reduction reactions occurring in their half cells. Oxidation occurs at the anode (negative electrode) and reduction at the cathode (positive electrode).

- A galvanic cell can be written in symbolic form as Anode |Electrolyte| |Electrolyte| Cathode.
- The emf of a cell is the potential difference between two electrodes in the open circuit.
- When a metal is dipped in its own salt solution then the potential of metal with respect to solution is called electrode potential. This potential is measured with respect to a reference electrode called Standard Hydrogen electrode.
- Electrochemical series is the arrangement of electrodes in the order of their increasing electrode potential.
- The cell emf is related to the electrode potential (reduction)

$$E_{cell} = E_{cathode} - E_{anode}$$

- The Nernst equation is

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[Red]}{[Oxi]}$$

- The standard Gibbs energy of the cell reaction ΔG^0 is related to the standard cell emf as $\Delta G^0 = -nFE^0$.

TERMINAL EXERCISE

1. Calculate the Oxidation number of the elements written in bold letters

   $[\mathbf{Cr}(H_2O)_6]^{3+}$, $[\mathbf{Fe}(CN)_6]^{3-}$, $H\mathbf{C}O_3^-$, $\mathbf{Pb}_3O_4$

2. Balance the following reactions by oxidation number method

   (a) $Fe_2O_3 + C \longrightarrow Fe + CO$

   (b) $C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$

3. Balance the following reactions by ion-electron method:

   (i) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$

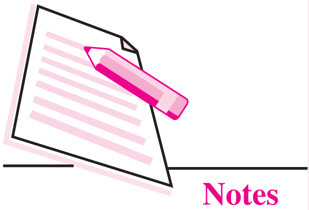
   (ii) $ClO_3^- + Mn^{2+} \longrightarrow MnO_2 + Cl^-$ in acidic medium

   (iii) $Fe(OH)_2 + H_2O_2 \longrightarrow Fe(OH)_3 + H_2O$ in basic medium

4. Define the following and give its units:

   (i) Conductivity

   (ii) Molar conductivity



5. Draw a graph showing the variation in molar conductivity in a weak and a strong electrolytes with concentration.

6. Explain why the molar conductivity of an electrolyte increases with dilution while conductivity decreases on dilution.

7. The measured resistance of a conductance cell containing 7.5×10^{-3}M solution of KCl at 25ºC was 1005 ohms. Calculate (a) Conductivity (b) Molar conductivity of the solution. Given the cell constant 1.25 cm^{-1}.

8. The conductivity of 0.05M solution of an electrolyte at 298 K is 0.0025 cm^{-1}. Calculate the molar conductivity.

9. How much aluminium will be deposited on passing a current of 25 A for 10 hr by electrolysis of malten Al_2O_3?

10. Equivalent mass of an element is 94 g. What is its electrochemical equivalent?

11. Two electrolytic cells A and B containing $ZnSO_4$ and $CuSO_4$ solutions respectively are connected in series on passing certain amount of electricity, 15.2 g of zinc was deposited in cell A. How much copper would be deposited in cell B?

12. Explain the term standard electrode potential. How is it determined experimentally.

13. Draw the diagram of the cell whose cell reaction is

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

14. For the cell

$$Mg \mid Mg^{2+} \parallel Zn^{2+} \mid Zn$$

   (i) Draw the cell diagram
   (ii) Identify anode and cathode
   (iii) Write cell reaction
   (iv) Write Nernst equation for the cell
   (v) Calculate E^0 use the data given the table 13.2

15. What are the functions of a salt bridge?

16. Using electro chemical series predict whether the following reaction is feasible or not

$$Ni(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Ni^{2+}(aq)$$

17. Explain with the help of electro-chemical series whether any reaction will take place when
    (i) Steam is passed over hot Cu.
    (ii) Tin is dipped in hydrochloric acid
18. Calculate ΔG^0 for the reaction

    $$2Al(s) + 3Sn^{4+}(aq) \longrightarrow 2Al^{3+}(aq) + 2Sn^{2+}(aq)$$

19. Calculate emf of the cell

    $$Cr \mid Cr^{3+}\ (.1M) \parallel Fe^{2+}\ (0.1M) \mid Fe$$

20. Calculate emf of the given cell reaction at 298k

    $$Sn^{4+}\ (1.5M) + Zn(s) \longrightarrow Sn^{2+}(0.5M) + Zn^{2+}\ (2M)$$

21. The blue colour of $CuSO_4$ is discharged when a rod of zinc is dipped in it? Explain.
22. Why oxidation cannot occur without reduction.
23. Knowing that

    $$Cu^{2+} + 2e \longrightarrow Cu\ ; \qquad E^0 = .34V$$

    $$2Ag^{+} + 2e \longrightarrow 2Ag\ ; \qquad E^0 = +.80V$$

    reason out whether 1M silver nitrate solution can be stored in copper vessel or 1M copper sulphate can be stored in silver vessel.

ANSWERS INTEXT QUESTION

13.1

Oxidation Number

1. –4, –3, +3, +2, +7, +5, 0, +5
2. In oxidation O.N. increases

   In reduction O.N. decreases
3. Oxidising agent HNO_3

   reducing agent H_2S
4. $I^{-}(aq) \longrightarrow I_2(s)$

(i) oxidation

$$\underset{+3}{Fe^{3+}}(aq) \longrightarrow \underset{+2}{Fe^{2+}}(aq) \quad \text{(Reduction)}$$

(ii)

reduction

$$Mg + Cl_2 \longrightarrow \underset{+2}{Mg}\ \underset{-1}{Cl_2}$$

oxidation

(iii) $I_2 \longrightarrow HIO_3$ oxidation

$HNO_3 \longrightarrow NO_2$ reduction

5.

oxidation

$$\underset{+2}{3CuO} + \underset{-3}{2NH_3} \longrightarrow \underset{0}{3Cu} + \underset{0}{N_2} + 3H_2O$$

reduction

(ii)

oxidation

$$\underset{+4}{MnO_2} + 4HCl^{-1} \longrightarrow \underset{+2}{MnCl_2} + \overset{0}{Cl_2} + 2H_2O$$

reduction

6. $Bi \longrightarrow Bi^{3+} + 3e^-$

(i) $NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O] \times 3$

$Bi + 3NO_3^- + 6H^+ \longrightarrow Bi^{3+} + 3NO_2 + 3H_2O$

(ii) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(iii) $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

$$\text{(iv)}\quad \text{Al} + 4\,0\text{H}^- \longrightarrow \text{NH}_3 + 9\,\text{OH}^-]\times 8$$

$$\text{NO}_3^- + 6\text{H}_2 0 + 8\text{e}^- \longrightarrow \text{NH}_3 + 9\,\text{OH}^-]\times 3$$

$$8\text{Al} + 3\text{NO}_3^- + 18\text{H}_2\text{O} + 5\text{OH}^- \longrightarrow 8\text{Al}(\text{OH})_4^- + \text{NH}_3$$

13.2

1. Electrolytes give ions in the solution and these ions conduct electricity by moving to their respective electrodes i.e. cations towards cathode and anions towards anode.

2. Specific conductance is the conductance of a solution taken in a cell in which two electrodes are 1cm apart and surface area of each one of them is 1cm^2.

   Equivalent conductance is the conductance of all the ions furnished by an equivalent of the electrolyte in a solution of given concentration.

3. Conductance S; specific conductance Scm^{-1}

4. Nature of electrolyte (strong or weak), valency of its ions, speed of ions, concentration and temperature.

5. See Fig. 13.2.

6. $\lambda_m^\infty\ \text{Al}_2(\text{SO}_4)_3 = 2\lambda_m^\infty\ \text{Al}^{3+} + 3\lambda_m^\infty\ \text{SO}_4^{2-}$

13.3

1. (i) non-spontaneous (ii) spontaneous

2. 1.12×10^{-3} g c^{-1}

3. See section 13.8.2

4. $\text{Fe(s)} \,|\, \text{Fe SO}_4\text{(aq)} \,||\, \text{CuSO}_4\text{(aq)} \,|\, \text{Cu(s)}$

5. In feasible since $\text{E}^\circ = -1.10\text{ V}$

13.4

1. In electrolytic cell electrical energy is used for carrying out redox reaction while in an electrochemical cell a redox reaction is used for producing electrical energy.

2. See sec. 13.6.2

3. See sec. 13.8

4. Mg > Al > Zn > Fe > Cu > Ag.

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14

CHEMICAL KINETICS

You know that a knowledge of Gibbs energy change in a given process can tell you whether the process is feasible or not. However, the Gibbs energy decrease does not indicate anything about the speed of a reaction. For example, the reaction between hydrogen and oxygen to give water is accompanied by a large decrease in Gibbs energy. However, you would not be able to observe the formation of water, even if hydrogen and oxygen are kept in contact with each other for ever. On the other hand, there are reactions which take place instantaneously. For example, when HCl is added to $AgNO_3$, white precipitate of AgCl is formed instantaneously. In this lesson we shall study the speed or rate of reactions which are neither very slow nor very fast. We shall also study the factors that control the rate of a reaction.

OBJECTIVES

After reading this lesson you will be able to :

- explain the rate of a chemical reaction;
- differentiate between average rate and instantaneous rate;
- correlate the average and instantaneous rates with changes in concentrations of various reactants and products;
- explain the factors that affect the rate of a reaction;
- define rate law and rate constant;
- define order and molecularity of a reaction;
- distinguish between order and molecularity;
- derive rate law for first order reaction and define half life period for first order reaction;

- derive a relationship between half life and rate constant for first order reaction;
- solve numericals on the relationships;
- explain collision theory of reaction rates.
- explain the effect of temperature on reaction rate, and
- explain Arrhenius equation and activation energy.

14.1 RATE OF A CHEMICAL REACTION

When the reactants are mixed to perform a reaction, there are no products present initially. As time passes, the concentration of the products increases and that of the reactants decreases. The rate of any chemical reaction can be expressed as the rate of the change in concentration of a reactant (or a product).

$$\text{Rate of a chemical reaction} = \frac{\text{Change in concentration}}{\text{Time taken}} \text{ of a reactant or a product}$$

$$= \frac{\text{mol litre}^{-1}}{\text{second}}$$

Let us consider the following chemical reaction :

$$2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$$

The rate for this reaction can be determined by measuring the increase in the molar concentration of NOBr at different time intervals.

Let us see how we can express the rate of this reaction. You know that molar concentration of a substance is expressed by enclosing the formula of the substance in square bracket.

For example, [NOBr] represents the molar concentration of NOBr.

Let us suppose that $[NOBr]_1$ is the molar concentration at time t_1 and $[NOBr]_2$ is the molar concentration at time t_2.

Then, change in molar concentration = $[NOBr]_2 - [NOBr]_1 = \Delta[NOBr]$

Time required for the change = $t_2 - t_1 = \Delta t$

Here, Δ means change in the respective quantity.

Therefore, the rate of formation of NOBr = $\dfrac{\Delta[NOBr]}{\Delta t}$

This expression gives the rate of reaction in terms of NOBr.

If the decrease in the molar concentration of NO or Br_2 is measured we can write the rate of the reaction with respect to NO as

$$= \frac{-\Delta[NO]}{\Delta t}$$

$$\text{and w.r.t. } Br_2 \text{ as } = \frac{-\Delta[Br_2]}{\Delta t}$$

Thus, the rate of a reaction can be expressed either in terms of reactants or products. We find in the reaction mentioned above that two moles of NO react with one mole of Br_2. Therefore, the change in concentration of NO in a given time Δt will be double than that for Br_2. Thus, in order to make the rates with respect to different reactants or products equal, the rate expression is divided by the storichrometric coefficient in the balanced chemical equation.

For example, in the equation,

$$2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$$

The rate of reaction with respect to reactants and products is expressed as

$$\text{rate of reaction } = +\frac{1}{2}\frac{\Delta[NOBr]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NOBr]}{\Delta t} = \frac{-\Delta[Br_2]}{\Delta t}$$

14.2 AVERAGE RATE AND INSTANTANEOUS RATE

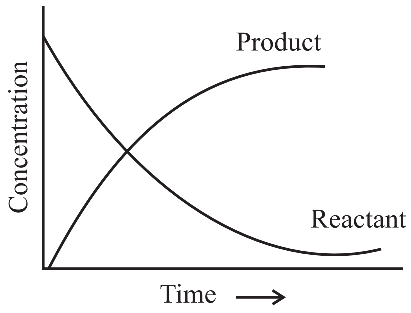
The rate of a reaction depends on the concentration of reactants. As the reaction proceeds the reactants get consumed and their concentration decreases with time. Therefore, the rate of reaction does not remain constant during the entire reaction.

The rate of a reaction given as $\frac{\Delta[\text{concentration}]}{\Delta t}$ gives an average rate.

For example, $\frac{\Delta[NOBr]}{\Delta t}$ gives the average rate of reaction. Instantaneous rate of a reaction is the rate of reaction at any particular instant of time, we express instantaneous rate by making Δt very small ϕ

$$\lim_{\Delta t \to 0} \frac{[NOBr]}{\Delta t} = \frac{d[NOBr]}{dt}$$

When concentration of any of the reactants or products is plotted against time, the graph obtained is as given below :



Notes

For the reaction,

$$2N_2O_5(g) \longrightarrow 2NO_2(g) + O_2(g)$$

Average rate of reaction

$$= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

and instantaneous rate $= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

14.3 FACTORS AFFECTING RATE OF A REACTION

The rate of a chemical reaction is affected by the following factors :

1. **The concentration of reactants** : Generally the rate of a reaction increases as the concentration of the reactants is increased.
2. **Temperature** – A reaction is faster when the reaction temperature is increased.
3. **Presence of a catalyst –** A catalyst alters the reaction rate without being consumed by the reaction.

For example :

(i) Reaction between hydrogen and oxygen to form water is extremely slow. It occurs very fast in the presence of platinum as catalyst.

You would study these effects in more detail in the following sections of this lesson.

Example 14.1 : Express the average and instantaneous rate of the following reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

in terms of (i) rate of formation of NH_3,

(ii) rate of disappearance N_2, and

(iii) rate of disappearance of H_2.

Write the different expressions for the rate of reactions.

Solution : The expression for the three rates are :

$$\text{Average rate of formation of } NH_3 = \frac{\Delta[NH_3]}{\Delta t}$$

$$\text{Average rate of disappearance of } N_2 = -\frac{\Delta[N_2]}{\Delta t}$$

$$\text{Average rate of disappearance of } H_2 = \frac{\Delta[H_2]}{\Delta t}$$

$$\text{Instantaneous rate of formation of } NH_3 = \frac{d[NH_3]}{dt}$$

$$\text{Instantaneous rate of disappearance of } N_2 = -\frac{d[N_2]}{dt}$$

$$\text{Instantaneous rate of disappearance of } H_2 = \frac{d[H_2]}{dt}$$

To equate the three rates, divide each rate by the coefficient of the corresponding substances in the balanced equation.

$$\text{Average rate} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$$

$$\text{Instantaneous rate} = \frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

INTEXT QUESTIONS 14.1

1. Which of the following units could be used to express the rate of reaction between magnesium and hydrochloric acid?
   (a) cm^{-3} s
   (b) cm^3 min^{-1}
   (c) cm^3 s^{-1}
   (d) mol dm^{-3} min^{-1}
2. For the following reaction,

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

   Write the expression for the average, rate of reaction in terms of :
   (a) rate of formation of NO_2F
   (b) rate of disappearance of NO_2
   (c) rate of disappearance of F_2
   (d) equivalent rate of formation of product and disappearance of reactants.
3. Express the instantaneous rates of formation of product and disappearance of reactants for the above reaction.
4. Explain why the reaction $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$ occurs more slowly when the volume of the system is increased.

14.4 DEPENDENCE OF REACTION RATE UPON CONCENTRATION

Rate law : If we follow a chemical reaction over a period of time, we find that its rate slowly decreases as the reactants are consumed. We can say that the rate is related to the concentration of the reactants. Rate is directly proportional to the concentration of the reactants raised to some power.

For example, consider the reaction

$$xA\ (g) + yB(g) \rightarrow \text{Products} \qquad \text{...(i)}$$

where a and b are coefficients of A and B respectively in the balanced equation. We can express the rate as

$$\text{Rate} \propto [A]^x\ [B]^y$$

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

where k is the constant of proportionality.

The above equation is known as the rate law for the reaction.

Rate law is defined as the mathematical relationship between rate of a reaction and the concentration of the reactants.

It is important to note that x and y are not necessarily equal to the stoichiometric coefficient of A and B in the reaction. The constant k in the rate law is called the **rate constant**. It is numerically equal to the rate of the reaction if all the concentrations were set equal to unity.

$$\text{rate} = k\ [1]^x\ [1]^y$$

$$\therefore \qquad \text{rate} = k$$

It means that large values of k indicate fast reaction and small values of k indicate slow reactions. Each reaction is characterised by its own rate constant, whose value is dependent on the temperature, but independent of concentration of the reactants.

14.5 ORDER AND MOLECULARITY OF A REACTION

Order and molecularity are two properties of a chemical reaction. In this section we shall learn about these.

14.5.1 Order of a Reaction

The powers to which the concentration terms are raised in the rate expression describes the order of the reaction with respect to that particular reactant

In the rate law,

$$\text{rate} = k\ [A]^x\ [B]^y$$

the values of x and y are order of the reaction with respect to the reactants A and B respectively. The sum of the powers $x + y$ represents the overall order of the reaction.

For example in the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

The rate law as found by experiment is

$$\text{rate} = k\,[NO]^2\,[O_2]^1$$

Here the order of reaction with respect to NO is 2 and with respect to O_2 is 1. The sum of the powers is termed as overall order of reaction. In the above example it is 2 + 1 = 3.

It must be remembered that order of a reaction *must be determined experimentally* and cannot be deduced from the coefficients in the balanced equation

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The overall order is 1 and it is termed as first order reaction.

The order of reaction can be 0, 1, 2, 3 called as zero order, first order, second order and third order respectively. The order of a reaction can be a fraction as well; for example the decomposition of ethanal to methane and carbon monoxide,

$$CH_3\,CHO\,(g) \xrightarrow{723\text{ K}} CH_4(g) + CO(g)$$

is experimentally found to the following rate law :

$$\text{rate} = k\,[CH_3CHO]^{3/2}$$

14.5.2 Difference between Rate of Reaction and Rate Constant

Rate of reaction	Rate constant
1. It is the speed at which the reactants are converted into products. It is measured as the rate of decrease of concentration of reactant or rate of incr透rease in the concentration of the products.	It is the proportionality constant in the rate law and is defined as the rate of the reaction when the concentration of each of the reactant is unity.
2. It depends upon the initial concentration of the reactant.	It is independent of the initial concentration of reactant.

14.5.3 Molecularity of a Reaction

A reaction occurs when its reactants are mixed. At molecular level, this ‘mixing’ occurs through molecular collisions. The balanced chemical equation does not always gives the correct picture of how a reaction is occurring at molecular level. For the following reaction to occur

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

apparently 14 ionic species must collide. However, the probability of a collision involving more than 3 particles is practically zero. Therefore, this reaction must be occurring in many steps, each step involving collision of not more than 3 species. Such reactions are called complex reactions and each step is called an **elementary reaction step**. Some reactions occur in a single step and such reactions are called **simple reactions**.

Molecularity is the number of molecules, atoms or ions taking part in an elementary reaction step, which must collide simultaneously in order to bring about the chemical reaction.

Molecularity of a reactions is its characteristic property and reactions are classified according the their molecularity.

(i) **Unimolecular reactions**

These are reactions whose molecularity is one. For example

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

(ii) **Bimolecular reactions**

These are the reactions with molecularity equal to two, for example:

$$2HI \rightarrow H_2 + I_2$$

$$CH_3COOC_2H_5 + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH.$$

(iii) **Termolecular or trimolecular reactions**

These reactions have molecularity equal to three, for example

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO + Cl_2 \rightarrow 2NOCl$$

Termolecular reactions are rare because the probability of three molecules colliding simultaneously is very small. Most of the reactions are unimolecular or bimolecular.

Molecularity of a reaction can only be a whole number, 1, 2 or 3. It is never zero, fractional or more than 3.

14.6 UNITS OF RATE CONSTANT

For zero order

$$\text{Rate} = k\,[A]^o$$

$$\text{Rate} = k$$

The unit for rate of a reaction is mol L^{-1} s^{-1}. The unit of k for zero order is same as that for rate.

For a first order reaction

$$\text{Rate} = k\,[A]^1$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k \text{ mol L}^{-1}$$

$$k = \text{s}^{-1}$$

For a first order reaction, the unit for rate constant is time^{-1}.

For second order reaction

$$\text{Rate} = k\,[A]^2$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k\,(\text{mol L}^{-1})^2$$

Therefore $$k = \text{mol}^{-1}\text{ L s}^{-1}$$

In general for any order n the unit for rate constant k is given as

$$k = (\text{mol L}^{-1})^{1-n}\text{ s}^{-1}$$

14.6.1 Zero Order Reactions

Zero order reactions are those whose rate is proportional to zeroth power of concentration, that is, the rate is independent of concentration of the reactant.

Table: Compession of Order and molecularity

Order	Molecularity
1. It is the sum of powers of concentration terms in the experimentally determined rate equation	It is the number of molecules, atoms or ions which must collide simultaneously in order to bring about the chemcal reaction.
2. Order of a reaction can be 1, 2, 3, zero or fractional.	Molecularity can be 1, 2 or 3 only. It cannot be zero or fractional.
3. It is an experimental quantity.	It is a theoretical quantity and depends on the mechanism of the reaction.
4. It is applicable to elementary as well as complex reaction.	It is applicable to only elementary reaction.
5. For complex reactions, order is determined by the slovest step and the order and molecularity of the slowest step are the same.	For complex reactions, molecularity has no meaning.

Examples of Zero Order Reactions

Some reactions show zero order *under certain conditions.*

(1) Decomposition of HI on the surface of gold catalyst when the *pressure of HI is high*.

(2) Photochemical combination of H_2 and Cl_2 to form HCl *when carried out over water*.

(3) Enzyme reactions *when the substrate concentration is high* in comparison to the enzyme concentration.

Consider the reaction:

$$\mathrm{A} \longrightarrow \text{Products.}$$

Since the order of the reaction is zero, its differential rate equation is

$$\text{Rate} = -\frac{\mathrm{d[A]}}{\mathrm{d}t} = k[\mathrm{A}]^0$$

Since anything raised to the power zero is equal to 1,

$$\text{Rate} = -\frac{\mathrm{d[A]}}{\mathrm{d}t} = k \qquad (1)$$

Separating the variables, we get

$$d[\mathrm{A}] = -k\mathrm{d}t$$

Integrating both sides

$$\int d[\mathrm{A}] = -k\int \mathrm{d}t$$

$$[\mathrm{A}] = -kt + \mathrm{I} \qquad (2)$$

Where [A] is the concentration of A at time t and I is the constant of integration. It can be evaluated from the initial conditions. When $t = 0$, $[\mathrm{A}] = [\mathrm{A}]_0$, where $[\mathrm{A}]_0$ is the initial concentration of the reactant. Substituting in equation (2)

$$[\mathrm{A}]_0 = -k \times 0 + I = 0 + I$$

$$\therefore \qquad [\mathrm{A}]_0 = \mathrm{I} \qquad (3)$$

Substituting for I in equation (2)

$$[\mathrm{A}] = -kt + [\mathrm{A}]_0 \qquad (4)$$

This equation is the **integrated rate equation for a zero order reaction.** This equation is an equation of a straight line and is of the form

$$y = mx + c$$

It [A] is plotted as a function of t, the plot is a straight line graph with intercept equal to $[A]_0$ and slope equal to $-k$.

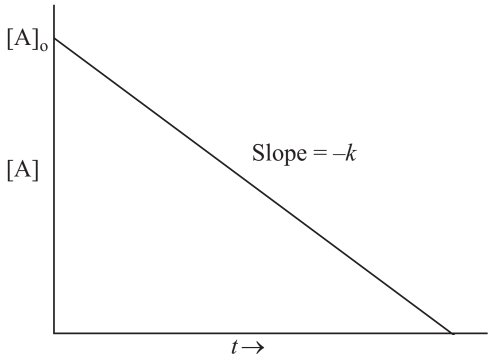


Fig. Concentration versus time plot for a zero order reaction.

Units of *k*

Equation (4) can be rearranged as

$$kt = [A]_0 - [A]$$

or
$$k = \frac{[A]_0 - [A]}{t} = \frac{\text{concentration}}{\text{time}} \tag{5}$$

$$= \text{Concentration time}^{-1} = \text{mol L}^{-1}\text{s}^{-1}$$

Half-Life Period, $t_{1/2}$

It is the time during which one-half of the initial amount of the reactant reacts. It is denoted by $t_{1/2}$ or $t_{0.5}$. It is also called **half-change period.** It can be obtained from equation (4). Rearranging it, we get

$$t = \frac{[A]_0 - [A]}{k} \tag{6}$$

when $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$

that is after half-life period, one-half of the reactant is consumed. Also, one-half reactant is left unreacted or $[A] = \frac{1}{2}[A]_0$.

Putting in equation (6)

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

$$t_{1/2} = \frac{[\mathrm{A}]_0}{2\mathrm{k}} \qquad (7)$$

Thus, the half-life period of a zero order reaction depends upon the initial concentration of the reactant $[\mathrm{A}]_0$ and from the above equation

$$t_{1/2} \propto [\mathrm{A}]_0$$

the half-life period is directly proportional to the initial concentration of the reactant.

Example: The rate constant of a zero order reaction is 2.4×10^{-3} mol $\mathrm{L}^{-1}\mathrm{s}^{-1}$. What would be the half-life of the reaction if the initial concentration of the reactant is 1.2×10^{-2} mol L^{-1}?

Solution

For a zero order reaction

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

Given: initial concentration of the reactant, $[\mathrm{A}]_0 = 1.2 \times 10^{-2}$ mol L^{-1} and $k = 2.4 \times 10^{-3}\ \mathrm{mol\ L^{-1}} s^{-1}$.

$$\therefore \qquad t_{1/2} = \frac{1.2 \times 10^{-2}\ \mathrm{mol\ L^{-1}}}{2 \times 2.4 \times 10^{-3}\ \mathrm{mol\ L^{-1} s^{-1}}}.$$

$$= 2.5\ \mathrm{s}.$$

14.6.2 First Order Reaction

We will now discuss how to determine the rate constant for a first order reaction. For the first order reaction, this equation would tell us how does the concentration vary with time. The predicted variations can then be compared with the experimental data to obtain the order of the reaction.

Let us consider for the reaction $\mathrm{A} \longrightarrow$ Product.

For first order reaction.

$$\text{rate} = \frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{dt}} = k_1[\mathrm{A}]$$

where k_1 is the rate constant,

Rearranging the rate expression, we have :

$$\frac{-d[A]}{[A]} = k_1 dt$$

Integrating the two sides we get :

$$-\ln [A] = k_1 t + \text{constant} \qquad \text{...(i)}$$

where the constant can be determined from the initial conditions.

Let $[A]_0$ be concentration of [A] when $t = 0$ i.e., at the beginning of the reaction, then $-\ln [A] = -\ln [A]_0$, when $t = 0$

or $$\text{constant} = -\ln [A]_0$$

Putting the value of the constant in equation

$$-\ln [A] = k_1 t - \ln [A]_0$$

or $$-\ln [A] + \ln [A]_0 = k_1 t$$

or $$\ln\frac{[A]_0}{[A]} = k_1 t$$

$$\text{Rate constant, } k_1 = \frac{1}{t}.\ln\frac{[A]_0}{[A]}$$

We can convert it in to log to the base 10

$$k_1 = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$\frac{k_1 t}{2.303} = \log [A]_0 - \log [A]$$

$$-\frac{k_1 t}{2.303} = \log [A] - \log [A]_0$$

$$\log [A] = -\left(\frac{k_1}{2.303}\right) t + \log [A]_0$$

The unit of $k_1 = \text{time}^{-1}$

This equation has the same form as the equation of a straight line.

$$y = mx + c$$

where m is the slope and c is the intercept. If we plot $\log_{10}$ [A] vs t, it would give a straight line with a slope equal to $-\frac{k_1}{2.303}$. The rate constant, k_1 can then be calculated from the slope as shown in Fig. 14.1.

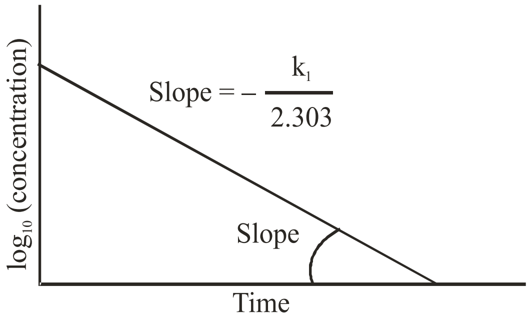


Fig. 14.1 : *A graph of log₁₀ (concentration) against time for a first-order reaction.*

14.6.3 Half-Life Period

The time taken for a reaction to reach the half-way stage i.e. when half of the starting material has reacted is called half-life period of the reaction. It is denoted by $t_{1/2}$ or $t_{0.5}$. Let us now see how the half-life period of a first order reaction is calculated.

You know that

$$\ln[A] = \ln[A]_0 - k_1t$$

when $[A] = \frac{1}{2}[A]_0$ (reactant reduces to half of the initial concentration)

then $t = t_{1/2}$ (half life period)

Therefore, we have

$$\ln\left\{\frac{[A]_0}{2}\right\} = \ln[A]_0 - k_1t_{1/2}$$

or $$\ln\left\{\frac{[A]_0}{2}\right\} - \ln[A]_0 = -k_1t_{1/2}$$

or $$\ln\frac{1}{2} = -k_1t_{1/2}$$

or $$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$$

You would notice that half-life period is independent of the initial concentration.

Example 14.2 : The decomposition of hydrogen peroxide to water and oxygen.

$$2H_2O_2(\ell) \longrightarrow 2H_2O(\ell) + O_2(g)$$

is a first order reaction with a rate constant of 0.0410 min^{-1}. If we start with 0.20 M solution of H_2O_2, what will be concentration after 10 minutes?

Solution : We have equation for first order reaction as

$$k = \frac{1}{t}\text{In}\frac{[A]_0}{[A]}$$

converting it into $\log_{10}$ base

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

If [A] = x, after 10 minutes then subsituting the values of *k* and *t*, we have

$$0.0410\ (\text{min}^{-1}) = \frac{2.303}{10(\text{min})}\log\frac{0.20}{x}$$

or $$\log\frac{0.20}{x} = \frac{10(\text{min})\ (0.0410\ \text{min}^{-1})}{2.303} = 0.178$$

Taking antilog

$$\frac{0.20}{x} = \text{antilog } 0.178 = 1.51$$

Solving $$x = \frac{0.20}{1.51} = 0.132\ \text{mol litre}^{-1}.$$

Example 14.3 : In example 14.2 if we start with initial concentration of 0.50 how long will it take for this concentration to drop to 0.10 M.

Solution : We have to find the time taken by the reaction starting from concentration of H_2O_2 of 0.5M to concentration of 0.1 M.

We have the equation,

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

Substituting the values of *k*, $[A]_0$ and [A] we have

$$0.0410\ \text{min}^{-1} = \frac{2.303}{t}\log\frac{0.50}{0.10}$$

$$t = \log 5 \times \frac{2.303}{0.0410\ \text{min}^{-1}} = \frac{0.699 \times 2.303}{0.041}\ \text{min}$$

or $$t = 39 \text{ minutes}$$

Example 14.4 : In example 14.2, how long will it take for the sample to decompose to 50%.

Solution : When half the sample has decomposed, we have

$$t_{1/2} = \frac{0.693}{k}$$

Putting the value of $k = 0.0414\ \text{min}^{-1}$ we have

$$t = \frac{0.693}{0.0414}\ \text{min} = 16.9\ \text{minutes}$$

INTEXT QUESTIONS 14.2

1. The rate of a certain reaction, $A \longrightarrow$ Product is 1.0×10^{-3} mol/litre.

   When conc. $A = 0.020M$, what is rate constant k, if the reaction is :

   (a) zero order

   (b) first order

2. For the following reaction

   $$C_2H_4\,(g) + I_2(g) \longrightarrow C_2H_4I_2(g)$$

   the rate equation is

   $$\text{rate} = k\,[C_2H_4(g)]\,[I_2(g)]^{3/2}$$

   (a) What is the order of reaction with respect to each reactant?

   (b) What is the overall order of reaction?

   (c) What is the unit of k, if concentrations are measured in mol dm^{-3}?

3. The first order rate constant for the decomposition of C_2H_5Cl at 700K is $2.5 \times 10^{-3}\ \text{min}^{-1}$. If the initial concentration is 0.01 mol L^{-1}, calculate the time required for the concentration of C_2H_5Cl to drop to half of its original value.

14.7 COLLISION THEORY OF REACTION RATES

Collision theory was proposed to explain the rates of reactions occurring in gas phase. It is largely based on kinetic molecular theory of gases. According to this theory:

1. A reaction would occur only when the reactant molecules collide with one another. Thus, the rate of a reaction would depend upon the *collision frequency*, Z_{AB} which is the number of collisions involving one molecule each of two reactants A and B occurring in unit volume of the gaseous reaction mixture and in unit time.

2. Not all molecular collisions result in chemical reaction. Only effective collisions can bring about chemical reaction. An effective collision is the one

in which the combined kinetic energy of colliding moleculas is equal to or more than the activation energy of the reaction E_a. The fraction of molecules possessing a minimum of activation energy E_a at a particular temperature T is given by $e^{-\frac{E_a}{RT}}$.

3. For a reaction to occur not only the collision should be energetically effective, the orientation of the colliding molecules should be such which would permit the formation of new bonds. Consider, for example, the decomposition reaction of HI

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The product would be formed only if during the collision the two H atoms are near each other and so are the two I atoms. (Fig 14.3(a)). This would permit the formation of bond between two H atoms and another bond between two I atoms. If orientation is not proper (Fig 14.3(b), it is not possible as two I atoms are too far apart for the bond formation. After the collision, the two HI molecules rebound back without any reaction. Only a certain fraction of energetically effective collisions would have proper orientation and would result in a chemical reaction. This fraction is represented in terms of probability P, that molecules during a given collision would have proper orientation. P is called **probability factor** or **steric factor.**

H — I   H — I

H — I   I — H

(a)   (b)

Fig. 14.3 (a) Proper orientation of two HI molecules (b) Improper orientation.

Taking these three factors into account, the rate of the reaction is given by the relation

$$\text{Rate} = Z_{AB} \cdot e^{-\frac{E_a}{RT}} \cdot P$$

14.7 DEPENDENCE OF REACTION RATE ON TEMPERATURE

You have learnt earlier that an increase in temperature causes an increase in the rate of reaction. The rate is about doubled, for many reactions, by a 10 degree rise in temperature. How can we explain this behaviour?

In order for a chemical reaction to occur, the reacting molecules must collide with each other. Only fast moving molecules i.e. the molecules having high energy are able to react. There must be some minimum energy possessed by the reacting molecules during the collision. This is called the **threshold energy**. All molecules having energy higher than the threshold energy are therefore, capable of reacting. What would happen if we increase the number of molecules having higher energy? More molecules will react. In other words rate of reaction would increase. Thus, if we increase the temperature, we increase the rate of reaction. Let us see if we can express it quantitatively.

The change in energy that takes place during the course of a reaction is shown in Fig. 14.2. The horizontal axis denotes the progress of the reaction and it indicates the extent to which the reaction has progressed towards completion. The graph indicates that the reactant molecules A and B must possess enough energy. This is known as Activation energy, to climb the potential energy hill to form the activated complex. All the reacting molecules do not possess energy equal to threshold energy in their normal energy state. Therefore a certain extra energy needs to be supplied so that their energy equals the threshold energy. The potential energy of activated complex is maximum. The reaction thereafter proceeds to completion (i.e. formation AB). Ea indicates the activation energy of forward reaction and Ea′ is the activation energy of the backward reaction.

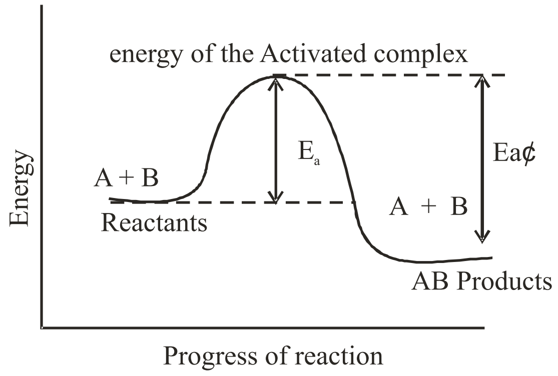


Fig. 14.2 *Energy diagram for a reaction*

You know that rate of reaction = k [concentration]. If we have value of concentration as unity, then rate of reaction is equal to the rate constant, k. The rate constant k depends on the magnitude of the activation energy, E_a, and also on the absolute temperature (T), k is small when E_a is very large or the temperature is low.

We can express this relationship by a mathematical equation known as *Arrhenius equation* after its discoverer, S. Arrhenius as follows :

$$k = Ae^{-Ea/RT}$$

Where A is a proportionality constant and is also known as frequency factor, R is the gas constant. How can we utilise this relationship between k, Ea and T? We can calculate activation energy, if we measure the rate constant at two different temperatures.

Taking natural logarithm of equation, we get

$$\ln k = \ln A - \frac{Ea}{RT}$$

We can compare this equation with that of a straight line $y = mx + c$ as follow :

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

The plot of in k vs 1/T gives a straight line whose slope is equal to –Ea/R and whose intercept is In A (in Fig. 14.3).

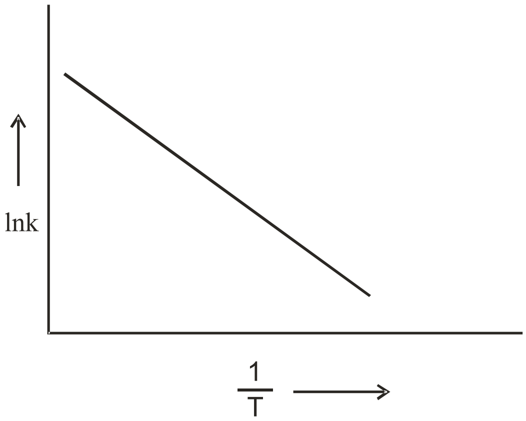


Fig. 14.3 *Graphical determination of E_a.*

We can also obtain Ea from k at two temperatures by direct computation.

At T_1, the equation becomes

$$k_1 = Ae^{-Ea/RT_1}$$

At T_2, we can write

$$k_2 = Ae^{-Ea/RT_2}$$

Dividing k_1 by k_2 we get

$$\frac{k_1}{k_2} = \frac{Ae^{-Ea/RT_1}}{Ae^{-Ea/RT_2}}$$

taking natural logarithm

$$\ell n \frac{k_1}{k_2} = \frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Converting into logarithm (base 10)

$$\log \frac{k_1}{k_2} = \frac{-E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 . T_2}\right)$$

Multiply by –1 on both sides and inverting the fraction

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 . T_2}\right)$$

This equation can also be used to calculate the rate constant at some specific temperature if E_a and k at some other temperature are known.

Example 14.5 : What must be the value of E_a if the rate constant for a reaction is doubled when the temperature increases from 300K to 310K?

Solution : Given $\frac{k_2}{k_1} = 2$, $R = 8.31\ JK^{-1}$

$$T_2 = 310\ K$$

$$T_1 = 300\ K$$

$$E_a = ?$$

We have equation :

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 \,.\, T_2}\right)$$

substituting the values we have

$$\log 2 = \frac{E_a}{2.303 \times 8.31\,JK^{-1}} \frac{(310 - 300)K}{(310K \times 300K)}$$

solving, we have

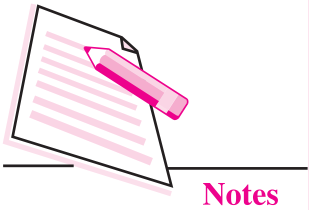
$$E_a = 53.5\ kJ$$

INTEXT QUESTIONS 14.3

1. As a rough rule of thumb, the rates of many reactions double for every 10ºC rise in temperature? Explain.
2. The rate constant of a reaction at 288 K is 1.3×10^{-5} litre/mol. While at 323K its rate constant is 8.0×10^{-3} lit./mol. What is the E_a for the reaction.
3. The rate of the reaction triples when temperature changes from 293 K to 323 K. Calculate the energy of activation for such a reaction.
4. $H_2(g)$ and $O_2(g)$ combine to form $H_2O(\ell)$ by an exothermic reaction. Why do they not combine when kept together for any period of time.
5. What is an effective collision?

WHAT YOU HAVE LEARNT

- The rate of a chemical reaction can be expressed as the rate of change in concentration of a reactant or product.



Notes

- The factors that affect the rate of a chemical reaction are : the concentration of the reactants, temperature and catalyst.
- Rate law is defined as the mathematical relationship between rate of a reaction with the concentration of the reactant.
- The constant k in the rate law is called the rate constant. It is numerically equal to the rate of the reaction if all the concentrations were set equal to unity.
- The sum of the powers to which the concentration terms are raised in the rate expression describe the order of the reaction.
- The rate constant of a first order reaction, k_1, is given by

$$k_1 = \frac{1}{t} \text{ In } \frac{[\text{A}]_0}{[\text{A}]}$$

- The time taken for a reaction to reach the half way stage, i.e., when half of the starting material has reacted is called half-life period of a reaction.
- According to the collision theory, a reaction occurs only when the reactant molecules collide provided they have sufficient energy and proper orientation.
- The dependence of the rate constant on the magnitude of the activation energy, E_a, and the absolute temperature, T, is given by the Arrhenius equation, $k = Ae^{-Ea/RT}$.
- The activation energy for the decomposition of a compound corresponds to the difference between the energy of the reactants and the maximum on the energy curve.

TERMINAL EXERCISE

1. Sketch an energy vs progress of reaction diagram for a reaction. Indicate the activation energy for both forward (E_a) and reverse reaction (E'_a).
2. For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, it is found that N_2O_5 is decomposing at the rate of 0.02 mol/litre sec. Calculate to rate of reaction defined as $\frac{\Delta[NO_2]}{\Delta t}$ with Δt in seconds.
3. The rate constant for a certain first order decomposition reaction is 0.23 s^{-1} at 673K. Calculate the half-change period for this reaction.

4. The rate constant for a certain first order reaction is 1.00×10^{-3} s^{-1} at 298K. The rate constant for the reaction is 1.4×10^{-2} s^{-1} at 323K. Calculate the activation energy for this reaction.

5. The rate of a reaction was found to be 3.0×10^{-4} mol/litre second. What will be the rate if it were expressed in the units mol/litre minute.

6. List the three factors that affect the rate of a chemical reaction.

7. For a certain first order reaction the concentration of the reactant decreases from 2.00 mol/litre to 1.50 mol/litre in 64 minutes. Calculate the rate constant for this reaction.

8. The rate constant for a certain first order reaction is 1.0×10^{-3} min^{-1} at 298K. If the activation energy is 10.0 k cal, calculate the rate constant at 323K.

9. The reaction

$$A_2 + B \longrightarrow C + D$$

Occurs in the following steps

(i) $A_2 \longrightarrow 2A$

(ii) $A + B \longrightarrow X$

(iii) $A + X \longrightarrow C + D$

The order of this reaction is one. What is its molecularity. What one of the three steps is the slowest or rate determining step?

ANSWERS TO INTEXT QUESTIONS

14.1

1. d

2. (i) $\dfrac{\Delta[NO_2F]}{\Delta t}$ (ii) $\dfrac{-\Delta[NO_2]}{\Delta t}$

(iii) $\dfrac{-\Delta[F_2]}{\Delta t}$ (iv) $\dfrac{1}{2}\dfrac{\Delta[NO_2F]}{\Delta t} = -\dfrac{1}{2}\dfrac{\Delta[NO_2]}{\Delta t} = \dfrac{-\Delta[F_2]}{\Delta t}$

3. $\dfrac{1}{2}\dfrac{d[NO_2F]}{dt} = -\dfrac{1}{2}\dfrac{d[NO_2]}{dt} = \dfrac{d[F_2]}{dt}$

4. Increase in volume would decrease the pressure which would decrease the rate of reaction.

14.2

1. (a) 1.0×10^{-3} mol litre^{-1} s^{-1}

   (b) 5.0×10^{-2} s^{-1}

2. (a) First order with respect to C_2H_4 and 1.5 with respect to I_2.

   (b) The over all order of reaction is 2.5

   (c) $k = \dfrac{\text{sec}^{-1}}{(\text{mol dm}^{-3})^{3/2}}$

   $= \text{mol}^{-3/2}\, dm^{9/2}\, \text{s}^{-1}$.

3. (a) $2.5 \times 10^{-3}\,(\text{min}^{-1}) = \dfrac{2.303}{10\text{ min}} \log_{10} \dfrac{0.01\text{ mol L}^{-1}}{x}$

   (b) When half of the sample is decomposed

   $t_{1/2} = \dfrac{0.693}{2.5 \times 10^{-3}}\text{ min} = 0.277 \times 10^3\text{ min} = 2.77 \times 10^2\text{ min}$

14.3

1. 10
2. 34.0 K cal mol^{-1}
3. 28.82 kJ
4. Molecules do not have enough energy to be equal to threshold energy.

15

313en15

ADSORPTION AND CATALYSIS

Surface of solids plays a crucial role in many physical and chemical phenomena. There are two main reasons for this special role. Firstly, the surface of a substance interacts first with its surroundings. Secondly, the surface molecules are in a different state as compared to the molecules in the interior of the solid. The surface molecules interact more readily with other substances which come close by and are responsible for many special properties. In this lesson we shall study about two such properties – adsorption and catalysis.

OBJECTIVES

After reading this lesson you will be able to :

- define adsorption;
- distinguish between physical adsorption and chemisorption;
- list and explain the various factors that affect adsorption;
- state Freundlich adsorption isotherm mathematically and explain it;
- explain Langmuir isotherm;
- define catalysis;
- distinguish between homogeneous and heterogeneous catalysis, and
- explain the role of activation energy in catalysis.

15.1 ADSORPTION

The surface of a solid attracts and retains molecules of a gas or a dissolved substance which comes in its contact. These molecules remain only at the surface and do not go deeper into the bulk Fig. 15.2(a).

The phenomenon of attracting and retaining the molecules of a gas or a dissolved substance by the surface of a solid, resulting in their higher concentration on the surface is called adsorption.

The substance which gets adsorbed is called the **adsorbate** and the solid substance which adsorbs is called the **adsorbent**.

A molecule in the interior of a solid is surrounded by other molecules in all directions (Fig. 15.1). However, a molecule at the surface is surrounded by other molecules within the solid phase but not from the outside.Therefore, these surface molecules have some unbalanced or residual forces.

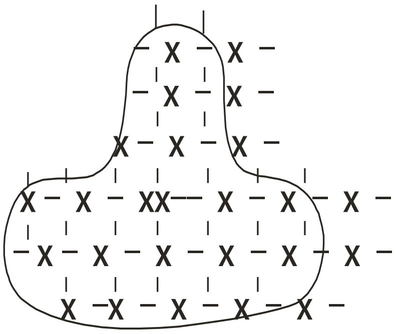


Fig. 15.1 : *Molecules in the interior and at the surface of a solid*

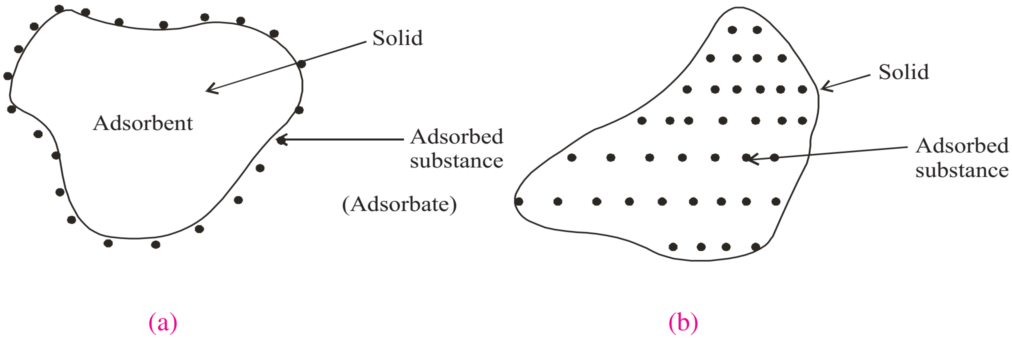


Fig. 15.2 : *(a) Adsorption (b) Absorption*

15.1.1 Adsorption and Absorption

The phenomenon of *adsorption* is different from that of *absorption*. The latter term implies that a substance is uniformly distributed throughout the body of a solid, Fig. 15.2(b). If we leave a small lump of calcium chloride in open, it absorbs water vapour (moisture) from air and after some time even starts dissolving in it. On the other hand if we keep a sample of silica gel in open, it adsorbs water vapour on its surface as shown in Fig. 15.2 (a).

15.1.2 Factors Affecting Adsorption

Adsorption occurs on the surface of almost all solids. However, the extent of adsorption of a gas on the surface of a solid depends upon the following factors:

(i) Nature and surface area of the adsorbent

(ii) Nature of the adsorbed gas

(iii) Temperature

(iv) Pressure of the gas

Let us now discuss these factors briefly.

(i) Nature and Surface Area of the Adsorbent

Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents.

The extent of adsorption also depends upon the surface area of the solid. Greater the surface area, more is the surface available for adsorption and greater is the adsorption. The surface area depends upon the particle size of the substance. A cube of each side equal to 1cm has six faces. Each of them is a square with surface area of 1cm^2. Thus, the total surface area of this cube is 6 cm^2 Fig. 15.3 (a). If its each side is divided into two equal halves, ½ cm long, and the cube is divided into two equal halves, ½ cm long, and the cube is cut along the lines indicated in the Fig (b), the cube would be divided into 8 smaller cubes with each side 0.5 cm long [Fig. 15.3 (b)]. Surface area of each small cube would be $(6 \times 0.5 \times 0.5) = 1.5$ cm^2 and the total surface area of all the 8 smaller cubes would be 12 cm^2 which is double the surface area of the original cube. If it is subdivided into smaller cubes, each of side equal to 1×10^{-6} cm the surface area will increase to 6×10^6 cm^2 or 600 m^2. The increase in surface area would result in greater adsorption.

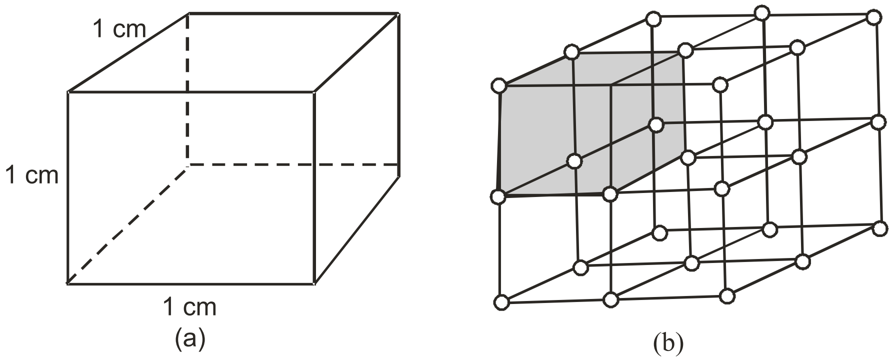


Fig. 15.3 : *Subdivision of a cube*

Now we can explain why the solids that are porous in nature and have rough surfaces are better adsorbents. It is so because each of these features increases the surface area.

(ii) The Nature of the Adsorbed Gas

The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquifiable or are more soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of SO_2 or NH_3 adsorbed by charcoal is much more than that of H_2 or O_2 gases. It is because the intermolecular forces are stronger in more easily liquifiable gases, therefore, they get adsorbed more strongly.

(iii) Temperature

The extent of adsorption decreases with rise in temperature. For example, under one atmosphere pressure, one gram of charcoal adsorbs about 10 cm^3 of N_2 gas at 272 K, 20 cm^3 at 248 K and 45 cm^3 at 195 K.

Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed, is called ***enthalpy of adsorption***. The adsorption process is similar to the condensation process. The reverse process is called **desorption** and is *endothermic* in nature. It is similar to the evaporation process. When a gas is kept in contact with a solid adsorbent in a closed container, a dynamic equilibrium is established in due course of time.

$$\underset{\text{adsorbate}}{\text{gas}} + \underset{\text{adsorbent}}{\text{solid}} \rightleftharpoons \text{gas adsorbed on the solid} + \textit{heat}$$

Since the forward process (adsorption) is exothermic in nature, according to the Le Chatelier's principle, it would be favoured at low temperature. Therefore, the extent of adsorption would increase on decreasing the temperature and would decrease on increasing the temperature.

(iv) Pressure of the gas

At a constant temperature the extent of adsorption increases with increase in the pressure of the gas (adsorbate). We shall study the relation between the two in detail a little later.

15.1.3 Physical and Chemical Adsorption

Adsorption can be divided into two main categories – physical and chemical adsorption.

(i) Physical Adsorption

It is the common type of adsorption. The basic feature of **physical adsorption** is that the adsorbate molecules are held at the surface of the adsorbent by weak van der Waals forces. These are the forces that exist between particles of all matter. Because of their universal nature, these forces would operate between any adsorbent and adsorbate pair. Therefore, the physical adsorption is observed on surface of any solid. Only, the extent of adsorption varies according to the nature of the adsorbent and adsorbate as discussed earlier.

Physical adsorption is characterized by low *enthalpy of adsorption*, that is about 10 – 40 kJ mol^{-1}.

Another feature of the physical adsorption of a gas by a solid is that it is *reversible* in nature and an equilibrium is established between the adsorbent and the adsorbate as discussed earlier. Increase of pressure increases the adsorption and the release of pressure desorbs the gas. When temperature is increased, the physical adsorption decreases and when it is lowered, the adsorption increases. In physical adsorption, several layers of adsorbate are adsorbed one over the other.

(ii) Chemisorption or Chemical Adsorption

We have seen earlier that some unsaturated valancies exist on the surface of a solid. Whenever a chemical combination takes place between the adsorbent and the adsorbate the adsorption becomes very strong. This type of adsorption caused by forces similar to chemical bonds between the adsorbent and the adsorbate is called **chemisorption** or **chemical adsorption**.

The enthalpy of chemisorption is as high as that of chemical bonds (bond enthalpies) and is in the range of 40 – 400 kJ mol^{-1}. Chemisorption is highly specific and is possible between a specific adsorbent – adsorbate pair. Like most of the chemical changes it is irreversible. Attempts to release the adsorbed gas gives the gas and some amount of a definite compound. For example, oxygen gas is chemisorbed on tungsten. It is released from the surface of tungsten as a mixture of oxygen and tungsten oxide. Unlike physical adsorption, chemisorption first increases and then decreases with rise in temperature [Fig. 15.4 (b)]. This shows that chemisorption has an energy of activation*. During chemisorption, only one layer of adsorbate molecules is adsorbed. The main distinctions between physical adsorption and chemisorption are summarized in Table 15.1.

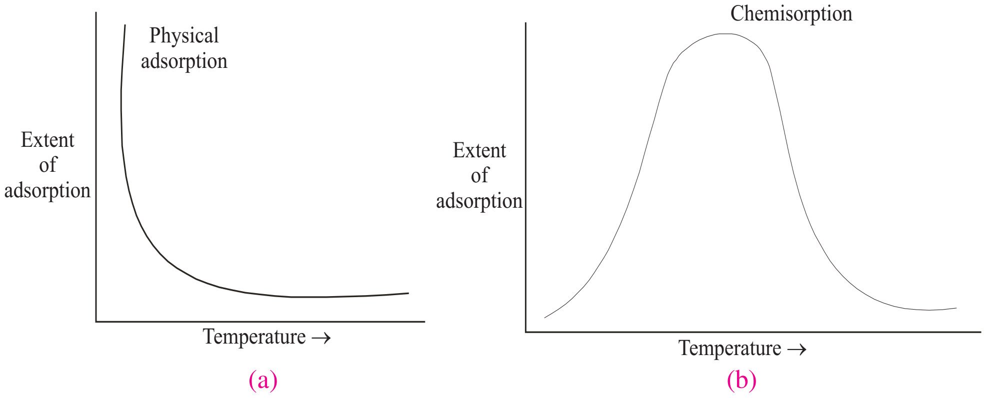


Fig. 15.4 : *Effect of temperature on (a) physical adsorption and (b) chemisorption.*

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* You will learn more about energy of activation later in this lesson.

Table 15.1 : Physical Adsorption and Chemisorption

Physical Adsorption	Chemisorption
1. The forces operating between adsorbate and adsorbent are the weak van der Waals forces.	1. The forces operating between adsorbate and adsorbent are strong and similar to chemical bonds.
2. The enthalpy of adsorption is low and ranges from 10 to 40 kJ mol^{-1}.	2. The enthalpy of adsorption is high and ranges from 40 to 400 kJ mol^{-1}.
3. No activation energy is involved.	3. Significant activation energy is involved.
4. Adsorption occurs more readily at low temperature and high pressure.	4. Chemisorption occurs at relatively high temperature and high pressure.
5. It is not specific in nature. All gases are adsorbed on all solids and no compounds are formed.	5. It is highly specific in nature and occurs between those adsorbents and adsorbates which have a possibility of compound formation between them.
6. It is reversible in nature. The gas is desorbed on increasing the temperature or decreasing the pressure.	6. It is irreversible in nature. Desorption also separates some amount of the compound formed.
7. Multilayer formation is common.	7. Monolayer formation occurs.

15.1.4 Adsorption Isotherms

The extent of adsorption is measured in terms of the quantity $\frac{x}{m}$ where, x is the mass of the gas (adsorbate) adsorbed at equilibrium on mass m of the adsorbent. $\frac{x}{m}$ is the mass of the adsorbate adsorbed per unit mass of the adsorbent. The graph showing variation in $\frac{x}{m}$ with pressure(p) at a constant temperature is called **adsorption isotherm**. Let us see the variation in extent of adsorption in case of gases and of solutes from their solutions.

(i) Adsorption of Gases

The adsorption isotherm of a gas which is adsorbed on a solid is shown in Fig. 15.5. It shows that the extent of adsorption of a gas on a solid increases with the increase in the pressure of the gas, p at three different constant temperatures. The curves also show that the extent of adsorption, decreases at a fixed pressure as the temperature is increased (see the dotted line).

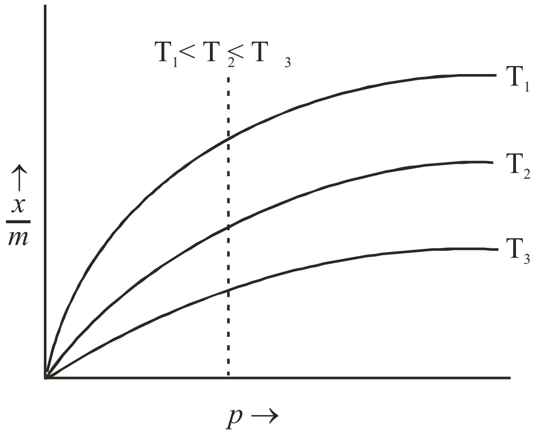


Fig. 17.5 : *Adsorption isotherm of a gas*

Freundlich Adsorption Isotherm

Freundlich gave an empirical mathematical relationship between the extent of adsorption $\left(\frac{x}{m}\right)$ and the equilibrium pressure (p) of the gas as :

$$\frac{x}{m} = k\,p^{\frac{1}{n}} \quad \text{where n > 1}$$

In this relation k is a constant at a given temperature and depends upon the nature of the adsorbate and adsorbent. The value of n changes with pressure. It is 1 at low pressures and increases with pressure. The relationship is valid at a constant temperature. Therefore, it is called **Freundlich Adsorption Isotherm**. On taking logarithm of the above equation, we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

This is an equation of a straight line and a plot of log $\frac{x}{m}$ against log p should be a straight line with slope $\frac{1}{n}$ as depicted in Fig. 15.6. In actual practice, a straight line is obtained provided the data at very low and very high pressures is neglected.

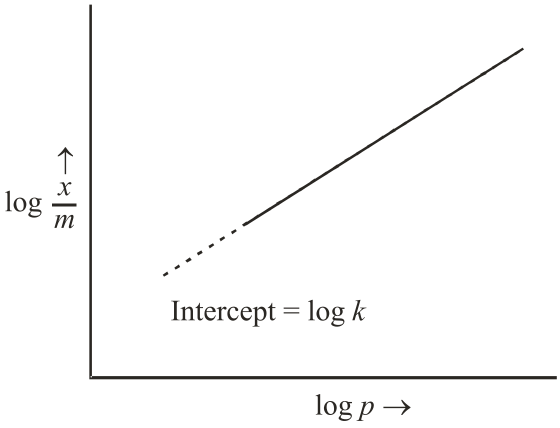


Fig. 15.6 : Plot of log $\frac{x}{m}$ against log p.

15.1.5 Langmuir Adsortion Isotherm

Adsorption Isotherm : One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas. Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases. This is named as the Langmuir adosrption isotherm. This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied. In his derivation, Langmuir considered adsorption to consist of the following two opposing processes :

Asorption of the gas molecules on the surface of the solid.

Desorption of the adsorbed molecules from the surface of the solid.

Langmuir believed that eventually a dynamic equilibrium is established between the above two opposing processes. He also assumed that the layer of the adsorbed gas is only one molecule thick i.e., unimolecular. Since such type of adsorption is obtained in the case of **chemisorption.** Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation.

$$\frac{x}{m} = \frac{a\,p}{1+bp} \qquad \text{...(15.1)}$$

where a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{b} \text{ (at very high pressure)} \qquad \text{...(15.2)}$$

At very low pressure, Eq. (15.1) is reduced to $x/m = ap$ (at very low pressure) ...(15.3)

In order to determine the parameters a and b, Eq. (15.1) may be written in its inverse form:

$$\frac{m}{x} = \frac{1+bp}{ap} = \frac{b}{a} + \frac{1}{ap} \qquad \text{...(15.4)}$$

A plot of m/x against $1/p$ gives a straight line the slope and intercept equal to 1/a and b/a, respectively. Thus, both parameters can be determined.

The Langmuir isotherm, in the form of Eq. (15.1) is generally more successful in interpreting the data than the Freundlich isotherm when a monolayer is formed. A plot of x/m versus p is shown in (Fig15.7). At low pressures, according to Eq. (15.3), pressure x/m increases linearly with p. At high pressure according to Eq. (15.2), x/m becomes constant i.e. the surface is fully covered and change in pressure has no effect and no further adsorption takes place, as is evident from Fig. 15.7.

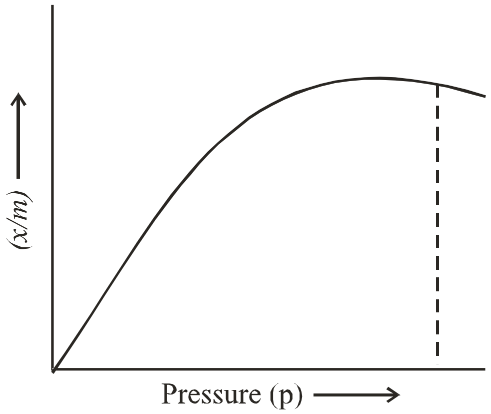


Fig. 15.7 : *Langmuir Adsorption isotherm.*

(ii) Adsorption from Solutions.

Adsorption occurs from solutions also. The solute gets adsorbed on the surface of a solid adsorbent. Charcoal, a good adsorbent, is often used to adsorb acetic acid, oxalic acid and organic dyestuffs from their aqueous solutions.

The extent of adsorption, $\frac{x}{m}$ depends upon the concentration c of the solute. Freundlich isotherm is applicable to adsorption from solutions when concentration is used in place of pressure as shown below.

$$\frac{x}{m} = k\,c^{\frac{1}{n}}$$

and in the logarithmic form as

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c$$

The plot of log $\frac{x}{m}$ against c is also a straight line, provided very low and very high concentrations are avoided.

15.1.6 Applications of Adsorption

The phenomenon of adsorption finds many applications, some of which are given below:

1. Activated charcoal is used in gas masks in which toxic gases are adsorbed and air passes through it.
2. Silica gel packed in small cloth bags is used for adsorbing moisture in bottles of medicine and in small electronic instruments.
3. Animal charcoal is used for decolourizing many compounds during their manufacture.

4. In chromatography, the selective adsorption of different solutes on the surface of solid adsorbent helps in their separation.
5. Mordants are used during dyeing process with certain dyes. In such cases, the mordants fix the dye on the fabric by adsorption.

INTEXT QUESTIONS 15.1

1. Indicate which of the following statements are true or false. (T/F)
   - (i) More easily liquifiable gases are adsorbed more strongly.
   - (ii) Non-porous adsorbents would adsorb more quantity of a gas than porous adsorbents under similar conditions.
   - (iii) The extent of adsorption increases with rise in temperature.
   - (iv) Chemisorption is highly specific in nature.
   - (v) Adsorption can occur from solutions also.

15.2 CATALYSIS

When hydrogen and oxygen gases are kept in contact with each other, no observable reaction occurs. If we add a small piece of platinum gauge in the mixture of these gases, the reaction occurs readily. Here platinum gauge speeds up the reaction and is called a **catalyst**.

A catalyst is a substance which changes the rate of a reaction but remains chemically unchanged at the end of the reaction.

The phenomenon of change of reaction rate by addition of a substance which itself remains unchanged chemically is called **catalysis**. The following are some more examples of catalysis:

(i) Decomposition of potassium chlorate occurs at high temperature. If a small amount of the manganese dioxide is added, the decomposition occurs at much lower temperature. Here, manganese dioxide acts as catalyst.

$$2\,KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

(ii) The evolution of hydrogen by the reaction between zinc and hydrochloric acid is catalysed by $Cu^{2+}(aq)$ ions.

$$Zn(s) + 2HCl(aq) \xrightarrow{Cu^{2+}(aq)} ZnCl_2(aq) + H_2(g)$$

(iii) The oxidation of hydrogen chloride gas by oxygen occurs more quickly if the gases are passed over cupric chloride.

$$4HCl(g) + O_2(g) \xrightarrow{CuCl_2(s)} 2H_2O(g) + Cl_2(g)$$

Notes

Auto-catalysis

In certain reactions, one of the products of the reaction acts as the catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate occurs as

$$2KMnO_4(aq) + 3H_2SO_4(aq) + 5(COOH)_2(aq) \longrightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(\ell) + 10\ CO_2(g)$$

At room temperature, the reaction is quite slow in the beginning. Gradually it becomes fast due to the catalytic action of Mn^{2+} ions which are one of the products as $MnSO_4$ in the reaction.

The phenomenon in which one of the products of a reaction acts as a catalyst is known as auto-catalysis.

Negative Catalysis

Some catalysts retard a reaction rather than speed it up. They are known as negative catalysts. For example :

(i) Glycerol retards the decomposition of hydrogen peroxide.

(ii) Phenol retards the oxidation of sulphurous acid.

Promoters and Poisons

Certain substances increase or decrease the activity of the catalyst, although, by themselves they do not show any catalytic activity.

The substances which increase the activity of a catalyst are called ***promoters*** *and those which decrease the activity of a catalyst are called* ***poisons***. For example:

(i) In Haber's process for the manufacture of ammonia, the catalytic activity of iron is enhanced by molybdenum which acts as promoter.

$$N_2(g) \quad + \quad 3H_2(g) \xrightleftharpoons[\text{Mo(s)}]{\text{Fe(s)}} 2NH_3(g)$$

(ii) Copper promotes the catalytic activity of nickel during hydrogenation of oils.

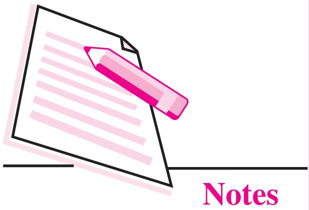
(iii) In Haber's process the catalyst iron is poisoned by hydrogen sulphide H_2S.

(iv) In contact process for the manufacture of sulphuric acid, the catalyst platinum is poisoned by even the traces of arsenious oxide As_2O_3.

15.2.1 General Characteristics of a Catalyst

The following are the general characteristics of a catalyst :

(i) A catalyst remains unchanged at the end of the reaction.



Notes

The amount and the chemical composition of a catalyst remain unchanged in a catalytic reaction. However, the catalyst may undergo a physical change. For example, manganese dioxide, which is used as a catalyst in thermal decomposition of potassium chlorate becomes powder during the course of the reaction.

(ii) A small quantity of the catalyst is generally enough.

In most of the reactions, only a minute amount of catalyst is required. Only one gram of Cu^{2+} ions is sufficient to catalyse the oxidation of 10^9 litres of sodium sulphite solution. In some cases, the rate of reaction is directly proportional to the concentration of catalyst present. Catalysis by acids or bases is usually of this type.

(iii) A catalyst does not alter the position of equilibrium state of a reversible reaction.

A catalyst allows the equilibrium to be reached faster. However, it does not alter the equilibrium composition of the reaction mixture. It is because, a catalyst increases the rates of forward and backward reaction equally.

(iv) Catalysts are generally specific in their action.

Generally, one catalyst will change the rate of only one reaction. For example, manganese dioxide catalyses the decomposition of potassium chlorate but not of potassium perchlorate.

(v) A catalyst cannot initiate a reaction.

A catalyst can change the rate of a reaction which occurs even in the absence of catalyst. It cannot start a reaction.

(vi) The activity of a catalyst can be increased by the presence of promoters and decreased by the presence of poisons.

Presence of a promoter increases the activity of a catalyst, while the presence of a poison decreases it.

15.2.2 Homogeneous and Heterogeneous Catalysis

The phenomenon of catalysis can be divided into two main types – homogeneous and heterogeneous catalysis, on the bases of the number of phases present in the reaction mixture (A phase is a homogeneous part of a system).

(a) Homogeneous Catalysis

When the catalyst is present in the same phase as the reactants, the phenomenon is called ***homogeneous catalysis***. For example :

(i) Nitric oxide catalyses the oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process.

$$2SO_2(g) \quad + \quad O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii) Hydrogen ions catalyse the *inversion of cane sugar*

$$C_{12}H_{22}O_{11}(aq) \quad + \quad H_2O(aq) \xrightarrow{H^+(aq)} \underset{\textbf{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\textbf{Fructose}}{C_6H_{12}O_6(aq)}$$

(b) Heterogeneous Catalysis

When the catalyst is present in a phase other than that of reactants the phenomenon is called ***heterogeneous catalysis***. For example :

(i) Iron (s) catalyses the formation of NH_3 gas.

$$N_2 + 3H_2 \xrightleftharpoons{Fe(s)} 2NH_3$$

(ii) In contact process for the manufacture of sulphuric acid, platinized asbestos is used as the catalyst

$$2\,SO_2(g) \quad + \quad O_2(g) \xrightleftharpoons{Pt(s)} 2SO_3(g)$$

15.2.3 Catalysis and Activation Energy

We have seen that a catalyst increases the rate of a reaction. We explain it by considering the Fig 15.8.

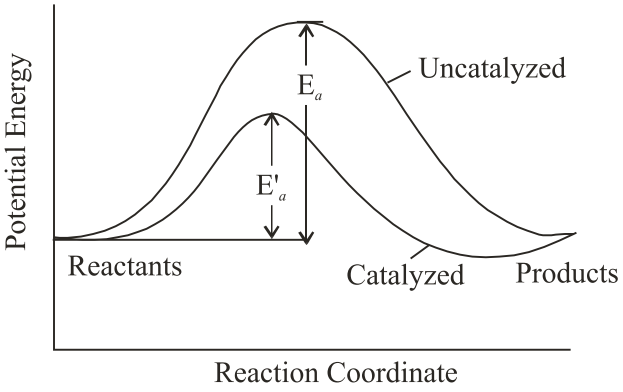


Fig. 15.8 : *Graphical representation of the effect of catalyst on a reaction.*

In this figure E_a is the activation energy of uncatalysed reaction and E'_a is the activation energy of the catalysed reaction. A catalyst lowers the activation energy as you can see in the figure ($E'a < Ea$). The reduction in activation energy is achieved by providing an alternative pathway of lower energy for the reaction.

You can also see in this figure that the relative energies of reactants and products are not changed. The enthalpy change is the same for the catalysed and uncatalysed reactions.

Notes

INTEXT QUESTIONS 15.2

1. List any two characteristics of a catalyst.
2. A small amount of alcohol when added to a solution of sodium sulphite slows down its oxidation to sodium sulphate. What type of catalyst is alcohol?
3. How would the activation energy be affected in the above reaction (given in Q.No.2) on adding the alcohol?
4. Addition of molybdenum enhances the catalytic activity of iron in the Haber's process for the manufacture of ammonia. What are the substances like molybdenum called?

WHAT YOU HAVE LEARNT

- The phenomenon of attracting and retaining the molecules of a gas or of a dissolved substance on the surface of a solid is called adsorption.
- The substance which gets adsorbed is called the adsorbate and the solid substance which adsorbs is called the adsorbent.
- The substances that are porous in nature and have rough surfaces are better adsorbent.
- Easily liquifiable gases are more readily adsorbed.
- Extent of adsorption decreases with rise in temperature and increases with the increase in pressure of the gas.
- Physical adsorption is due to van der Waal forces and chemisorption is due to forces similar to chemical bonds.
- Pressure dependence of adsorption of a gas at a constant temperature is given by Freundich Adsorption Isotherm

$$\frac{x}{m} = k\,p^{\frac{1}{n}}$$

- A catalyst is the substance which changes the rate of a reaction, but itself remains chemically unchanged during the reaction.
- The catalysts which increase the rate of a reaction are called the positive catalysts while those which decrease the rate are called the negative catalysts.
- Auto catalysed reactions are those in which one of the products acts as the catalyst.

- A promoter enhances the activity of a catalyst while a poison hampers it.
- A catalyst can't initiate a reaction, nor can it alter the position of equilibrium state of a reversible reaction.
- When the catalyst is present in the same phase as the reactants it is called a homogeneous catalyst.
- When the catalyst is present in a phase other than that of reactants it is called a heterogenous catalyst.
- A catalyst changes the rate of a reaction by changing its path and the activation energy.

TERMINAL EXERCISE

1. What is the difference between adsorption and absorption?
2. Distinguish between physical and chemical adsorption.
3. List the factors that affect adsorption.
4. What type of solids make better adsorbents?
5. Easily liquifiable gases are adsorbed more readily. Explain.
6. What is 'extent of adsorption'?
7. How does extent of adsorption vary with temperature in case of (i) physical adsorption and (ii) chemisorption? Depict graphically.
8. What is enthalpy of adsorption?
9. Explain the effect of temperature on extent of physical adsorption with the help of Le Chatelier's Principle.
10. What is an adsorption isotherm?
11. State mathematically Freundlich Adsorption Isotherm and depict it graphically. Under what conditions is it applicable.
12. Give the mathematical equation of Frundlich Isotherm for adsorption of solutes from solutions.
13. Give any three applications of adsorption.
14. What is a (i) catalyst and (ii) negative catalyst?
15. What are promoters and poisons? Give one example of each.

16. What is auto catalysis. Give one example.
17. Give any five characteristics of catalysis.
18. Distinguish between homogeneous and heterogeneous catalysis.
19. Give two examples each of homogeneous and heterogenous catalysis.
20. How does a catalyst change the rate of reaction. Explain with the help of appropriate example.

ANSWERS TO THE INTEXT QUESTIONS

15.1

(i) T, (ii) F, (iii) F, (iv) T, (v) T

15.2

1. See text section 15.2.1
2. Negative catalyst
3. Increase
4. Promoters

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16

OCCURRENCE AND EXTRACTION OF METALS

Metals and their alloys are extensively used in our day-to-day life. They are used for making machines, railways, motor vehicles, bridges, buildings, agricultural tools, aircrafts, ships etc. Therefore, production of a variety of metals in large quantities is necessary for the economic growth of a country. Only a few metals such as gold, silver, mercury etc. occur in free state in nature. Most of the other metals, however, occur in the earth's crust in the combined form, i.e., as compounds with different anions such as oxides, sulphides, halides etc. In view of this, the study of recovery of metals from their ores is very important. In this lesson, you shall learn about some of the processes of extraction of metals from their ores, called metallurgical processes.

OBJECTIVES

After reading this lesson, you will be able to :

- differentiate between minerals and ores;
- recall the occurrence of metals in native form and in combined form as oxides, sulphides, carbonates and chlorides;
- list the names and formulae of some common ores of Na, Al, Sn, Pb ,Ti, Fe, Cu, Ag and Zn;
- list the occurrence of minerals of different metals in India;
- list different steps involved in the extraction of metals;

---

* An alloy is a material consisting of two or more metals, or a metal and a non-metal. For example, brass is an alloy of copper and zinc; steel is an alloy of iron and carbon.

- list and explain various methods for concentration of ores (gravity separation, magnetic separation, froth floatation and chemical method);
- explain different metallurgical operations : roasting, calcination and smelting with suitable examples;
- choose the reducing agent for a given ore;
- differentiate between flux and slag, and
- explain different methods for refining of metals : poling, liquation, distillation and electrolytic refining.
- explain the process involved in the extraction of Al, Fe, Cu, and Zn.

16.1 OCCURRENCE OF METALS

Metals occur in nature in free as well as combined form. Metals having low reactivity show little affinity for air, moisture, carbon dioxide or other non-metals present in nature. Such metals may remain in elemental or native (free) state in nature. Such metals are called "noble metals" as they show the least chemical reactivity. For example gold, silver, mercury and platinum occur in free state.

On the other hand, most of the metals are active and combine with air, moisture, carbon dioxide and non-metals like oxygen, sulphur, halogens, etc. to form their compounds, like oxides, sulphides, carbonates, halides and silicates. i.e., they occur in nature in a combined state.

A naturally occurring material in which a metal or its compound occurs is called a *mineral*. A mineral from which a metal can be extracted economically is called an *ore*.

An ore is that mineral in which a metal is present in appreciable quantities and from which the metal can be extracted economically.

The main active substances present in nature, expecially in the atmosphere are oxygen and carbon dioxide. In the earth's crust, sulphur and silicon are found in large quantities. Sea-water contains large quantities of chloride ions (obtained from dissolved sodium chloride). Most avtive metals are highly electropositive and therefore exist as ions. It is for this reason that most of the important *ores* of these metals occur as (i) oxides (ii) sulphides (iii) carbonates (iv) halides and (v) silicates. Some sulphide ores undergo oxidation by air to form sulphates. This explains the occurrence of sulphate ores.

Ores are invariably found in nature in contact with rocky materials. These rocky or earthy impurities accompanying the ores are termed as *gangue* or *matrix.*

Some important ores and the metals present in these ores are listed in Table 16.1

Table 16.1: Some Important Ores

Type of Ore	Metals (Common Ores)
Native Metals	Gold (Au), silver (Ag)
Oxide ores	Iron (Haematite, Fe_2O_3); Aluminium (Bauxite, $Al_2O_3 . 2H_2O$); Tin (Cassiterite, SnO_2); Copper (Cuprite, Cu_2O); Zinc (Zincite, ZnO); Titanium (Ilmenite, $FeTiO_3$, Rutile, TiO_2)
Sulphide ores	Zinc (Zinc blende, ZnS); Lead (Galena, PbS); Copper (Copper glance, Cu_2S); Silver (Silver glance or Argentite, Ag_2S); Iron (Iron pyrites, FeS_2)
Carbonate ores	Iron (Siferite, $FeCO_3$); Zinc (Calamine, $ZnCO_3$) , Lead (Cerrusite, $PbCO_3$)
Sulphate ores	Lead (Anglesite, $PbSO_4$)
Halide ores	Silver (Horn silver, AgCl); Sodium (Common salt or Rock salt, NaCl); Aluminium (Cryolite, Na_3AlF_6)
Silicate ores	Zinc (Hemimorphite, $2ZnO.SiO_2.H_2O$)

16.1.1 Mineral Wealth of India

India possesses large deposits of minerals of some important metals such as iron, manganese, aluminium, magnesium, chromium, thorium, uranium, titanium and lithium. They constitute one-quarter of the world's known mineral resources.Mineral fuels (like coal ,petroleum and natural gas) constitute more than 80% while metallic minerals constitute only about 10% of the total volume of mineral production in a year. In this section, we shall list some of the important minerals of a few common metals such as Fe, Cu, Ag, Zn, Ti, Al Sn, Pb and Na and their locations in India.

Important Ores of Some Common Elements

Iron	Iron ore reserves in the country are estimated at 1750 crore tonnes. Major iron ore mining is done in Goa, Madhya Pradesh, Bihar, Karnataka, Orissa and Maharashtra.
Aluminium	Its chief ore, bauxite is available in India in abundance. The annual production of bauxite is estimated to be more than 2 million tonnes. Important deposits of bauxite in the country occur in Bihar, Goa, Madhya Pradesh, Maharashtra, Tamil Nadu, Gujarat, Karnataka, Orissa, Uttar Pradesh, Andhra Pradesh, Jammu & Kashmir and Rajasthan.

Copper	India does not have rich copper ore deposits. The total reserves of the ore in the country are estimated around 60 crore tonnes. Major ore producing areas are Singhbum district (Bihar), Balaghat district (Madhya Pradesh) and Jhunjhunu district (Rajasthan).
Zinc and Lead	India has no significant deposits of lead ores. Lead and Zinc have been located at Zawar mines near Udaipur (Rajasthan) and at Hazaribagh (Jharkhand), Sargipalli mines in Orissa and Bandalamottu lead project in Andhra Pradesh. Some reserves have been located in Gujarat and Sikkim.The total reserves are estimated at about 360 million tonnes in which lead content is estimated to be around 5 million tonnes and zinc to be around 16 million tonnes.
Tin	Deposits of tinstone (SnO_2) are found in Hazaribagh (Jharkhand) and Orissa.
Silver	India does not possess rich silver deposits. Gold from Kolar fields and Hutti gold fields (Karnataka) and lead-zinc ores of Zawar mines (Rajasthan) contain some silver.
Titanium	Ilmenite $(FeTiO_3)$ is recovered from beach sands of Kerala and Tamil Nadu. The estimated reserves are around 100 to 150 million tonnes.
Sodium :	Tincal or Native borax $(Na_2B_4O_7.10H_2O)$ is found in Ladakh and Kashmir.

16.2 GENERAL PRINCIPLES OF EXTRACTION OF METALS

The process of extracting the metals from their ores and refining them is called *metallurgy*. The choice of the process depends upon the nature of the ore and the type of the metal. The metal content in the ore can vary depending upon the impurities present and chemical composition of the ore. Some common steps involved in the extraction of metals from their ores are :

(i) Crushing and pulverization

(ii) Concentration or dressing of the ore

(iii) Calcination or roasting of the ore

(iv) Reduction of metal oxides to free metal

(v) Purification and refining of metal.

16.2.1. Crushing and Pulverization

The ore is generally obtained as big rock pieces. These big lumps of the ore are crushed to smaller pieces by using *jaw-crushers* and *grinders*. It is easier to work with crushed ore. The big lumps of the ore are brought in between the plates of a crusher forming a jaw. One of the plates of the crusher is stationary while the other moves to and fro and the crushed pieces are collected below (Fig. 16.1).

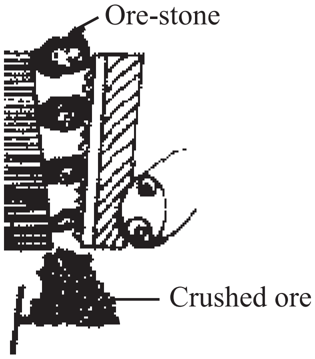


Fig. 16.1 : *Jaw Crusher*

The crushed pieces of the ore are then pulverized (powdered) in a stamp mill shown in Fig. 16.2. The heavy stamp rises and falls on a hard die to powder the ore. The powdered ore is then taken out through a screen by a stream of water. Pulverization can also be carried out in a ball mill. The crushed ore is taken in a steel cylinder containing iron balls. The cylinder is set into revolving motion. The striking balls pulverize the crushed ore into fine powder.

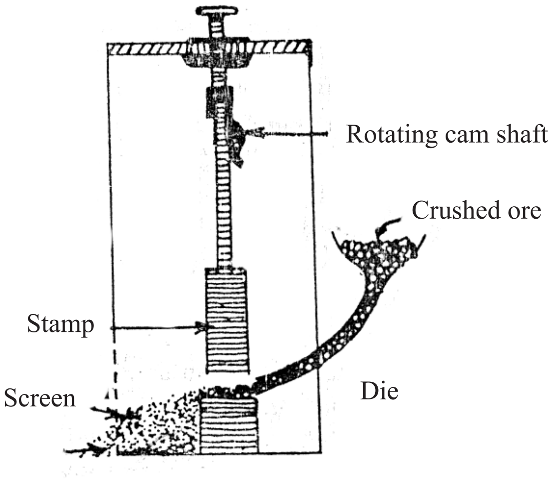


Fig. 16.2 : *The Stamp mill*

16.2.2 Concentration or Dressing of the Ore

Generally, the ores are found mixed with earthy impurities like sand, clay, lime stone etc. These unwanted impurities in the ore are called *gangue* or *matrix.*

The process of removal of gangue from powdered ore is called concentration or ore dressing.

There are several methods for concentrating the ores. The choice of method depends on the nature of the ore. Some important methods are :

(i) **Gravity separation (Hydraulic washing) :** In this method, the light (low specific gravity) earthy impurities are removed from the heavier metallic ore particles by washing with water. It is therefore, used for the concentration of heavier oxide ores, like haematite (Fe_2O_3) tinstone (SnO_2) and gold (Au). In this method, as shown in the Fig. 16.3 the powdered ore is agitated with water or washed with a strong current of water. The heavier ore settles down rapidly in the grooves and the lighter sandy and earthy materials (gangue particles) are washed away.

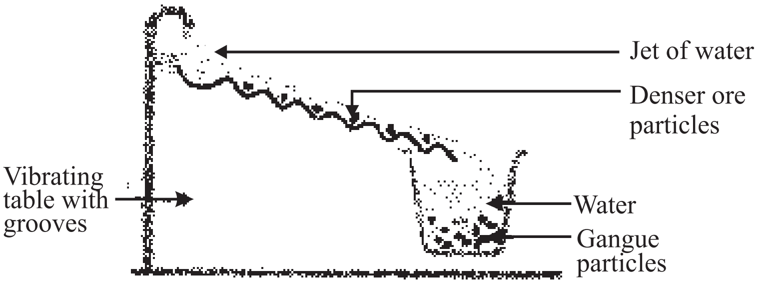


Fig. 16.3 : *Gravity Separation (Hydraulic Washing)*

(ii) Magnetic separation method :

By this method, those ores can be concentrated which either contain impurities which are magnetic or are themselves magnetic in nature.

For example, the tin ore, tin stone (SnO_2) itself is non-magnetic but contains magnetic impurities such as iron tungstate $(FeWO_4)$ and manganese tungstate $(MnWO_4)$.

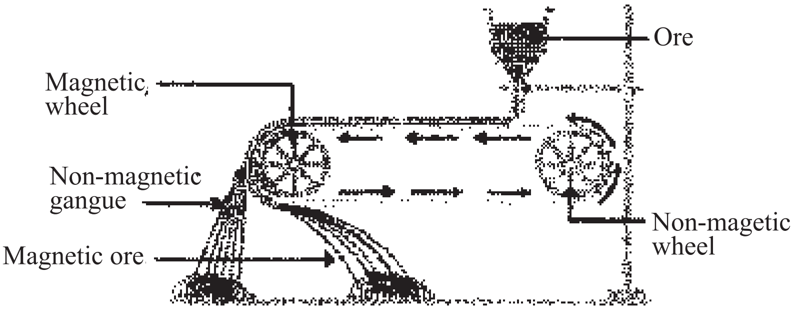


Fig. 16.4. : *Magnetic Separation*

The finely powdered ore is passed over a conveyer belt moving over two rollers, one of which is fitted with an electromagnet (Fig. 16.4). The magnetic material is attracted by the magnet and falls in a separate heap. In this way magnetic impurities are separated from non-magnetic material.

(iii) Froth floatation method :

This method is especially applied to sulphide ores, such as **galena** (PbS), **zinc blende** (ZnS), or **copper pyrites** $(CuFeS_2)$. It is based on the different wetting properties of the surface of the ore and gangue particles. The sulphide ore particles are wetted preferentially by oil and gangue particles by water. In this process, finely powdered ore is mixed with either pine oil or eucalyptus oil. It is then mixed with water. Air is blown through the mixture with a great force. Froth is produced in this process which carries the weted ore upwards with it. Impurities (gangue particles) are left in water and sink to the bottom from which these are drawn off (Fig. 16.5).

(iv) Chemical method :

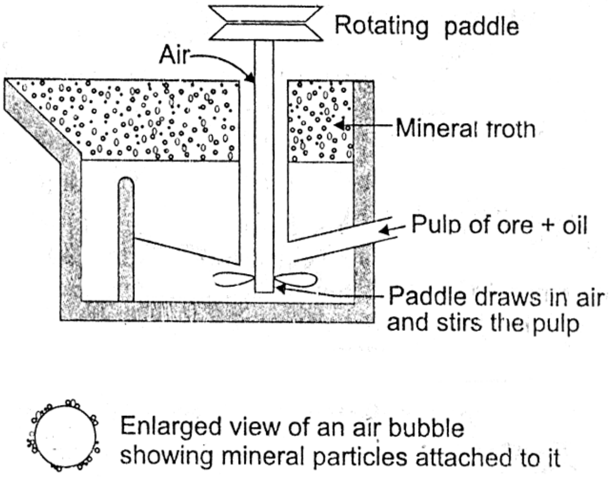


Fig. 18.5 : *Froth floatation*

In this method the ore is treated with a suitable chemical reagent which dissolves the ore leaving behind insoluble impurities. The ore is then recovered from the solution by a suitable chemical method. This is applied for extraction of aluminium from bauxite $(Al_2O_3.2H_2O)$.

Bauxite is contaminated with iron (III) oxide (Fe_2O_3), titanium (IV) oxide (TiO_2) and silica (SiO_2). These impurities are removed by digesting the powdered ore with aqueous solution of sodium hydroxide at 420 K under pressure. Aluminium oxide dissolves in sodium hydroxide, whereas, iron (III) oxide, silica and titanium (IV) oxide remain insoluble and are removed by filtration.

$$Al_2O_3 + 6NaOH \longrightarrow \underset{\textbf{Sodium aluminate}}{2Na_3AlO_3} + 3H_2O$$

Sodium aluminate is diluted with water to obtain precipitate of aluminium hydroxide. It is filtered and ignited to obtain pure alumina.

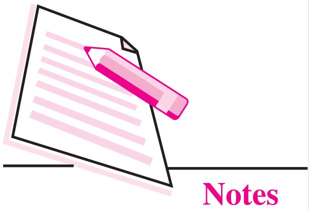
$$Na_3AlO_3 + 3H_2O \longrightarrow Al(OH)_3 + 3NaOH$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

INTEXT QUESTIONS 16.1

1. Write the names of eight important metals. Give an example of one important ore of each metal.
2. What is the difference between an ore and a mineral?
3. Name some important methods of concentrating the ores.
4. Which method of concentration is applied in the following cases?

   (i) Magnetic ores (ii) Sulphide ores (iii) Bauxite ore
5. Which metal is extracted from the mineral zinc blede ?


Notes

16.2.3 Calcination and Roasting of the Ore

The concentrated ore is converted into metal oxide by calcination or roasting.

(A) Calcination :

Calcination involves heating of the concentrated ore in a limited supply of air so that it loses moisture, water of hydration and gaseous volatile substances. The ore is heated to a temperature so that it does not melt. Two examples of calcination are given below:

(i) Removal of water of hydration

$$Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$$

(ii) Expulsion of CO_2 from carbonate

$$ZnCO_3 \longrightarrow ZnO + 2CO_2$$

(B) Roasting :

Roasting is a process in which the concentrated ore is heated in a free supply of air at a temperature insufficient to melt it. The following changes take place during roasting :

(i) Drying of the ore.

(ii) Removal of the volatile impurities like arsenic, sulphur, phosphorus and organic matter.

$$4As + 3O_2 \longrightarrow 2As_2O_3(g)$$

$$S + O_2 \longrightarrow SO_2(g)$$

$$4P + 5O_2 \longrightarrow P_4O_{10}(g)$$

(iii) Conversion of the sulphide ores into oxides

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

Calcination and roasting are generally carried out in a reverberatory furnace or in a multiple hearth furnace.

16.2.4 Reduction of the Metal Oxides to Free Metal

This process is carried out after calcination or roasting of ores. In this process called *smelting,* the oxide ores are converted into the metallic state by reduction.

(A) **Smelting** :

Smelting is a process in which the oxide ore in molten state is reduced by carbon or other reducing agents to free metal.

(i) *By using carbon as a reducing agent :*

This method is used for the isolation of iron, tin and zinc metals from their respective oxides. The oxide ores are strongly heated with charcoal or coke. Reduction occurs by the action of carbon and/or carbon monoxide which is produced by the partial combustion of coke or charcoal.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$ZnO + C \longrightarrow Zn + CO$$

Although the ore has been concentrated in an earlier step, it is still contaminated with some gangue material which is finally removed in the reduction process by the addition of *flux* during smelting.

Flux is a chemical substance which combines with gangue at higher temperatures to form easily fusible material called *slag* which is not soluble in the molten metal. Flux are of two types :

Basic Flux :

On heating, lime stone is converted into calcium oxide used as basic flux which combines with acidic impurities like silica in metallurgy of iron and forms fusible calcium silicate $(CaSiO_3)$.

$$\underset{\textbf{(Limestone)}}{CaCO_3} \longrightarrow CaO + CO_2(g)$$

$$\underset{\textbf{(Basic flux)}}{CaO} + \underset{\textbf{(Acidic gangue)}}{SiO_2} \longrightarrow \underset{\textbf{(Slag)}}{CaSiO_3}$$

Acidic flux :

SiO_2 is used as acidic flux to remove basic impurity of FeO in metallurgy of Cu.

$$\underset{\textbf{(Acidic flux)}}{SiO_2} + \underset{\textbf{(Basic gangue)}}{FeO} \longrightarrow \underset{\textbf{(Slag)}}{FeSiO_3}$$

The fusible slag, such as calcium silicate formed during smelting floats over the molten metal and is thus easily removed. Another advantage is that the slag provides a covering to the molten metal thus preventing it from getting oxidized by air.

(ii) *Other reducing agents :*

Oxide ores which cannot be reduced by carbon or metals which show affinity to carbon by forming metal carbides, are reduced by reducing agents like aluminium, sodium, magnesium or hydrogen. *Oxide* like chromium oxide (Cr_2O_3) or manganese oxide (Mn_3O_4) are reduced by aluminium powder is a highly exothermic reaction. This process is known as *Goldschmidt's Alumino-thermite reduction method.*

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + Heat$$

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + Heat$$

Heat is generated in the process due to the formation of Al_2O_3 which is a highly exothermic reaction.

Titanium is obtained by the reduction of $TiCl_4$ (produced by the action of carbon and chlorine on TiO_2) by Mg in an inert atmosphere of argon (Kroll process).

$$TiCl_4 + 2Mg \xrightarrow[1103\ K]{Heat} Ti + 2MgCl_2$$

Titanium can also be obtained by the reduction of TiO_2 by sodium

$$TiO_2 + 4Na \rightarrow Ti + 2Na_2O$$

Tungsten and molybedenum can be obtained by the reduction of their oxides by hydrogen,

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$

(iii) Self-reduction :

This is applied to the sulphide ores of copper, mercury and lead . The ores are heated in air, a part of these sulphide ores is changed into the oxide or sulphate which then reacts with the remaining part of the sulphide ore to give the metal and sulphur dioxide. The reactions showing their extraction are given below :

(1) $$\underset{\textbf{Copper glance}}{2Cu_2S} + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Copper produced at this stage is called *Blister copper*. The evolution of sulphur dioxide produces blisters on the surface of solidified copper metal.

(2) $$\underset{\textbf{Cinnabar}}{2HgS} + 3O_2 \longrightarrow 2HgO + 2SO_2$$

$$2HgO + HgS \longrightarrow 3Hg + SO_2$$

(3) $$\underset{\textbf{Galena}}{2PbS} + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

$$PbS + 2PbO \longrightarrow 3Pb + SO_2$$

$$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$$

(B) Reduction of concentrated ores by other methods:

Some metals cannot be obtained from their ores by using common reducing agents such as C, CO, H_2 etc. Other methods of reduction are used for such cases.

(i) *Reduction by precipitation :*

Noble metals like silver and gold are extracted from their concentrated ores by dissolving metal ions in the form of their soluble complexes. The metal ions are then regenerated by adding a suitable reagent. For example, concentrated argentite ore (Ag_2S) is treated with a dilute solution of sodium cyanide (NaCN) to form a soluble complex :

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

This solution is decanted off and treated with zinc to precipitate silver,

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$$

(ii) *Electrolytic Reduction :*

Active metals like sodium, potassium and aluminium etc., are extracted by the electrolysis of their fused (*molten*) salts. For example, sodium is obtained by the electrolysis of fused sodium chloride (Down's process). The reactions taking place in the electrolytic cell are :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Na^+ ions move towards the cathode and Cl^- ions move towards the anode. Following reactions take place at the electrodes :

At the Cathode $Na^+ + e^- \longrightarrow \underset{\textbf{(metal)}}{Na}$ (Reduction)
(Negative electrode)

At the Anode $Cl^- \longrightarrow Cl + e^-$ (Oxidation)
(Positive electrode)

$$Cl + Cl \longrightarrow Cl_2$$

Aluminium is extracted from molten alumina (Al_2O_3) by electrolysis. The melting point of alumina is quite high (2323K) which is inconvenient for electrolysis. It dissolves in molten cryolite (Na_3AlF_6) at around 1273 k. The reactions which take place in the cell are:.

At the Cathode $Al^{3+} + 3e^- \longrightarrow Al\,(\text{metal})$

At the Anode $C + 2O^{2-} \longrightarrow CO_2 + 4e^-$

INTEXT QUESTIONS 16.2

1. Explain the following terms :

   Calcination, Roasting, Smelting, Flux and Slag.
2. Which is the cheapest and most abundant reducing agent employed in the extraction of metals ?
3. Name the process which is used for converting sulphide ores into oxides.
4. How are oxide ores reduced ?
5. Name few materials which are used as flux in metallurgical processes.
6. What happens to (i) Bauxite and (ii) Calamine ores during calcination ?

16.2.5 Refining of Metals

Except in the electrolytic reduction method, metals produced by any other method are generally impure. The impurities may be in the form of (i) other metals (ii) unreduced oxide of the metal (iii) non-metals like carbon, silicon, phosphorus, sulphur etc. and (iv) flux or slag. Crude metal may be refined by using one or more of the following methods :

(i) *Liquation :* Easily fusible metals like tin, lead etc. are refined by this process. In this method, the impure metal is poured on the sloping hearth of a reverberatory furnace (Fig.16.6) and heated slowly to a temperature little above the melting point of the metal. The pure metal drains out leaving behind infusible impurities.

Fig. 16.6 : *Liquation*

(ii) *Poling :* Poling involves stirring the impure molten metal with green logs or bamboo. The hydrocarbons contained in the pole reduce any metal oxide present as impurity. Copper and tin are refined by this method (Fig. 16.7).

(iii) *Distillation :* Volatile metals like zinc and mercury are purified by distillation. The pure metal distils over, leaving behind non-volatile impurities.

(iv) *Electrolytic Refining :* A large number of metals like copper, silver, zinc, tin etc. are refined by electrolysis. A block of impure metal is made the anode and a thin sheet of pure metal forms the cathode of the electrolytic cell containing suitable metal salt solution which acts as an electrolyte (Fig. 16.8). On passing current, pure metal deposits at the cathode sheet while more electropositive impurities are left in solution. Less electropositive metals do not dissolve and fall away from the anode to settle below it as *anode mud.*

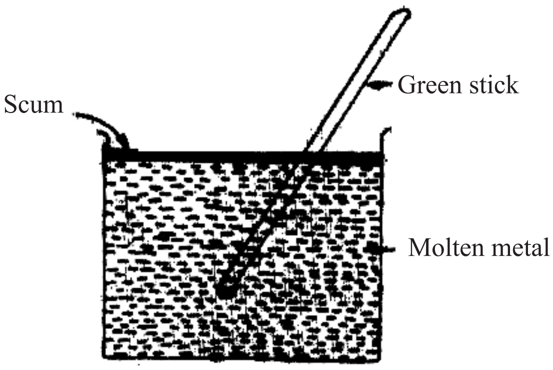


Fig. 18.7 : *Polling*

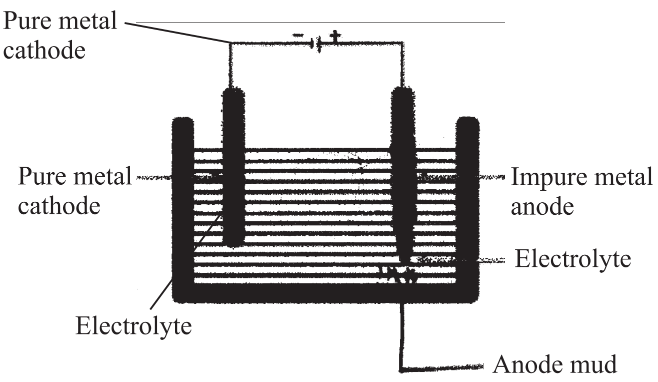


Fig. 16.8 : *Electrolytic Refining*

For example, in the electrolytic refining of crude copper (blister copper), a large piece of impure copper is made anode and a thin piece of pure copper is made the cathode. An acidified solution of copper sulphate is used as an electrolyte. On passing an electric current of low voltage through the solution copper (II) ions obtained from copper sulphate solution go to the cathode where they are reduced to the free copper metal and get deposited.

$$Cu^{2+} + 2e^{-} \longrightarrow Cu \quad \text{(at cathode)}$$

An equivalent amount of the metal from the anode dissolves into the electrolyte as Cu^{2+} ions

$$Cu \longrightarrow Cu^{2+} + 2e^{-} \quad \text{(at anode)}$$

As the process goes on, anode becomes thinner while the cathode becomes thicker. The impurities like silver, gold settle down at the bottom of the cell as *'anode mud'*.

16.3 EXTRACTION OF Al, Fe, Cu AND Zn

Aluminium

Extraction of Aluminium

Aluminium is the most abundant metallic element in the earth's crust, occurring in a variety of aluminosilicatcs such as clay, micas and feldspars. The only ore of aluminium from which it is profitable to extract the metal is bauxite.

The bauxite is first freed from silica and iron (III) oxide impurities by dissolving it in sodium hydroxide (iron(III) oxide remains undissolved) and then precipitating aluminium hydroxide by seeding the solution with a little aluminium hydroxide (silica remains dissolved):

$$A1_2O_3(s) + 2OH^-(aq) + 3H_2O(1) \longrightarrow \underset{\text{aluminate ion}}{2A1(OH)_4^-(aq)}$$

$$Al(OH)_4^-(aq) \longrightarrow Al(OH)_3(s) + OH^-(aq) \text{ (takes place on seeding)}$$

Pure aluminium oxide is now obtained by heating the hydroxide:

$$2A1(OH)_3(s) \longrightarrow A1_2O_3(s) + 3H_2O(I)$$

It is dissolved in molten cryolite, $(Na^+)_3A1F_6^{3-}$, and electrolysed at about 900°C, using a number of graphite blocks as anodes and a graphite lined bath as the cathode. Aluminium is discharged at the cathode and collects at the bottom of the molten electrolyte as a liquid, from where it can be tapped off and allowed to solidify. Oxygen is evolved at the anodes, which are slowly burnt away as carbon dioxide.

The extraction of aluminium is only economic where cheap electricity is available from water power. A low voltage is used to avoid decomposing the molten cryolite which acts as a solvent; a very high current density is used. One theory assumes that aluminium oxide dissociates into $A1^{3+}$ and $A1O_3^{3-}$

$$A1_2O_3 \rightleftharpoons A1^{3+} + A1O_3^{3-}$$

Cathode	**Anode**
$A1^{3+}$ discharged	AlO_3^{3-} discharged
$4A1^{3+} + 12e- \rightarrow 4A1$	$4A1O_3^{3-} \rightarrow 2A1_2O_3 + 3O_2 + 12e-$

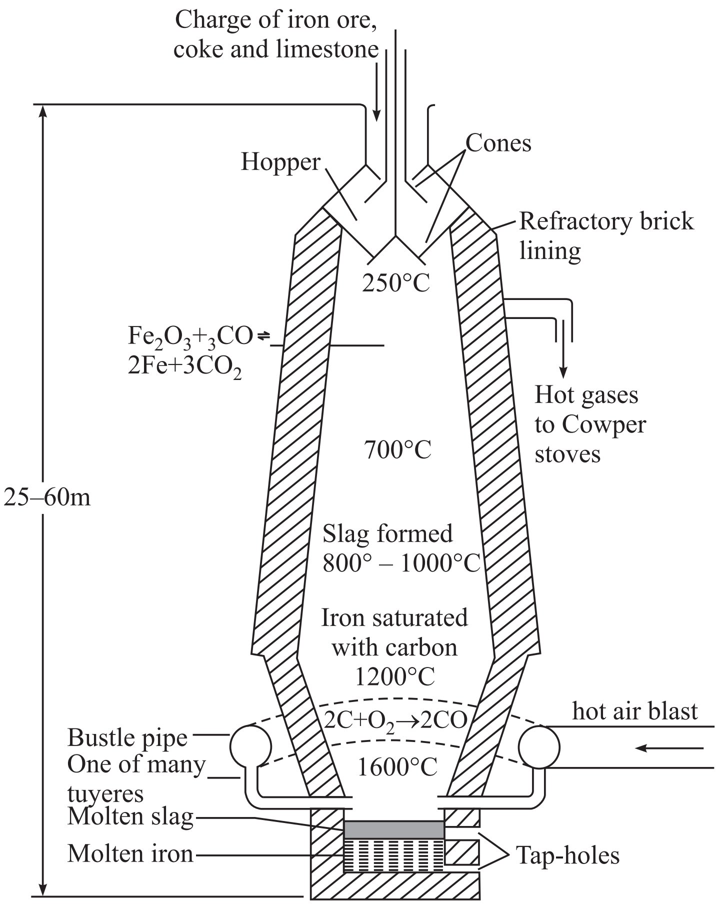
$$\underset{\text{Molten cryolite solvent}}{(Na^+)_3\ A1F_6^{3-}}$$

The process, however, is probably much more complex.

Iron

Iron, which is the second most abundant metal occurring in the earth's crust, is extracted from its oxides, haematite, Fe_2O_3. and magnetite, Fe_3O_4, and also from the carbonate siderite, $FeCO_3$. Iron pyrites, FeS_2, is not considered to be an important ore of iron.

The extraction of iron is carried out in a blast furnace which can vary in size and can be between 25 and 60 metres in height and up to 10 metres in diameter. It is constructed from steel with the inner regions lined with firebricks. A charge of iron ore, limestone and coke in the correct proportions is fed into the top of the furnace through a cone and hopper arrangement. Preheated air at a temperature of about 600°C is injected into the furnace through a number of pipes called tuyeres; the tuyeres are fed from a 'bustle' pipe encircling the blast furnace. The blast furnace is provided with two tap holes which are plugged with clay; molten iron is tapped from the lower one and molten slag from the other. The production of iron is a continuous process and, depending upon its size, a blast furnace can produce from 1000 to 1800 tonnes of iron every twenty-four hours.



The energy and reducing agent required for the smelting of iron are obtained by the combustion of coke, the temperature of the charge increasing steadily as it falls through the ascending combustion gases:

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

At a temperature of about 700°C the iron ore is reduced to spongy iron by the carbon monoxide:

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g)$$

Since this reaction is reversible a high CO/CO_2 pressure ratio favours the reduction to iron.

The limestone decomposes at about 800°C and the calcium oxide reacts with sandy impurities to form a slag of calcium silicate. More carbon monoxide is produced by the reduction of carbon dioxide:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + \underset{\text{impurity}}{SiO_2(s)} \longrightarrow \underset{\text{slag}}{CaSiO_3(l)}$$

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

The reduction of the iron oxide is completed by the coke at a temperature in the region of 1200°C and cementite, Fe_3C, and graphite enter the iron. Other reactions also occur at high temperatures, for instance silica is reduced to silicon and this enters the iron as ferrosilicon:

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

The molten metal is either run out into moulds of sand, when it is known as pig-iron, or more generally conveyed directly in the liquid form to steelmaking plants. The slag is tapped from the furnace as a liquid and can be used in concrete or blown into a ‘woolly’ material and used for insulation.

The hot gases emerging from the top of the furnace contain appreciable amounts of carbon monoxide and are burnt in Cowper stoves to preheat the air for the blast.

Cast iron

Iron castings are made by igniting a mixture of pig-iron, scrap iron and coke in cupola furnaces by a blast of hot air. The molten iron is poured into moulds to make articles such as manhole covers, guttering, machinery frames and drainpipes. Cast iron expands slightly on solidifying and therefore faithfully reproduces the shape of the mould. It is extremely hard, but unfortunately is very brittle and will fracture if struck by a sharp blow. The impurities in cast iron lower the melting point from 1535°C for pure iron to approximately 1200°C.

Wrought iron

This is made by heating impure iron with haematite so that impurities are oxidised. Carbon is converted to carbon monoxide and silicon and manganese to a slag.

$$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(l) + 3CO(g)$$

As the impurities are removed, the melting point of the iron rises to about 1500°C and the pasty mass is removed from the furnace as balls and worked under a hammer to squeeze out the slag. Wrought iron is tough, malleable and ductile; it can be worked by a blacksmith into chains, railway carriage couplings and ornamental gates, etc.

Copper

Although copper does not occur abundantly in nature, many copper-containing ores are known. It is principally extracted from copper pyrites, $CuFeS_2$, copper glance, Cu_2S, and cuprite, Cu_2O. The extraction of copper from copper pyrites will be considered.

The pulverized ore is concentrated by the froth flotation process and roasted in a limited supply of air to convert the iron into iron (II) oxide :

$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 3SO_2(g) + 2FeO(s)$$

After the addition of silica, SiO_2, the mixture is heated in the absence of air to convert the iron (II) oxide into a slag of iron (II) silicate, $FeSiO_3$,

which is poured away. The copper (I) sulphide is now reduced to copper by heating in a controlled amount of air:

$$Cu_2S(s) + O_2(g) \longrightarrow 2Cu(s) + SO_2(g)$$

Zinc

Zinc is usually extracted from its ore zinc blende, ZnS and calamine $ZnCO_3$. The zinc ores are first concentrated and then roasted in air to convert them into the oxide:

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

$$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$$

The sulphur dioxide produced is used to manufacture sulphuric acid. The zinc oxide is mixed with powdered coke and heated to 1400°C. Zinc oxide is reduced by the coke and the mixture of zinc vapour and carbon monoxide pass through an outlet near the top of thee retort:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$

Liquid zinc is run out into moulds and solidifies. The hot carbon monoxide is used to preheat the briquettes.

INTEXT QUESTIONS 16.3

1. State the nature of materials used for constructing cathodes and anodes in the electrolytic cell for refining of copper. Write chemical equations for the reactions which take place.
2. Which method is used for the refining of metals that are easily fused ?
3. Which metals are refined by poling ?
4. Name a metal which is purified by distillation.
5. Name any three elements which are refined by electrolytic refining.
6. What is role of cryolyte in the extraction of Al.
7. Which one is responsible to reduce Fe_2O_3 to Fe C or CO.

WHAT YOU HAVE LEARNT

- Metals play an extremely useful role in day-to-day life.
- Most metals are found in nature in combined form. Only a few noble metals such as gold, silver, occur in nature in free state,
- The process of extraction of metals from their ores is called *metallurgical process*.
- A naturally occurring material in which a metal or its compound occurs is called a mineral. A mineral from which a metal can be extracted economically is called an ore. Thus all minerals do not serve the purpose of ores.
- Most active metals are highly electropositive and exist as M^{n+} ions. Therefore, they are found in nature in association with some common anions, i.e., as salts like *oxides, sulphides, carbonates, halides, silicates* etc. Some sulphides slowly undergo oxidation by air to form *sulphates.*
- India possesses rich mineral wealth with abundance of iron, aluminium and some amount of copper, tin, lead, silver and gold.
- Various steps involved in the extraction of metal are :
  (i) Crushing and pulverization
  (ii) Concentration or dressing of the ore
  (iii) Calcination or Raosting of the concentrated ore
  (iv) Reduction of the oxides to free metal
- The metals thus obtained are then purified by employing some suitable method, viz. *liquation, poling, distillation or electrolytic refining.*
- Metallurgical uperations involved in the extraction of Fe, Al, Cu & Zn.

TERMINAL EXERCISE

1. Name the metal oxides that are not reduced to metallic state by heating with carbon. Which reducing agent is used for these ores ?
2. Which metal sulphide combines with its oxide to form metal ? Give reactions.
3. Name four reducing agents other than carbon, used during smelting.
4. What is the difference between calcination and roasting ?
5. Give the name and formula of at least one ore, of the following metals :

   (i) copper (ii) zinc (iii) iron (iv) tin
6. What happens when
   - (i) Calamine is calcined.
   - (ii) Zinc blende is roasted.
   - (iii) Silica is heated with lime stone.
7. Describe the froth floatation method for the concentration of sulphide ore.
8. Give chemical equations involved in the self reduction method for the extraction of copper.
9. How will you obtain iron from its ore?
10. Explain the process involved in the extraction of al from $Al_2O_3.2H_2O$.

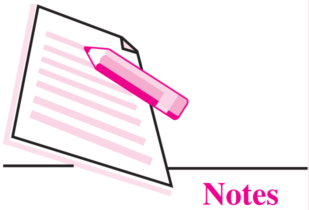
ANSWERS TO INTEXT QUESTIONS

16.1

1. Sodium (Na), Aluminium (Al), Silver (Ag), Iron (Fe), Zinc (Zn), Lead (Pb), Gold (Au), Mercury (Hg).

   Ores : rock salt, bauxite, argentite, haematite, zincite, galena, native gold, cinnabar, respectively.
2. *Mineral* is a naturally occurring material in which a metal or its compound occurs.

   An *ore* is that mineral in which metal is present in large quantity and from which the metal can be extracted in pure and high quality, economically.
3. Gravity separation, magnetic separation, froth floatation and chemical method.
4. (i) Magnetic separation method
   (ii) Froth floatation method
   (iii) Chemical method
5. Zinc.



16.2

1. *Calcination :* it involves heating of the ore in a limited supply of air to a temperature that the ore does not melt.

   Roasting : It involves heating of the ore in a free supply of air to a temperature that the ore does not melt.

   Smelting : The extraction of metal in the fused state is termed smelting. The ore is reduced by carbon to the free metal.

   Flux : it is a chemical substance which combines with gangue at higher temperatures to form easily fusible material called slag.

   Slag is a fusible chemical compound formed by the reaction of flux with gangue. Slag is not soluble in the molten metal and is thus separated.
2. Carbon in the form of coke.
3. Roasting ; $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2(g)$
4. Oxide ores are reduced to metal by heating them with coke.
5. Silica, borax and other non-metallic oxides are acidic fluxes. Lime stone $(CaCO_3)$ is a basic flux.
6. (i) $Al_2O_3.\ 2H_2O \longrightarrow Al_2O_3 + 2H_2O$

   (ii) $ZnCO_3 \longrightarrow ZnO + CO_2$

16.3

1. Cathode : Pure metal — At Cathode : $Cu^{2+} + 2e \rightarrow Cu$

   Anode : Impure metal — At Anode : $Cu \rightarrow Cu^{2+} + 2e$
2. Liquation
3. Copper and tin
4. Zinc
5. Copper, Silver and Tin
6. (i) decrease the melting point of alumino

   (ii) To increase the conductance
7. CO

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17

HYDROGEN AND s-BLOCK ELEMENTS

Hydrogen, alkali metals (like sodium and potassium) and alkaline earth metals (like magnesium and calcium) are the essential parts of the world we live in. For example, hydrogen is used in making vanaspati. Yellow glow of street light is due to sodium. Sodium choloride, potassium chloride and compounds of alkali metals are essential for life. Sodium hydroxide sold under the name of caustic soda is used in the manufacture of soap. Plaster of paris, a compound of calcium is used as a building material as well as by doctors in setting of fractured bone.

In this lesson we shall study occurrence, physical and chemical properties and uses of hydrogen and s-block elements (alkali metals and alkaline earth metals).

OBJECTIVES

After reading this lesson, you will be able to:

- explain the unique position of hydrogen in the periodic table;
- list the sources of hydrogen;
- compare and contrast the properties of different isotopes of hydrogen;
- recall the various physical and chemical properties and uses of hydrogen with chemical reactions;
- explain the structure of water molecule and ice;
- list the uses of heavy water;
- list the different methods of preparation of hydrogen peroxide;
- list oxidizing and reducing properties of hydrogen peroxide with at least two examples of each;
- list the uses of hydrogen peroxide;
- explain the different types of hydrides;

- describe the use of hydrogen as fuel;
- recall the names and formulae of some common ores of alkali and alkaline earth metals;
- recall the electronic configuration of alkali and alkaline earth metals;
- write reactions of alkali and alkaline earth metals with oxygen, hydrogen, halogens and water;
- explain the trend of basic nature of oxides and hydroxides;
- explain the solubility and thermal stability of their carbonates and sulphates.
- explain diagonal relationship between Li and Mg;
- describe the biological importance of sodium and potassium;
- explain anomalous nature of beryllium;
- explain the digonal relationship between Be and Al;
- describe the biological role of Mg^{2+} and Ca^{2+}; and
- describe the manufacturing processes for NaOH, Na_2CO_3 and $NaHCO_3$.

17.1 HYDROGEN

Hydrogen is the first element of the periodic table. Hydrogen has the simplest atomic structure and consists of a nucleus containing one proton with a charge +1 and one orbital electron. The electronic structure may be written as $1s^1$.

17.1.1 History and Occurrence of Hydrogen

Turquet de Mayerne (1655) and Boyle (1672) collected an inflammable gas by reacting iron with sulphuric acid. A century later Cavendish investigated the properties of this gas and called it 'inflammable air', but it was Lavoisier who called it by its present name, hydrogen.

Hydrogen occurs in the free state in some volcanic gases and in the outer atmosphere of the sun; other stars are composed almost entirely of hydrogen. The extremely high temperatures that are common place in stars (10^6—10^7°C) enable nuclear fusion of hydrogen atoms to occur, resulting in a colossal liberation of energy; several reaction schemes have been put forward for this process which ultimately results in the formation of helium

$$4{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\underset{\text{positive electron or positron}}{{}^{0}_{+1}e} \text{ (energy released)}$$

The hydrogen liberated during chemical reactions is lost very readily, since the mass of the hydrogen molecule is so small and its speed so high that it can escape from the earth's gravitational field. The main sources of hydrogen are water, and petroleum and natural gas, where it occurs in combination with carbon. The element is an essential ingredient in all living matter, being found in proteins and fats.

17.1.2 Position in the Periodic Table

Where is hydrogen placed in the periodic table?

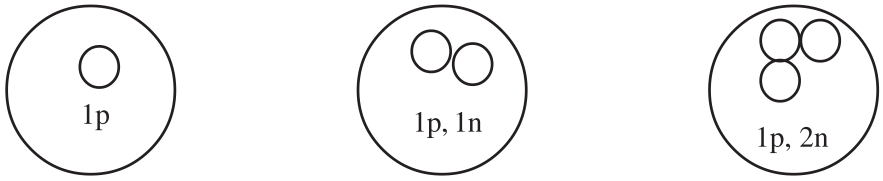
Elements are placed in the periodic table according to their outermost electronic configuration. So hydrogen ($1s^1$) may be placed with alkali metals (ns^1). But hydrogen attains noble gas configuration of helium atom ($1s^2$) by gaining one electron. It forms the hydride ion H^- ($1s^2$) like halogens (ns^2np^5) by gaining one electron. On electrolysis of used alkali hydride, hydrogen is liberated at anode just as chlorine is liberated at anode during electrolysis of sodium chloride. Thus hydrogen ought to be placed in group 17 along with halogens. Hydrogen also resembles group 14 elements, since both have a half filled shell of electrons. So where should hydrogen be placed? This problem is solved by placing hydrogen neither with alkali metals nor with halogens. It has been given a unique position in the periodic table (see Periodic Table in lesson 4).

17.1.3 Isotopes of hydrogen

If atoms of the same element have different mass numbers they are called isotopes. This difference in mass number arises because the nucleus contains a different number of neutrons.

Naturally occurring hydrogen contains three isotopes: protium ${}^1_1H$ or H, deuterium ${}^2_1H$ or D and tritium ${}^3_1H$ or T. These three isotopes contain one proton and 0, 1 and 2 neutrons, respectively in the nucleus (Fig 17.1). Protium is by far the most abundant.

Naturally occurring hydrogen contains 99.986% of the ${}^1_1H$ isotope, 0.014% of D and $7 \times 10^{-16}\%$ of T, therefore the properties of hydrogen are essentially those of the lightest isotope. Tritium is radioactive and emits low energy β particles ($t_{1/2}$ = 12.33yrs).



Protium
Atomic number = 1
Mass number = 1
${}^1_1H$

Deutirium
Atomic number = 1
Mass number = 2
${}^2_1H$ or D

Tritium
Atomic number = 1
Mass number = 3
${}^3_1H$ or T

Fig 17.1: *Isotopes of hydrogen*

Due to difference in mass of different isotopes, there arise a few differences in their properties. For example:

1. H_2 is more rapidly adsorbed on the metal surface than D_2.
2. H_2 reacts over 13-times faster with Cl_2 than does D_2.

Difference in properties that arises from the difference in mass is called *isotope effect*. Since the percentage difference in the mass of isotopes of hydrogen is very large. The difference in properties of isotopes of hydrogen is very large the difference in properties of compounds containing these isotopes is also large.

17.1.4 Physical properties

Hydrogen is a diatomic gas, H_2. It is colourless and has no smell. It is lightest of all the gases known. It is insoluble in water, acids and most of the organic solvents. It is adsorbed when passed over platinum and palladium.

17.1.5 Chemical properties

1. Combustion: Hydrogen is combustible and burns in air with pale blue flame.

$$2H_2 + O_2 \rightarrow 2H_2O$$

2. Reducing property: Hydrogen reduces heated metal oxides to metals.

$$ZnO + H_2 \rightarrow Zn + H_2O$$

$$CuO + H_2 \rightarrow Cu + H_2O$$

3. Reaction with non-metals: Hydrogen combines with nitrogen, carbon, oxygen and chlorine under appropriate conditions to form ammonia, methane, water and hydrogen chloride, respectively.

$$3H_2 + N_2 \rightarrow 2NH_3$$

$$2H_2 + C \rightarrow CH_4$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

Reaction with metals: Hydrogen reacts with highly electropositive metals to from the corresponding hydrides.

$$2Na + H_2 \rightarrow 2NaH$$

$$2Li + H_2 \rightarrow 2LiH$$

17.1.6 Uses

Hydrogen is used:

1. for conversion of coal into synthetic petroleum.
2. in the manufacture of bulk organic chemicals, particularly methanol.
3. in the hydrogenation of oils. Vegetable oils change in to vegetable ghee when hydrogen is passed through the oils at 443K in presence of nickel as catalyst.
4. in the manufacture of ammonia, which is used in the production of fertilizers.
5. as primary fuel for heavy rockets.
6. for filling balloons.

INTEXT QUESTIONS 17.1

1. Name the isotopes of hydrogen.
2. Name the isotope of hydrogen which is radioactive?
3. Why is hydrogen used for filling balloons?
4. Which gas is produced, when hydrogen combines with carbon?
5. Name the gas which is used for the production of fertilizers.
6. How are vegetable oils changed into vegetable ghee?

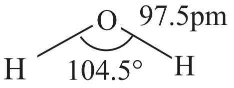
17.2 COMPOUNDS OF HYDROGEN

Hydrogen forms a large number of compounds: here we will consider only two of them, namely water (H_2O) and hydrogen peroxide (H_2O_2).

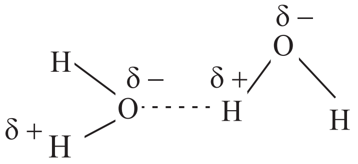
17.2.1 Water (H_2O)

This oxide of hydrogen is essential to all life. It occurs in the form of snow, as water in rivers, lakes, sea etc. and as vapour in the atmosphere. Water is a covalent compound made up of two hydrogen atoms linked with one oxygen atom through covalent bonds. Its Lewis structure and molecular structure are shown below.

$H:\ddot{\underset{\cdot\cdot}{O}}:H$



Because of the large electronegativity of oxygen, water molecule is highly polar. It has partial negative charge (δ^-) on the oxygen atom and partial positive charge (δ^+) on the hydrogen atom. An electrostatic attraction between H of one molecule with O of other molecule results in the formation of intermolecular hydrogen bonds.



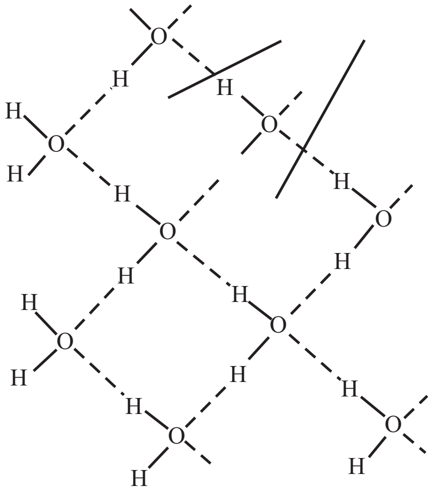


Fig. 17.2: *Tetrahedral arrangement of oxygen atoms in ice.*

Structure of ice:

The remarkable characteristic of water is that in solid form, it is less dense than liquid form. Consequently an ice cube floats on water. Water molecules are joined together in an extensive three dimensional network in which oxygen atom is bonded to four hydrogen atoms, two by hydrogen bonds and two by normal covalent bonds, in a near tetrahedral hydrogen bonded structure (Fig. 17.2), which has got open spaces. This is responsible for low density.

17.2.2 Heavy water and its applications

Water containing deuterium in place of ordinary hydrogen (protium) is termed as heavy water (D_2O). Heavy water is separated from water by electrolysis. The equilibrium constant for the dissociation of water containing protium is very high (1.0×10^{-14}) as compared to water containing deuterium (3.0×10^{-15}) e.g.

$$H_2O \rightarrow H^+ + OH^-$$

$$D_2O \rightarrow D^+ + OD^-$$

O–H bonds are broken more rapidly than O–D bonds. Thus when water is electrolyzed, H_2 is liberated much faster than D_2, and the remaining water thus becomes enriched in heavy water D_2O. In order to obtain one litre of almost pure D_2O, we have to electrolyze about 30000 litres of ordinary water.

Uses:

1. Heavy water is used as a moderator in nuclear reactors. In this process the high speed neutrons are passed through heavy water in order to slow down their speed.
2. It is used in the study of mechanism of chemical reactions involving hydrogen.
3. It is used as the starting material for the preparation of a number of deuterium compounds, for example:

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

17.2.3 Hydrogen peroxide (H_2O_2)

Hydrogen peroxide is an important compound of hydrogen. Its chemical formula is H_2O_2.

Methods of preparation:

Two methods of preparation of hydrogen peroxide are given below:

1. By the action of dilute mineral acids (H_2SO_4) on metallic peroxides (barium peroxide, sodium peroxide)

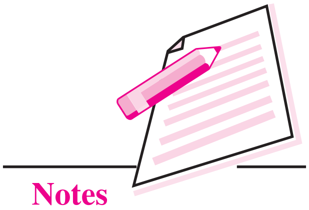
$$BaO_2 . 8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + 8H_2O$$

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

2. By the electrolysis of H_2SO_4 (50% W/W) followed by distillation

At cathode: $2H^+ + 2e^- \rightarrow H_2$

At anode: $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^{-1}$



The anodic solution which contains persulphate ions $(S_2O_8)^{2-}$ is distilled with sulphuric acid at reduced pressure yielding H_2O_2:

$$S_2O_8^{2-} + 2H^+ + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

Properties:

Hydrogen peroxide is a clolourless syrupy liquid and has sharp odour. It has a boiling point of 423K. It is miscible in all proportions with water, alcohol and ether. The oxidation state of oxygen in hydrogen peroxide is –1, a value, which lies between the oxidation state of oxygen in O_2 (zero) and water (–2). Therefore, hydrogen peroxide acts as an oxidizing agent as well as a reducing agent in acidic and alkaline media.

Oxiding Properties:

(a) Oxidizing action in acid solution:

(i) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(ii) $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$

(b) Oxidizing action in alkaline solution:

$MnCl_2 + H_2O_2 + 2KOH \rightarrow 2KCl + 2H_2O + MnO_2$

(c) Reducing action in acid solution:

$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

(d) Reducing action in alkaline solution:

(i) $2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2KOH$

(ii) $Cl_2 + H_2O_2 + 2KOH \rightarrow 2KCl + 2H_2O + O_2$

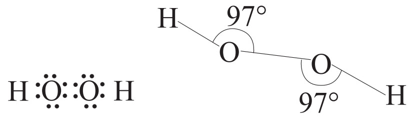
Uses:

Hydrogen peroxide is used:

1. for bleaching hair, leather and wool etc.
2. as a germicide and disinfectant.
3. as an explosive when mixed with alcohol.
4. in the preparation of foam rubber.
5. in pollution control e.g. treatment of drainage and sewage water for dechlorination.

Structure:

The Lewis structure and molecular structure of hydrogen peroxide are shown below:



17.2.4 Hydrides

Hydrogen reacts with metals and nonmetals to forms hydrides. Hydrides can be calssified as:

(1) Ionic hydrides

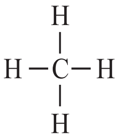
Only the Group l and 2 metals are sufficiently electropositive to force the hydrogen atom to accept an electron. These hydrides, which are white crystalline solids, are formed by heating the metal in hydrogen at temperatures up to 700°C. The Group 1 hydrides, e.g. Na^+H^-, have the sodium chloride structure, i.e. each cation is surrounded by six equidistant hydride ions and vice versa; the structures of the Group 2 hydrides, e.g. $Ca^{2+}(H^-)_2$, are more complex.

Except for lithium hydride they decompose before their melting points are reached, and the fact that they contain the hydride ion is proved by electrolysing them in fused alkali halides, when hydrogen is evolved at the anode. The hydride ion is a very reactive entity and all ionic hydrides are decomposed by water and air (probably initiated by traces of water vapour in the air)

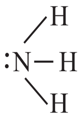
$$H^- + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$$

(2) Covalent Hydrides

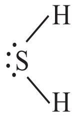
By far the greatest number of hydrides come under this classification and, except for a few, they are gaseous at ordinary temperature. They are formed by the elements from Group 13 to Group 17 in the Periodic Table.



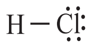
methane



ammonia



hydrogen sulphide



hydrogen chloride

The stability of the hydrides of the elements of a particular periodic group decreases with increasing atomic number (as the element becomes more 'metallic'); thus hydrogen chloride is stable to heat while hydrogen iodide is easily decomposed into its elements. Some are so unstable in the presence of small traces of air, e.g. stannane, SnH_4, that special methods are necessary for their preparation.

In the covalent hydrides, hydrogen is showing its natural tendency to acquire the stable electronic configuration of helium by electron sharing.

(3) Interstitial hydrides

These are ill-defined compounds formed by a number of transition metals in which hydrogen is accommodated in the lattice of the transition element. Some expansion of the metal lattice occurs, since the density of the hydride is less than that of the parent metal. No definite chemical formula can be allocated to these substances, i.e. they are non-stoichiometric. Although the composition can be varied by changes in temperature and pressure, formulae such as $TiH_{1.73}$ and $ZrH_{1.92}$ have been reported. The uptake of hydrogen is reversible and can in all cases be removed by pumping at a sufficiently high temperature. The use of finely divided palladium for making extremely pure hydrogen depends on this reversibility.

17.2.5 The Hydrogen Economy (Hydrogen as Fuel)

The total volume of ocean water is about 1×10^{21} L. Thus, the ocean contains an almost inexhaustible supply of hydrogen.

The world's fossil fuel reserves are being depleted at an alarmingly fast rate. Faced with this dilemma,, scientists have made intensive efforts in recent years to develop a method of obtaining hydrogen gas as an alternative energy source. Hydrogen gas could replace gasoline to power automobiles (after considerable modification of the engine, of course) or be used with oxygen gas in fuel cells to generate electricity. One major advantage of using hydrogen gas in these ways is that the reactions are essentially free of pollutants; the end product formed in a hydrogen-powered engine or in a fuel cell would be water, just as in the burning of hydrogen gas in air:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Of course, success of a hydrogen economy would depend on how cheaply we could produce hydrogen gas and how easily we could store it.

Although electrolysis of water consumes too much energy for large-scale application, if scientists can devise a more practical method of "splitting" water molecules, we could obtain vast amounts of hydrogen from seawater. One approach that is currently in the early stages of development would use solar energy. In this scheme a catalyst (a complex molecule containing one or more transition metal atoms, such as ruthenium) absorbs a photon from solar radiation and becomes energetically excited. In its excited state the catalyst is capable of reducing water to molecular hydrogen.

INTEXT QUESTIONS 17.2

1. Why does ice float on water?
2. What is heavy water? Write its important uses.
3. Give one method of preparation of hydrogen peroxide.
4. Give two uses of hydrogen peroxide.

5. How does hydrogen peroxide decolorize potassium permaganate?
6. Name the types of hydrides
7. NaH is covalent or ionic hydride?

17.3 *s*-BLOCK ELEMENTS

The *s*-block elements have an outer electronic configuration ns^1or ns^2 and are placed in the group 1 and 2 of the periodic table. Group 1 consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals after the Arabic word *al-qis* meaning plant ashes. These ashes are particularly rich in carbonates of calcium, strontium, barium and radium. The elements beryllium, magnesium, calcium, strontium, barium and radium belong to group 2 and are known as alkaline earth metals.

17.3.1 The alkali metals

In this group all the elements are electropositive metals and there exists resemblance between the elements owing to their similar outer electron configuration. The occurrence and properties of alkali metals are discussed below:

17.3.1.1 Occurrence

Sodium and potassium are abundant. Sodium is found as sodium chloride in the sea water and as sodium nitrate (Chile saltpeter) in the deserts of Chile. Potassium too, is found in sea water, and also as carnallite ($KCl.MgCl_2.6H_2O$). Lithium, rubidium and caesium occur in a few rare aluminosilicates. Francium is radioactive; its longest-lived isotope ^{223}Fr has a half life of only 21 minutes.

17.3.1.2 Electronic configuration

The alkali metals with their symbols, atomic numbers and electronic configurations are listed below in Table 17.1:

Table 17.1: Electronic configuration of alkali metals

Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	$1s^2, 2s^1$
Sodium	Na	11	$1s^2, 2s^2p^6, 3s^1$
Potassium	K	19	$1s^2, 2s^2p^6, 3s^2p^6, 4s^1$
Rubidium	Rb	37	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$
Caesium	Cs	55	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^1$

17.3.1.3 Physical properties of Alkali Metals

Alkali metals are placed in group 1 of periodic table. They readily form unipositive ions. As we go down the group the alkali metals show steady increase in size due to the addition of a new shell at each step. The increase in size of the atoms or ions, directly influences the physical and chemical properties of the alkali metals. Some physical properties are given in Table 17.2.

Table 17.2: Physical properties of alkali metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol^{-1})	Electro negativity	Density (g cm^{-3})	M.P. K	Electrode Potential (E° volts)
Li	76	520.1	1.0	0.54	454	–3.05
Na	102	495.7	0.9	0.97	371	–2.71
K	138	418.6	0.8	0.86	336	–2.83
Rb	152	402.9	0.8	1.53	312	–2.89
Cs	167	375.6	0.7	1.90	302	–2.93

The trends in physical properties are listed in Table 17.3.

Table 17.3: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +1 oxidation state
2.	Atomic/ionic radii	Li < Na < K < Rb < Cs Atomic and ionic radii increases since number of shells increase as we go down the group.
3.	Ionization energy	Li > Na > K > Rb > Cs As the size increases it becomes easier to remove an electron from the outermost shell.
4.	Electronegativity	Li > Na > K > Rb > Cs The electropositive character increases due to decrease in ionization enthalpy therefore electronegativity decreases.
5.	Metallic character	Li < Na < K < Rb < Cs Metallic character increases as we go down the group due to increase in electropositive character.

<table>
<tr><td>6.</td><td>Density</td><td colspan="5">$Li < Na > K < Rb < Cs$
Generally density increases from Li to Cs as the atomic mass increases (exception K).</td></tr>
<tr><td>7.</td><td>Melting point &
boiling points</td><td colspan="5">$Li > Na > K > Rb > Cs$
Decreases down the group because of increasing size and weak intermetallic bond.</td></tr>
<tr><td>8.</td><td>Flame coloration</td><td colspan="5">They show characteristic colors in the flame. The outermost electron absorbs energy and is excited to a higher energy level. This absorbed energy is remitted when the electron comes back to ground state. The difference in energy falls in the visible range of radiation hence the colors are seen.</td></tr>
<tr><td></td><td></td><td>Li
Crimson red</td><td>Na
Yellow</td><td>K
Pale violet</td><td>Rb
Violet</td><td>Cs
Violet</td></tr>
</table>

17.3.1.4 Chemical Properties

Alkali metals are the most reactive metals in the whole periodic table due to their ease in losing outermost electron hence getting oxidized easily. As the ease of losing electrons increases, the reactivity increases down the group.

(i) Oxides: All alkali metals form oxides, which are basic in nature. Lithium forms only one type of oxide, lithium monoxide Li_2O. Sodium peroxide Na_2O_2 is formed when sodium is heated with oxygen. Other metals of this group also form superoxides MO_2 on reaction with oxygen.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

$$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

$$K(s) + O_2(g) \rightarrow KO_2(s)$$

The formation of a particular oxide is determined by the size of the metal ion. Tiny lithium ion is not able to come in contact with sufficient number of peroxo ions. However, the ions of potassium, rubidium, caesium are large enough to come in close contact with peroxo ions and form stable structures as superoxides.

(ii) Reactivity towards water: Although lithium has the most negative E°, its reaction with water is considerably less vigorous than that of sodium which has the least negative E° among the alkali metals (Table 17.2). The low reactivity of lithium is due to small size and high ionization enthalpy. All the metals of the group react with water explosively to form hydroxide and liberate hydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

Basic character of oxides and hydroxides: The basic character of oxides and hydroxides of alkali metals increases with the increase in size of metal ion. So, lithium oxide and hydroxide are least basic whereas, caesium oxide and hydroxide are most basic in nature.

(iii) Hydrides: The alkali metals react with hydrogen at about 637K to form hydrides (MH), where M stands for alkali metals.

$$2M + H_2 \rightarrow 2MH$$

(iv) Halides: Alkali metals react with halogens to form halides:

$$2M + X_2 \rightarrow 2MX (X = F, Cl, Br, I)$$

17.3.1.5 Diagonal Reltionship between Lithium and Magesium

The similarity between first member of one group and the second member of succeeding group is called diagonal relationship. Thus lithium shows properties similar to magnesium. Likewise Beryllium and aluminium have similar characteristics.

The closeness of the diagonal elements arises due to their comparable polarizing power. Mathematically,

$$\text{Polarizing power} \propto \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

On going from lithium to sodium, the ionic charge remains the same, the ionic radius increases and, therefore, the polarizing power decreases. On going from lithium to beryllium, the ionic charge increases, the ionic radius decreases and, therefore, the polarizing power increases.

On going from beryllium to magnesium, the polarizing power decreases–and becomes comparable to that of lithium.

In other words, the ratio between ionic charge to the square of ionic radius is nearly the same for lithium and magnesium. So are their physical and chemical properties, as shown in the following examples.

1. Both elements have nearly the same values of electronegativities.
2. The melting and boiling points of the two elements are comparable.
3. Lithium and magnesium possess nearly the same degree of hardness.
4. Both the elements form nitrides when heated directly with nitrogen.
5. Both the elements form carbides when heated directly with carbon.
6. Both the elements form normal oxides when heated in air.
7. The carbonates, nitrates and hydroxides of both the elements undergo thermal decomposition to their respective oxides.

8. The halides of both the elements are appreciably soluble in organic solvents.
9. Oxyacid salts of both the elements are sparingly soluble in water.

17.3.1.6 Anamodous behaviour of Lithium

1. Lithium salts of large polarizable anions are less stable than those of other alkali metals, as expected

   $$Li_2CO_3 \xrightarrow{700°C} Li_2O + CO_2 \qquad \text{Na etc., no reaction below 800°C}$$

   $$LiNO_3 \longrightarrow Li_2O + NO_2 \qquad NaNO_3 \longrightarrow NaNO_2 + \tfrac{1}{2}O_2$$

   $$2LiOH \longrightarrow Li_2O + H_2O \qquad \text{Na etc., no reaction.}$$

   In each case, the more stable salts of the heavier alkali metals decompose at a temperature higher than that normally obtainable in the laboratory. Lithium forms no solid bicarbonate, triiodide, hydrosulphide, or superoxide. These are unstable at room temperature, whereas those of the other alkali metals require a higher temperature to effect their decomposition.
2. Solubility differences: The lithium salts of anions of high charge density are less soluble than those of the other alkali metals, for example LiOH, LiF, Li_3PO_4, Li_2CO_3. The halides of lithium are more covalent than the other halides and are more soluble in organic solvents.
3. Complex formation: Lithium forms more stable covalent bonds than the other alkali metals and therefore forms more stable complex compounds (Section 20.4) not only with oxygen donor ligands, but also with nitrogen donors. For example, lithium cannot be recovered unchanged from its liquid ammonia solution, owing to the formation of $Li(NH_3)_4$.
4. Lithium reacts only very slowly with water.
5. Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For example, in air lithium forms the normal oxide, whereas the others form higher oxides such as peroxides and superoxides. Lithium reacts with nitrogen to form the nitride, Li_3N; the others do not react. Lithium hydride is more stable than the other hydrides, and lithium carbide forms more easily (with acetylene).
6. Lithium compounds are more covalent. Thus the halides are more soluble in organic solvent and the alkyls and aryls are more stable than those of the other alkali metals.

   The so-called "anomalous" properties of lithium occur because lithium is "unexpectedly" much less electropositive than sodium.

17.3.1.7 Sodium Hydroxide

Manufacture of sodium hydroxide by the Castner-Kellner process

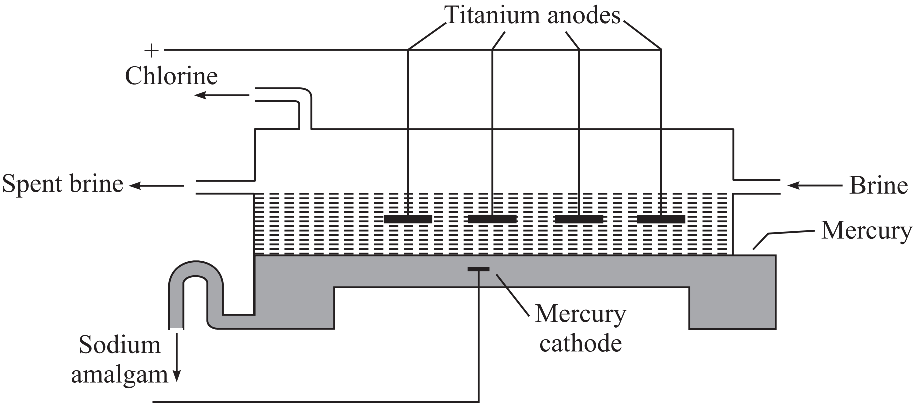


Fig. 17.3 The Castner-Kellner cell

In this process a saturated solution of sodium chloride (brine) flows through the cell (Fig. 17.3) in the same direction as a shallow stream of mercury which constitutes the cathode; the anode consists of a number of titanium blocks. On electrolysis chlorine is discharged at the anode and sodium at the cathode, where it dissolves in the mercury and is removed from the cell. The sodium amalgam is passed through water where the sodium reacts to form 50 per cent sodium hydroxide solution of high purity, the reaction being catalysed by the presence of iron grids. The mercury is then returned to the cell. The products are thus sodium hydroxide, chlorine and hydrogen.

Cathode		**Anode**
Na^+ discharged $\longleftarrow$	Na^+Cl^- $\longrightarrow$	Cl^- discharged
$2Na^+ + 2e^- \rightarrow 2Na$	$H_2O \rightleftharpoons H^+ + OH^-$	$2Cl^- \rightarrow 2Cl\bullet + 2e^-$
$Na + Hg \rightarrow Na/Hg$		$2Cl\bullet \rightarrow Cl_2$
$2Na/Hg + 2H_2O \longrightarrow 2Na^+OH^- + H_2 + 2Hg$		

Sodium is discharged in preference to hydrogen in the cell, since hydrogen has a high overvoltage at a mercury electrode. This amounts to saying that the discharge of hydrogen ions or the combination of hydrogen atoms to give molecules is difficult to achieve at a mercury surface, i.e. mercury is a poor catalyst for either or both of these processes. Since sodium dissolves in mercury which is circulated through the cell, the formation of sodium hydroxide and hydrogen in the electrolytic cell itself is prevented.

Reactions of sodium hydroxide

Sodium hydroxide is a white deliquescent solid which is caustic and slimy to touch: it dissolves readily in water with vigorous evolution of heat. In aqueous solution this is completely dissociated and its reactions are essentially those of the hydroxide ion which is a strong base, i.e. it will neutralise acids and displace ammonia from ammonium salts when heated :

$$Na^+OH^-(aq) + H^+Cl^-(aq) \longrightarrow Na^+Cl^-(aq) + H_2O(1)$$

$$\text{or} \quad OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$$

$$Na^+OH^-(aq) + NH_4{}^+Cl^-(aq) \longrightarrow Na^+Cl^-(aq) + H_2O(l) + NH_3(g)$$

$$\text{or} \quad OH^-(aq) + NH_4{}^+(aq) \longrightarrow H_2O + NH_3(g)$$

In aqueous solution it reacts with many salts and precipitates the corresponding basic hydroxide, e.g.

$$Cu^{2+}SO_4{}^{2-}(aq) + 2Na^+OH^-(aq) \longrightarrow Cu(OH)_2(s) + (Na^+)_2SO_4{}^{2-}(aq)$$

$$\text{or} \quad Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$$

The hydroxides of the less electropositive metals are amphoteric and dissolve in an excess of alkali, e.g. the hydroxides of aluminium (III), lead (II), tin (11) and zinc(II):

$$A1^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow \underset{\text{aluminate ion}}{Al(OH)^-{}_4(aq)}$$

$$Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$$

$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow \underset{\text{zincate ion}}{Zn(OH)_4{}^{2-}(aq)}$$

Sodium reacts with a variety of non-metals, e.g. the halogens, silicon, sulphur, white phosphorus; sodium salts are formed in which the non-metal is incorporated into the anion.

Uses of Sodium hydroxide

Sodium hydroxide is used in the laboratory for absorbing carbon dioxide and other acidic gases, in a number of organic reactions involving hydrolysis and in volumetric analysis. Industrially it is used in the manufacture of soap (essentially sodium stearate) and sodium formate (obtained by heating sodium hydroxide with carbon monoxide under pressure).

17.3.1.8 Sodium Carbonate

The manufacture of sodium carbonate – the Solvay process

It is manufactured by the ammonia-soda or Solvay process. In theory the process involves the reaction between sodium chloride and calcium carbonate to produce sodium carbonate and calcium chloride, but in practice other chemicals are required, since the reaction as given below does not take place:

$$CaCO_3(s) + 2NaCl(s) \longrightarrow Na_2CO_3(s) + Ca(Cl)_2(s)$$

The raw materials are sodium chloride. calcium carbonate, a fuel and ammonia. The calcium carbonate is strongly heated to give quicklime and carbon dioxide:

$$Ca^{2+}CO_3^{2-}(s) \longrightarrow Ca^{2+}O^{2-}(s) + CO_2\ (g) \qquad (1)$$

The carbon dioxide is now passed up a large tower, fitted with perforated plates, down which a concentrated aqueous solution of sodium chloride saturated with ammonia trickles. The reactions taking place in the tower can be represented by the equations:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_3.H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad (2)$$

$$Na^+(aq) + Cl^-(aq) + NH_4^+(aq) + OH^-(aq) + CO_2(g) \longrightarrow$$
$$Na^+(aq) + HCO_3^-(aq) + NH_4^+(aq) + Cl^-(aq) \qquad (3)$$

$$Na^+(aq) + HCO_3^-(aq) \longrightarrow Na^+HCO_3^-(s) \qquad (4)$$

Sodium hydrogen carbonate, which is not very soluble in sodium chloride solution, due to the common ion effect is filtered and heated to produce sodium carbonate:

$$2Na^+HCO_3^-(s) \longrightarrow (Na^+)_2CO_3^{2-}(s) + H_2O(1) + CO_2(g) \qquad (5)$$

The sodium carbonate at this stage is contaminated with ammonium salts. If required pure, it is dissolved in water and carbon dioxide is blown through the solution. The precipitate of sodium hydrogen carbonate is filtered and heated to produce pure sodium carbonate; recrystallisation from water produces washing soda, $(Na^+)_2CO_3^-.10H_2O$.

$$(Na)_2CO_3^2(aq) + H_2O(1) + CO_2(g) \longrightarrow \underset{\text{precipitated leaving ammonium salts in solution}}{2NaHCO_3(s)} \qquad (6)$$

The Solvay process is a very economical process since:

(a) sodium chloride and calcium carbonate are cheap;

(b) quicklime and ammonium chloride formed in reactions (1) and (3) respectively are reacted together to produce ammonia so that, apart from making up small losses, no additional ammonia is required;

(c) carbon dioxide formed in reactions (5) is reintroduced into the Solvay tower.

Properties and uses of sodium carbonate

Sodium carbonate is freely soluble in water and gives an alkaline reaction. It reacts with some salts in solution and precipitate the corresponding carbonates, e.g.

$$Ca^{2+}(Cl^-)_2(aq) + (Na^+)_2CO_3{}^{2-}(aq) \longrightarrow Ca^{2+}CO_3{}^{2-}(s) + 2Na^+Cl^-(aq)$$

Because of its alkaline reaction in solution, sodium carbonate frequently precipitate basic carbonates, e.g.

$$3Zn^{2+}(aq) + CO_3{}^{2-}(aq) + 4OH^-(aq) + 2H_2O(1) \longrightarrow ZnCO_3.2Zn(OH)_2.2H_2O(s)$$

In these instances the normal carbonate can usually be obtained by using sodium hydrogen carbonate solution.

Sodium carbonate is often used in the laboratory as a volumetric reagent. Industrially it is used in a wide variety of ways, including the manufacture of glass, in the preparation of sodium salts, in the treatment of hard water, for the manufacture of soap, and in paper making.

17.3.1.9 Sodium hydrogen carbonate

This can be obtained by passing carbon dioxide through a cold concentrated solution of the corresponding carbonate, e.g.

$$(Na^+)_2CO_3{}^{2-}(aq) + CO_2(g) + H_2O(1) \longrightarrow 2Na^+HCO_3{}^-(s)$$

Because sodium hydrogen carbonate solution is less alkaline than sodium carbonate solution, the former is often used to precipitate normal carbonates which would otherwise be formed as basic carbonates, e.g.

$$Cu^{2+}(aq) + 2HCO_3{}^-(aq) \longrightarrow CuCO_3(s) + H_2O(s) + CO_2(g)$$

17.3.1.10 Biological Importance of Sodium and Potassium

1. To keep normal osmotic pressure of body matter and to save many matter from loss
2. To increase nanomuscular
3. Sodium and potassium salt combine weak acid to give respective extracellular and intracellular matter. They form buffer.

17.3.1.11 Stability and Solubility of Carbonates and Sulphates:

The carbonates and sulphates of alkali metals are generally soluble in water and thermally stable. The carbonates are highly stable to heat and melt without decomposing. As the electropositive character increases down the group, the stability of the carbonates increases. Carbonate of lithium is not so stable to heat due to the small size of lithium.

INTEXT QUESTIONS 17.3

1. Name the important ores of sodium.
2. Arrange the alkali metals in order of increasing ionization enthalpy.
3. Which of the alkali metals forms only monoxide?
4. Write down the chemical equation for the reaction of sodium with water.
5. What type of bond exists in the hydrides of alkali metals?
6. Name the element which forms (i) peroxide, (ii) superoxide.
7. Write chemical equation when $NaHCO_3$ is heated.
8. Li^+ resembles Mg^{2+}. Why?
9. Name the common ore of Mg.
10. Arrange the alkaline earth metals in order of increasing reactivity.
11. Name an amphoteric oxide of alkaline earth metals.
12. Arrange the carbonates of alkaline earth metals in order of thermal stability.
13. What is the biological role of Ca^{2+}.

17.3.2 The Alkaline Earth Metals

You have seen a gradual increase in the size of the alkali metals as we move down the group 1 of the periodic table. Identical observations may be made in the case of alkaline earth metals placed in group 2 of the periodic table. Some physical properties of the alkaline earth metals are given in Table 17.4.

Table 17.4: Physical properties of the alkaline earth metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol^{-1})	Electro negativity	Density (g cm^{-3})	M.P. K	Electrode Potential (E°) volts
Be	89	899	1.5	1.85	1562	–1.70
Mg	136	737	1.2	1.74	924	–2.38
Ca	174	590	1.0	1.55	1124	–2.76
Sr	191	549	1.0	2.63	1062	–2.89
Ba	198	503	0.9	3.59	1002	–2.90

An alkaline earth metal atom is smaller in size compared to its adjacent alkali metal. This is due to the added proton in the nucleus, which exerts a pull on the electrons in an atom resulting in squeezing of the atom. This reduction in size shows higher control of the nucleus on the electrons in the shells.

The ease of losing electrons makes the alkaline earth metals good reducing agents. But this property is less prominent as compared to the corresponding alkali metals.

17.3.2.1 Occurrence

The alkaline earth metals are too reactive to occur native. Magnesium is the second most abundant metallic element in the sea, and it also occurs as carnallite ($KCl.MgCl_2.6H_2O$) in earth crust. Calcium occurs as calcium carbonate (marble, chalk etc) and with magnesium as dolomite ($CaCO_3.MgCO_3$). Other ores of calcium are anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$). Strontium and barium are rare and are found as carbonates and sulphates. Beryllium too is rare and is found as beryl ($Be_3Al_2(SiO_3)_6$).

17.3.2.2 Electronic Configuration

The electronic configurations of the alkaline earth metals are listed in Table 17.5.

Table 17.5: Electronic configuration

Element	Symbol	Atomic number	Electronic configuration
Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2p^6, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2p^6, 3s^2p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^2$

17.3.2.3 Physical properties of alkaline earth metals

Alkaline earth metals are less electropositive than alkali metals. The electropositive character of alkaline earth metals increases down the group. They achieve an inert gas configuration by the loss of two electrons. Some physical properties and their trends are given in Table 17.6.

Table 17.6: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +2 oxidation state
2.	Atomic/ionic radii	Be < Mg < Ca < Sr < Ba Size of alkaline earth metals increases from top to bottom due to increase in the number of shells.
3.	Ionization enthalpy	Be > Mg > Ca > Sr > Ba As the size increases it becomes easier to remove an electron from the outermost shell.
4.	Electronegativity	Be > Mg > Ca > Sr > Ba As the electropositive character increases from top to bottom due to decrease in ionization energy, electronegativity decreases from top to bottom.

5.	Metallic character	Be < Mg < Ca < Sr < Ba Metallic character increases as we go down the group due to increase in electropositive character.
6.	Density	Generally density increases from top to bottom as the atomic mass increases.
7.	Melting point & boiling point	They show higher values of melting and boiling points as compared to alkali metals because of the smaller size and stronger metallic bonds. There is no regular trend down the group. It depends upon packing.
8.	Flame coloration	Except Be and Mg (due to small size and higher ionization enthalpy) all other alkaline earth metals impart characteristic colours to the Bunsen flame. Ca – Brick red Sr – Crimson red Ba – Sea green

17.3.2.4 Chemical Properties of Alkaline Earth Metals

The alkaline earth metals are reactive metals, though less reactive than alkali metals. The reactivity increases from top to bottom in a group due to increase in electropositive character.

(i) **Reactivity and E° values:** The near constancy of the E° (M^{2+}/M) values for group 2 metals (Table 17.4) is somewhat similar to that for group 1 metals. Therefore, these metals are electropositive and are strong reducing agents. The less negative value for Be arises from, the large hydration energy associated with the small size of Be^{2+} being countered by relatively large value of the enthalpy of atomization of beryllium

(ii) **Oxides:** The alkaline earth metals burn in oxygen forming the ionic oxides of the type MO where M stands for alkaline earth metals except Sr, Ba, and Ra which form peroxides. Peroxides are formed with increasing ease and increasing stability as the metal ions become larger.

$$2Mg + O_2 \rightarrow 2MgO$$

$$2Be + O_2 \rightarrow 2BeO$$

$$2Ca + O_2 \rightarrow 2CaO$$

$$Ba + O_2 \rightarrow 2BaO$$

Basic character of the oxides increases gradually from BeO to BaO. Beryllium oxide is amphoteric, MgO is weakly basic while CaO is more basic.

(iii) Hydrides: The alkaline earth metals combine with hydrogen to form hydrides of general formula MH_2

$M + H_2 \rightarrow MH_2 (M = Mg, Ca, Sr, Ba)$

(iv) Reaction with water: Usually the alkaline earth metals react with water to liberate hydrogen. Be does not react with water or steam even at red heat and does not get oxidized in air below 837K.

$Mg + H_2O \rightarrow MgO + H_2$

Ca, Sr, and Ba react with cold water with increasing vigour.

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

(v) Halides: All the alkaline earth metals combine directly with the halogens at appropriate temperature forming halides, MX_2 where M stands for alkaline earth metals.

$M + X_2 \rightarrow MX_2$

(vi) Solubility and stability of carbonates and sulphates:

Carbonates: The carbonates of alkaline earth metals are sparingly soluble in water. They decompose if heated strongly. Their thermal stability increases with increase in the size of the cation. Decomposition temperatures of carbonates are given below:

$BeCO_3$	**$MgCO_3$**	**$CaCO_3$**	**$SrCO_3$**	**$BaCO_3$**
<373K	813K	1173K	1563K	1633K

Sulphates: The sulphates of alkaline earth metals are white solids, stable to heat. The sulphates, $BeSO_4$ and $MgSO_4$ are readily soluble and the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration energies of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore, their sulphates are soluble.

The sulphates decompose on heating, giving the oxides.

$MSO_4 \rightarrow MO + SO_3$

The thermal stability of sulphates increases with the increase in the size of cation.

This is shown by the temperature at which decomposition occurs:

$BeSO_4$	**$MgSO_4$**	**$CaSO_4$**	**$SrSO_4$**
773K	1168K	1422K	1647K

(vii) Complex compounds: Smaller ions of the group 2 elements form complexes. For example chlorophyll is a complex compound of magnesium. Beryllium forms complexes like $[BeF_4]^{2-}$.

17.3.2.5 Anomalous Nature of Beryllium: Diagonal Relationship to Aluminium

Beryllium, the first member of the group, appears to be very different from the other members, in the same way as lithium differs from the other alkali metals, and for the same reasons. In fact, the anomalous nature of the first member of the s- and p-block groups becomes more pronounced towards the middle of the table: beryllium differs more from magnesium than lithium does from sodium. Also, beryllium shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium; and the properties in which beryllium differs from magnesium, it shares with aluminium (in general). The cohesive properties of beryllium are much greater than those of magnesium: beryllium has higher melting and boiling points, enthalpy of fusion, etc., and density, and it is much harder. Similarly its attraction for outer electrons is greater than that of magnesium, leading to much lower atomic radii, higher electron affinity and ionization energy, etc. Its higher polarizing power leads to all its compounds being largely covalent, with lower melting and boiling points, enthalpies of formation etc., and with greater solubility in organic solvents than the corresponding magnesium compounds. The hydration enthalpy of the small Be^{2+} ion is very high and its salts are among the most soluble known. Despite this, its electrode potential is not high, because of its very high second ionization enthalpy. Nevertheless, it would be expected to react with water, and react vigorously with acids ($E^{\phi} = -1.70$). In fact, it does not react with water, and is resistant to acid. This must be a kinetic effect: perhaps an oxide film protects the metal. Certainly this is one of the metals rendered passive by concentrated nitric acid. The halides are hygroscopic and fume in air, and alll soluble salts are largely hydrolysed and polymerized in water except in strong acid or strong alkali solutions (beryllium is amphoteric, unlike magnesium, etc.):

$$2[Be(H_2O)_4]^{2+} \xrightleftharpoons[H_3O^+]{H_2O} 2H_3O^+ + [(H_2O)_3BeOBe(H_2O)_3]^{2+} \xrightarrow{OH^-}$$

$$Be(OH)_2(s) \xrightarrow{OH^-} [Be(OH)_4]^{2-}\ (aq).$$

Beryllium is a poor reducing agent, and does not dissolve in ammonia to give blue reducing solutions.

17.3.2.6 Calcium oxide (CaO)

Manufacture of CaO

CaO (quick lime) is manufactured in enormous quantities (126 million tonnes in 1988) by roasting $CaCO_3$ in lime Kiln.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

CaO reacts exothermally with water, forming hydroxide

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$Ca(OH)_2$ is called slaked lime

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3$$

17.3.2.7 $CaCO_3$ Calcium Carbonate

$CaCO_3$ occurs in two different crystalline forms, calcite and aragonite. Both forms occur naturally as minerals. Calcite is the more stable: each Ca^{2+} is surrounded by six oxygen atoms from $CO_3{}^{2-}$ ions. Aragonite is a metastable form, and its standard enthalpy of formation is about 5 kJ mol^{-r} higher than that of calcite. In principle aragonite should decompose to calcite, but a high energy of activation prevents this happening. Aragonite can be made in the laboratory by precipitating from a hot solution. Its crystal structure has Ca^{2+} surrounded by nine oxygen atoms. This is a rather unusual coordination number.

Uses of Lime:

1. In steel making to remove phosphates and silicates as slag.
2. By mixing with SiO_2 and alumina or clay to make cement.
3. For making glass.
4. In the lime-soda process, which is part of the chlor-alkali industry, converting Na_2CO_3 to NaOH or vice versa.
5. For 'softening' water.
6. To make CaC_2.
7. To make slaked lime $Ca(OH)_2$ by treatment with water.

17.3.2.8 Biological Role of Mg^{2+} and Ca^{2+}

Mg^{2+} ions are concentrated in animal cells, and Ca^{2+} are concentrated in the body fluids outside the cell. They are also essential for the transmission of impulses along nerve fibres. Mg^{2+} is important in chlorophyll, in the green parts of plants. Ca^{2+} is important in bones and teeth as apatite $Ca_3(PO_4)_2$, and the enamel on teeth as fluoroapatite $[3(Ca_3(PO_4)_2) \bullet CaF_2]$. Ca^{2+} ions are important in blood clotting, and to maintain the regular beating of the heart.

WHAT YOU HAVE LEARNT

- Hydrogen can either be placed with alkali metals or with halogens.
- Hydrogen exists in three isotopic forms namely hydrogen, deuterium and tritium.

- Hydrogen is a combustible gas and has reducing property.
- There are two important oxides of hydrogen: water and hydrogen peroxide.
- Cage-like structure of ice makes it float on water.
- Water containing deuterium in place of ordinary hydrogen is known as heavy water.
- Heavy water can be separated from ordinary water by electrolysis or distillation.
- Heavy water is used as moderator in nuclear reactors.
- Hydrogen peroxide acts both as oxidizing and reducing agent.
- Different types of hydrides i.e. ionic, covalent etc.
- Hydrogen as fuel.
- The alkali and alkaline earth metals show regular variation in various properties along a group and period.
- Alkali metals react with hydrogen, water and halogens to form hydrides, hydroxides and halides respectively.
- Diagonal relationship betrween Li^+ Mg^{2+}
- Manufacture of NaOH, Na_2 CO_3, $NaHCO_3$
- Biological role of alkali metals.
- Basic nature of oxides and hydroxides of group 1 and group 2 elements.
- Thermal stability and solubility of carbonates and sulphates.
- Manufacture of CaO and $CaCO_3$
- Biological role o alkaline earth metals.

TERMINAL EXERCISE

1. Write three general characteristics of the s-block elements which distinguish them from the elements of other blocks.
2. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?
3. What happens when?

   (a) sodium metal is dropped in water.

   (b) sodium metal is heated in free supply of air.

   (c) sodium peroxide dissolves in water.

4. Explain why hydrogen is best placed separately in the periodic table of elements.
5. Describe the industrial applications of hydrogen.
6. Discuss the importance of heavy water in nuclear reactor and how is it prepared from normal water?
7. Name the isotopes of hydrogen. What is the importance of heavier isotopes of hydrogen?
8. Why is ice less dense than water and what kind of attractive forces must be overcome to melt ice?
9. Show by proper chemical reactions how hydrogen peroxide can function both as an oxidizing and a reducing agent?
10. Compare the properties of alkali metals and alkaline earth metals with respect to:
    (a) atomic radii
    (b) ionization energy
    (c) melting points
    (d) reducing behavior
11. Explain the trends of solubility and stability of the carbonates and sulphates of alkaline earth metals.
12. Explain the process involved in the manufacture of NaOH, Na_2CO_3 and $NaHCO_3$ (Give Chemical equations only)
13. Explain the biological role of Ca^{2+} and Mg^{2+}.

ANSWERS TO INTEXT QUESTIONS

17.1

1. Three isotopes of hydrogen are (a) protium ${}^1_1H$, deuterium D or ${}^2_1H$ and (c) tritium T or ${}^3_1H$.
2. Tritium.
3. It is lightest of all the gases known.
4. Methane (CH_4).
5. Ammonia (NH_3).
6. Vegetable oils $+H_2 \xrightarrow[Ni]{443K}$ Vegetable ghee.

17.2

1. Ice is less dense as compared to water. It has open spaces in the hydrogen bonded structure.
2. D_2O; Moderator is nuclear reactors.
3. $BaO_2.8H_2O + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 + 8H_2O$
4. (a) as a bleaching agent.

   (b) germicide and disinfectant.
5. H_2O_2 reduces $KMnO_4$

   $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

   Mn(+7) is reduced to Mn(+2)
6. Three types of hydrides : ionic, covalent and interstitial
7. Ionic hydride

17.3

1. NaCl and $NaNO_3$.
2. $Cs < Rb < K < Na < Li$
3. Lithium
4. $2Na + 2H_2O \rightarrow 2NaOH + H_2$
5. Ionic.
6. (i) Sodium (ii) potassium
7. $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
8. Same polarising power.
9. Carnallite ($KCl.MgCl_2.6H_2O$).
10. $Be < Mg < Ca < Sr < Ba$
11. BeO
12. $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
13. Teeth enamal

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18

GENERAL CHARACTERISTICS OF THE P-BLOCK ELEMENTS

The *p*-block of the periodic table consists of the elements of groups 13,14, 15, 16, 17 and 18. These elements are characterised by the filling up of electrons in the outermost *p*-orbitals of their atoms. Some of these elements and their compounds play an important role in our daily life. For example:

- Nitrogen is used in the manufacture of ammonia, nitric acid and fertilizers. Trinitrotoluene (TNT), nitroglycrine, etc., are compounds of nitrogen, which are used as explosives.
- Oxygen present in air is essential for life and combustion processes.
- Carbohydrates, proteins, vitamins, enzymes, etc., which contain chain of carbon atoms, are responsible for the growth and development of living organism.

The usual trends (vertical as well as horizontal) in various properties observed in the *s*-block are observed in this block, too. As we move from top to bottom through a vertical column (group) some similarities are observed in the properties. However, this vertical similarity is less marked in the *p*-block than that observed in the *s*-block, especially in groups 13 and 15; vertical similarity is increasingly shown by the later groups. As far as the horizontal trend is concerned, the properties vary in a regular fashion as we move from left to right across a row (period).

In this lesson we shall study some important physical properties w.r.t. the of electronic configuration of the atom. Finally, we shall relate the periodicity in atomic properties to the observed chemical behaviour of their compounds, with special reference to their oxides, hydrides and halides.

OBJECTIVES

After reading this lesson you will be able to:

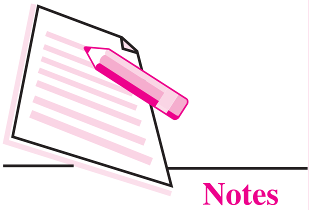
- describe the general mode of occurrence of these elements in nature;
- recall the electronic configurations of the p-block elements;
- explain the variations in atomic and physical properties such as
  - (i) atomic and ionic sizes;
  - (ii) ionization enhalpy;
  - (iii) electronegativity;
  - (iv) electron-gain enthalpy;
  - (v) metallic and non-metallic behaviours along the period and in a group of the periodic table;
- correlate the properties of the elements and their compounds with their positions in the periodic table;
- explain the anomalous properties of the first element in each group of this block and
- explain inert pair effect.

18.1 OCCURRENCE OF THE *P*-BLOCK ELEMENTS IN NATURE

The *p*-block elements do not follow any set pattern of mode of occurrence in nature. Some of them occur free as well as in the combined state in nature. For example, elements such as oxygen, nitrogen, carbon, sulphur occur in both the forms. Noble gases occur in free state only. All other elements usually occur in the combined state. The distribution of these elements in nature is also far from any uniform pattern. Some of them are quite abundant, *e.g*., oxygen, silicon, aluminium, nitrogen etc. On the other hand the heavier members in each group of the block are generally much less abundant. The important minerals associated with elements will be considered whenever it is necessary at the appropriate places in the text.

18.2 ELECTRONIC CONFIGURATION

Among the elements of *p*-block, the *p*-orbitals are successively filled in a systematic manner in each row. Corresponding to the filling up of 2*p*, 3*p*, 4*p*, 5*p* and 6*p* orbitals five rows of *p*-block elements are there. The outer electronic configuration of the atoms of these elements is ns^2np^{1-6}.



18.3 ATOMIC SIZE

The atomic radius of the of *p*-block elements generally decreases on moving across a period from left to right in the periodic table. It is because the addition of electrons takes place in the same valence shell and are subjected to an increased pull of the nuclear charge at each step. The variation in atomic size along a period is shown in Table 18.1.

Table 18.1 : Variation in Atomic Size in a row from boron to fluorine

Element	**Boron**	**Carbon**	**Nitrogen**	**Oxygen**	**Fluorine**
Outer electronic configuration	$2s^2\ 2p^1$	$2s^2\ 2p^2$	$2s^2\ 2p^3$	$2s^2\ 2p^4$	$2s^2\ 2p^5$
Nuclear charge	+5	+6	+7	+8	+9
Effective nuclear charge	+ 2.60	+ 3.25	+ 3.90	+ 4.55	+ 5.20
Atomic size (pm)	88	77	70	66	64

On moving down a group, the atomic radius of the elements increases as the atomic number increases. This is due to the increase in the number of shells as we move from one element to the next down the group. The increase in nuclear charge is more than compensated by the additional shell. The variation in atomic size on moving down a group is shown in Table 18.2.

Table 18.2 : Variation in atomic size down a group

Elements of Group 13	**Outer electron configuration**	**Nuclear charge**	**Effective nuclear charge**	**Atomic size (pm)**
Boron	$2s^2\ 2p^1$	+ 5	+ 2.60	88
Aluminium	$3s^2\ 3p^1$	+ 13	+ 11.60	118
Gallium	$4s^2\ 4p^1$	+ 31	+ 29.60	124
Indium	$5s^2\ 5p^1$	+ 49	+ 47.60	152
Thallium	$6s^2\ 6p^1$	+ 81	+ 79.60	178

18.4 IONIZATION ENTHALPY

It is the amount of energy required to remove the most loosely bound electron from the outermost shell of a neutral gaseous atom. It is measured in kJ mol^{-1} and is known as first ionization enthalpy.

The first ionization enthalpy of the *p*-block elements generally increases on moving from left to right along a period. It is because as we move from left to right along a period, the atomic size decreases. In a small atom, the electrons are held tightly. The larger the atom, the less strongly the electrons are held by the nucleus. The ionization enthalpy, therefore, increases with decrease in atomic size. However, there are certain exceptions, e.g., the first ionization enthalpy of a group 16 element is lower than that of a group 15 element. It is because in case of a group 15 element, the electron is to be removed from the half-filled *p*-orbitals. A comparison of first ionization energies of some elements is given in Table 18.3.

Table 18.3 : Comparison of first ionization enthalpies (kJ mol^{-1})

B	C	N	O	F	Ne
801	1086	1403	1310	1681	2080
AI	Si	P	S	CI	Ar
577	796	1062	999	1255	1521

In general the first ionization enthalpy decreases in a regular way on descending a group. It is because on descending a group, the atomic size increases. As a result the electrons are less tightly held by the nucleus and therefore, first ionization enthalpy decreases.

INTEXT QUESTIONS 18.1

1. Which of the following atoms is expected to have smaller size?
   (i) $_9$F and $_{17}$CI (ii) $_6$C and $_{14}$Si (iii) $_5$B and $_6$C (iv) $_6$C and $_7$N
2. Which atom in the following pairs of atoms is expected to have higher ionization enthalpy?
   (i) $_4$Be and $_5$B (ii) $_{16}$S and $_{17}$CI (iii) $_2$He and $_{10}$Ne (iv) $_8$O and $_{16}$S
3. Arrange the following atoms in order of increasing ionization enthalpy: $_2$He, $_4$Be, $_7$N, $_{11}$Na.
4. How does the ionization enthalpy vary in general in a group and in a period of the *p*-block elemetns?

18.5 ELECTRON GAIN ENTHALPY

When an electron is added to a neutral gaseous atom, heat enegy is either released or absorbed. The amount of heat energy released or absorbed when an extra electron is added to a neutral gaseous atom is termed as electron gain enthalpy, i.e., energy change for the process :

$$X(g) + e^{-} \longrightarrow X^{-}(g)$$

Generally for most of the atoms, the electron gain enthalpy is negative, *i.e.*, energy is released when an electron is added to a neutral gaseous atom. But for some atoms, the electron gain enthalpy is a positive quantity, *i.e.*, energy is absorbed during the addition of an electron.

Electron affinity generally becomes more negative on moving from left to right along a period. It is because on moving across a period, the atomic size decreases. As a result the force of attraction exerted by the nucleus on the electron increases.

Consequently the atom has a greater tendency to gain an electron. Hence, electron gain enthalpy becomes more negative.

On moving down a group, the electron gain enthalpy becomes less negative. This is due to the increase in atomic size and thus, less attraction for the electrons; the atom will have less tendency to gain an electron. Hence, electron gain enthalpy becomes less negative. But in the halogen group, the electron gain enthalpy of chlorine is more negative than that of fluorine. It is because the size of the F atom is very small which makes the addition of electron less favourable due to inter electronic repulsion. Similar situation exists for the first element of each group.

Table 18.4 : Electron gain enthalpies of some p-block elements in kJ mol^{-1}

B	C	N	O	F
– 0.30	– 1.25	+ 0.20	– 1.48	– 3.6
AI	Si	P	S	CI
– 0.52	– 1.90	– 0.80	– 2.0	– 3.8

18.6 ELECTRONEGATIVITY

Electronegativity is defined as a measure of the ability of an atom to attract the shared electron pair in a covalent bond to itself.

Electronegativity increases along the period and decreases down the group.

Fluorine is the most electronegative of all the elements. The second most electronegative element is *oxygen* followed by *nitrogen* in the third position.

18.7 METALLIC AND NON-METALLIC BEHAVIOUR

The elements can be broadly classified into metals and non-metals. Metals are electropositive in character i.e., they readily form positive ions by the loss of electrons, whereas non-metals are electronegative in character i.e., they readily form negative ions by the gain of electrons. The metallic and non-metallic character of *p*-block elements varies as follows:

Along the period the metallic character decreases, whereas non-metallic character increases. It is because on moving across the period, the atomic size decreases due to the increased nuclear charge and hence, ionization energy increases.

On moving down the group the metallic character increases, whereas non-metallic character, decreases. It is because on moving down a group, the atomic size increases. As a result the ionization energy decreases and tendency to lose electrons increases. Therefore, metallic character increases and non-metallic character decreases.

18.8 ANOMALOUS BEHAVIOUR OF THE FIRST ELEMENT IN EACH GROUP OF THE *p*-BLOCK

The elements comprising *s*-block and *p*-block are called main groups or representative elements.

Since the atomic radii decrease across a period, the *p*-block atoms are smaller than their nearest *s* or *d* block atoms; thus F atom has the smallest radius. Associated with small atom the 2*p* orbitals are very compact and influence the bonds formed. Interelectronic repulsions are thus more significant in 2*p* than in *np* orbitals (where n > 2). This results in the N–N, O–O and F–F bonds being comparatively weaker than the P–P, S–S and CI–CI bonds, respectively.

The small size of the atoms of N, O and F results in their high electonegativity values. This is reflected in the formation of relatively strong hydrogen bonds in X – H....Y, where X and Y may be N, O or F.

Carbon, nitrogen and oxygen differ from other elements of their respective groups due to their unique ability to form *p*π–*p*π multiple bonds. For example C=C, C≡C, N=N, O=O, etc. The later members such as Si, P, S, etc., do not form pπ–*p*π bonds because the atomic orbitals (3p) are too large to achieve effective overlapping.

The valence shell capacity of the *p*-block elements in the second period limits the coordination number to a maximum of 4. However, in compounds of the heavier members the higher coordination numbers are attainable. Thus BH_4^- and BF_4^- contrast with $[AlF_6]^{3-}$; CF_4 contrasts with $[Si\,F_6]^{2-}$ and NH_4^+ contrasts with $[PCl_6]^-$. In the heavier members of each group *d*-orbitals are available for bonding and their participation may be envisaged in the attainment of the higher coordination number.

18.9 INERT PAIR EFFECT

Among the elements of *p*-block, in groups 13,14 and 15, there is a general trend that the higher oxidation states become less stable in going down the group. Thus although boron and aluminium are universally trivalent, gallium, indium and thallium exhibit +1 state as well. In fact +1 state of thallium is very stable. Similar situations are noticed in groups 14 and 15. Though carbon is universally tetravalent, it is possible to prepare divalent germanium, tin and lead compounds. The stable state of +3 in antimony and bismuth in group 15 is another example.

Outer electron configurations of group 13, 14 and 15 elements are ns^2np^1, ns^2np^2 and ns^2np^3, respectively. They are thus expected to show the higher oxidation state of +3, +4 and +5 respectively. But the preference of heavier elements of these groups to show +1, +2 and +3 states, respectively indicate that two electrons do not participate in bonding. The reluctance of *s*-electrons to take part in chemical bonding is known as *inert pair effect*.

The so called "inert pair effect" is therefore, ascribed to two factors.

1. The increase in the promotion energy from the ground state ($ns^2 np^1$) to the valence state ($ns^1 np^2$)
2. Poorer overlap of the orbitals of the large atoms and hence poorer bond energy.

The net result is the lesser stability of higher oxidation state with the increasing atomic number in these groups. Once the involved energies are taken into consideration, the so called "inert pair effect" term loses its significance.

INTEXT QUESTIONS 18.2

1. Why does fluorine have electron gain enthalpy lower than chlorine?
2. Which atom in the following pair of atoms has greater electron gain enthalpy?

   (i) F, Cl (ii) Br, I (iii)I, Xe (iv) O, F (v) O,S
3. Give two reasons for the fact that the first element in each group of *p*-block exhibits unique behaviour.
4. Explain why oxygen exists as a gas whereas sulphur exists as a solid.
5. Mention two reasons which are responsible for the so called "inert pair effect".
6. What is the consequence of "inert pair effect" on the oxidation states of Tl and Pb?

18.10 GENERAL TRENDS IN THE CHEMISTRY OF THE P-BLOCK ELEMENTS

The *p*-block elements except noble gases react with hydrogen, oxygen and halogens to form various hydrides, oxides and halides respectively. A more or less regular trend is observed in the properties of these compounds on moving down any particular group. The noble gases have almost zero electron afinity and have very high ionization enthalpies. Therefore, under normal conditions, the atoms of noble gases have little tendency to gain or lose electrons.

18.10.1 Hydrides

The hydrides of the *p*-block elements are listed in table 18.5. They are covalent molecules and their bond angles are consistent with VSEPR theory. The angles decrease from 109.5^0 in CH_4 to 107^0 in NH_3 and 104^0 in H_2O.

These hydrides are volatile in nature. Generally their acid strength increases from left to right and from top to bottom.

Table 18.5 : Hydrides of p-block elements

Group				
13	14	15	16	17
B_2H_6	CH_4	NH_3	H_2O	HF
$(AIH_3)x$	SiH_4	PH_3	H_2S	HCI
Ga_2H_6	GeH_4	AsH_3	H_2Se	HBr
InH_3	SnH_4	SbH_3	H_2Te	HI
TIH_3	PbH_4	BiH_3	H_2Po	–

18.10.2 Oxides

p-Block elements form a number of oxides on reacting with oxygen. The oxides E_2O_n ($n = 3$, 5 or 7) are the highest oxides formed by the elements in the groups 13, 15 or 17 respectively. The oxides EO_n ($n = 2$, 3 or 4) are formed by the elements in groups 14, 16 or 18 respectively. Thus, nitrogen forms NO, NO_2, N_2O_3, and N_2O_5; phosphorus forms P_4O_6 and P_4O_{10}, xenon forms XeO_3 and XeO_4.

- In any particular group, the basic nature of the oxides (oxidation state of the element remaining same) increases with increase in atomic number.
- In a particular period the acidity increases with increase in the oxidation state of the element.

18.10.3 Halides

A review of the properties of halides of *p*-block elements reveals that most of them are covalent halides. In a group the covalent character of halides decreases down the group. Where an element exhibits more than one oxidation state, the covalent character of a halide increases with the increase in the oxidation state of the element forming halides. For example, whereas $PbCl_2$ is an ionic halide, $PbCl_4$ is covalent. Similarly the covalent character of halides of a particular element increases from fluoride to chloride to bromide.

Covalent halides are generally gases, liquids or solids with low melting points. These halides usually hydrolyse to give the oxoacid of the element. For example $SiCl_4$ reacts vigorously with water

Notes

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

In general the chlorides, bromides and iodides are found to be more stable with lower oxidation state of the element, whereas fluorides are formed in the higher oxidation states. The halides are usually formed by the direct union of the element with the halogen. For example

$$C_{(s)} + Cl_2(g) \longrightarrow CCl_4(l)$$

$$2As_{(s)} + Cl_2(g) \longrightarrow AsCl_3(s)$$

INTEXT QUESTION 18.3

1. Which of the following oxides is the most acidic?

   (i) Al_2O_3 (ii) CO_2 (iii) SO_2

2. Which of the following hydrides of main group elements is the most acidic?

   (i) H_2Se (ii) H_2O (iii) HCl (iv) HI

3. Arrange the following in the increasing order of covalent character.

   $SiCl_4$, CCl_4, $SnCl_4$, $GeCl_4$

4. What happens when $SiCl_4$ reacts with water. Write complete chemical equation for the reaction.

5. How do the bond angles vary among the following hydrides NH_3, PH_3, AsH_3, SbH_3

6. Give equations for the formation of the following from the elements:

   (i) Al_2O_3 (ii) $SiCl_4$ (iii) CCl_4

7. Which is more covalent in each of the following pairs?

   (i) $AlCl_3$ and BCl_3 (ii) $PbCl_2$ and $PbCl_4$

WHAT YOU HAVE LEARNT

- The elements of groups 13, 14, 15, 16, 17 and 18 constitute the *p*-block of the periodic table.
- Some of the elements of the *p*-block are widely and abundantly found in nature, viz., oxygen, silicon, aluminium, etc.
- Many physical and chemical properties of the *p*-block main group elements show periodic variation with atomic number.

- The *ionization enthalpy* is the energy required to remove the outermost electron from a neutral gaseous atom.
- The electron *gain enthalpy* is the energy change when a neutral atom in a gaseous state accepts an electron.
- *Electronegativity* is the ability of an atom in a molecule to attract the electrons of a covalent bond to itself.
- The top element in each group shows a unique behaviour.
- The reluctance of *s*-electrons to take part in bond formation is known as "inert pair effect".
- *p*-Block elements form a number of oxides on reacting with oxygen.
- Most of the elements of the *p*-block form covalent halides.
- General characteristies of the *p*-block hydrides, halides and oxides.

TERMINAL EXERCISE

1. Which groups of the 'periodic table' constitute *p*-block?
2. How does the magnitude of ionization energy of an atom vary along the group in the periodic table?
3. How does electronegativity change along a row of elements in the periodic table?
4. Explain 'Metallic character decreases along a period but increases on moving down a group'.
5. Discuss the trends in the chemistry of *p*-block elements with respect to:

   (i) acidic and basic nature of the oxides;

   (ii) ionic and covalent nature of the hydrides.
6. What is the cause of anomalous behaviour of the top element in each group of the *p*-block elements.
7. What is 'inert pair effect'? Is there any inert pair present or is it a misnomer?
8. Comment on the nature (ionic/covalent) of the hydrides of the *p*-block elements
9. How does the covalent character of halides of an element change with oxidation state of the element?
10. Which is likely to form higher halides with an element exhibiting variable oxidation state, F_2 or Cl_2?

ANSWERS TO INTEXT QUESTIONS

18.1

1. (i) $_9F$ (ii) $_6C$ (iii) $_6C$ (iv) $_7N$
2. $_4Be$ (ii) $_{17}Cl$ (iii) $_2He$ (iv) $_8O$
3. Na < Be < N < He
4. In a group, it decreases down the group and it usually increases along a period.

18.2

1. The unexpectedly low value of electron gain enthalpy for F as compared to that of Cl atom may be attributed to the extremely small size of F atom vis-a-vis Cl atom. The addition of an electron produces a negative ion which has a high electron density and leads to increased interelectronic repulsions.
2. (i) Cl (ii) Br (iii) I (iv) F (v) S
3. (i) Small size (ii) absence of *d*-orbitals
4. Because oxygen can form multiple bonds ($O = O$).
5. (i) Lower bond energy in the compounds of heavier atoms and (ii) the higher energy involved in promotion from the ground state (s^2p^1) to the valence state (s^1p^2).
6. Lower oxidation states become more stable.

   For Tl, +1 and for Pb, +2.

18.3

1. SO_2
2. HI
3. $SnCl_4 < Ge\,Cl_4 < SiCl_4 < CCl_4$
4. $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$
5. The bond angle decreases from 107° to almost 90°.
6. (i) $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3\,(s)$

   (ii) $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$

   (iii) $C(s) + 2Cl_2(g) \rightarrow CCl_4(l)$
7. (i) BCl_3 (ii) $PbCl_4$

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19

p-BLOCK ELEMENTS AND THEIR COMPOUNDS – I

You have already studied the general characteristics of the p-block elements in the previous lesson. Now, we shall discuss some of the important elements and their compounds. Groups 13, 14 and 15 of the periodic table will be considered in this lesson and groups 16, 17 and 18 in the next lesson.

OBJECTIVES

After reading this lesson, you will be able to

- describe some general characteristics of Group 13, 14 and 15;
- describe the methods of preparation of boric acid, borax, diborane and boron trifluoride;
- explain the structure of diborane,boric acid and boron trifluoride;
- list the uses of borax, boric acid and boron trifluoride;
- list examples of double salts;
- describe the preparation and uses of aluminium trichloride and potash alum;
- explain the structure of aluminium trichloride;
- list the allotropes of crystalline carbon;
- compare the structures of diamond and graphite;
- explain the structure and properties uses of carbon monoxide, carbon dioxide and silicon dioxide;
- compare hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride;
- describe preparation and uses of silicon carbide;

- describe silicones, silicates and zeolite;
- explain the preparation properties and uses of nitrogen;
- explain the processes for manufacture of ammonia and nitric acid;
- explain allotropic forms of phosphorons;
- list the properties and uses of ammonia and nitric acid;
- explain nitrogen fixation: natural and industrial and
- list a few nitrogenous, phosphatic and mixed fertilizers with their importance.

19.1 SOME GENERAL CHARACTERISATICS OF ELEMENTS OF GROUP 13

This group consists of B, Al, Ga, In and Tl.

All these elements exhibit a group valency of three, but because of the very large input of energy that is necessary to form the 3-valent ions–the sum of the first three ionisation energies–their compounds when anhydrous are either essentially covalent or contain an appreciable amount of covalent character. Boron never forms a B^{3+} ion since the enormous amount of energy required to remove three electrons from a small atom.

The electronic configurations of the boron and aluminium atoms are similar in as much as the penultimate shell has a noble gas configuration. whereas the penultimate shell of the gallium, indium and thallium atoms contains eighteen electrons. (Table 19.1)

Boron, which is non-metallic, and aluminium, which is clearly metallic, are best considered separately. Gallium, indium and thallium are weakly metallic.

Table 19.1: Physical properties of Group 13 elements

	Atomic Number	**Electronic Configuration**	**Ionisation Energy/ $kJmol^{-1}$**			**Standard Electrode Potential/V**	**Atomic Radius/nm**	**Ionic Radius/nm**	**M.P. /°C**	**B.P. /°C**
			First	**Second**	**Third**					
B	5	2.3 $1s^2 2s^2 2p^1$	800	2427	3650		0.080 Estimated value	0.020	2300	3930
Al	13	2.8.3 $\ldots 2s^2 2p^6 3s^2 3p^1$	578	1816	2744	–1.66	0.125	0.050	660	2470
Ga	31	2.8.18.3 $\ldots 3s^2 3p^6 3d^{10} 4s^2 4p^1$	579	1979	2962	–0.52	0.125	0.062	29.8	2400
In	49	2.8.18.18.3 $\ldots 4s^2 4p^6 4d^{10} 5s^2 5p^1$	558	1820	2705	–0.34	0.150	0.081	157	2000
T1	81	2.8.18.32.18.3 $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^1$	589	1970	2880	+0.72	0.155	0.095	304	1460

Occurrence and Abundance

Boron is a fairly rare element, but it is well known because it occurs as concentrated deposits of borax $Na_2B_4O_7.10H_2O$ and kernite $Na_2B_4O_7.4H_2O$.

Aluminium is the most abundant metal, and the third most abundant element (after oxygen and silicon) by weight in the earth's crust (Table 19.2). It is well known and is commercially important. Aluminium metal is produced on a vast scale. Primary production was 17.6 million tonnes, and an additional 4 million tonnes is recycled. The most important ore of aluminium is bauxite. This is a generic name for several minerals with formulae varying between $A1_2O_3 \bullet H_2O$ and $Al_2O_3{\cdot}3H_2O$.

Table 19.2: Abundance of the elements in the earth's crust by weight

	ppm	Relative abundance
B	9	38
Al	83000	3
Ga	19	33
In	0.24	63
Tl	0.5	60

Gallium is twice as abundant as boron, but indium and thallium are much less common. All three elements, Ga, In and Tl, occur as sulphides. Ga. In and Tl are not very well known.

18.1.1 Boron

Boron can be obtained as an amorphous brown powder by treating borax with hydrochloric acid, igniting the boric acid, H_3BO_3 obtained, to give the oxide, B_2O_3, and finally reducing the latter with magnesium at a high temperature:

$$B_2O_3(s) + 3Mg(s) \longrightarrow 2B(s) + 3Mg\ O(s)$$

It is used in the construction of high impact-resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.

A crystalline form of boron can be obtained by thermal decomposition of boron tri-iodide on a tantalum filament:

$$2BI_3(s) \longrightarrow 2B(s) + 31_2(s)$$

Properties of boron

Amorphous boron is a very reactive element combining directly with oxygen, sulphur, nitrogen and the halogens to give respectively, an oxide, sulphide, nitride and a halide.

Reactions of Boron

Pure crystalline boron is very unreactive. However, it is attacked at high temperatures by strong oxidizing agents such as a mixture of hot concentrated H_2SO_4 and HNO_3, or by sodium peroxide. In contrast, finely divided amorphous boron (which contains between 2% and 5% of impurities) is more reactive. It burns in air or oxygen, forming the oxide. It also burns at white heat in nitrogen, forming the nitride BN. This is a slippery white solid with a layer structure similar to graphite. Boron also burns in the halogens, forming trihalides. It reacts directly with many metals, forming borides, which are hard and refractory. It reduces strong HNO_3 and H_2SO_4 slowly, and also liberates H_2 from fused NaOH. At red heat it will reduce steam to hydrogen:

$$2B(s) + 3H_2O(l) \longrightarrow B_2O_3(s) + 3H_2(g)$$

Some reactions of amorphous boron

Reaction	Comment
$4B + 3O_2 \rightarrow 2B_2O_3$	At high temperature
$4B + 3S \rightarrow B_2S_3$	At 1200°C
$2B + N_2 \rightarrow 2BN$	At very high temperature
$2B + 3F_2 \rightarrow 2BF_3$	At high temperature
$2B + 3Cl_2 \rightarrow 2BC1_3$	
$2B + 3Br_2 \rightarrow 2BBr_3$	
$2B + 3I_2 \rightarrow 2BI_3$	
$2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$	When fused with alkali
$2B + 2NH_3 \rightarrow 2BN + 3H_2$	At very high temperature
$B + M \rightarrow M_x.B_Y$	Many metals form borides (not group I) often nonstoichiometric

Notes

Reactions of Aluminium

Reaction with water and air

Thermodynamically Al should react with water and with air, but in fact, it is stable in both. The reason is that a very thin oxide film forms on the surface which protects the metal from further attack. This layer is only 10^{-4} to 10^{-6} mm thick. If the protective oxide covering is removed, for example by amalgamating with mercury, then the metal readily decomposes cold water, forming Al_2O_3 and liberating hydrogen.

Aluminium articles are often 'anodized' to give a decorative finish. This is done by electrolysing dilute H_2SO_4 with the aluminium as the anode. This produces a much thicker layer of oxide on the surface (10^{-2} mm). This layer can take up pigments, thus colouring the aluminium.

Aluminium burns in nitrogen at high temperatures, forming AlN.

Reaction with acids and alkalis

Aluminium dissolves in dilute mineral acids liberating hydrogen.

$$2Al + 6HCl \rightarrow 2Al^{3+} + 6Cl^- + 3H_2$$

However, concentrated HNO_3 renders the metal passive because it is an oxidizing agent, and produces a protective layer of oxide on the surface. Aluminium also dissolves in aqueous NaOH (and is therefore amphoteric), liberating hydrogen and forming aluminates.

$$2Al + 2NaOH + 6H_2O \rightarrow \underset{\text{Sodium aluminate}}{NaAl(OH)_4 \text{ or } NaAlO_2{\cdot}2H_2O} + 3H_2$$

Uses of aluminium

1. As structural metals in aircraft, ships, cars, and heat exchangers.
2. In buildings (doors, windows, cladding panels and mobile homes).
3. Container such as cans for drinks, tubes for toothpaste etc. and metal foil.
4. For cooking utensils.
5. To make electric power cables (on a weight for weight basis they conduct twice as well as copper).
6. Finely divided aluminium powder is called 'aluminium bronze', and is used in preparing aluminium paint.

19.2 COMPOUND BORON AND ALUMINIUM

Boron and aluminium are the first two members of Group 13 of the periodic table. Though the outermost electronic configurations of boron and aluminium are similar yet there is a big difference between the properties of their compounds. This will become clear when we study the compounds of boron and aluminium.

19.2.1 Boric Acid

Preparation : Boric acid (also called orthoboric acid) H_3BO_3, $[B(OH)_3]$ is prepared by the action of sulphuric acid on concentrated solution of borax ($Na_2B_4O_7 . 10H_2O$). Boric acid separates as white flaky crystals.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$

Properties and Structure : Boric acid is a white crystalline solid. It is soluble in water. It behaves as a weak Lewis acid rather than a protonic acid because it combines with hydroxyl ions (OH^-) of water to liberate hydronium ions (H_3O^+). Thus

$$B(OH)_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$$

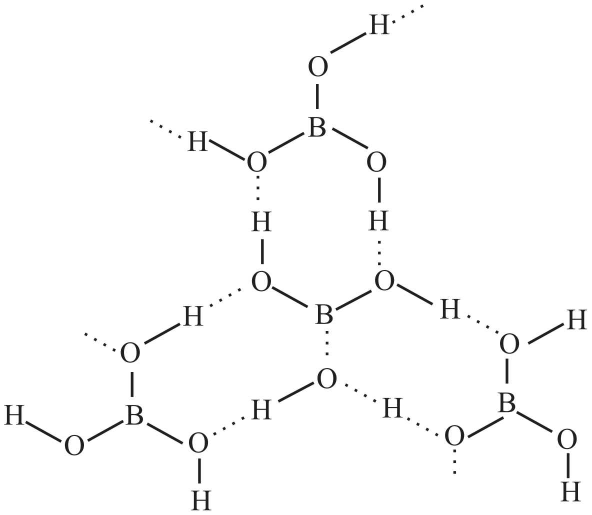


Fig. 19.1: *Structure of boric acid; the dotted lines represent hydrogen bonds*

When heated, it decomposes to metaboric acid and finally to boric anhydride (or boric oxide) at red heat

$$2B(OH)_3 \xrightarrow[H_2O]{375K} 2BO(OH) \xrightarrow[-H_2O]{\text{Red heat}} B_2O_3 (\uparrow) \text{ (Boric oxide)}$$

In boric acid, $B(OH)_3$ units are linked by hydrogen bonds to give two dimensional sheets (Fig. 19.1). The sheets are held together by weak van der Waals forces which are responsible for the cleavage of solid structure into flakes.

Uses: Boric acid is used:

(i) as an antiseptic,

(ii) as a food preservative, and

(iii) in making enamels, pottery glazes and glass.

19.2.2 Borax, $Na_2B_4O_7.10H_2O$

In crude form borax occurs as *tincal* in dried up lakes of India. It is also prepared from the mineral colemanite, $Ca_2B_6O_{11}$ by the action of concentrated solution of sodium carbonate

$$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow 2CaCO_3 + Na_2B_4O_7 + 2Na\,BO_2$$

Borax is crystallised from the filtrate. Borax is a white crystalline solid of the formula $Na_2B_4O_7$. $10H_2O$. On heating it loses water of crystallisation.

It is used:

(i) as an alkaline buffer in dyeing and bleaching processes

(ii) as a preservative

(iii) in the manufacture of optical and borosilicate glasses

(iv) as a flux, and

(v) in making glazes for pottery and tiles.

19.2.3 Diborane, B_2H_6

Diborane is the most important hydride of boron.

Preparation:

It is prepared by the following methods:

(i) By the action of lithium aluminium hydride on boron trichloride

$$4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(ii) By the action of lithium hydride on boron trifluoride

$$8BF_3 + 6LiH \rightarrow B_2H_6 + 6LiBF_4$$

Properties:

- Diborane is a toxic gas and has a foul smell.
- It burns in oxygen to give enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O; \ \Delta H = -1976 \text{kJ mol}^{-1}$$

- It is readily hydrolysed by water

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

Structure : The molecular structure of diborane is shown below. The two boron atoms and the four terminal hydrogen atoms lie in one plane, the two bridging hydrogen atoms lie symmetrically above and below the plane. If we consider the bonding situation in B_2H_6, there are eight B–H bonds but only twelve valence electrons. Obviously there are not enough electrons to fill all the available orbitals to form eight normal covalent (two-centre) bonds. Thus bonding in diborane is described in terms of two multi centre bonds, i.e., 3c–2e or three centre two electron B–H–B bonds and four normal B–H bonds.

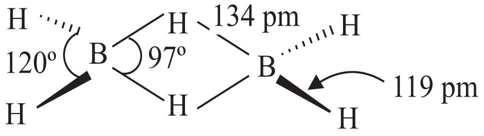


Fig. 19.2 : *Structure of diborane, B_2H_6*

19.2.4 Boron Trifluoride

Boron forms halides BX_3 (X = F, Cl, Br, I). All these halides with exception of fluoride, are formed by the action of appropriate halogen on boric oxide at high temperature. Boron trifluoride is formed by the action of hydrofluoric acid on boron oxide. Thus

$$B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$$

BF_3 hydrolyses according to the following equation

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HBF_4$$

BF_3 acts as an electron acceptor (Lewis acid) since B does not have an octet of electrons in its valence shell; infact it has a sextet. It forms complexes with nitrogen and oxygen donors, e.g. NH_3 and ether, thus completing the octet of boron.

$$F_3B \leftarrow NH_3 \quad \text{and} \quad F_3B \leftarrow OEt_2$$

Boron trifluoride is used as a catalyst in Friedel-Crafts reaction such as alkylation and acylation and in polymerization reactions.

The structure of boron trifluoride is shown in Fig 19.3:

B–F bond in BF_3 has a multiple bond character since its structure is a resonance hybrid of three resonating structures.

Note that in the resonating structures boron completes its octet.

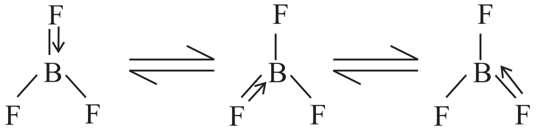


Fig 19.3 : *Resonatimg structures of boron trifluoride*

19.2.5 Aluminium trichloride

Aluminium trichloride exists as a dimer as Al_2Cl_6 at room temperature and as a monomer at high temperatures and is made by passing hydrogen chloride or chlorine over heated aluminium under anhydrous condition.

$$2Al + 6HCl \rightarrow Al_2Cl_6 + 3H_2$$

$$2Al + 3Cl_2 \rightarrow Al_2Cl_6$$

When pure, it is a white solid which sublimes at 453K. Aluminium has only three valence electrons. When these are used to form three covalent bonds, the atom has only six electrons in its valence shell. Since it is electron deficient it, therefore, exists as a dimer. The aluminium atoms complete their octets by dative bonding from two chlorine atoms. The arrangement of chlorine atoms about each aluminium atom is roughly tetrahedral. The structure of the dimer is shown in Fig. 19.4.

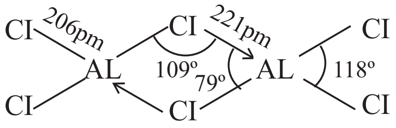


Fig.19.4 : *Structure of* $AlCl_3$

When treated with water it gives hydrated aluminium ions and Cl^- ions:

$$Al_2\,Cl_6 + 6H_2O \rightarrow 2[Al\,(H_2O)_6]^{3+} + 6Cl^-$$

Anhydrous aluminium chloride is used as a catalyst in Friedel-Crafts reaction because of its Lewis acid character.

19.2.6 Double Salts: Alums and Potash Alum

When two salts capable of indendent existence are mixed and the solution of the mixture is allowed to crystallise, crystals comprising both the salts are characteristically formed. However, in solution all the ions exist freely. Such substances are called double salts. For example, when a solution containing potassium sulphate and aluminium sulphate is allowed to crystallise, transparent octahedral crystals of potash alum, $K^+ Al^{3+} (SO^{2-}{}_4)_2 \cdot 12\,H_2O$ are obtained. The solid contains $[K(H_2O)_6]^+$, $[Al\,(H_2O)_6]^{3+}$ and SO_4^{2-} ions and it is a double salt since it gives the tests of its constituent ions in solutions. The double sulphate with similar composition and properties are called alums.

It is possible to replace the trivalent aluminium cation by trivalent metal ion of the similar ionic size, e.g. Ti^{3+}, Cr^{3+}, Fe^{3+} and Co^{3+}. It is also possible to prepare a series of alums in which potassium ion is replaced by ammonium ion, NH_4^+.

The alums are isomorphous, a few typical ones are given below:

Ammonium alum	$(NH_4)\,Al\,(SO_4)_2 \cdot 12H_2O$
Chrome alum	$KCr\,(SO_4)_2 \cdot 12H_2O$
Ammonium chrome alum	$(NH_4)Cr\,(SO_4)_2 \cdot 12H_2O$
Ferric alum	$K\,Fe\,(SO_4)_2 \cdot 12H_2O$

Potash alum, $K\,Al\,(SO_4)_2 \cdot 12H_2O$, is by far the most important of all the alums. It is used as a mordant in dyeing industry and also in purifying water. (Often it is formulated as $K_2SO_4 \cdot Al_2\,(SO_4)_3 \cdot 24\,H_2O$).

INTEXT QUESTIONS 19.1

1. Write the formula of the following:
   (i) Boric acid (ii) Borax
2. Write one reaction for the preparation of diborane.
3. What is the general formula of alums?
4. Write the formula of anhydrous solid aluminium trichloride and its structure.
5. Mention one use each of
   (i) borax (ii) boric acid (iii) boron trifluoride
5. Why aluminium become non-reactive after reacting with HNO_3.
6. Orthoboric acid is monoprotonic or triprotonic.

19.3 SOME GENERAL REMARKS ABOUT GROUP 14

All these elements exhibit a group valency of four, but because an enormous amount of energy is needed to remove four electrons from their atoms, they form compounds which are predominantly covalent. Similarly the gain of four electrons to give the 4-valent anion is energetically impossible.

Germanium, tin and lead form 2-valent compounds in which the two s electrons are inert (inert pair effect). The stability of this state relative to the 4-valent state increases steadily from germanium to lead, i.e. 2-valent germanium compounds tend to be strongly reducing and revert to the 4-valent state, while for lead this is the predominant valency state. 2-valent compounds of tin and lead are often predominantly ionic.

Carbon is non-metallic and so too is silicon; germanium has properties of both metals and non-metals (it is a metalloid), while the elements tin and lead are definitely metallic. There is a smooth transition from non-metallic to metallic properties on passing down the series silicon, germanium, tin and lead, but the first member carbon differs considerably from silicon. The chemistry of silicon is very similar to that of boron, its diagonal neighbour in the Periodic Table.

Table 19.3: Physical properties of Group-14 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm		M.P. /°C	B.P. /°C
				M^{2+}	M^{4+}		
C	6	2.4 $1s^22s^22p^2$	0.077				3580 (subl.)
Si	14	2.8.4 $\dots 2s^22p^63s^23p^2$	0.117		0.041	1410	2360
Ge	32	2.8.18.4 $\dots 3s^23p^63d^{10}4s^24p^2$	0.122	0.093	0.053	937	2830
Sn	50	2.8.18.18.4 $\dots 4s^24p^64d^{10}5s^25p^2$	0.140	0.112	0.071	232	2270
Pb	82	2.8.18.18.8.4 $\dots 5s^25p^65d^{10}6s^26p^2$	0.154	0.120	0.084	237	1744

The chemistry of carbon is dominated by its tendency to form chains and rings of carbon atoms in which other atoms, particularly hydrogen. play an important part. The chemistry of silicon is completely different.

Chemical properties of carbon

Carbon in any form will react with oxygen at a sufficiently high temperature to give carbon dioxide; in a deficiency of oxygen, carbon monoxide is formed as well. Charcoal will combine directly with sulphur, some metals and fluorine.

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$

$$Ca(s) + 2C(s) \longrightarrow Ca^{2+}(C{\equiv}C)^{2-}(s)$$

$$C(s) + 2F_2(g) \longrightarrow CF_4(g)$$

It will reduce steam, forming water gas and many oxides of metals; these reductions are of industrial importance.

It is not attacked by dilute acids, but concentrated nitric acid and sulphuric acid are reduced if warmed with carbon according to the equations

$$C(s) + 4HNO_3(aq) \longrightarrow 2H_2O(l) + 4NO_2(g) + CO_2(g)$$

$$C(s) + 2H_2SO_4(l) \longrightarrow 2H_2O(l) + 2SO_2(g) + CO_2(g)$$

19.4 CARBON AND SILICON

Carbon and silicon belong to Group 14 of the periodic table. Both elements show significant differences in their chemistry. There are thousands of hydrocarbons (alkanes and other compounds of carbon and hydrogen) but only a few silanes (compounds of silicon and hydrogen are known). It is because carbon has the unique ability to form compounds in which the carbon atoms are bonded to each other in chains or rings. This property is called *catenation* which is due to the fact that C–C bond is much stronger than Si- Si bond.

19.4.1 Allotropic Forms of Carbon

Diamond and Graphite : Structures and Properties

Diamond and graphite, both are crystalline forms of carbon. But they are structurally different. Due to the difference in the arrangement of carbon atoms, they show different properties. In diamond, each carbon atom is sp^3 hybridized and is linked to four other carbon atoms by strong covalent bonds in a tetrahedral fashion. It gives rise to a three-dimensional arrangement (Fig.19.5). On the other hand, in graphite, the carbon atoms are arranged in layers. In each layer a particular carbon atom is sp^2 hybdridized and is linked to three other carbon atoms in a hexagonal arrangement. The fourth electron is free and does not participate in bonding. The different layers are held together by weak van der Waals forces (Fig 19.6).

Chemically speaking diamond is unreactive and burns in oxygen only if heated above 800^0C, forming carbon dioxide. It reacts with fluorine (but not with chlorine) at 973 K giving carbon tetrafluoride. Alkalies and acids have no action on diamond. It is the hardest natural substance.

Graphite, on the other hand, is reactive. It burns in air at 873 K to form CO_2. It is not attacked by dilute acids but concentrated sulphuric acid reacts with graphite to give graphite bisulphate in solution. It does not react with chlorine also.

Diamond is used for cutting and grinding hard substances such as rocks, glass, etc., and in die for drawing wire for watch springs and lamp filaments. Beside all these, diamond is widely used in jewellery.

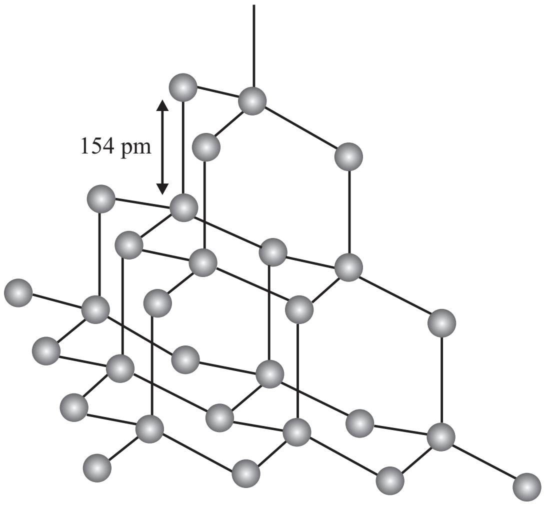


Fig. 19.5 : *Structure of diamond*

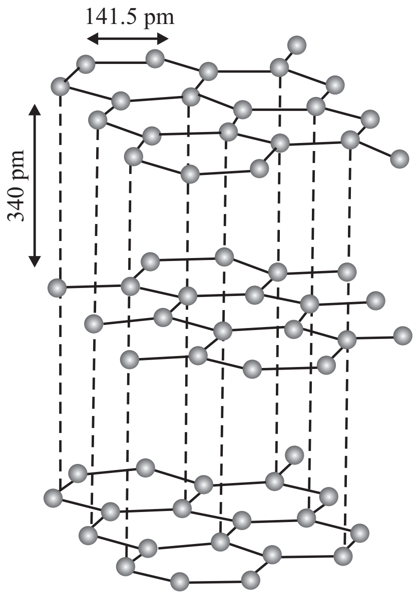


Fig. 19.6 : *Structure of graphite*

Graphite is used as electrodes,as lubricant, for making crucibles, for casting of metals, for lead pencils and as a constituent of heat resistant paints.

Fullerenes

Fullerene, a newly discovered allotrope of carbon is called "Buckminster Fullerene" after the name of American architect Buckminster Fuller. The most common Fullerene molecule has 60 carbon atoms and the carbon atoms are linked to create the shape of a hollow soccer ball. The outer surface of fullerenes can be altered by chemical reactions.

19.4.2 Oxides of Carbon and Silicon

Structure

Carbon forms two oxides, viz., carbon monoxide and carbon dioxide. The bonding in carbon monoxide may be represented as, three electron pairs shared between the two atoms. The three electron pairs consist of one sp hybridized σ bond and two π bonds.

$:C\,\vdots\vdots\,O:$ or $:C\overset{\leftarrow}{=}O:$

The structure of carbon dioxide on the other hand is linear O=C=O. There are two σ bonds and two π bonds in the molecule CO_2. The carbon atom uses sp hybrid orbitals to form σ bonds with oxygen atoms. The remaining two 2p orbitals of carbon overlap with 2p orbitals one each from the two O atoms to form the π bonds

$$O = C = O$$

Silicon also forms two oxides : SiO and SiO_2. Not much is known about silicon monoxide as its existence is only known at high temperatures. Silica (SiO_2) is widely found as sand and quartz.

Properties

Carbon monoxide is a neutral oxide. It is a colourless, odourless and a poisonous gas and burns with a blue flame. It is toxic because it forms a complex with the haemoglobin in the blood which prevents the haemoglobin from carrying oxygen around the body. This leads to oxygen deficiency resulting in unconsciousness or death. Carbon monoxide is an important industrial fuel and is also a strong reducing agent.

Carbon dioxide is an acidic oxide. It is a colourless and odourless gas and can be liquified under pressure at low temperature. Solid carbon dioxide is called dry ice.

SiO_2 is an acidic oxide and is unreactive in all its forms. It shows very limited reactions. It dissolves slowly in aqueous alkalies and more rapidly in fused alkalies or fused carbonates forming silicates. Silica also reacts with fluorine and HF to form silicon tetrafluoride

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

Uses of oxides of carbon

Carbon monoxide

(i) It is used as a reducing agent in metallurgical processes to reduce metal oxides. For example, in the blast furnace, it is used to reduce iron oxide to iron.

$$Fe_2O_3\ (s) + 3CO\ (g) \longrightarrow 2Fe\ (s) + 3CO_2(g)$$

(ii) In the presence of a catalyst, it can combine with hydrogen to give methanol (CH_3OH).

(iii) It forms carbonyl compounds. The nickel carbonyl $Ni(CO)_4$ is involved in the refinement of nickel.

(iv) It is used as a fuel.

(v) It is used in the synthesis of several organic compounds.

The main uses of carbon dioxide are as follows:

(i) Solid carbon dioxide also called *dry ice* is used as a refrigerant because when it is cooled at atmospheric pressure, it condenses into a solid rather than as a liquid. This solid sublime at –78°C

(ii) It is used in the production of *carbonated drinks.*

(iii) It is used in the production of washing soda ($Na_2CO_3.10H_2O$) and baking soda ($NaHCO_3$).

SiO_2 is a high melting solid and it exists in twelve different forms, each of which, has different structure. The main forms are quartz and cristobalite, each of which has a different structure at different temperatures. In all these forms silicon is tetrahedrally surrounded by four oxygen atoms and each oxygen is attached to two silicon atoms. The sp^3 orbitals of Si overlap with 2p orbitals of O atoms. Each corner of tetrahedron is shared by other tetrahedra. This gives an infinite structure – a macromolecule.

19.4.3 Halides of Carbon and Silicon

Carbon and silicon form tetrahalides like CCl_4 and $SiCl_4$, respectively. In the tetrahalides of these elements there are four covalent bonds, with a tetrahedral arrangement; the central atom is sp^3 hybridized. Carbon tetrachloride can be rightly called as tetrachloromethane and silicon tetrachloride as tetrachlorosilane.

- Carbon tetrachloride is prepared by the action of chlorine on carbon disulphide in the presence of a catalyst (usually $MnCl_2$)

$$CS_2 + 3Cl_2 \xrightarrow{MnCl_2} CCl_4 + S_2Cl_2$$

Silicon tetrachloride, $SiCl_4$, is formed by heating amorphous silicon in a current of dry chlorine.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

It can also be obtained by passing dry chlorine over an intimate mixture of silica and carbon strongly heated in a crucible. Thus

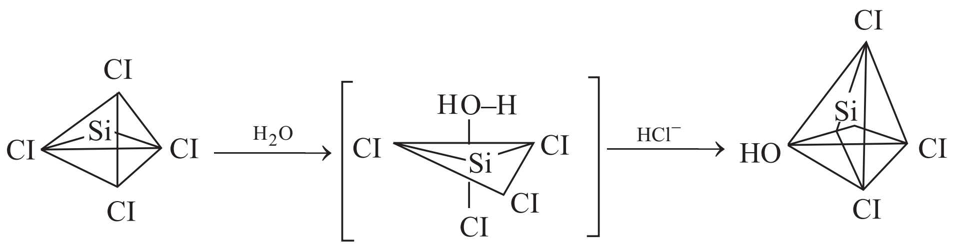
$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

Carbon tetrachloride is not hydrolysed by water whereas silicon tetrachloride is readily hydrolysed.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{silicic acid}}{Si(OH)_4} + 4HCl$$

The difference in the behaviour of CCl_4 and $SiCl_4$ towards water can be explained as follows.

A lone pair of electrons from the O atom of H_2O molecule is donated to the empty 3*d* orbital on Si. Subsequently one of the hydrogen atoms of water molecule combines with a chlorine atom of $SiCl_4$. This process goes on till all the chlorine atoms are replaced by –OH groups.



Since, there is no *d*-orbital in carbon in CCl_4 does not hydrolyse.

Silicon forms complex ion like SiF_6^{2-} but carbon does not form similer ions like CF_6^{2-}. It is because unlike carbon there are empty 3*d* orbitals in silicon. The availabity of *d* orbitals is responsible for the ability of silicon and not carbon to form complex ion SiF_6^{2-}

19.4.4 Silicon Carbide, SiC

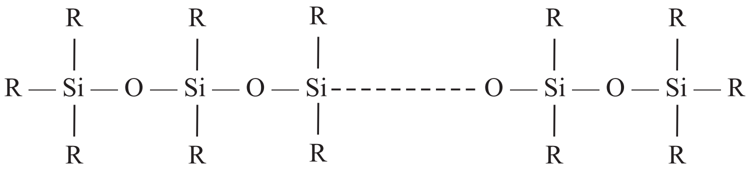
Silicon carbide (SiC) is commonly known as *carborundum*. It is extremely hard and chemically a very stable material. It is made by heating silica with excess of carbon in an electric furnace

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

In silicon carbide, there are three dimensional arrays of Si and C atoms, each atom of Si or C is tetrahedrally surrounded by four of the other type. Thus, this structure is very much similar to that of diamond. Silicon carbide or carborundum is widely used as an abrasive.

19.4.5 Silicones

These compounds are polymeric, the polymer chain containing alternately linked silicon and oxygen atoms. Alkyl or aryl groups, e.g. CH_3 or C_6H_5, are attached to the polymer backbone by means of covalent bonds to the silicon atoms. A typical silicone has the formula:



$$R-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}----------O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-R$$

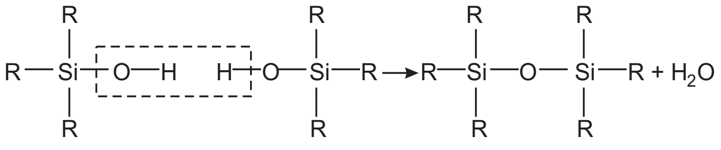
where R is an alkyl or aryl group.

Silicones are obtained by reacting a chloroalkane or a chlorobenzene with silicon in the presence of a copper catalyst and at a temperature of about 300°C. A mixture of alkyl or aryl chlorosilanes results:

$$RCl + Si \xrightarrow{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$$

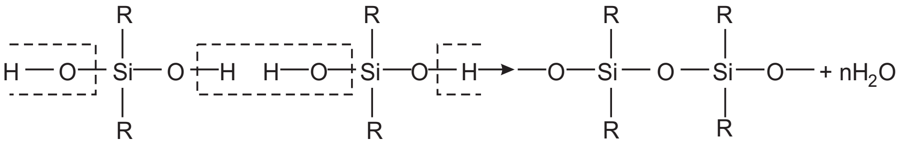
After fractional distillation, the silane derivatives are hydrolysed and the ‘hydroxides’ immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:

$$R_3SiCl + H_2O \longrightarrow R_3SiOH + HCl$$



a dimer

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$



a polymer chain

The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

Hydrolysis of the trichlorosilane derivative gives a two-dimensional structure. By blending a mixture of chlorosilanes before hydrolysis, it is possible to produce polymers of varying chain length, R_3SiOH acting as a chain stopper and $RSi(OH)_3$ as a cross-linking agent.

The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent. Silicone fluids are thermally stable and their viscosity alters very little with temperature, and silicone rubbers retain their elasticity at much lower temperatures than ordinary rubber.

19.4.6 Silicates

The tendency of silicon to form single covalent bonds with oxygen atoms has been observed in the structures of silica and polysilicic acid. These structures and also those of a bewildering variety of silicates arc now readily understood in terms of the linking together of tetrahedral SiO_4 units. Paining considers the silicon-oxygen bond to be about 50 per cent ionic, and it is sometimes convenient to discuss the structures of silicates in terms of Si^{4+} ions tetrahedrally surrounded by four much larger oxygen atoms. Examples of some typical silicates are given below (Fig. 19.7).

Silicates containing discrete SiO_4^{4-} anions

Orthosilicates contain the simple SiO_4^{4-} ion, one example being beryllium orthosilicate, $(Be^{2+})_2SiO_4^{4-}$. As mentioned above, the SiO_4^{4-} group is tetrahedral, as would be expected.

19.4.6.1 Silicates containing $Si_2O_7^{6-}$ anions (one oxygen atom shared)

When one oxygen atom is shared between two tetrahedra, the pyrosilicate anion, $Si_2O_7^{6-}$ is the result. A typical pyrosilicate is $(Sc^{3+})_2Si_2O_7^{6-}$.

19.4.6.2 Silicates containing extended anions (two oxygen atoms shared) and (d))

When each tetrahedron shares two oxygen atoms, it is possible to have closed ring anions such as $Si_3O_9^{6-}$. Another possibility is the formation of infinite chains, the formula of these anions approximating to $(SiO_3)n^{2n-}$ Examples of silicates containing these anions are $Be^2Ti^4Si_3O_9^{6-}$ and $Ca^{2+}Mg^2(SiO_3^{2-})_2$.

When each tetrahedron shares three oxygen atoms, silicates in the form of extended sheets result. The empirical formula of these polysilicate anions is $SiO_{2\frac{1}{2}}^-$ or $Si_4O_{10}^{4-}$ Anions of this type are found in micas and clays and account for their ready cleavage into thin slices.

(a) The structure of the orthosilicate anion	(a)	$SiO4^4$
(b) The structure of the pvrosilicate anion (one oxygen anion shared)	(b)	$Si_2O_7^{6-}$
(c) The structure of a ring silicate anion (two oxygen atoms shared)	(c)	$Si_3O_9^{6-}$
(d) The structure of an extended silicate anion (two oxygen atoms shared)	(d)	$(SiO_3)_n^{2n-}$
(e) The structure of an extended silicate anion (three oxygen atoms shared). In this structure the silicate atoms are joined to four oxygen atoms. The fourth oxygen atom carries a single negative charge and is above the plane.	(e)	$Si_4O_{10}^{4-}$ or $SiO_{2\frac{1}{2}}$

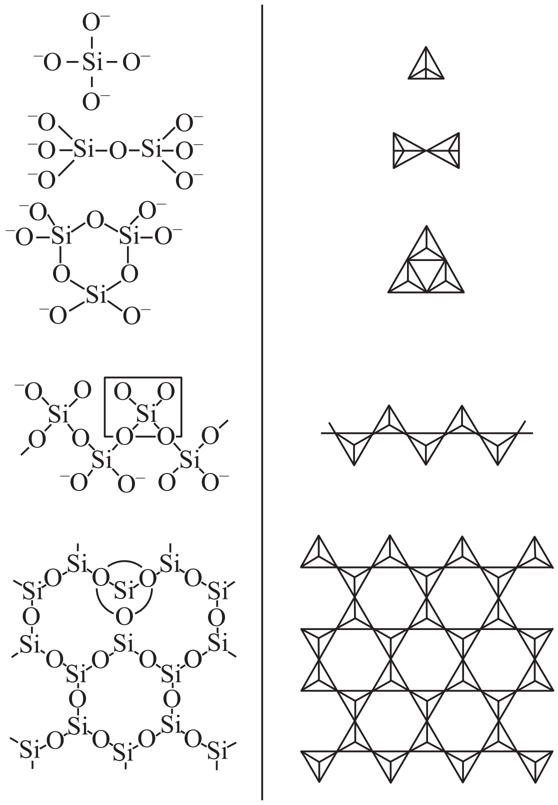


Fig. 19.7: Structure of Silicates

19.4.6.3 Zeolites

Zeolites have a much more open structure than the feldspars. The anion skeleton is penetrated by channels, giving a honeycomb-like structures These channels are large enough to allow them to exchange certain ions. They can also absorb or lose water and other small molecules without the structure breaking down. Zeolites are often used as ion-exchange materials, and as molecular sieves. Natrolite $Na_2[A1_2Si_3O_{10}]2H_2O$ is a natural ion exchanger. Permutit water softeners use sodium zeolites. Zeolites take Ca^{2+} ions from hard water and replace them by Na^+, thereby softening the water. The sodium zeolite (natrolite) gradually becomes a calcium zeolite, and eventually has to be regenerated by treatment with a strong solution of NaCl, when the reverse process takes place. In addition to naturally occurring minerals, many synthetic zeolites have been made. Zeolites also act as molecular sieves by absorbing molecules which are small enough to enter the cavities, but not those which are too big to enter. They can absorb water, CO_2, NH_3 and EtOH, and they are useful for separating straight chain hydrocarbons from branched chain compounds. Some other zeolites are healandite $Ca[A1_2Si_7O_{18}]6H_2O$, chabazite $Ca[A1_2Si_4O_{12}]6H_2O$, and analcite $Na[AISi_2O_6]H_2O$. Molecular sieves can be made with pores of appropriate size to remove small molecules selectively.

INTEXT QUESTIONS 19.2

1. Write two properties of diamond which are not exhibited by graphite.
2. What is the state of hybridization of carbon in (i) diamond (ii) graphite?
3. What is the nature of bond in carborundum?
4. Write the state of hybridization of carbon in CCl_4
5. Which one is affected by water and why; CCl_4 or $SiCl_4$?
6. Which is an acidic oxide, CO or CO_2?
7. What happens when SiO_2 is attacked by F_2?

19.5 SOME GENERAL CHARACTERISTICS OF ELEMENTS OF GROUP 15

This group consists of N, P, As, Sb and Bi.

Group 15 elements can complete the octet in chemical combination by gaining three electrons to form the 3-valent anion, by forming three covalent bonds, or by losing five electrons; the last possibility is ruled out on energetic grounds. Only nitrogen (and possibly phosphorus to a slight extent) forms the 3-valent ion and reactive metals are required for it to be possible; the N^{3-} ion is present in ionic nitrides, e.g. $(Li^+)_3N^{3-}$ and $(Ca^2+)_3(N^{3-})_2$. The majority of compounds formed by this group of elements are covalent.

Antimony and bismuth can form the 3-valent cation X^{3+} (the inert-pair effect), the Sb^3+ ion being present in $(Sb^{3+})_2(SO_4{}^{2-})_3$ and the Bi^{3+} ion in $Bi^{3+}(F^-)_3$ and $Bi^{3+}(N0_3{}^-)_3$. 5H_2O.

Because phosphorus, arsenic, antimony and bismuth have vacant *d* orbitals they are able to form 5-covalent compounds which are not possible for nitrogen, e.g. in the formation of PCl_5, one of the 3*p* electrons of the phosphorus atom is promoted to the 3*d* level. giving five unpaired electrons for valency purposes.

Nitrogen and phosphorus are non-metallic; metallic properties first become apparent with arsenic and become progressively more important for antimony and bismuth. Of these elements only nitrogen is able to multiple bond with itself, the triple bond being present in the nitrogen molecule, N≡N.

Tabe 19.4: Physical properties of Group 15 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm M^{3+}	M.P. /°C	B.P. /°C
N	7	2.5 $1s^22s^22p^3$	0.074		–210	–196
P	15	2.8.5 $\ldots 2s^22p^63s^23p^3$	0.110		44.1 (white)	280 (white)
As	33	2.8.18.5 $\ldots 3s^23p^63d^{10}4s^24p^3$	0.121	0.069		613 (sublimation)
Sb	51	2.8.18.18.5 $\ldots 4s^24p^64d^{10}5s^25p^3$	0.141	0.090	630	1380
Bi	83	2.8.18.18.8.5 $\ldots 5s^25p^65d^{10}6s^26p^3$	0.152	0.120	271	1560

Occurrence

Nitrogen occurs as an inert diatomic gas, 78 percent by volume in the atmosphere. Inorganic nitrogen compounds are usually soluble and are rarely found in nature except Chile saltpetre. Both nitrogen and phosphorus are essential constituents of all plant and animal tissue: nitrogen is present in proteins; and phosphorus is present as calcium phosphate in bones and teeth.

Dinitrogen

Preparation of dinitrogen

Nitrogen can be obtained :

(A) From air by the removal of oxygen etc., by physical or chemical means.

(B) By the decomposition of nitrogen compounds.

(A) *From air* : (a) The gas left after the removal of oxygen and carbon dioxide from air is almost nitrogen. Air is passed through two wash bottles one containing a solution of sodium hydroxide and the other sulphuric acid which remove carbon dioxide and moisture respectively. The dry air is now passed over heated iron or copper to remove oxygen.

$$2Cu + O_2 \rightarrow 2CuO$$

Nitrogen so collected in gas jars or holders contains about 1 per cent of noble gases.

(b) *By fractional evaporation of liquid air* : Nitrogen for industrial requirements is manufactured by this method. The boiling point of liquid nitrogen is –195.8°C, and of liquid oxygen is –183°C. Thus, the difference of 12.8°C in their boiling points, is sufficient to allow their separation from liquid air. T

(B) *From nitrogen compounds* : Nitrogen prepared from chemical compounds is usually called “*chemical nitrogen*”. It is conveniently prepared in the laboratory by the following methods :

(i) When a solution of ammonium nitrite is heated in a flask, nitrogen is obtained.

$$NH_4NO_2 \rightarrow 2H_2O + N_2$$

(ii) *By the oxidation of* ammonia : When chlorine is passed into an excess of concentrated ammonia solution, nitrogen is evolved which is bubbled through water to remove ammonia and ammonium chloride.

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

$$6NH_3 + 6HCl \rightarrow 6NH_4Cl$$

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

If ammonia is not present in excess or the action is prolonged, nitrogen trichloride is also formed which is highly explosive.

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

(iii) Very pure nitrogen is evolved by heating sodium or barium azide in vacuum.

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

$$2NaN_3 \rightarrow 2Na + 3N_2$$

Properties

Physical: Nitrogen is a colourless, odourless and tasteless diatomic gas. Its specific gravity in the gaseous state is 0’96737, in the liquid state 0.804, and in the solid state 1.0265. It is slightly soluble in water, 100 volumes of water at 20°C dissolve only 1·64 volumes of gas. At –1955°C it is condensed to a colourless liquid which freezes to a white snow-like mass at –210°C. The gas is non-poisonous, but simply dilutes the oxygen of the air. Animals die in nitrogen for want of oxygen only. The gas is neither combustible nor a supporter of combustion,

It has been noted that at 3500°C about 5 per cent of nitrogen is dissociated into atoms.

$$N_2(95\%) \rightleftharpoons 2N\ (5\%)$$

Chemical : It is inert at room temperature because a large amount of energy is required to break N ≡ N bond. However, the compounds of nitrogen show great chemical activity.

(i) When nitrogen is passed over heated metals like lithium, calcium, magnesium and aluminium, it forms nitrides.

$$2Al + N_2 \rightarrow 2AlN$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

These nitrides are readily decomposed by water.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

(ii) At 200 atmospheres and in presence of a catalyst, finely divided iron and molybdenum as promotor at 450°-500°C, nitrogen combines with hydrogen. This reaction is utilized for the manufacture of ammonia by the Haber process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24000 \text{ cals.}$$

(iii) It combines with carbides to form cyanamides which react with superheated steam to evolve ammonia.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

(iv) In presence of lightning discharge or an electric spark, nitrogen combines with oxygen to form nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO - 43.2 \text{ Cals.}$$

This reaction is utilized for the manufacture of nitric acid.

Uses

(i) Nitrogen is used on a large scale for the manufacture of ammonia, nitric acid and other important nitrogen compounds.

(ii) It is used for filling electric bulbs,

(iii) In the manufacture of high temperature thermometers.

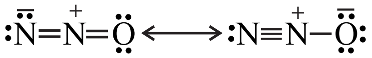
(iv) It is also used for providing an inert atmosphere in metallurgy and other industrial processes.

(v) It is the basis of two important activities of man *(a) agriculture* and (b) explosive.

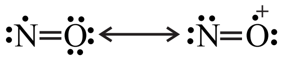
(vi) It is used as a source of cold when liquefied.

Structure of the Oxides of Nitrogen

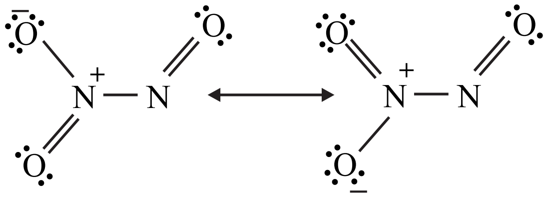
Dinitrogen Oxide, N_2O



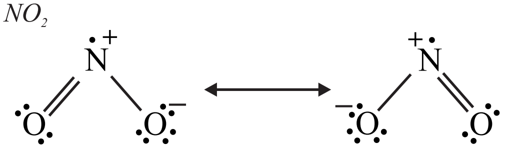
Nitrogen Oxide, NO



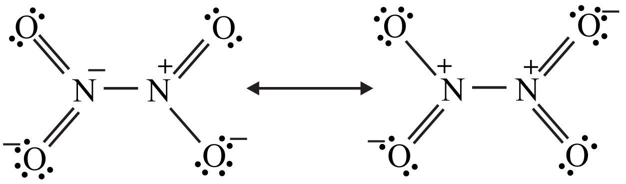
Dinitrogen trioxide, N_2O_3



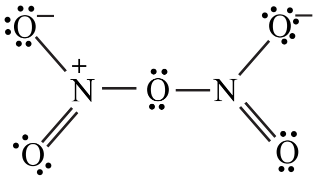
Nitrogen dioxide, NO_2



Dimer of NO_2 (N_2O_4)



Dinitrogen Pentaoxide



19.6 NITROGEN AND PHOSPHORUS

Nitrogen and phosphorus belong to Group 15 of the periodic table. They form a number of industrially important compounds like ammonia, nitric acid and fertilizers. Let us study about them.

19.6.1 Ammonia

Ammonia is prepared in the laboratory by heating an ammonium salt with a base:

$$2NH_4^+ + OH^- \rightarrow 2NH_3 + H_2O$$

or

$$2NH_4^+ + CaO \rightarrow Ca^{2+} + 2NH_3 + H_2O$$

It may also be prepared by treating a nitride with water.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

It is manufactured industrially by passing nitrogen and hydrogen over an iron catalyst at 750 K and under a pressure of about 200 atmospheres (Haber's process).

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H = –46 \text{ kJ mol}^{-1}$$

In the actual process the hydrogen required is obtained from water gas and the nitrogen from the fractional distillation of liquid air. The mixture of nitrogen and hydrogen (1 : 3 by volume) is compressed to 200-300 atm and then passed into the catalytic tubes packed with the catalyst. The catalyst in made by fusing Fe_3O_4 with KOH and Al_2O_3. The temperature of the catalytic tubes is maintained at 673 –773K by heating them electrically. The issuing gas containing about 10 per cent ammonia is cooled and the liquid ammonia condenses. The unconverted mixture of hydrogen and nitrogen is returned to the inlet and passed again over the catalyst. A typical plant might be arranged as shown in Fig.19.7

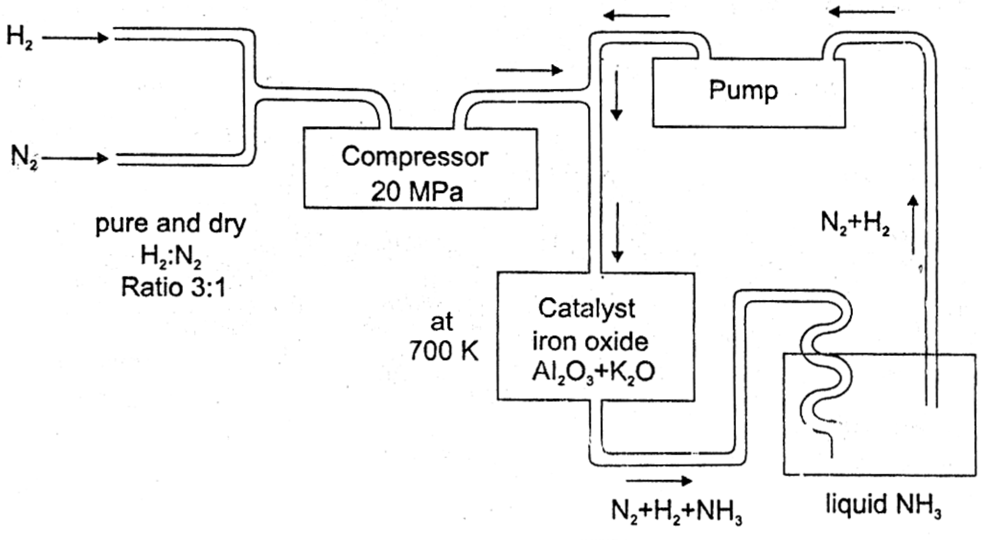


Fig. 19.7 : *The Haber process for the manufacture of ammonia*

Properties

Ammonia is a colourless and pungent smelling gas. It is readily liquified at a pressure of about nine atmospheres at ordinary temperatures. The liquid boils at –239.6K and freezes at –96K. Liquid ammonia resembles water in being highly associated because of its polar nature and strong hydrogen bonding.

Ammonia is extremely soluble in water. The hydrated ammonia molecule, $NH_3.H_2O$, is loosely called ammonium hydroxide, NH_4OH, which is a weak base, the ionization reaction being

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

The undissociated molecule, NH_4OH, is essentially a non-existent entity. It can only exist as NH_4^+ and OH^- ions.

Chemical reactions

(i) **Action of heat:** When heated above 500^0C it begins to decompose into its elements. The decomposition is accelerated by metallic catalysts

$$2NH_3 \rightarrow N_2 + 3H_2$$

(ii) **With oxygen :** Ammonia does not burn in air but freely burns in pure oxygen with a yellowish flame giving nitrogen and steam

$$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$$

In the presence of a catalyst, e.g. hot platinum, ammonia burns in air to give nitric oxide

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$

(iii) **As a reducing agent.** If ammonia is passed over those heated metallic oxides which are reducible by hydrogen, e.g. CuO, PbO, etc, it is oxidised to nitrogen and water :

$$3PbO + 2NH_3 \rightarrow 3Pb + N_2 + 3H_2O$$

(iv) **With acids.** It is easily absorbed by acids to form ammonium salts, e.g.:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The reaction can occur even if the acid is a gas, e.g.:

$NH_3 + HCl \rightarrow NH_4Cl$ (i.e. $NH_4^+Cl^-$)

(v) **With chlorine.** Ammonia reacts with chlorine, the products varying according to conditions :

$$\left.\begin{array}{l} 2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl \\ 6HCl + 6NH_3 \rightarrow 6NH_4Cl \end{array}\right\} \text{(with excess of ammonia)} \qquad ...(1)$$

$$\left.\begin{array}{l} NH_3 + 3Cl_2 \rightarrow \underset{\text{nitrogen trichloride}}{NCl_3 + 3HCl} \\ HCl + NH_3 \rightarrow NH_4Cl \end{array}\right\} \begin{array}{l}\text{(when chlorine is in} \\ \text{large excess)}\end{array} \qquad ...(2)$$

(vi) **With metal salts**. With some metal salts, aqueous ammonia reacts to form metal hydroxides which are precipitated.

For example, ammonia solution precipitates copper(II) hydroxide when treated with a copper salt,

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

In excess of ammonia, the precipitate of $Cu(OH)_2$ dissolves to form tetraammine complex

$$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_3$$

$$\rightarrow \underset{\textbf{tetraamminecopper(II) sulphate}}{[Cu(NH_3)_4]^{2+}SO_4^{2-}} + 2H_2O$$

Similar complexes are formed with many metallic salts and complex ions such as $[Ag(NH_3)_2]^+$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$ and $[Ni(NH_3)_6]^{2+}$ are well known.

Uses :

Ammonia is used for a number of purposes, some important uses are :

(i) In the manufacture of ammonium sulphate for use as a fertilizer.

(ii) In the manufacture of nitric acid (Ostwald process)

(iii) In the manufacture of sodium carbonate by Solvay process.

(iv) Liquid ammonia is used in refrigerators.

(v) Ammonia solution is used as a domestic cleaner : as a grease remover and in laundry.

Structure : Ammonia molecule is trigonal pyramid with the nitrogen at the apex. The nitrogen atom is sp^3 hybridized in which a lone pair of electrons occupies one of the tetrahedral positions. The angle $H\hat{N}H$ becomes 107^0 instead of 109^0 (in CH_4) due to lone pair-bond pair repulsion (Fig. 19.8).

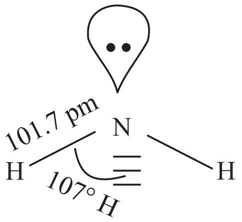


Fig. 19.8 : *Structure of ammonia*

19.6.2 Oxoacids of Nitrogen

There are several oxoacids of nitrogen such as nitrous acid, HNO_2, hyponitrous acid, $H_2N_2O_2$ and nitric acid, HNO_3. Of these nitric acid is the most important and will be considered here in detail.

Nitric Acid, HNO_3

Preparation

In the laboratory, nitric acid can be prepared by heating $NaNO_3$ or KNO_3 with concentrated H_2SO_4 in a glass retort and condensing the vapours coming out of the retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

In industry it is manufactured by the catalytic oxidation of ammonia which involves the following reactions (Ostwald process) :

$$4NH_3 + 5O_2 \xrightarrow[Pt]{1173\ K} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The aqueous nitric acid can be concentrated by distillation followed by dehydration with conc. H_2SO_4.

Properties

Physical : It is a colourless liquid of density 1.50 g cm^{-3} at 248 K. The acid is freely miscible with water forming a constant boiling mixture containing 98% of acid, b.p.393K.

Chemical : (a) In aqueous solution, nitric acid is a strong acid and dissociates to give hydronium and nitrate ions.

$$H_2O + HNO_3 \longrightarrow H_3O^+ + NO_3^-$$

(b) It is neutralised by appropriate alkalies to yield nitrates.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

(c) On heating it gives NO_2

$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

(d) It is a good oxidizing agent and oxidizes non metals, metals and organic compounds, some examples of which are given below :

(i) $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

(ii) $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

(iii) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(v) $Cu + \underset{\textbf{conc.}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$3Cu + \underset{\textbf{dil.}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

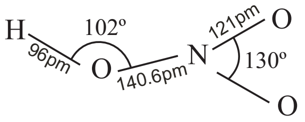
(vi) $4Zn + \underset{\textbf{dil.}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

(vii) $Mg + \underset{\textbf{dil.}}{2HNO_3} \longrightarrow Mg(NO_3)_2 + H_2$

(viii) Aluminium loses its normal reactivity i.e. becomes passive after being dipped in conc. HNO_3. This is due to the formation of a thin protective layer of aluminium oxide on its surface which prevents further action.

(ix) $\underset{\textbf{glycerine}}{C_3H_5(OH)_3} + 3HNO_3 \xrightarrow{\text{conc. } H_2SO_4} \underset{\textbf{trinitroglycerine (explosive)}}{C_3H_5(NO_2)_3} + 3H_2O$

Structure : In the gaseous state HNO_3 exists as a planar molecule with the structure: (Fig. 19.9):



Fig, 19.9 : *Structure of nitric acid molecule*

Uses : Nitric acid is used in the manufacture of nitrates which are used as fertilizers, and explosives, trinitroglycerine and trinitrotoluene (TNT)

- It is used as an oxidizing agent in labortory, e.g. Fe(II) gets oxidized to Fe(III)
- Conc. HNO_3 is a constituent of aqua regia ($HNO_3 : HCl = 1 : 3$)
- HNO_3 (100%) is a constituent of rocket propellant.

19.6.3 Allotropic forms of Phosphorus

The allotropy of phosphorus is rather complex but, essentially, there are three allotropic forms known as white, red and black phosphorus.

White phosphorus is formed as a soft, waxy solid whenever phosphorus vapour is condensed; structurally it contains tetrahedral P_4 units held together by van der Waals' forces. Since the P–P–P bond angles are 60° in each of these P_4 units there is a considerable amount of strain, and this makes itself felt in the high chemical reactivity of this allotrope.

White phosphorus very slowly changes into the red variety in the course of many years; this change can be accelerated by raising the temperature, and commercially this allotrope is made from white phosphorus by heating in the absence of air to 270°C for several days. Its structure is not known with certainty but it is certainly macromolecular; it is denser than white phosphorus.

The third allotrope, black phosphorus, can be obtained by subjecting white phosphorus to high pressures at 200°C in the absence of air. It too is macromolecular, with each phosphorus atom surrounded by three more atoms. It is an electrical conductor resembling graphite in this respect and also in its flakiness. Its density is higher than that of red phosphorus.

Only white and red phosphorus are normally encountered in the laboratory.

19.6.4 Phosphorus Halides

Phosphorus trichloride, PCl_3

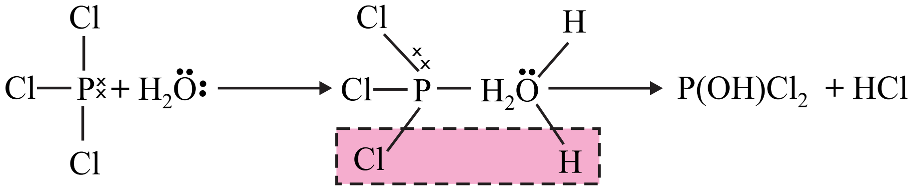
The trichloride, is obtained by passing chlorine over white phosphorus. The phosphorus burns with a pale green flame and phosphorus trichloride distils and is condensed as a colourless liquid. Since it is attacked by air and water, it is necessary to displace the air from the apparatus with a stream of carbon dioxide and to include a soda-lime drying tube.

$$P_4(s) + 6C1_2(g) \longrightarrow 4PC1_3(l)$$

Phosphorus trichloride is readily hydrolysed by water to phosphonic acid, H_3PO_3, and hydrogen chloride:

$$PCl_3(1) + 3H_2O(1) \longrightarrow H_3PO_3(aq) + 3HCl(g)$$

It is thought that the reaction takes place in stages, with the formation of complexes in which the oxygen atom of a water molecule is attached to the phosphorus atom (expansion of the octet can occur since the phosphorus atom has *d* orbitals available):



$$P(OH)C1_2 + H_2O \longrightarrow P(OH)_2Cl + HCl$$

$$P(OH)_2Cl + H_2O \longrightarrow P(OH)_3 + HCl$$

Phosphorus trichloride reacts with many compounds containing the –OH group, and it is used in organic chemistry for the preparation of acid chlorides and alkyl chlorides, e.g.

$$3CH_3COOH(l) + PCI_3(1) \longrightarrow 3CH_3COC1 + H_3PO_3$$

$$3C_2H_5OH(1) + PC1_3(1) \longrightarrow 3C_2H_5C1 + H_3PO_3$$

It readily combines with oxygen and chlorine (reversibly), the phosphorus atom increasing its covalency from three to five:

$$2PC1_3(1) + O_2(g) \longrightarrow \underset{\text{phosphorus trichloride oxide}}{2POCl_3(l)}$$

$$PC1_3(1) + Cl_2(g) \rightleftharpoons PCl_5(s)$$

Phosphorous pentachloride, PCl_5

Phosphorus pentachloride is prepared by passing chlorine through a flask into which phosphorus trichloride is dripping. Since it dissociates into the trichloride and chlorine very readily, the experiment is conducted in an ice-cooled apparatus.

$$PCl_3(l) + Cl_2(g) \rightleftharpoons PC1_5(s)$$

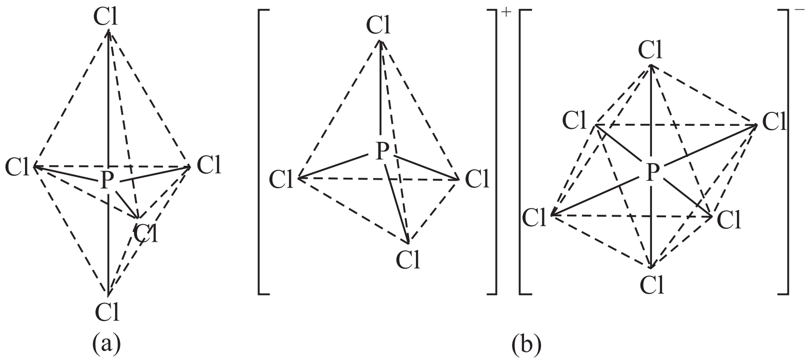
Like the trichloride it is attacked by compounds containing the hydroxyl group, e.g.

$$PCl_5(s) + H_2O(l) \longrightarrow POCl_3(1) + 2HCl(g)$$

$$POCl_3(1) + 3H_2O(l) \longrightarrow H_3PO_4(aq) + 3HCl(g)$$

$$CH_3COOH(l) + PCl_5(s) \longrightarrow CH_3COCl(1) + POC1_3(1) + HCl(g)$$

In the vapour state the phosphorus pentachloride molecule has a trigonal bipyramidal structure (Fig. 18.10(a)); in the solid state it is ionic, having the structure $(PCI_4^+)(PCl_6^-)$ (Fig. 18.10(b)).



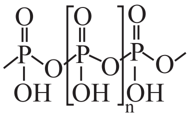
(a) (b)

Table 19.10: The acids of phosphorus and their properties.

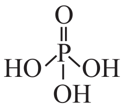
Acid	Nature	Preparation		Anion
H_3PO_2 or $H_2P(OH)O$ hypophosphorous	crystalline white solid	white P_4 + alkali $H_2PO_2^-$ + H_2	$H_2PO_2^-$ hypophosphite	strongly reducing monobasic pK = 2
H_3PO_3 or $HPO(OH)_2$ orthophosphorous	deliquescent colourless solid	P_2O_3 or PCl_3 + H_2O	H_2PO3^-, HPO_3^{2-} phosphite	reducing,but slow dibasic pK_1 = 2 pK_2 = 6

H_3PO_4 Orthophosphoric	white solid	$P_2O_5 + H_2O$	$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} phosphate	not oxidizing, tribasic
$H_2P_2O_4$ pyrophosphoric	colourless solid	heat phosphates or phosphoric acid heating	$P_2O_7^{4-}$ pyrophosphate	tetrabasic pK-$_1$ = 2
	linear and cyclic anions	phosphates	$[PO_3(PO_3)n\bullet OPO_3]^{(4+n)-}$ $[PO_3]_n^{n-}$ polyphosphate	

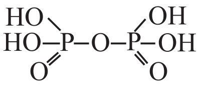
Structure of Oxyacids of Phosphorous



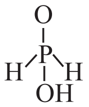
$[HPO_o]_n$
metaphosphoric acid



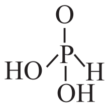
H_3PO_4
orthophosphoric acid



$H_1P_2O_7$
pyrophosphoric acid



H_3PO_2
hypophosphorous
acid



H_3PO_3
orthophosphorous
acid

INTEXT QUESTIONS 19.3

1. Does 'NH_4OH' exist as a molecule?
2. What is the bond angle in NH_3 molecule?
3. What is the state of hybridization of N in NH_3?
4. Draw the structure of pyrophosphoric acid.
5. What happen when PCl3 is treated with water.

WHAT YOU HAVE LEARNT

- General Characteristic of Group 13, 14, & 15.
- Method of preparation of boric acid. The acidic nature and structure of boric acid.
- Method of preparation and uses of borax.

- Methods of preparation and uses of boron trifluoride and diborane.
- The Lewis character and use of boron trifluoride.
- Preparation of aluminium trichloride and its structure
- Method of preparation of alums and uses
- The comparison of diamond and graphite.
- The structure and properties of carbon monoxide, carbon dioxide and silicon dioxide and their uses.
- Comparison of the hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride.
- Preparation and uses of silicon carbide (carborundum)
- Preparation and uses of silicons.
- Preparation and structure of silicates and zerolites.
- Preparation, properties and uses of nitrogen.
- Structure of oxides of nitrogen.
- The methods of preparation, properties and uses of ammonia and nitric acid.
- Structure of the oxides and oxoacids of nitrogen Halides of phosphorus Allotropic forms of phosphorus oxyacids of phosphorous.

TERMINAL QUESTIONS

1. Why is boric acid not a protonic acid?
2. Discuss the structure of boric acid.
3. Draw the Lewis structure of CO and CO_2 molecules.
4. Why does BF_3 act as a Lewis acid?
5. What is catenation ? Why does carbon show catenation but silicon does not?
6. Compare the structure of CO_2 and SiO_2.
7. Describe briefly the Haber process for the manufacture of ammonia.
8. Why is graphite a conductor of electricity but diamond is not?
9. Explain different types of silicones.
10. Explain ortho and pro silicates.

ANSWERS TO INTEXT QUESTIONS

19.1

1. (i) $B(OH)_3$ (ii) $Na_2B_4O_7.10H_2O$
2. $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$
3. $NM(SO_4)_2\ .12H_2O$

   Where N = monovalent large cation like K^+ or NH_4^+ and M = trivalent cation like Al^{3+}, Fe^{3+}, Cr^{3+}
4. Al_2Cl_6
5. (i) as a flux, for glazing pottery and tiles : in the manufacture of optical and borosilicate glasses.

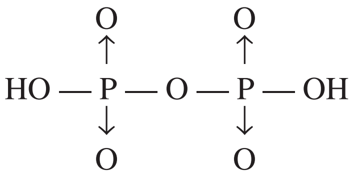
   (ii) as an antiseptic, as a food preservative, for making enamels

   (iii) as a catalyst in Friedel-Crafts reaction.
6. Monoprotonic
7. Due to the formation of oxide layer

19.2

1. Hardness and conducting nature. Diamond : hard, non conducting; graphite: soft, conducting.
2. sp^3 in diamond and sp^2 in graphite.
3. Covalent
4. sp^3
5. $SiCl_4$, as silicon can accept electron pair in its d-orbitals from water molecule.
6. CO_2
7. $SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$

19.3

1. No. Nitrogen cannot increase its covalency beyond 4.
2. 107^0.
3. sp^3
4. 

$$HO - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{P}} - O - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{P}} - OH$$

5. $PCl_3 + 3H_2O \longrightarrow H3PO_3 + 3HCl$

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20

p-BLOCK ELEMENTS AND THEIR COMPOUNDS - II

You have already studied the chemistry of the elements of Groups 13, 14 and 15. In this lesson we shall deal with the chemistry of the elements of Groups 16, 17 and 18.

OBJECTIVES

After reading this lesson you will be able to:

- explain general characteristics of group 16, 17 and 18 elements;
- classify oxides into acidic, basic and amphoteric types;
- recall the preparation, properties and uses of ozone;
- explain the allotripic forms of sulphur;
- describe the manufacture of sulphuric acid;
- proporation properties and uses of SO_2;
- structure oxoacids of sulphur;
- recall the characteristics of hydrogen halides (HF, HCl);
- list the oxides and oxoacids of chlorine;
- compare the acidic behaviour of oxoacids of chlorine;
- write the general molecular formulae of interhalogen compounds;
- discuss the structures of interhalogen compounds;
- list a few chloro fluoro carbons and explain their uses and their effect on environment;
- explain the unreactive nature of noble gases;
- explain occurance of noble gases;
- recall the preparation of xenon fluorides and oxides, and
- illustrate the structures of XeF_2, XeF_4, XeF_6, XeO_3 and XeO_4.

20.1 SOME CHARACTERISTIC PROPERTIES OF THE ELEMENTS OF GROUP 16

The Group 16 elements show the usual gradation from non metallic to metallic properties with increasing atomic number that occurs in any periodic group. Oxygen and sulphur are non-metals, selenium and tellurium are semiconductors and polonium is metallic.

These elements can enter into chemical combination and complete their octets by gaining two electrons to form the 2 di-valent ions, e.g. O^{2-}, S^{2-}, except for polonium which is too metallic, or by forming two covalent bonds, e.g. the hydrides H_2O, H_2S, H_2Se, H_2Te and H_2Po.

The two heavier members of this group can form the 4-valent cation X^{4+} e.g. there is evidence of the presence of Te^{4+} ions in the dioxide TeO_2 and of Po^{4+} ions in the dioxide, PoO_2, and sulphate, $Po(SO_4)_2$.

Because sulphur, selenium, tellurium and polonium have vacant *d* orbitals that can be utilised without too great an energy change, they are able to form covalent compounds in which the octet of electrons is expanded; for instance, the valencies of sulphur in H_2S, SCl_4 and SF_6 are two, four and six, respectively. Oxygen, in common with other first row members of the Periodic Table, cannot expand its octet.

Oxygen exists in the form of discrete molecules, a double bond uniting two oxygen atoms together, $O = O$. The atoms of the other Group elements do not form multiple bond to themselves and sulphur, in particular, shows a strong tendency to catenate, puckered S_8 rings being present in rhombic and monoclinic sulphur. There are two forms of selenium corresponding in structure to rhombic and monoclinic sulphur in which Se_8 rings, are present. These forms, however, are readily converted into a 'metallic' form of the element called grey selenium. As far as is known, there is only one form of tellurium which has the same structure as grey selenium. Polonium is truly metallic.

Table 20.1: Properties of Group 16 elements

	Atomic Number.	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm	M.P. /°C	B.P. /°C
O	8	2.6 $\mathrm{L}s^2 2s^2 2p^4$	0·074	0.140	–218	–183
S	16	2.8.6 $....2s^2 2p^6 3s^2 3p^4$	0.104	0.184	119^*	445
Se	34	2.8.18.6 $....3s^2 3p^6 3d^{10} 4s^2 4p^4$	0·117	0.198	217^{**}	685

Te	52	2.8.18.18.6 ....$4s^24p^64d^{10}5s^25p^4$	0.137	0·221	450	990
Po	84	2.8.18.32.18.6 .... $5s^25p^65d^{10}6s^26p4$	0.140		254	960

* For monoclinic sulphur

** For grey selenium

Occurrance

Oxygen occurs in the atmosphere to the extent of about 21 per cent by volume (23 per cent by weight). This percentage remains constant by the operation of the highly complex process termed photosynthesis, The element is present in the earth's crust and in water to the extent of about 50 per cent and 89 per cent by weight, respectively. It is an essential ingredient in all living matter and is of prime importance in respiration and combustion processes. Although only slightly soluble in water, enough oxygen dissolves to support marine life.

Preparation of dioxygen

1. By heating chlorates, nitrates and permanganates :

$$2KC1O_3 + (MnO_2) \rightarrow 2KC1 + 3O_2 + (MnO_2)$$

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

2. By heating metallic oxides :

$$2HgO \rightarrow 2Hg + O_2$$

$$2Pb_3O_4 \rightarrow 6PbO + O_2$$

$$2Ag_2O \rightarrow 4Ag + O_2$$

3. By the action of bleaching powder on hydrogen peroxide solution.

$$Ca(OCl)_2 \rightarrow 2H_2O_2 \rightarrow CaCl_2 + 2H_2O + 2O_2$$

4. By the action of hot and concentrated sulphuric acid on potassium dichromate or potassium permanganate.

$$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

5. By the action of sodium peroxide on water.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

Manufacture of oxygen :

(1) By the electrolysis of water : Where ever electricity is cheap, oxygen can be conveniently manufactured by the electrolysis of water. The electrolysis is carried out in iron tanks containing a solution of caustic soda or acidified water. The electrodes used are of iron or nickel and a current of 1000 amperes is used. Oxygen is evolved at the anode and hydrogen at the cathode. A porous diaphragm is used to prevent the mixing of hydrogen and oxygen.

2. From air : When barium oxide is heated in air to about 500°C it combines with oxygen to form barium peroxide, BaO_2. On raising the temperature to about 800°C, the peroxide decomposes to give barium oxide and oxygen.

$$2BaO + O_2 \rightarrow 2BaO_2 \qquad \text{(at about 500°C)}$$

$$2BaO_2 \rightarrow 2BaO + O_2 \qquad \text{(at about 800°C)}$$

It can be prepared from liquified air. There is a difference of 12·5°C in the boiling points of oxygen and nitrogen ; oxygen boils at –182.5°C while nitrogen at –195°C. This difference is sufficient to enable a separation of the two by fractional distillation.

PROPERTIES

Physical

Oxygen is colourless, tasteless and odourless gas and slightly heavier than air. Liquid oxygen is pale blue with boiling point–182·5°C and specific gravity 1·2386 at –210°C. The liquid solidifies on cooling at –218·4°C to a light blue solid. It is somewhat soluble in water (about 3%), a fact responsible for aquatic life. Liquid oxygen is paramagnetic and is strongly attracted by magnet.

Chemical

Oxygen is essentially required for the burning or combustion of substances in air. Combustion is much more brilliant in pure oxygen. Molecular oxygen combines directly with most of the elements, exceptions being the inert gases, the halogens, gold and platinum. It is a fairly good oxidising agent in aqueous solution and directly oxidises Cr^{2+}, Fe^{2+}, SO_3^{2-}, V^{2+}, and Ti^{3+} ions. The gas oxidises some substances at ordinary temperature, some at higher temperatures, and some in presence of suitable catalysts.

(i) *At ordinary temperatures* : Phosphorus is slowly oxidised in oxygen to form its pentoxide at room temperature. The oxidation of alkali and alkaline earth metals and the rusting of iron take place at ordinary temperatures. Nitric oxide quickly combines with oxygen to give brown fumes of dioxide, NO_2

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$4Na + O_2 \rightarrow 2Na_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

One of the most important reactions of molecular oxygen is the one that takes place between the inspired oxygen and the protein haemoglobin at the body temperature.

(ii) *At higher temperatures* : At higher temperatures it combines with almost all the elements to form compounds with the evolution of much energy. The binary compounds so obtained are known as oxides.

$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

$$C + O_2 \rightarrow CO_2$$

$$2Mg + O_2 \rightarrow 2MgO$$

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Uses : Apart from it being an absolute necessity for terrestrial life, oxygen is used for many industrial purposes.

(i) *For the production of high temperature flames* :

Oxy-hydrogen flame = 2400°—2800°C

Oxy-coal gas flame = 2200°—2400°C

Oxy-acetylene flame = 3100°—3300°C

Oxy-acetylene flame produces hydrogen which prevents the oxidation of metals during welding or cutting.

$$C_2H_2 + O_2 \rightarrow 2CO + H_2$$

(ii) *For medical purposes* : When even a patient is unable to breath sufficient air, oxygen is given for artificial respiration.

(iii) *In iron and steel industry* : Addition of oxygen to the air blast in blast furnace raises the temperature required for the manufacture of iron and steel.

(iv) *In rocket fuels* : Liquid oxygen is an important constituent of the fuels used in rockets.

(v) It is also used for bleaching purposes.

(vi) Oxygen is used as an oxidizing agent in laboratories and in many industries.

20.2 OXYGEN AND SULPHUR

Oxygen and sulphur are the first two members of the 16th group of the periodic table.

In this section you will learn about some compounds of oxygen and sulphur including environmentally important ozone and industrially important sulphuric acid.

20.2.1 Classification of Oxides

The binary compounds of oxygen with other elements (metals or non-metals) are called oxides. An understanding of the nature of an oxide provides a clue to the nature of the element which forms the oxide. Depending upon the acid-base behaviour of the oxides, they can be classified into the following categories.

(1) Acidic oxides

(2) Basic oxides

(3) Amphoteric oxides

(4) Neutral oxides

(1) Acidic Oxides : Acidic oxides are generally formed by non-metallic elements and some metals in higher oxidation states. Examples of some acidic oxides are CO_2, SO_2, N_2O_5, P_4O_{10}, Cl_2O_7, Mn_2O_7, etc. These oxides combine with water to form acids whereas with alkalies they form salt and water.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

However, certain acidic oxides do not form acids on reacting with water. But they react with alkalies to form salt and water, e.g., SiO_2

$$SiO_2 + 2\,NaOH \longrightarrow \underset{\textbf{Sodium silicate}}{Na_2SiO_3} + H_2O$$

(2) Basic oxides : Metals combine with oxygen to form basic oxides. The basic oxides react with acids to form salt and water.

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

The oxides of the metals of Groups 1 and 2 react with water to form hydroxides known as **alkalies**.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

(3) Amphoteric oxides : Almost all metallic oxides are basic oxides. But some metallic oxides show the characteristics of both acidic as well as basic oxides, i.e., they react with both acids as well as bases to form salt and water. Such oxides are called *amphoteric oxides*. The oxides of zinc, aluminium, lead and tin are amphoteric in nature.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnO + 2NaOH \longrightarrow \underset{\textbf{Sodium zincate}}{Na_2ZnO_2} + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\textbf{Sodium aluminate}}{2NaAlO_2} + H_2O$$

(4) Neutral oxides : These oxides are neither acidic nor basic. Examples are carbon monoxide, (CO), nitric oxide (NO), nitrous oxide (N_2O) , etc.

INTEXT QUESTIONS 20.1

1. Give one example each of basic oxide, acidic oxide and amphoteric oxide.
2. Classify the following oxides into acidic, basic or amphoteric oxides : K_2O, SiO_2, SO_2, FeO, Al_2O_3, ZnO, CrO_3.
3. Give chemical equations to illustrate the amphoteric behaviour of ZnO.
4. Name the compound formed when the oxide of an element of Group 1 or 2 reacts with acid?
5. Oxygen is a gas but Sulphur is solid why?

20.3 OZONE

Ozone is an allotrope of oxygen. You must have learnt through the media that ozone layer depletion in the upper atmosphere is causing a great environmental concern. We will now study the preparation, properties, importance and uses of ozone.

Ozone is formed around high voltage electrical installations. Traces of ozone are formed in forests by decay of organic matter. Ozone is prepared industrially by Siemen's ozonizer.

Siemens ozonizer : In this apparatus metal electrodes are used to produce an electric field. Two coaxial glass tubes are fused together at one end. The outer tube has an inlet for oxygen or air and an outlet for ozone (with oxygen or air). The inner side of the inner tube and the outer side of the outer tube are coated with tinfoil (T). These are connected to the terminals of an induction coil or high voltage transformer.

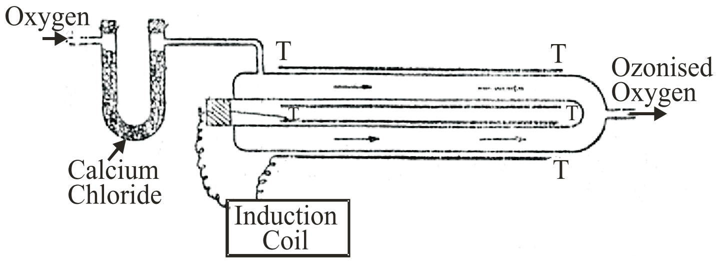
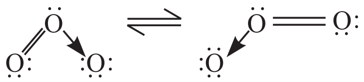


Fig. 20.1 : *Siemen's Ozonizer*

Pure, dry and cold oxygen or air is passed through the inlet in a slow current. Electrical energy is absorbed and about 5 to 10 percent of oxygen is converted into ozone.

All rubber and cork fittings are avoided because of the corrosive action of ozone on these materials.

Structure of Ozone : Ozone forms a V-shaped molecule. The central O atom uses sp^2 hybrid orbitals for bonding. The structure of ozone can be explained as a resonance hybrid of the following two structures, (oxygen – oxygen bond length 128 pm and bond angle 117º)



Properties of Ozone

(a) **Physical :** Ozone is a pale blue gas which turns into blue liquid at 161K. At 80K it freezes to a violet black solid. It is ten times as soluble in water as oxygen.

(b) **Chemical :** The chief characteristic of ozone is that it is unstable and that it gives energy loaded nascent oxygen. Its reactions are closely paralleled to the reactions of hydrogen peroxide.

1. *Catalytic decomposition :* Ozone in aqueous solution decomposes on standing. Above 373K ozone decomposes very rapidly. Even at ordinary temperature it decomposes in the presence of chlorine, bromine, nitrogen pentoxide and other acidic oxides and oxides of transition metals.

$$2O_3 \rightarrow 3O_2.$$

2. *Oxidizing properties :* In the presence of reducing agents ozone furnishes active atom of oxygen according to the equation.

$$O_3 \rightarrow O_2 + O$$

In most of the reactions, oxygen gas is liberated as the reduction product from ozone.

(i) It oxidizes black lead sulphide to white lead sulphate

$$4O_3 + PbS \rightarrow PbSO_4 + 4O_2$$

(ii) Ozone oxidizes acidified ferrous sulphate to ferric sulphate

$$O_3 + 2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O + O_2$$

(iii) Ozone oxidizes moist sulphur to sulphuric acid and phosphorus to phosphoric acid.

$$3O_3 + S + H_2O \rightarrow H_2SO_4 + 3O_2$$

$$5O_3 + 2P + 3H_2O \rightarrow 2H_3PO_4 + 5O_2$$

(iv) *Ozone tails mercury.* Normally mercury does not stick to glass but if exposed to ozone it loses its convex meniscus and leaves a 'tail' or trail of minute droplets on a glass surface. This is supposed to be due to the formation of stray molecules of mercurous oxide which affect the surface only.

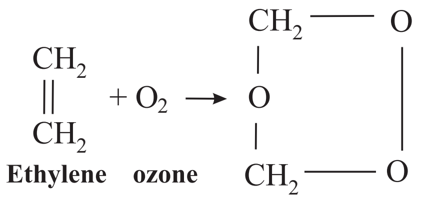
$$O_3 + 2Hg \rightarrow Hg_2O + O_2$$

The 'tailing' effect can be removed by washing with dilute acid.

(v) Ozone oxidizes stannous chloride to stannic chloride. Note that no oxygen is produced in this reaction.

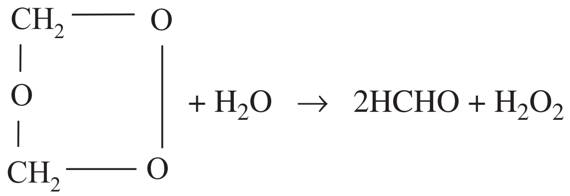
$$O_3 + 3SnCl_2 + 6HCl \rightarrow 3SnCl_4 + 3H_2O$$

3. *Ozonides :* All unsaturated organic compounds combine with ozone to form unstable compounds called ozonides, e.g.



Ethylene **ozone** **Ethylene ozonide**

The ozonides are hydrolysed by water to give aldehydes or ketones or both.



This technique is called *ozonolysis* and is widely used to locate the position of double bond in organic compounds.

Uses of Ozone

Some of its applications are given below :

1. ***Water purification :*** Small ozone-air plants function as part of the water purification set up. Ozone is a powerful germicide and it can purify a water spray effectively; it does not produce the unwanted by-products that other sterilizing agents do.
2. ***Air purification :*** Ozone is also used to purify air in tunnels, wells and crowded subways and cinema halls.
3. ***Refining oils :*** Vegetable oil and ghee go rancid when stored for a long time. This is caused by bacterial growth in the small water content present in them. If ozone is bubbled through oil, all such growing organisms are destroyed and we get purified oil.
4. ***Dry bleach*** **:** Ozone is also used to bleach waxes, flour, sugar and starch. Hydrogen peroxide, which produces water and other agents which act only in solution, cannot be used in these cases.
5. ***In Industry and in the Laboratory*** **:** It is widely used in certain organic preparation. Its use in ozonolyses has already been mentioned.

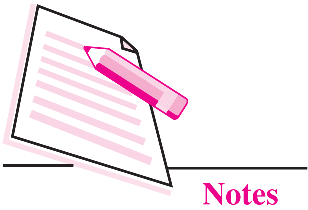
INTEXT QUESTIONS 20.2

1. What are ozonides? What happens when an ozonide is hydrolysed?
2. Write the reactions which occur when ozone reacts with (i) ferrous sulphate (ii) stannous chloride
3. Which is more soluble in water, oxygen or ozone?
4. Draw the structure of ozone molecule, O_3.
5. What is meant by "tailing of mercury"? How is it removed?

20.4 ALLOTROPIC FORMS OF SULPHUR

Rhombic sulphur

This is the form of sulphur normally encountered and consists of S_8 structural units packed together to give crystals whose shape is shown in Fig. Fairly large crystals can be obtained by allowing a solution of powdered sulphur in carbon disulphide to evaporate slowly; they are yellow, transparent and have a density of 2.06 g cm^{-3}.



Monoclinic sulphur

This form of sulphur is formed when molten sulphur is allowed to crystallise above 95.6°C. Like rhombic sulphur it consists of S_8 structural units, but these are arranged differently in the crystal lattice. The temperature of 95.6°C is the transition temperature for sulphur; below temperature, 95.6°C rhombic sulphur is the more stable allotrope and above it, the monoclinic sulphur is the more stable of the two forms.

$$\text{Rhombic sulphur} \xrightleftharpoons{95.6^\circ C} \text{Monoclinic sulphur}$$

Crystals of monoclinic sulphur are amber-yellow in colour and have a density of 1.96 g cm^{-3}.

Amorphous sulphur

A number of forms of sulphur which possess no regular crystalline form can be obtained when sulphur is liberated in chemical reactions, e.g. by the action of dilute hydrochloric acid on a solution of sodium thio-sulphate:

$$S_2O_3^{\,2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g) + S(s)$$

Plastic sulphur

This is obtained, by pouring nearly boiling sulphur into cold water. It consists of a completely random arrangement of chains of sulphur atoms which, when stretched, align themselves parallel to each other. On standing, it slowly changes over into rhombic sulphur, as the chains of sulphur atoms break and reform the S_8 cyclic units.

The action of heat on sulphur

Both rhombic and monoclinic sulphur melt to a yellow liquid. Owing to the conversion of rhombic to monoclinic sulphur, and also to possible variations in the percentage of allotropes of liquid sulphur formed, the melting points are not sharp: rhombic sulphur melts at approximately 113°C and monoclinic sulphur at approximately 119°C. As the temperature rises the colour of the liquid darkens until it is nearly black, and it becomes viscous. At about 200°C the viscosity begins to fall and at its boiling point of 445°C the liquid is again mobile.

There is still some doubt concerning a complete explanation of these observations, but a recent theory runs as follows: as the sulphur melts the S_8 rings begin to open and it is possible that other ring systems containing possibly six and four sulphur atoms form. It is known, however, that sulphur chains begin to form and reach their maximum chain length at 200°C, corresponding to the maximum viscosity of liquid sulphur. The decrease in viscosity of liquid sulphur that occurs above 200°C is explained as being due to the breakdown of these long chains and the re-formation of S_8 rings. Sulphur vapour contains S_8 rings, together

with smaller fragments such as S_8, S_4 and S_2. At very high temperatures atomic sulphur is formed.

Sulphur Dioxide, SO_2

Priestley (1774) obtained this gas by heating mercury with concentrated sulphuric acid and called it *vitriolic acid air.* Lavoisier in 1777 determined its composition.

It is found in volcanic gases and in traces in the air of towns; being derived from the burning of iron pyrites present as impurity in coal.

Preparation : *By the reduction of sulphuric acid ' It is* prepared in the *laboratory* by reducing hot concentrated sulphuric acid with copper turnings.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

The gas is dried by concentrated sulphuric acid, calcium chloride or phosphorus pentoxide and is collected by upward displacement of air or over mercury.

The reduction of concentrated sulphuric acid may also be brought about by heating with mercury, silver, sulphur or charcoal.

$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + 2H_2O + SO_2$$

$$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$$

$$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

$$C + 2H_2SO_4 \longrightarrow 2H_2O + CO_2 + 2SO_2$$

(ii) By the action of aliab on sulphites or bisulphites :

$$NaHSO_3 + 2H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$$

(iii) By burning sulphur or sulphide ores :

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

(iv) Now-a-days, it is commercially prepared by heating *anhydrite* ($CaSO_4$) with clay and coke at 1200°C.

$$2CaSO_4 + C \longrightarrow 2CaO + 2SO_2 + CO_2$$

Properties : It is a colourless gas with an odour well known as that of burning sulphur. It is $2\frac{1}{4}$ times as heavy as air. It is easily liquified by compression (2.5 atm at 15°C) or by cooling in a freezing mixture. Its critical temperature is 157.15°C and critical pressure 77.65 atm. The liquid is colourless, boils at —10°C and freezes at –75'5°C. Liquid sulphur dioxide is a good solvent for iodine, sulphur, phosphorus etc.

(i) Incombustible and non-supporter of combustion : It is incombustible and does not support combustion in the ordinary sense, but heated potassium, magnesium, tin and iron burn in the gas.

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

(ii) Decomposition : When heated to 1200°C it decomposes to an appreciable extent giving sulphur trioxide and sulphur.

$$3SO_2 \longrightarrow 2SO_2 + S$$

It is also decomposed in a strong beam of light.

(iii) Acidic nature : It is highly soluble in water forming unstable sulphurous acid.

$$HO_2 + SO_2 \rightleftharpoons H_2SO_3$$

Being an acidic oxide, it combines with basic oxides forming sulphites, e.g.,

$$CaO + SO_2 \longrightarrow CaSO_3$$

(*iv*) It combines with certain metallic dioxides yielding metallic sulphates, e.g.,

$$PbO_2 + SO_2 \longrightarrow PbSO_4$$

(*v*) It combines with oxygen and with chlorine

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

(vi) Reducing properties : In presence of moisture, it acts as a fairly strong reducing agent. For example

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

$$I_2 + SO_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 2H_2$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + H_2SO_4$$

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + 2HCl + H_2SO_4$$

$$2KIO_3 + 5SO_2 + 2H_2O \longrightarrow 2I_2 + 2KHSO_4 + 3H_2SO_4$$

$$Hg_2(NO_3)_2 + SO_2 + 2H_2O \longrightarrow 2Hg + 2HNO_3 + 3H_2SO_4$$

(vii) Oxidising properties : It also acts as an oxidising agent. Such as

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

$$C + SO_2 \longrightarrow CO_2 + S$$

(viii) Bleaching properties : In presence of moisture it acts as a mild bleaching agent;

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

the nascent hydrogen bleaches the colour of the substance. Thus sulphur dioxide bleaches by *reduction*

Uses:

It is used

(i) in the manufacture of sulphuric acid.

(ii) in the refining of sugar and kerosene oil.

(iii) in fumigation and in preserving fruits since it has antiseptic properties.

(iv) As a refrigerant in the liquid state.

(v) For bleaching delicate articles such as wool, silk and straw.

(vi) In the preparation of sodium and calcium bisulphites which are used in paper industry.

(viii) As an *antichlor* in removing excess chlorine from bleached materails.

20.5 SULPHURIC ACID

The most important compound of sulphur is sulphuric acid. Sulphuric acid or the 'oil of Vitriol' was known to the alchemists and their predecessors. Before the coming of Chamber process in the last century, it was obtained by heating hydrated sulphates.

Manufacture : The two main processes used for the manufacture of sulphuric acid are (1) Lead Chamber process and (2) the Contact process. Nowadays sulphuric acid is mostly manufactured by Contact process.

Manufacture of sulphuric acid by Contact Process involves the following steps:

(i) Sulphur dioxide gas is produced by burning sulphur in air or by roasting of pyrites.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(ii) Sulphur dioxide produced is then freed from dust and other impurities such as arsenic compounds.

(iii) The purified sulphur dioxide in then oxidized by atmospheric oxygen to sulphur trioxide in the presence of a catalyst, vanadium (V) oxide, V_2O_5 heated to 720K.

$$2SO_2 + O_2 \xrightarrow[720K]{V_2O_5} 2SO_3$$

The plant is operated at a pressure of 2 atmosphere and temperature of 720K.

(iv) The sulphur trioxide gas in then absorbed in conc. H_2SO_4 to form *oleum* ($H_2S_2O_7$). If SO_3 is directly dissolved in water, a highly corrosive mist of sulphuric acid is formed.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

(v) Oleum is then diluted with water to obtain sulphuric acid of desired strength.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The sulphuric acid obtained from the contact process is about 96-98% pure.

Properties of Sulphuric acid

(i) Physical properties : Pure sulphuric acid is a thick colourless oily liquid. Its melting point is 283.5K. Concentrated sulphuric acid dissolves in water with the liberation of a large amount of heat. While preparing dilute H_2SO_4, water must not be added to conc. H_2SO_4. Dilute sulphuric acid is prepared by adding conc. H_2SO_4 slowly and with constant stirring to water. If water is added to the acid, the heat produced is so large that it could throw out drops of sulphuric acid and burn you.

Chemical properties : The most important properties of sulphuric acid are its oxidizing and dehydrating properties.

(i) **Oxidizing properties :** Hot concentrated sulphuric acid acts as an oxidizing agent and oxidizes metals, non-metals and compounds.

Oxidation of metals.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2$$

Oxidation of non-metals

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

Oxidation of compounds

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$

$$8HI + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$$

$$3H_2S + H_2SO_4 \longrightarrow 4S + 4H_2O$$

Dehydrating properties : Conc. H_2SO_4 is a strong dehydrating agent. It removes water of crystallization from copper sulphate (which is blue in colour) and turns it to white colour.

$$\underset{\textbf{blue}}{CuSO_4.5H_2O} \xrightarrow[-5H_2O]{\text{conc. } H_2SO_4} \underset{\textbf{white}}{CuSO_4}$$

It also removes water from carbohydrates leaving behind, black mass of carbon.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

Uses of Sulphuric Acid

Sulphuric acid is known as the king of chemicals. It is practically used in every industry. It is used in the manufacture of fertilizers, paints and pigments, detergents, plastics and fibres, etc.

Structures of Oxyacids of Sulphur

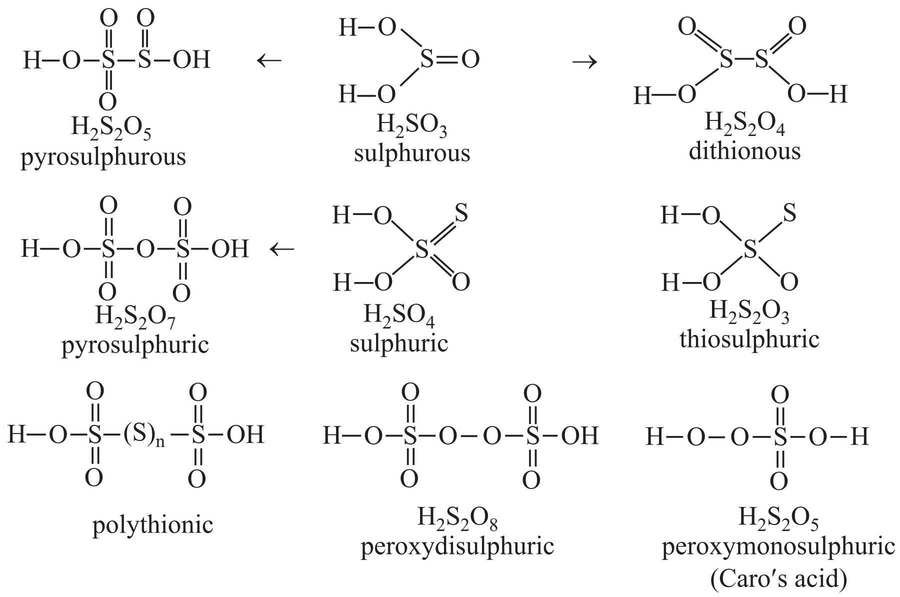


Fig. 20.2: *Some oxyacids of sulphur.*

INTEXT QUESTIONS 20.3

1. Write a reaction to show the

   (i) oxidizing property of sulphuric acid

   (ii) dehydrating property of sulphuric acid

2. In the manufacture of sulphuric acid by Contact process, SO_3 is dissolved in conc. H_2SO_4 and not in water. Why?

3. Write the reaction that takes place in the presence of a catalyst in the contact process.

20.6 SOME GENERAL CHARACTERISTICS PROPERTIES OF ELEMENTS OF GROUP 17

All members of Group 17 are non-metallic, although there is the usual increase in 'metallic' character with increasing atomic number, e.g. dipyridine iodine nitrate can be written as $[1(\text{pyridine})_2]^+NO_3^-$, containing the 1^+ ion as part of a complex. Fluorine and chlorine are gases, bromine is a volatile liquid, and iodine is a dark shiny coloured solid. Astatine is radioactive and very short-lived; what little chemistry that has been carried out with this element has employed tracer techniques.

These elements can enter into chemical combination and complete their octets by gaining one electron to form the 1-valent ion, e.g. F^-, Cl^-, etc., and by forming one covalent bond, e.g. the elements themselves F_2, Cl_2, Br_2, I_2 and their hydrides HF, HCl, HBr and HI.

Because chlorine, bromine and iodine have easily accessible *d* orbitals available, they are able to form covalent compounds in which the octet of electrons is expanded; for instance, iodine shows valencies of 1, 3, 5 and 7 respectively in the compounds ICI, ICI_3, IF_5 and IF_7. Like nitrogen and oxygen (the first members of Group 15 and 16, respectively), fluorine cannot expand its octet and is thus restricted to a covalency of 1.

The molecules of the halogens are diatomic with only weak van der Waals' forces operating between the individual molecules; however, in the case of iodine these forces are sufficiently strong to bind the iodine molecules into a three dimensional lattice (fig.). This structure is easily broken down on heating, and in fact, iodine sublimes at one atmosphere pressure if warmed gently.

The Structure of iodine

There is sufficient difference between fluorine and chlorine in chemical behavior to warrant a separate treatment of the former element. Chlorine, bromine and iodine are treated as a group.

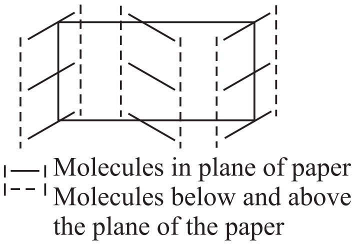


Table 20.2: Physical properties of Group 17 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm M^{3+}	M.P. /°C	B.P. /°C
F	9	2.7 $\ldots 1s^2 2s^2 2p^5$	0.072	0.136	–220	–188
Cl	17	2.8.7 $\ldots 2s^2 2p^6 3s^2 3p^5$	0.099	0.181	–101	–34.7
Br	35	2.8.18.7 $\ldots 3s^2 3p^6 3d^{10} 4s^2 4p^5$	0.114	0.195	–7.2	58.8
I	53	2.8.18.18.7 $\ldots 4s^2 4p^6 4d^{10} 5s^2 5p^5$	0.133	0.216	114	184
At	85	2.8.18.32.18.5 $\ldots 5s^2 5p^6 5d^{10} 6s^2 6p^5$				

Occurrence

Fluorine and chlorine are fairly abundant, bromine and iodine less so,. Fluorine is present mainly in the insoluble fluorides of calcium: calcium fluoride; cryolite, Na_3AlF_6; and fluoroapatite, $3Ca_3(PO_4)_2 . CaF_2$. Sea-water contains the chlorides, bromides, and iodides, of sodium, potassium, magnesium, and calcium. The deposits of dried-up seas contain these compounds, mainly the chlorides, for example sodium chloride and carnallite, $KCl{\cdot}MgCl_2$. Certain forms of marine life concentrate iodine in their systems.

20.7 FLUORINE AND CHLORINE

Fluorine and chlorine are the first two members of Group17. Fluorine is the most electronegative element. In this section we shall briefly learn about fluorine and chlorine and study in some detail about the hydrogen halides, oxides and oxoacids of chlorine and interhalogen compounds.

Fluorine is extremely difficult to prepare owing to its highly reactive nature. It is the strongest chemical oxidizing agent hence cannot be prepared by oxidation of fluoride ions. It is prepared by the electrolysis of potassium hydrogen fluoride (KHF_2) in anhydrous hydrogen fluoride. Hydrogen fluoride undergoes electrolytic dissociation.

$$2HF \rightarrow F_2 + H_2$$

The fluorine obtained is contaminated with hydrogen fluoride which may be removed by passing the gas over solid NaF.

Fluorine is a pale yellow gas which fumes in air.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2.$$

Fluorine is highly reactive. It combines with various metals and non-metals to form fluorides. With hydrogen halides it acts as an oxidizing agent, e.g.

$$2HX + F_2 \rightarrow 2HF + X_2 \text{ (X = Cl, Br or I)}$$

Fluorine is widely used in the preparation of fluorinated hydrocarbons which in turn find various uses in industry.

Chlorine is usually prepared by the oxidation of chlorides by strong oxidizing agents, such as MnO_2, $KMnO_4$.

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O + Cl_2$$

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

On a large scale chlorine is obtained as a by product in the electrolysis of sodium chloride.

Chlorine is a greenish yellow gas and can be liquified by pressure alone at room temperature, It is quite reactive and forms chlorides of metals and nonmetals when reacted with them. It also oxidizes ammonia to nitrogen

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

Large quantities of chlorine are used in bleaching industry and in the manufacture of plastics, synthetic rubbers, antiseptics and insecticides.

20.7.1 Hydrogen Halides and Hydrohalic Acids

The hydrogen halides under consideration are HF, HCl, HBr and HI. The bond distance H–X increases with the size of halogen atom. The bond also becomes more covalent and less ionic. Since the bond length increases, the hydrogen halide in aqueous solution loses hydrogen ion more easily with increasing size of halogen, and the acid strength increases in the order HF < HCl < HBr < HI

The aqueous solutions of hydrogen halides are, in general, known as hydrohalic acids or simply halogen acids (hydrofluoric, hydrochloric hydrobromic, and hydroiodic acids)

Preparation of Hydrogen Halides

Industrially HF is made by heating CaF_2 with strong H_2SO_4.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Hydrogen chloride is made by heating a mixture of NaCl and conc. H_2SO_4 at 423 K.

$$NaCl + H_2SO_4 \xrightarrow{423\text{ K}} HCl + NaHSO_4$$

$$NaCl + NaHSO_4 \xrightarrow{823\text{ K}} HCl + Na_2SO_4$$

High purity HCl is made by the direct combination of the elements (H_2 and Cl_2)

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Phosphoric acid is used to make HI

$$H_3PO_4 + NaI \longrightarrow HI + NaH_2PO_4$$

HBr is made by a similar method. Also we use red phosphorus for making HBr and HI

$$2P + 3Br_2 \longrightarrow 2PBr_3$$

$$PBr_3 + 6H_2O \longrightarrow 6HBr + 2H_3PO_3$$

$$2P + 3I_2 \longrightarrow 2PI_3$$

$$2PI_3 + 6H_2O \longrightarrow 6HI + 2H_3PO_3$$

Properties of the Halogen Halides

- HF is a liquid at room temperature (b.p. 293 K), whereas HCl, HBr and HI are gases.
- The boiling point of HF is unexpectedly high as compared to HCl (189K), HBr (206K) and HI (238K). This is due to the formation of hydrogen bonds between the F atom of one molecule and the H atom of another molecule (Fig. 20.2).

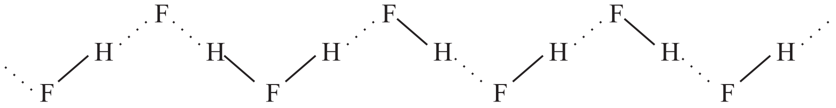


Fig. 20.2 : *Hydrogen bonded chain in HF*

In the gaseous state, the hydrogen halides are essentially covalent. In the aqueous solutions they ionize to form ions but HF ionizes to a very small extent

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$

The bond dissociation energy of the hydrogen halides follow the order HF>HCl>HBr>HI.

The stability of hydrogen halides to thermal decomposition therefore decreases in the order HF > HCl > HBr > HI. The acid strength of the acids increases in the order HF < HCl < HBr < HI. The aqueous solution known as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid possess the usual property of acids, e.g. they react with bases to form salts and water and with metals to form salts and hydrogen.

Uses of Hydrogen Halides

Hydrogen fluoride is used to prepare certain fluorides mainly fluorocarbons or freons. It is also used in etching glass and in removing sand from casting. Hydrogen chloride is primarily used for preparing chlorides. Large quantities of hydrochloric acid are used in the manufacture of aniline dyes and for cleaning iron before galvanization. Hydrogen bromide and hydrogen iodide are used to prepare bromide and iodide salts. Hydrogen iodide is also used as a reducing agent in organic chemistry.

20.7.2 Oxides and Oxoacids of Halogens

There are several compounds containing halogen and oxygen. Oxygen is less electronegative than fluorine, hence the compounds of oxygen with fluorine are known as oxygen fluorides (e.g. OF_2). Other halogens are less electronegative than oxygen. Thus they are known as halogen oxides. Only the oxides of chlorine are important and they are described here.

Oxides of chlorine The main oxides are listed below :

Chlorine monoxide, Cl_2O

Chlorine dioxide, ClO_2

Chlorine hexoxide, Cl_2O_6

Chlorine heptoxide, Cl_2O_7

Chlorine monoxide, Cl_2O, is prepared by passing chlorine over freshly prepared mercury (II) oxide

$$2\,Cl_2 + 2\,HgO \longrightarrow Cl_2O + HgO.\,HgCl_2$$

It is a pale yellow gas which decomposes violently on heating and dissolves in water forming hypochlorous acid. $Cl_2O + H_2O \longrightarrow 2HOCl$

It is a powerful oxidizing agent.

Chlorine dioxide, ClO_2, is prepared by the action of concentrated sulphuric acid on potassium chlorate

$$KClO_3 + H_2SO_4 \longrightarrow \underset{\textbf{chloric acid}}{HClO_3} + KHSO_4.$$

$$3HClO_3 \longrightarrow \underset{\textbf{perchloric acid}}{HClO_4} + 2ClO_2 + H_2O$$

It is an orange gas and explosive in nature.

Chlorine hexoxide, Cl_2O_6, is prepared by the action of ozone on chlorine at low temperature. It is a red liquid and dissolves in alkalies producing chlorate and perchlorate

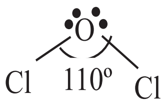
$$Cl_2O_6 + 2OH^- \longrightarrow ClO_3^- + ClO_4^- + H_2O$$

Chlorine heptoxide, Cl_2O_7, is prepared by the action of phosphorus pentoxide on anhydrous perchloric acid at 263 K.

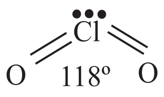
$$P_4O_{10} + 4HClO_4 \longrightarrow 4\,HPO_3 + 2Cl_2O_7$$

It is a colourless oil which explodes on heating or striking.

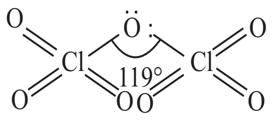
The structures of chlorine oxides are as follows :



Cl_2O



ClO_2



Cl_2O_7

Oxoacids of chlorine

Chlorine forms four oxoacids, HOCl, HOClO, $HOClO_2$ and $HOClO_3$

Hypochlorous acid, HOCl is known only in solution - It is prepared by shaking chlorine water.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

Its salt NaOCl is used as a bleaching agent.

Chlorous acid, HOClO is also known in solution, certain chlorite salts of alkali and alkaline earth metals are known in solid state, e.g., $NaClO_2, 3H_2O$. The acid is prepared by the action of barium chlorite with sulphuric acid.

$$\underset{\textbf{barium chlorite}}{Ba\,(ClO_2)_2} + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4$$

Chloric acid, $HOClO_2$ is prepared by the action of barium chlorate with sulphuric acid.

$$\underset{\textbf{barium chlorate}}{Ba\,(ClO_3)_2} + H_2SO_4 \longrightarrow HClO_2 + BaSO_4$$

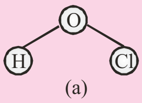
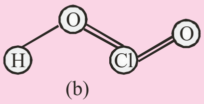
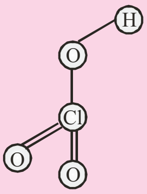
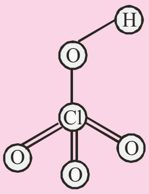
Perchloric acid, $HOClO_3$, is prepared by distilling potassium perchlorate with concentrated sulphuric acid under reduced pressure

$$\underset{\textbf{potassium perchlorate}}{2KClO_4} + H_2SO_4 \longrightarrow 2HClO_4 + K_2SO_4$$

It is a colourless oily liquid and combines vigonously with water forming hydronium perchlorate ($H_3O^+ ClO_4^-$). It is one of the strong acids. It is also an oxidizing agent.

The oxoacids of chlorine are listed in the following table showing their structures.

Table 20.3 : Oxoacids of chlorine

Name	Hypochlorous acid (a)	Chlorous acid (b)	Chloric acid (c)	Perchloric acid (d)
Formula of oxoacid	HOCl	HOClO	$HOClO_2$	$HOCl\ O_3$
Oxidation state of chlorine	+1	+3	+5	+7
Structure	 (a)	 (b)	 (c)	 (d)

The acid strength of the oxoacids of chlorine increases as the number of O-atoms present in the acid increases.It is because oxygen is more electronegative then chlorine. As the number of O atoms bonded to the Cl atom increases, more electrons will be pulled away more strongly from the O–H bond. As a result the O–H bond will be weakened. Thus $HOClO_3$ require the least energy to break the O–H bond and form H^+. Thus, HOCl is a very weak acid whereas $HOClO_3$ is the strongest acid, thus the acid strength increases in the order.

$$HOCl < HOClO < HOClO_2 < HOClO_3$$

20.7.3 Chlorofluorocarbons (CFC)

Chlorofluorocarbons are the compounds of carbon where chlorine and fluorine are substituted for hydrogen in saturated hydrocarbons e.g. CCl_2F_2, $CFCl_3$, $C_2F_4Cl_2$ etc. These compounds have very high capacity to retain heat. It is believed that the capacity to retain heat is about 10,000 times more than that of carbon-dioxide. Thus these molecules are capable of cooling other systems by taking away their heat.

Chlorofluorocarbons are also termed as **freons**. About 5 thousand metric tonnes of CFC's are still being produced in our country annually. In addition to their usage as aerosols, solvents, foam blowing agents and refrigerants, they are also known to cause environmental hazard. CFCs react with protective ozone layer in the stratosphere, thus causing perforation through which radiations from outer sphere enter our atmosphere and cause damage to our life systems. The destruction of ozone layer is termed as *ozone depletion* and it is creating a ozone hole.

20.7.4 Interhalogen Compounds

The halogens form a series of mixed binary compounds called the interhalogens. These compounds are of the type XX', XX_3', XX_5', and XX_7'. The compounds of the type XX' are known for all combinations. Compounds of XX_3', and XX_5' types are known for some, and of XX_7' type only IF_7 is known.

Preparation

The interhalogen compounds can be prepared by direct reaction between the halogens. They can also be prepared by the action of a halogen on a lower interhalogen.

$$Cl_2 + F_2 \text{ (equal volumes)} \xrightarrow{473K} 2ClF$$

$$Cl_2 + 3F_2 \text{ (excess } F_2\text{)} \xrightarrow{573K} 2ClF_3$$

$$I_2 + 5F_2 \xrightarrow{293K} 2IF_5$$

$$I_2 + 7F_2 \xrightarrow{523-573K} 2IF_7$$

INTEXT QUESTIONS 20.4

1. Name the most electronegative halogen.
2. Name the halogen that can react with an inert gas.
3. Write a chemical reaction used for the laboratory preparation of chlorine.
4. Arrange the hydroacids of halogens in the decreasing order of their strength.
5. What group of carbon compounds is supposed to cause ozone depletion.

20.8 THE NOBLE GASES

The gaseous elements helium, neon, argon, krypton, xenon and radon constitute the 18 group of the periodic table. Because of their low, abundance on the earth, they have been called *rare gases*, and due to their chemical inertness, they have been called inert or noble gases. With the discovery that some of them can form compounds under suitable conditions, we no longer refer to them as inert gases. All of them, except helium, have the closed shell, np^6, configurations Helium has the ls2 configuration. The electronic configuration accounts for their high degree of chemical inertness in ordinary chemical reactions.

Occurrence

All the noble gases, except radon, are present in atmosphere. The relative percentages of the noble gases in dry air are given in the following table.

Table 20.4: Relative Abundance of 18 Group Elements in Dry Air

Element	Percentage
Helium (He)	5.2×10^{-4}
Neon (Ne)	1.8×10^{-3}
Argon (Ar)	9.3×10^{-1}
Krypton (Kr)	1.1×10^{-4}
Xenon (Xe)	8.7×10^{-6}
Radon (Rn)	–

In addition helium is present up to l0 per cent in natural gas. It also results from the decay of certain radioactive elements and is found in some uranium minerals. Radon is produced in the radioactive decay of radium.

Properties

The outer electronic configuration and the general trends in properties of the noble gases are summarised in Table

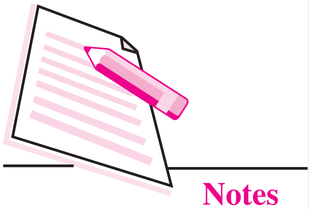
Table 20.5: Relative Abundance of 18 Group Elements in Dry Air

***	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	[He] $2s^2 2p^6$	[Ne] $3s^3 3p^6$	[Ar] $3d^{10} 4s^2 4p^6$	[Kr] $4d^{10} 5s^2 5p^6$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$
Atomic radii	**120**	**160**	**190**	**200**	**220**	**-**
Ionic radii/kJmol^{-1}	2372	2080	1520	1351	1170	1037
Election gain enthalpy/kJmol^{-1}	48	116	96	96	77	68
Den (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
M.P.	-	24.6	83.8	115.9	161.3	202
B.P.	4.2	27.1	87.2	119.7	165.0	211
Fraction in Air (% volume) radiactive	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

20.9 COMPOUNDS OF NOBLE GASES

The group 18 of the periodic table consists of six elements – helium, neon, argon, krypton, xenon and radon. These elements are termed as **'noble gases'**. The name noble gases implies that they tend to be unreactive and are reluctant to react just like noble metals. Except helium which has 2 electrons and forms a complete shell $1s^2$, the other elements of the group have a closed octet of electrons in their outer shell $ns^2 np^6$. This electronic configuration is very stable and the ionization energies of the atoms of these elements are very high. Therefore, the atoms of noble gases have a little tendency to gain or lose electrons. Hence these elements exhibit lack of chemical reactivity.

The first compound of noble gases was made by Neil Bartlett in 1962 by the reaction of xenon with PtF_6. Since then several other xenon compounds, mainly with the most electronegative elements (fluorine and oxygen), have been prepared. He, Ne and Ar do not form any compounds whereas Kr does form KrF_2. Radon is a radioactive element and all its isotopes have very short half lives.



Notes

Xenon Compounds

Xenon reacts with fluorine to form binary fluorides, XeF_2, XeF_4 and XeF_6. The product formed depends on the temperature and xenon-fluorine ratio. Thus

$$\underset{(2:1\ \text{ratio})}{Xe + F_2} \xrightarrow{873\ \text{K},\ 1\ \text{bar}} XeF_2(s)$$

$$\underset{(1:5\ \text{ratio})}{Xe + 2F_2} \xrightarrow{873\ \text{K},\ 7\ \text{bar}} XeF_4(s)$$

$$\underset{(1:20\ \text{ratio})}{Xe + 3F_2} \xrightarrow{573\ \text{K},\ 60\ \text{bar}} XeF_6\ (s)$$

XeF_2, XeF_4 and XeF_6 are all white solids. They readily sublime at 298 K. They differ in their reactions with water

XeF_2 dissolves in water and undergoes slow hydrolysis in water.

$$2\ XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

XeF_4 and XeF_6 react with water violently to give xenon trioxide and hydrogen fluoride.

$$6\ XeF_4 + 12H_2O \longrightarrow 4\ Xe + 2XeO_3 + 24\ HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeF_6 on partial hydrolysis gives, xenon oxofluorides.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

The xenon fluorides react with strong Lewis acids to form complexes.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+\ [PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+\ [SbF_6]^-$$

XeF_6 may also act as a fluoride accepter from fluoride ion donors to form fluoroxenate anions.

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^-\ (M = Na, K, Rb, Cs)$$

XeO_3 can be prepared by hydrolysis of XeF_6

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeO_4 can be prepared by the reaction of barium peroxenate with conc. sulphuric acid

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

Structure of Xenon compounds

The structures and shapes of the common xenon fluorides and oxides are shown below. The shapes of these molecules can be explained in terms of VSEPR theory which you have already learnt in chemical bonding.

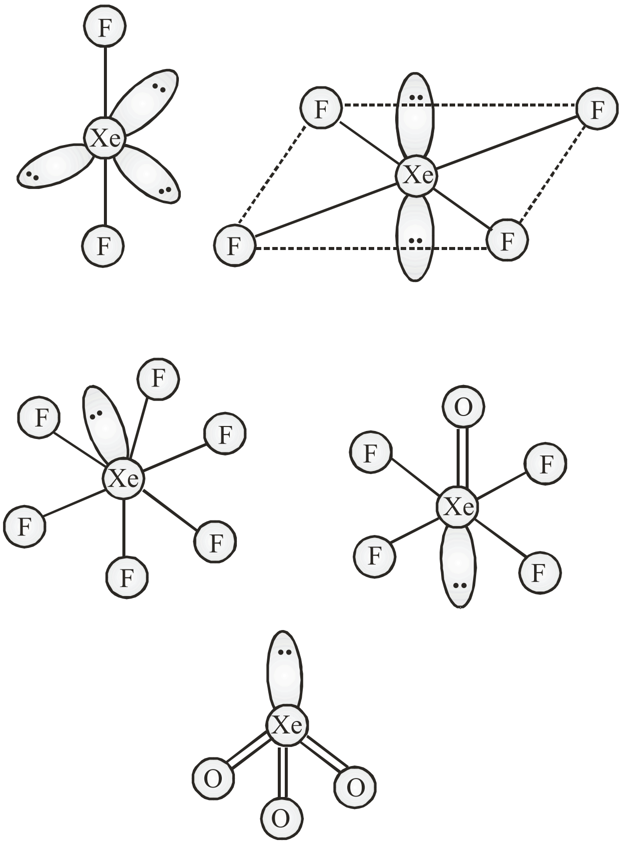


Fig. 20.3 : *The structures of* XeF_2, XeF_4, XeF_6, XeO_3 *and* $XeOF_4$

WHAT YOU HAVE LEARNT

- General characterics of the elements o Group 16, 17 & 18.
- While sulphur exists as S_8 molecules oxygen exists as O_2 molecules. Both these elements form divalent anions however sulphur also shows +4 and +6 oxidation state. Oxygen and sulphur are non-metals of group number 16.
- The binary compounds of oxygen with other elements are known as oxides. The oxides can be classified as : acidic oxides, basic oxides and amphoteric oxides.
- Ozone, an allotrope of oxygen is prepared by Siemen's ozonizer.
- Allotropic forms of Sulphur preparation properties and uses of SO_2.

- Sulphuric acid displays strong acid character and possesses oxidizing and dehydrating properties.
- Structure of oxoacids of Sulphur.
- Chlorine forms a number of oxoacids : HOCl, $HClO_2$, $HClO_3$ and $HClO_4$.
- The binary compounds of halogens with one another are called inter halogen compounds.
- Halogens are placed in group number 17 of the periodic table. All members of the group are very reactive. They show variable oxidation states. Halogens react with other halogen forming interhalogens. Halogen (Fluorine) can even react with noble gases. Halogens react with hydrogen forming hydracids.
- Fluorochlorocarbons are called freons which decompose ozone and are therefore environmentally hazardous.
- Occurance of noble gases.
- Helium, neon, argon, krypton, xenon and radon are the members of Group number 18 and are collectively called noble gases.
- Xenon is known to react with fluorine to form XeF_2, XeF_4 and XeF_6.

TERMINAL EXERCISES

1. Which one of the following oxides can react with an acid as well as with an alkali : SO_2, CaO, ZnO, MgO?
2. Write two oxides which do not react with either acids or alkalies. Which type of oxides are they?
3. Is ozone an allotrope of oxygen? Which is more soluble in water oxygen or ozone?
4. What is the state of hybridization of the central oxygen atom in O_3 molecule?
5. Why does ozone tail mercury?
6. Which property of ozone makes it useful for bleaching?
7. Write the conditions which are required to convert SO_2 to SO_3 in the manufacture of sulphuric acid by contact process.
8. What is oleum?
9. Why is sulphuric acid known as king of chemicals?
10. Write down the structure of oxo acids of sulphur.

11. Fluorine never acts as a central atom in any interhalogen compounds. Why?
12. Draw the structure of BrF_4^-.
13. Arrange the hydrogen halides in order of their acid strength in aqueous solution.
14. Why is F_2O not known as fluorine oxide? Instead it is known as oxygen fluoride, OF_2.
15. Which is the strongest acid among the oxoacids of chlorine and why?
16. What happens when XeF_4 reacts with SbF_5? Write the complete equation for the reaction.

ANSWERS TO INTEXT QUESTIONS

20.1

1. Basic oxide : CaO; acidic oxide : SO_2 ; amphoteric oxide : ZnO.
2. Acidic oxide : SiO_2, SO_2, CrO_3

   Basic oxide : K_2O, FeO

   Amphoteric oxide : Al_2O_3, ZnO
3. $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

   $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$
4. An oxide of group 1, K_2O and of Gr 2 BaO

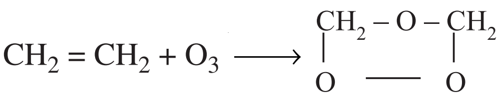
   $K_2O + 2HCl \longrightarrow 2KCl + H_2O$

   $BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$

   Oxygen has multiple bonds but sulphur has single bond.

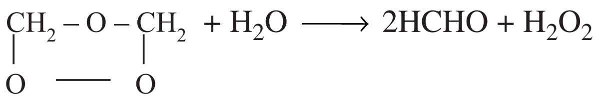
20.2

When ethene combines with O_3, an ozonide is formed, thus



$$CH_2 = CH_2 + O_3 \longrightarrow \begin{array}{ccc} CH_2 & -O- & CH_2 \\ | & & | \\ O & — & O \end{array}$$

On hydrolysis it gives HCHO,

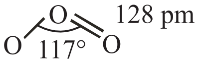


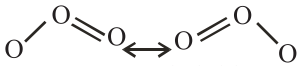
$$\begin{array}{ccc} CH_2 & -O- & CH_2 \\ | & & | \\ O & — & O \end{array} + H_2O \longrightarrow 2HCHO + H_2O_2$$

2. (i) $2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2$

   (ii) $3SnCl_2 + O_3 + 6HCl \longrightarrow 3\,SnCl_4 + 3H_2O$

3. Ozone is 10 times more soluble than O_2.

4. 



resonance hybrids

5. Mercury loses its convex meniscus and leaves a “tail” or a trail of minute droplets on a glass surface when exposed to ozone. This is due to the formation of mercurous oxide. The tailing effect can be removed by washing the mercury with a dilute acid.

20.3

1 (i) Oxidizing property of conc. H_2SO_4

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(ii) Dehydrating property : It removes water from sugar

$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + 11\,H_2O$

2. A corrosive mist of sulphuric acid is formed.

3. $2SO_2 + O_2 \xrightarrow[720\,K]{V_2O_5} 2SO_3$

20.4

1. Fluorine
2. Fluorine
3. $2\,NaCl + 3H_2SO_4 + MnO_2 \longrightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + Cl_2$
4. $HI > HBr > HCl > HF$
5. Chlorofluorocarbons (or freons)

313en21

21

d-BLOCK AND f-BLOCK ELEMENTS

You have already learnt in lesson 3 on periodic classification, that each period (except the first period) of the periodic table starts with the filling of *ns* subshell and ends with the filling of *np* subshell (*n* is the principal quantum number and also the number of the period). The long form of the periodic table is based on the filling of electrons in various levels in order of increasing energy as given by Aufbau principle. In the fourth period, filling of the 4th shell commences with the filling of 4*s* subshell followed by 3*d* and 4*p* subshells. For the first time, we come across a group of elements in which a subshell of the previous principal quantum number (3*d*) starts getting filled instead of the expected subshell 4*p*. This group of elements that occurs in between the *4s* and *4p* elements is referred to as *3d* elements or elements of first transition series (see periodic table). *4f* Series consist of 14 members from Ce to Lu (At. No. 58-71), where the penultimate subshell, *4f* subshell is filled up. They have general electronic configuration [Xe] $4f^{1-14}\ 5d^{1,2}\ 6s^2$. La is also included in this series: it is the prototype for the succeeding 14 elements. In this lesson you will study more about these elements and also about the preparation, properties and uses of potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$).

OBJECTIVES

After reading this lesson, you will be able to:

- define transition metals and write their electronic configuration;
- list the general and characteristic properties of the transition elements;
- explain the properties of 3d transition series: metallic character, variable oxidation state, variation in atomic and ionic radii, catalytic properties,

coloured ions, complex formation, magnetic properties, interstitial compounds and alloy formation;

- recall the preparation of potassium permanganate from pyrolusite ore;
- write the chemical equations illustrating the oxidizing properties of $KMnO_4$ in acidic, alkaline and neutral media (acidic: $FeSO_4$, SO_2, alkaline: KI and ethene, neutral: H_2S and $MnSO_4$);
- recall the preparation of potassium dichromate from chromite ore;
- write the oxidation reactions of potassium dichromate with SO_2 and ferrous sulphate in acidic medium;
- write electronic configuration of lanthanoides (4f-elements) and actinoids (5f-elements);
- explain oxidation states of lanthanoids and actinoids;
- explain the comparison between lanthanoids and actinoids;
- explain lanthanoide contraction.

21.1 OCCURRENCE OF THE FIRST-ROW TRANSITION METAL ELEMENTS

Only a few of the transition elements occur in free state e.g. Au and Pt. Most of the these elements occur as oxides, sulphides and carbonates in nature. (See module 6, lesson 18)

21.2 *d*-BLOCK ELEMENTS

d-Block elements occupy the middle portion of the periodic table i.e. between *s*- and *p*- block elements. They include elements from groups 3 to 12. In these elements the outermost shell contains one or two electrons in their outer most i.e, ns orbital but the last electron enters into the inner d-subshell i.e. $(n\text{-}1)\ d$ orbital. The elements of the *d-block* are metallic in nature. Their general characteristic properties are intermediate between those of the s-block elements, on one hand and of the p-block elements on the other. We can say that *d*-block elements represent a change (or transition) from the most electropositive *s*-block elements to the least electropositive *p*-block elements and are, therefore, also named as transition elements.

Transition elements are elements in which the *d* subshell is partially filled either in atomic state or in ionic state.

There are four series of transition elements in the periodic table. The first transition series begins with scandium (At. No. 21) and ends at copper (At. No. 29) whereas the second, third and fourth series begin with yttrium (At. No. 39), lanthanum (At. No. 57) and actinium (At. No. 89) and end at silver (At. No. 47), gold (At. No. 79) and at the element having atomic number 112 (a synthetic element), respectively. These series are also referred to as *3d, 4d, 5d* and *6d* series, respectively. It may be noted that although elemental copper, silver and gold as well as Cu^{1+}, Ag^{1+} and Au^{1+} have a d^{10} configuration but Cu^{2+} has a $3d^9$, Ag^{2+} a $4d^9$ and Au^{3+} a $5d^8$ configuration and that is why these elements are classified as transition elements. On the other hand, zinc, cadmium and mercury do not have partially filled *d* subshell either in the elemental state or in any of their common ions. These elements, therefore, are not transition elements. However, zinc, cadmium and mercury are often considered along with *d*- block elements.

INTEXT QUESTIONS 21.1

1. What are transition elements?
2. How many elements comprise the first transition series? Give names of all these elements.
3. Whereas copper is a transition element, zinc is not included amongst transition elements. Explain.
4. Although Cu^+, Ag^+ and Au^+ have d^{10} configuration but Cu, Ag and Au are transition elements, why?

21.2 ELECTRONIC CONFIGURATION

The general electronic configuration of transition elements is $(n\text{-}1)\, d^{1\text{-}10}\, ns^{1\text{-}2}$. The (n-1) stands for inner shell and the *d*-orbitals may have one to ten electrons and the *s*-orbital of the outermost shell (n) may have one or two electrons. It is observed from the Fig. 21.1 that 4*s* orbital ($l = 0$ and $n = 4$) is of lower energy than 3*d* orbitals ($l = 2$ and $n = 3$) upto potassium (At. No.19). The energy of both these orbitals is almost same in case of calcium (At. No. 20), but the energy of 3*d* orbitals decreases with further increase of nuclear charge and becomes lower than *4s,* and 4*p,* (in case of scandium At. No.21). Thus after filling of 4*s* orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to 3*d* orbital instead of 4*p,* as the former is of lower energy than the latter. This means that 21st electron enters the underlying principal quantum level with $n = 3$ rather than the outermost level with $n = 4$ which started filling at potassium (At. No.19), the first element of the fourth period. In the case of next nine elements following calcium, the incoming electron is filled in the *d*- subshell. Since half filled and completely filled subshells are stabler than the one in which one electron is short, an electron gets transferred from 4*s* to 3*d* in case of the elements with atomic number 24 and 29. Consequently, configuration of chromium and copper have only one 4*s* electron (Table 21.1).

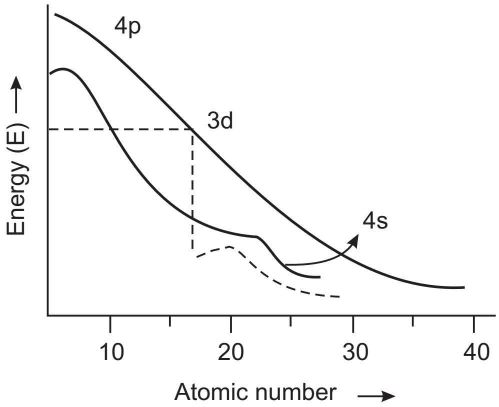


Fig. 21.1 : *Variation of energy of orbitals vs atomic number*

Table 21.1: Electronic configuration of first series(or 3*d*) transition elements

Element	Symbol	Z	Electronic Configuration
Scandium	Sc	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
Titanium	Ti	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
Vanadium	V	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Chromium	Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Manganese	Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Iron	Fe	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Cobalt	Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Nickel	Ni	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Copper	Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

As can be seen, in case of zinc, the 30th electron goes to 4*s* level and not 3*d* level which is already full. Thus by definition, zinc cannot be called a member of *d*block elements. Besides, no compound of zinc is known to have a partially filled 3*d* subshell. Thus it does not fit into the definition of a transition element either. Hence zinc cannot be rightly called either a *d*-block element or transition element. However, zinc and other members of group 12, viz., cadmium and mercury are discussed along with 3*d,* 4*d* and 5*d* transition elements for the sake of convenience.

It is important to understand at this point, the process of ionization (i.e. oxidation) of transition elements. From what has been said above regarding filling of the orbitals, it is logical to conclude that during ionization electrons should be lost first from the (n-1) *d* subshells and then from the 4*s* level. This, however, is not the case. The reason for the deviation from the expected behavior is that once the filling of the *3d* subshell commences at scandium (At. No.21) energy of 3*d* subshell decreases and becomes lower than that of 4*s* subshell. Consequently, on ionization, the first row transition elements lose electrons from the 4*s* subshell followed by the loss from 3*d* level. For example vanadium (Z = 23) has electronic configuration V= [Ar]$3d^3\,4s^2$ and the electronic configuration of V^{2+} is [Ar]$3d^3$, Similarly electronic configuration of V^{3+} and V^{4+} are [Ar]$3d^2$ and [Ar]$3d^1$, respectively. In some cases, however, for example scandium, all the electrons beyond the core of 18 electrons are lost in single step. It is important to note that though 3*d* orbitals are of higher energy than 4*s* orbitals (as is evident from the order of filling) the difference is so little that these are considered almost of same energy.

INTEXT QUESTIONS 21.2

1. Write the general electronic configuration of transition elements.
2. Write down the electronic configuration of the following elements in ground state: Sc, Cr, Cu and Zn.
3. Write down the electronic configuration of the following ions: Cr^{3+}, Ti^{4+}, Ni^{3+} and Cu^{2+}.
4. Why the electronic configuration of Mn^{2+} is $3d^5$ and not $3d^2\,4s^2$?

21.3 PHYSICAL PROPERTIES

Some important physical properties of *d*-block elements are listed in Table 21.2. Like *s*-block elements, *d*-block elements are also metals. But properties of these elements are markedly different from those of *s*-block elements. The interesting feature of the chemistry of transition elements is that similarities in the properties of transition elements are much more marked as compared to those in *s*-block. Almost all transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lusture. All the transition elements have typical metallic structure except mercury, which is liquid at room temperature.

Transition elements show high melting and boiling points. They typically melt above 1356 K. It is due to the small atomic size and strong interatomic bonding. All the transition elements are hard except zinc, cadmium and mercury. They show high enthalpy of atomization (Table 21.2). Densities of transition elements are very high as compared to those of s-block elements. The density of the elements in a given transition series increases across a period and reaches a maximum value at groups 8,9 and 10. This trend can be explained on the basis of small radii and close packed structure of the elements.

Atomic radii

The radii of the elements decrease from left to right across a row in the transition series until near the end, then the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra electrons are added. The

Table 21.2: Some important physical properties of 1st transition series

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Outer electronic configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$	$3d^{10} 4s^2$
Atomic radius (pm)	160	146	131	125	129	126	125	124	128	133
Ionic radius M^{2+} (pm)	–	90	88	84	80	76	74	72	69	79
Ionic radius M^{3+} (pm)	81	76	74	69	66	64	63	63	–	–
Crystal structure	fcc	hcp	bcc	bcc	bcc	bcc,fcc	hcp,fcc	fcc	fcc	hcp
Density (g ml^{-1})	3.1	4.5	6.1	7.2	7.6	7.9	8.7	8.9	8.9	7.1
Melting point (K)	1817	1998	2173	2148	1518	1809	1768	1726	1356	693
Boiling point (K)	3003	3533	3723	2138	2423	3273	3173	3003	2868	1179
Stable oxidation states	+3	+4	+3,+4,+5	+2,+3,+6	+2,+3,+4,+7	+2,+3	+2,+3	+2	+1,+2	+2
Ist ionization enthalpy (kJ mol^{-1})	632	659	650	652	717	762	758	736	745	906
Electronegatively	1.3	1.5	1.05	1.6	1.05	1.8	1.8	1.8	1.8	1.6
Heat of fusion (kJ mol^{-1})	15.9	15.5	17.6	13.8	14.6	15.3	15.2	17.6	13.0	7.4
Heat of vaporization (kJ mol^{-1})	338.9	445.6	443.6	305.4	224.7	353.9	389.1	380.7	338.9	114.6
Reduction potential $(E^0)M^{2+}/M(V)$	–	–1.63	–1.20	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34	–0.76

d-orbital electrons shield the nuclear charge poorly. Thus the effective nuclear charge increases and, therefore, electrons are attracted more strongly, hence contraction in size occurs. There is an increase in atomic radii with increase in atomic number in a given group, for example Ti (146 pm), Zr (157 pm) and Hf (157 pm). The very close similarity between the radii of elements of second and third transition series is a consequence of the filling of the 4*f*- subshell (causing lanthanide contraction which you will study later in this lesson).

INTEXT QUESTIONS 21.3

1. Why do transition elements show higher melting and boiling points?
2. Why do the radii of transition elements decrease along a period?
3. Why do transition elements show higher density as compared to *s*-block elements?

21.4 CHARACTERISTIC PROPERTIES

These are the properties shown only by transition elements. On the basis of these properties transition elements can be distinguished from *s* and *p*-block elements.

21.4.1 Variable Oxidation States

s-block, *d*-block and *f*-block elements show positive oxidation states (except H which shows –1 oxidation state also) whereas, most of the *p*-block elements show both positive and negative states. The number of electrons used for bonding by an electropositive element is equal to its positive oxidation state. A characteristic property of *d*-block elements is their ability to exhibit a variety of oxidation states in their compounds. This is due to the fact that for bonding, in addition to ns electrons, these elements can use inner (n-1)d electrons as well because of very small difference in their energies. Thus, depending upon the number of d electrons involved in bonding, different oxidation states arise. The lowest oxidation state is usually equal to the number of *s*-electrons present (except Sc). For example, copper has an electronic configuration of $3d^{10}4s^1$ and shows oxidation state of + 1 besides the usual oxidation state of +2. The highest oxidation states are observed in compounds with fluorine and oxygen, which are the two most electronegative elements. The different oxidation states of elements of the first transition series are given below:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn*
+3	(+2)	+2	+2	+2	(+1)	(+1)	(+1)	+1	(+1)
	+3	+3	+3	(+3)	+2	+2	+2	+2	+2
	+4	+4	+4	+4	+3	+3	(+3)	(+3)	
		+5	(+5)	(+6)	+6	(+4)	(+4)		
			+6	+7					

Notes

(* Given for comparison only.) Here the rare oxidation states are given in parentheses.

An examination of the common oxidation states given above, reveals the following:

Except for scandium, the most common oxidation state of 3*d* elements is +2 which arises from the loss of two 4*s* electrons. This means that after scandium, *d* orbitals become more stable than *s* orbital. Compounds having oxidation states +2 and +3 of these elements have ionic bonds whereas bonds are essentially covalent in higher oxidation states. For example, in case of permanganate ion, MnO_4^-, bonds formed between manganese and oxygen are covalent. Considering the acid base character of the oxides, it can be inferred that increase in oxidation state leads to decrease in basic character of the oxide and vice-versa. For example, MnO is a basic oxide whereas Mn_2O_7 is an acidic oxide.

Since transition metals exhibit multiple oxidation states, their compounds in the higher oxidation states are strong oxidizing agents as they tend to accept electrons and come to stable lower oxidation states.

21.4.2 Magnetic Properties

Substances possess two types of magnetic behaviour, either diamagnetism or paramagnetism. Diamagnetic substances are either repelled or remain unaffected by an applied magnetic field whereas, paramagnetic substances are attracted towards the applied field.

There is a strong co-relation between the magnetic behaviour, electronic configuration and oxidation state. Paramagnetism arises due to the presence of unpaired electrons (Table 21.3). Since transition metal ions generally contain unpaired electrons a large number of transition metal ions exhibit paramagnetic behavior.

Magnetic moment (μ) of paramagnetic material can be calculated (in B.M., Bohr Magneton) by using the expression: $\mu = \sqrt{n\,(n+2)}$ where n is the number of unpaired electrons.

For example, Ni^{2+} ion has two unpaired electrons (i.e. n = 2). The magnetic moment can be calculated as $\mu = \sqrt{2\,(2+2)} = \sqrt{8} = 2.83$ B.M The mangentic moments of some 3*d* metals ions are listed in Table 21.3 which shows that greater the number of unpaired electrons, greater is the magnetic moment.

Table 21.3 : Magnetic moments of some ions of the transition elements:

Ion	Electronic configuration	Number of unpaired electrons	Calculated magnetic moments (B.M.)
Sc^{3+}	$3d^0$	0	0
Ti^{3+}	$3d^1$	1	1.73

Ti^{2+}	$3d^2$	2	2.83
V^{2+}	$3d^3$	3	3.87
Cr^{2+}	$3d^4$	4	4.90
Mn^{2+}	$3d^5$	5	5.92
Fe^{2+}	$3d^6$	4	4.90
Co^{2+}	$3d^7$	3	3.87
Ni^{2+}	$3d^8$	2	2.83
Cu^{2+}	$3d^9$	1	1.73

Compounds containing Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+} and Cu^{+} ions are diamagnetic since these ions do not contain any unpaired electron.

21.4.3. Colour of Ions and Compounds

Most of the compounds of *d*-block elements are coloured or they give coloured solution when dissolved in water (Table 21.4). This property of transition elements is in marked contrast to that of the *s*- and *p*-block elements, which often yield white compounds. In transition metal compounds colour is generally associated with incomplete (n-1) *d* subshell of the transition metal. When white light, which has colored constituents, interacts with a substance, a part of it is absorbed by the substance. For example, if red portion of white light is absorbed by a substance, it would appear blue (the complementary colour of red). This is observed in case of copper sulphate solution. Since most compounds of transition elements are coloured, there must be energy transition, which can absorb some of the energy of the visible light. The colour of transition metal ions containing unpaired electrons is attributed to electronic transitions from one energy level to another in the *d*-subshell. In these metals the energy difference between the various *d*-orbitals is in the same order of magnitude as the energies of the radiation of white light (A. = 4000 to 8000 A).

Table 21.4 : Colours of hydrated ions of some transition elements

Hexahydrated ion of	Number of d electrons	Color of solid/solution
Ti^{3+}	1	Violet
V^{3+}	2	Blue
V^{2+}	3	Violet
Cr^{3+}	3	Green
Mn^{3+}	4	Violet
Fe^{3+}	5	Yellow/colorless
Mn^{2+}	5	Yellow/colorless
Fe^{2+}	6	Pale green

Notes

Co^{2+}	7	Pink
Ni^{2+}	8	Green
Cu^{2+}	9	Blue

21.4.4 Alloy and Interstitial Compound Formation

In the Table 21.2 it may be observed that the atomic size of the elements of first transition series is quite close to each other. Thus, in the crystal lattice, anyone of these elements can easily replace another element of similar size forming solid solutions and smooth alloys. Transition elements, therefore, form a number of alloys. Cr, V and Mn are used to produce alloy steel and stainless steel, copper forms brass, bronze etc. Besides, transition metals also form a number of interstitial compounds in which they take up atoms of small size, like hydrogen, carbon and nitrogen etc. These are located in the vacant spaces of metal lattices and are bound firmly there in. The products thus obtained are hard and rigid. For example, steel and cast iron become hard due to formation of an interstitial compound with carbon. In such compounds, malleability and ductility may marginally decrease but tenacity is considerably enhanced. Some examples of alloys are given in Table 21.5.

Table 21.5 : Examples of some alloys

Alloy	Composition
Brass	Cu (50%-80%) and Zn (50%-20%)
Bronze	Cu (90%-93%) and Sn (10%-7%)
Gun metal	Cu (88%), Sn (10%) and Zn (2%)
Bell metal	Cu (80%) and Sn (20%)

21.4.5 Complex Formation

Transition metals exhibit a strong tendency to form complexes with different ligands due to the following reasons:

1. Small size and high charge density.
2. Variable oxidation states.
3 . Availability of vacant d-orbitals to accept electron pairs from ligands.

You will learn more about complexes in the next lesson

21.4.6 Catalytic Properties

The catalytic activity of transition metals and their compounds is associated with their variable oxidation states. Typical catalysts are vanadium(V) oxide (contact process for sulphuric acid), finely divided iron (Haber's process), nickel (catalytic hydrogenation) and palladium(II) chloride and a copper(II) salt for the production of ethanol from ethane and water (Wacker's process). Haemoglobin, a large molecule containing Fe(II), acts as a catalyst for the respiration process.

Catalysis at a solid surface involves the formation of bonds between reactant molecules and the catalyst surface atoms, this has the effect of increasing the concentration of the reactants at the catalyst surface and also of weakening the bonds in the reactant molecules (the activation energy is lowered).

Transition metal ions function as catalysts by changing their oxidation states, e.g., Fe(III) cations catalyse the reaction between iodide and peroxodisulphate ions:

$$2I^{-}(aq) + S_2O_8^{2-}(aq) \xrightarrow{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

An oversimplified, explanation of this catalysis reaction might be:

$$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$

It is known that both the above reactions can take place, and it would be expected that two reactions between ions of opposite charge would be faster than one reaction between ions of the same type of charge.

INTEXT QUESTIONS 21.4

1. Why do transition elements act as good catalysts?
2. Name some of the common catalysts you have studied.
3. Which of the following compounds are expected to be diamagnetic: $CrCl_3$, $ScCl_3$, $CuSO_4$, $CoCl_2$, $TiCl_4$ and $ZnCl_2$?
4. Which of the following do you expect to be colored and why, Cr^{+} and Cu^{+}?
5. Name any two alloys of transition elements.
6. Calculate in B.M., magnetic moments expected for the following ions:

   V^{4+}, Ni^{3+}, V^{4+}, Ni^{3+}, Cr^{3+} and Ti^{4+}.

21.5 IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

The preparation, properties and applications of two important compounds of transition elements viz. $K_2Cr_2O_7$ and $KMnO_4$ which are widely used in industry and laboratory are discussed below:

21.5.1 Potassium Dichromate ($K_2Cr_2O_7$)

Mineral chromite ($FeO.Cr_2O_3$) is the starting material for the manufacture of all chromates and dichromates. Soluble chromates are prepared using alkali metal oxides, hydroxides or carbonates whereas insoluble chromates are made by double decomposition of soluble chromates.

Large Scale Production of Potassium Dichromate from Chromite ore

A mixture of finely powdered chromite, sodium carbonate and quick lime is heated in a reverberatory furnace in free supply of air. Carbon dioxide is evolved and sodium chromate is formed. The function of quick lime is to keep the mass porous and prevent fusion.

$$\underset{\textbf{Chromite}}{4FeO.Cr_2O_3} + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

The mass after roasting is extracted with water, which dissolves soluble sodium chromate leaving behind insoluble ferric oxide. After concentrating the solution containing sodium chromate, concentrated sulphuric acid is added.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Sodium sulphate produced, crystallizes out and is removed. On further concentrating the solution, deliquescent red crystals of sodium dichromate separate out slowly on cooling. When a hot saturated solution of sodium dichromate is mixed with a saturated solution of potassium chloride, sodium chloride separates out, followed by separation of garnet red triclinic crystals of potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Since potassium dichromate is moderately soluble in cold water (100 gL^{-1} at 298 K) but easily soluble in hot water (1000 g L^{-1}) at 373 K, it is readily purified by recrystallization from water.

Physical Properties

$K_2Cr_2O_7$ forms orange red prismatic crystals. Its specific gravity is 2.676 and its melting point is 696 K. It is moderately soluble in cold water but highly soluble in hot water and insoluble in alcohol.

Chemical Properties

1. Since chromium forms stable compounds in low oxidation states as well, potassium dichromate in which oxidation number of chromium is +6, acts as a powerful oxidizing agent. For this reason, it is used as a primary standard in volumetric analyses. In acidic solutions, one molecule of potassium dichromate furnishes three atoms (i.e. six equivalents) of available oxygen as follows:

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$

The available oxygen then oxidizes ferrous, iodide ions and sulphur dioxide as follows:

$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$

$2HI + [O] \rightarrow H_2O + I_2$

$SO_2 + [O] + H_2O \rightarrow H_2SO_4$

These reactions can also be shown as ionic equations.

In acidic solution, the oxidizing action of $K_2Cr_2O_7$ can be represented as follows:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

The ionic equation for the reducing action of Fe(II) can be represented as:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

The complete ionic equation may be obtained by adding the half reaction of dichromate ion to the half reaction of Fe(II):

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3-} + 7H_2O \\ (Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 6 \\ \hline Cr_2O_7^{2-}.+ 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

Similarly the reactions of dichromate with iodide ion and sulphur dioxide can be written as given below:

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ (2I^- \rightarrow I_2 + 2e^-) \times 3 \\ \hline Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O \end{array}$$

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ (SO_2 + 2H_2O \rightarrow SO_4^{2+} + 2e^-) \times 3 \\ \hline Cr_2O_7^{2-} + 3SO_2 + 14H^+ \sim 2Cr^{3+} + 3SO_4^{2-} + H_2O \end{array}$$

2. Potassium dichromate when heated with concentrated sulphuric acid with an ionic chloride (such as NaCl, KCl etc.) forms red vapours of chromyl chloride, (CrO_2Cl_2) as follows:

$$\begin{array}{l} K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O \\ [NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4 \\ [CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O] \times 2 \\ \hline K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O \end{array}$$

Red vapours of chromyl chloride, a derivative of chromic acid is absorbed in dilute solution of NaOH . A yellow solution of sodium chromate is formed. On acidifying this solution with acetic acid and adding lead acetate, a yellow precipitate of lead chromate, is formed which is soluble on heating and reappears on cooling. This is used as a confirmatory test to detect the presence of chloride ions in qualitative analysis.

3. When concentrated sulphuric acid is added to a solution of chromate or dichromate, a red coloured solution of chromic trioxide often called “chromic acid”, is obtained. In the acidic solution it exists as dichromic acid ($H_2Cr_2O_7$). Chromium trioxide is a very powerful oxidizing agent.
4. Oxidation number of chromium is +6 in both chromates and dichromates. However, *in* neutral aqueous solution, dichromate ions exist in equilibrium with chromate ions as:

$$\underset{\textbf{Orange}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\textbf{Yellow}}{2CrO_4^{2-}} + 2H^+$$

Thus in an acidic medium, equilibrium shifts to the left and dichromate ions exist whereas in alkaline medium, only monomeric chromate ions exist.

Uses:

1. Potassium dichromate is used as an important volumetric reagent for the estimation of Fe^{2+}, I^-, SO_3^{2-} etc.
2. It is used in the manufacture of chrome alum, which is an important compound used for tanning of leather and dyeing of fabrics.

INTEXT QUESTIONS 21.5

1. Name the starting materials used in preparation of soluble chromate and dichromates.
2. Write down the formula of chromite ore.
3. How is sodium dichromate converted into potassium dichromate?
4. What happens when potassium dichromate is heated with an alkali metal chloride and concentrated sulphuric acid?
5. Give the molecular formula of chrome alum. What are its uses?
6. Why does dichromate act as an oxidizing agent?
7. What happens when a base is added to dichromate?
8. What is the oxidation state of chromium in (i) K_2CrO_4 and (ii) $K_2Cr_2O_7$?

21.5.2 Potassium Permanganate ($KMnO_4$)

Pyrolusite ore (MnO_2) is the starting material for the manufacture of potassium permanganate. Pyrolusite is first converted into potassium manganate which is then oxidized to potassium permanganate.

Conversion of pyrolusite into potassium manganate

When pyrolusite is fused with hydroxide of sodium or potassium in the presence of air manganite first formed is converted into a dark green mass of corresponding manganate as follows :

$$MnO_2 + 2KOH \rightarrow \underset{\textbf{Potassium manganite}}{K_2MnO_3} + H_2O$$

$$2K_2MnO_3 + O_2 \rightarrow \underset{\textbf{Potassium manganate}}{2K_2MnO_4}$$

The dark green mass of potassium manganate is dissolved in a small quantity of cold water to form a dark green solution from which dark green crystals of potassium manganate may be obtained on concentraion.

Conversion of potassium manganate to potassium permanganate :

Any of the following methods can be used for preparing potassium permanganate.

1. When green concentrated solution of potassium manganate is gently warmed, or largely diluted with water, the green color changes to pink owing to the formation of potassium permanganate. Potassium manganate is stable in alkaline solutions or in pure water. But even a trace of acid, like carbonic acid, is enough to bring about its disproportionation :

   $$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

2. Potassium manganate may also be converted into potassium permanganate by oxidation either chemically with chlorine or ozone or electrolytically at the anode.

Chemical oxidation:

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2.$$

Anodic oxidation:

$$\underset{\text{green}}{MnO_4^{2-}} \rightarrow \underset{\text{purple}}{MnO_4^-} + e^- \text{ (at anode)}$$

Physical properties

Potassium permanganate forms dark purple red rhombic prisms. It is sparingly soluble in water (5.31 g in 100 mL at 298K) giving a deep purple colored solution which is opaque until very dilute. The crystals on heating evolve oxygen and form a black powder of potassium manganate and manganese dioxide.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

Chemical properties

Potassium permanganate is a powerful oxidizing agent. The action is different in acidic, neutral and alkaline solutions.

(i) In acidic solution, two molecules of permanganate furnish five atoms of oxygen as follows :

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

In ionic form the equation is:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Ferrous sulphate is oxidized to ferric sulphate by acidified potassium permanganate.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

or

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Sulphur dioxide is oxidized to sulphuric acid:

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

or

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

(ii) In neutral solution the main reaction is:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$KMnO_4$ oxidises Mn^{2+} salts to MnO_2 and H_2S to S and SO_4^{2-} as follows:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow K_2SO_4 + 5MnO_2 + 2H_2SO_4$$

$$2KMnO_4 + 4H_2S \rightarrow 2MnS + S + K_2SO_4 + 4H_2O$$

(ii) In alkaline solutions the main reaction is:

$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$$

In ionic form the equation is:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

However, MnO_4^{2-} is further reduced to MnO_2 hence the complete equation representing the oxidizing behaviour of $KMnO_4$ in alkaline solution is same as in neutral medium

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2^- + 4OH^-$$

Alkaline permanganate oxidizes iodides to iodates and ethene to ethylene glycol:

$$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$$

$$2KMnO_4 + 3CH_2 = CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2 - CH_2OH + 2KOH$$

Uses:

1. Potassium permanganate is used as an oxidizing agent in the laboratory and in industry.
2. Because of its oxidizing properties, it is used for disinfecting wells and lake water, as mouthwash, for washing wounds and gargling during throat infections.
3. It is used as a reagent in volumetric analyses for estimating Fe(II) ion, oxalic acid, oxalate ion, sulphites and hydrogen peroxide.

INTEXT QUESTIONS 21.6

1. How is potassium manganate converted into potassium permanganate?
2. Give reactions of $KMnO_4$ to show that it acts as an oxidizing agent in neutral, alkaline and acidic medium.
3. Why is $KMnO_4$ added to wells and lakes from where water is drawn for drinking?
4. Write down the chemical formulae of pyrolusite ore, potassium permanganate and potassium manganate.
5. In which medium (acidic, basic or neutral), $KMnO_4$ acts as better oxidizing agent?
6. What is the color of K_2MnO_4 and of $KMnO_4$?
7. What are the oxidation states of Mn in MnO_2, K_2MnO_4 and $KMnO_4$?

21.6 *f*-BLOCK ELEMENTS (LANTHANOIDES)

In addition to *d*-block elements, there are two rows of elements shown separately at the bottom of the periodic table. The elements from La to Lu (14 elements) are called lanthanoides. They are characterised by the filling up of the anti penultimate 4*f* orbitals. They are extremely similar to each other in properties. Earlier these were called the rare earths. This name is not appropriate because many of these elements are not particularly rare. Now these elements are known as inner transition elements (because they form transition series within the *d*-block transition elements) or lanthanoids.

21.6.1 Electronic Configuration

Lanthanum is the first member of the third transition series, and it has one 5*d* and two 6*s* electrons. The next element is cerium, which while still retaining two 6*s* electrons, has two electrons in the 4*f* orbitals and none in the 5*d* orbitals. There are 7 separate 4*f* orbitals, each of which can accommodate two electrons with opposite spins. The atoms of the elements from cerium to lutetium have two to fourteen electrons in 4*f*- orbitals, respectively. These elements constitute the first inner transition series known as lanthanides and, although lanthanum itself does not possess any 4*f* electrons, it is customary to include this element in this series.

The filling up of the 4*f* orbitals is regular with some exceptions (Table 21.6); the element europium has the outer electronic configuration $4f^7 5s^2 5p^6 5d^0 6s^2$ and the next element gadolinium has the extra electron in the 5*d* orbital. The element ytterbium has a full compliment of 4*f* electrons ($4f^{14} 5s^2 5p^6 5d^0 6s^2$) and the extra electron in the lutetium atom enters the 5d orbitals ($4f^{14} 5s^2 5p^6 5d^1 6s^2$). Except for lanthanum, gadolinium and lutetium, which have a single 5d electron, the lanthanoides do not have electrons in the 5*d* orbitals.

Table 21.6: Electronic configuration of lanthanides

Element	Symbol	Z	Electronic configuration
Lanthanum	La	57	$[Xe]4f^0 5d^1 6s^2$
Cerium	Ce	58	$[Xe]4f^2 6s^2$
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$
Neodymium	Nd	60	$[Xe]4f^4 6s^2$
Promethium	Pm	61	$[Xe]4f^5 6s^2$
Samarium	Sm	62	$[Xe]4f^6 6s^2$
Europium	Eu	63	$[Xe]4f^7 6s^2$
Gadolinium	Gd	64	$[Xe]4f^7 5d^1 6s^2$
Terbium	Tb	65	$[Xe]4f^9 6s^2$
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$
Erbium	Er	68	$[Xe]4f^{12} 6s^2$
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$
Lutetium	Lu	71	$[Xe]4f^{14} 5d^1 6s^2$

21.6.2 The lanthanoide contraction

Each succeeding lanthanoide differs from its immediate predecessor in having one more electron in the 4*f* orbitals (except for some exceptions as discussed above) and one extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus; thus there is a gradual increase in the attraction of the nucleus for the peripheral electrons as the nuclear charge increases, and a consequent contraction in atomic radius is observed. For example, the ionic radii of the +3 cations decrease steadily from a value of 115 pm for La^{3+} to a value of 93 pm for Lu^{3+}. The regular decrease in atomic radii with increase in atomic number is known as lanthanoide contraction.

The lanthanoide contraction considerably influences the chemistry of the elements, which succeed the lanthanides in the periodic table; for instance the atomic radii of zirconium (At. No. 40) and hafnium (At. No. 72) are almost identical and the chemistry of these two elements is strikingly similar. Incidentally, the density of hafnium (which immediately follows the lanthanides) is almost twice the density of zirconium (which is in the same group).

21.6.3 Oxidation states of lanthanIODS

Table 21.7: Electronic configuration and oxidation states

Element		**Electronic configuration of atoms**				**Oxidation states**		
Lanthanum	La	[Xe]		$5d^1$	$6s^2$	+ III		
Cerium	Ce	[Xe]	$4f^1$	$5d^1$	$6s^2$		+ III	+ IV
Praseodymium	Pr	[Xe]	$4f^3$		$6s^2$		+ III	(+ IV)
Neodymium	Nd	[Xe]	$4f^4$		$6s^2$	(+II)	+ III	
Promethiurm	Pm	[Xe]	$4f^5$		$6s^2$	(+II)	+ III	
Samarium	Sm	[Xe]	$4f^6$		$6s^2$	(+II)	+ III	
Europium	Eu	[Xe]	$4f^7$		$6s^2$	+ II	+ III	
Gadolinium	Gd	[Xe]	$4f^8$	$5d^1$	$6s^2$		+ III	
Terbium	Th	[Xe]	$4f^9$		$6s^2$		+ III	(+ IV)
Dysprosium	Dy	[Xe]	$4f^{10}$		$6s^2$		+ III	(+ IV)
Holmium	Ho	*[Xe]*	$4j^{11}$		$6s^2$		+ III	
Erbium	Er	[Xe]	$4f^{12}$		$6s^2$		+ *III*	
Thulium	Tm	[Xe]	$4f^{13}$		$6s^2$	(+ II)	+ III	
Ytterbium	Yb	[Xe]	$4f^{14}$		$6s^2$	+ II	+ III	
Lutetium	Lu	[Xe]	4*f*14	$5d^1$	$6s^2$	+ III		

The sum of first three ionization enthalpies of the lanthanoids are comparatively low so these elements are highly electropositive and the compounds of these elements are essentially all ionic in nature.The characteristic oxidation state of these elements is +3, however some of them also show +2 and +4 oxidation states which are less stable as compared to +3.. Like transition elements, fluorides and oxides stabilize higher oxidation states whereas bromides and iodides stabilize lower oxidation states. The elements show (+ II) and (+ IV) oxidation states, particularly when they lead to:

(a) Noble gas electronic configuration, *e.g.,* Ce^{4+} ($4f^0$).

(b) Half filled *f*-orbital, *e.g.,* Eu^{2+} and Tb^{4+} ($4f^7$).

(c) Completely filled *f*-orbital, *e.g.,* Yb^{2+} ($4f^{14}$).

Due to only one stable oxidation states, *i.e.,* + III, lanthanoid elements resemble each other much more than the transition elements.

21.7 ACTINOIDS

Electronic Configuration

The electronic configuration of actinoids do not follow the simple patternn found in the lanthanoids. It might have been expected that after Ac the 5*f* orbitals would become lower in energy than the 6*d* orbitals. However, for the first four actinide elements Th, Pa, U and Np the difference in energy between 5*f* and 6*d* orbitals is small. Thus in these elements electrons may occupy the 5*f* or the 6*d* orbitals or sometimes both. Later in the actinide series the 5*f* orbital becomes appreciably lower in energy, thus from Pu onwards the 5*f* orbital fills in a regular way.

Oxidation states of actinoids are given in the Table below.

Table 21.8: The elements and their oxidation states

Atomic Number	Element	Symbol	Outer electronic structure	Oxidation states*
89	Actinium	Ac	$6d^1$ $7s^2$	III
90	Thorium	Th	$6d^2$ $7s^2$	III IV
91	Protactinium	Pa	$5f^2$ $6d^1$ $7s^2$	III IV V
92	Uranium	U	$5f^3$ $6d^1$ $7s^2$	III IV V VI
93	Neptunium	Np	$5f^4$ $6d^1$ $7s^2$	III IV V VI VII
94	Plutonium	Pu	$5f^6$ $7s^2$	III IV V VI VII
95	Americium	Am	$5f^7$ $7s^2$	II III IV V VI

96	Curium	Cm	$5f^7$	$6d^1$	$7s^2$		III	IV
97	Berkelium	Bk	$5f^9$		$7s^2$		III	IV
98	Californium	Cf	$5f^{10}$		$7s^2$		III	IV
99	Einsteinium	Es	$5f^{11}$		$7s^2$	II	III	
100	Fermium	Fm	$5f^{12}$		$7s^2$	II	III	
101	Mendelevium	Md	$5f^{13}$		$7s^2$	II	III	
102	Nobelium	No	$5f^{14}$		$7s^2$	II	III	
103	Lawrencium	Lr	$5f^{14}$	$6d^1$	$7s^2$	II		

21.7.1 Oxidation States

As seen in the table +2 oxidation state is quite rare. Am^{2+} has $5f^7$ electronic configuration.

Like lanthanoids all the actinoids show +3 oxidation state. This +3 oxidation state is not the most stable oxidation state for Th, Pu, U and Np. For example, U^{3+} is readily oxidized in air, and in solution. +III is the most stable oxidation state for higher actinoids *i.e., from* $_{95}$Am to $_{103}$Lw (except$_{102}$ No]. They show similar properties to that of lanthanoids. The higher oxidation states involve all the outer electrons for bonding (including 5*f* electrons). Oxidation states other than +3 are also exhibited by some of these elements e.g. Np and Pu show as high as +VII oxidation state and Am and heavy actinoids show +II oxidation state. Np in + VII oxidation state acts as an oxidizing agent.

21.7.2 Comparison between lanthanoids and actinoids

Similarlity

1. Orbitals are filled progressively in both the series.
2. +III is the prominent oxidation state for both the series.
3. In both the series, 4*f* and 5*f* electrons imperfectly shield, therefore both show contraction in size.
4. They show line like spectra.
5. Both 4*f* and 5*f* block elements show ion exchange behavior.
6. Hydroxides, carbonates and fluorides of bivalent actinoids as well as lanthanoids are soluble whereas nitrates, perchlorates and sulphates are insoluble.

Differences

1. There is large energy gap between 4*f* and 5*d* sub-shells, the energy gap between 5*f* and 6*d* is small so the chemistry of actionoids is not similar to that of lanthanoids.

2. Pm is the only radioactive elements among the lanthanoids, whereas almost all the actinoids are radioactive elements.
3. The maximum oxidation shown by the lanthanoids +IV, whereas antioids show upto +VII oxidation state.
4. Lathanoids do not form complexes easily but actinoids form complexes.
5. 4*f* electrons have greater screening effect as compared to 5*f* electrons.
6. Lanthanoids do not from oxocations but auinoids form oxocations such as UO^{2+}, UO_2^+, NPO_2^+ and PuO_2^+.
7. The compounds of lanthanoids are less basic as compared to the compounds of actinoids.

INTEXT QUESTIONS 21.7

1. How many elements constitute lanthanoide series?
2. Why Zr and Hf show almost same properties?
3. Write down the electronic configuration of the following in the ground state: Gd, Lu, Ho, Er.
4. Write down the electronic configuration of the following ions: Eu^{3+}, Yb^{3+}, Ce^{4+}.
5. Which is characteristic oxidation state of Lanthanoids?
6. Actinoids show variable oxidation state why?
7. Are actinoids form oxocation?

WHAT YOU HAVE LEARNT

- Transition elements have partially filled *d*-orbitals either in atomic or ionic state.
- They show general electronic configuration $(n-1)d^{1-10}ns^{1,2}$.
- They show high M.P. and B.P. due to strong inter-atomic bonding.
- They show variable oxidation states.
- They form colored ions and compounds.
- They show paramagnetic behaviour.
- They form complexes.
- They form alloy and interstitial compounds.

- Manufacture of $K_2Cr_2O_7$ and $KMnO_4$.
- $K_2Cr_2O_7$ and $KMnO_4$ act as oxidizing agents.
  These compounds are used in volumetric analysis.
- Electronic configuration of lanthanoids and actinoids.
- Lanthanoid contraction oxidation states of lanthanoids and actinoids.
- Comparison between lanthanoids and actinoids.

TERMINAL EXERCISES

1. What distinguishes a transition metal from a representative metal?
2. Why is zinc not considered a transition metal?
3. Explain why atomic radii decrease very gradually from Sc to Cu.
4. Write down the ground state electronic configuration of the first row transition elements. Explain the irregularities.
5. Write down the electronic configuration of the following ions:
   V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Cu^{2+}, Sc^{3+} and Ti^{4+}
6. Why do transition elements have more oxidation states than other elements?
7. Give the highest oxidation states for the elements from Sc to Cu.
8. How would you define transition elements? List the properties associated with transition elements.
9. How do the following properties vary in transition elements?
   (a) Stability of the various oxidation states.
   (b) Ability to form complexes.
10. What do you understand by the terms paramagnetism and diamagnetism? Predict the magnetic moments for Fe^{2+}, Co^{3+}, Ni^{3+} and Cu^{+} ions.
11. 4*s* sub-shell is filled prior to 3*d*- sub-shell but on ionization 4*s* electrons are removed first. Explain.
12. Why does Mn(II) show maximum paramagnetic character amongst the bivalent ions of first transition series?
13. Why is Cu^{2+} ion colored and paramagnetic while Zn^{2+} ion is colorless and diamagnetic.
14. Why do transition elements.
   (a) show variable oxidation states?
   (b) form a large number of coordination compounds?
   (c) give colored and paramagnetic ions?
   (d) exhibit good catalytic properties?

15. Discuss the main characteristic features of the transition elements with special reference to their atomic size, variable oxidation states, magnetic and catalytic properties.

16. Explain the trends of variations of:

    (a) melting and boiling points.

    (b) atomic radius in the first transition series.

17. A solution of $KMnO_4$ on reduction yields either a colorless solution or a brown precipitate or a green solution depending on the pH of the solution. What different stages of the reduction do these represent and how are they carried out?

18. A black color compound [X] of manganese when fused with KOH under atmospheric oxygen gave a green colored compound [Y]. When the compound [Y] was treated with an oxidizing agent (chlorine or ozone), it gave a purple colored solution [Z]. Identify X, Y, Z and write the chemical equation.

19. Compound [A] of chromium when treated with sodium carbonate in the presence of atmospheric oxygen gave a yellow colored compound [B]. Compound [B] on treatment with acid gave an orange colored compound [C]. [B] can also be obtained by treatment of [C] with alkali. Identify the compound A, B, C and write the chemical equations.

20. Why do transition elements form a large number of alloys and interstitial compounds?

21. What are lanthanides? Why are they called inner transition elements?

22. What is lanthanide contraction and what are its consequences?

23. Write the electronic configurations of the following in ground state:

    Eu, Ho and Gd.

24. Describe two oxidizing properties of potassium dichromate.

25. Describe two oxidizing properties of potassium permanganate.

26. Compare between the properties of lanthanoids and actinoids.

ANSWERS TO INTEXT QUESTIONS

21.1

1. Transition elements are defined as “Elements whose atoms have partially filled *d*-orbitals either in the atomic or in ionic state (common oxidation state).

2. 10 elements constitute the first transition series. These are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn.
3. Since zinc does not have partially filled *d*-orbitals either in atomic or in ionic state.
4. Because there are partially filled *d*-orbitals in Cu^{2+}, Ag^{2+} and Au^{3+}.

21.2

1. General electronic configuration of transition elements is: $(n-1)d^{1-10}\, ns^{1 \text{ or } 2}$.
2. $Sc = [Ar]3d^1 4s^2$, $Cr = [Ar]3d^5 4s^1$, $Zn = [Ar]3d^{10} 4s^2$, $Cu = [Ar]\ 3d^{10}\ 4s^1$
3. $Cr^{3+} = [Ar]3d^3$, $Ti^{4+} = [Ar]3d^0$, $Ni^{3+} = [Ar]3d^7$ and $Cu^{2+} = [Ar]3d^9$
4. Because less amount of energy is required to remove an electron from 4*s* instead of 3*d* orbital. It is due to the fact that after Sc, 3*d*, becomes lower in energy than 4*s*.

21.3

1. due to strong interatomic bonding.
2. due to increase in effective nuclear charge.
3. due to small size. Size does not increase in the same proportion as the atomic mass.

21.4

1. due to variable oxidation states.
2. V_2O_5 (contact process for H_2SO_4) and iron (Haber's process)
3. $ScCl_3(3d^0)$, $TiCl_4(3d^0)$ and $ZnCl_2(3d^{10})$.
4. Cr^+ because it has partially filled *d*-orbital i.e. $3d^5$.
5. Nichrome and brass.
6. $V^{4+}3d^1\ \sqrt{n(n+2)} = \sqrt{n(1+2)} = \sqrt{3} =$ 1.73 B.M., $Ni^{3+}3d^7 n = 3$, $\sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M

21.5

1. Chromite ore, Na_2CO_3 and O_2
2. $FeO.Cr_2O_3$.
3. $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$
4. $K_2Cr_2O_7 + 4NaCl = 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$

5. $KCr(SO_4)_2.12H_2O$ or $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, tanning of leather and dyeing fabrics.
6. For Cr, +3 is the stable oxidation state but in $K_2Cr_2O_7$ the oxidation state of Cr is +6.
7. $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$. Dichromate changes to chromate.
8. (i) +6 (ii) +6.

21.6

1. By oxidation with ozone or chlorine

   $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$

   $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$
2. Alkaline:

   $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

   Neutral:

   $2MnO_4^- + 2H_2O + 3Mn^{2+} \rightarrow 5MnO_2 + 4H^+$

   Acidic:

   $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2 = O$
3. Because it is used as disinfectant (kill microorganisms)
4. Pyrolusite MnO_2, potassium permanganate $KMnO_4$, potassium manganate K_2MnO_4.
5. In acidic medium, because it liberates 5O atoms or change in oxidation state of Mn is from +7 to +2.
6. K_2MnO_4, green and $KMnO_4$, purple.
7. $MnO_2 = +4$, $K_2MnO_4 = +6$ and $KMnO_4 = +7$.

21.7

1. 14.
2. Due to lanthanide contraction. (Due to same size)
3. Gd$[Xe]5f^7 5d^1 6s^2$, Lu$[Xe]4f^{14} 5d^1 6s^2$, Ho $[Xe]4f^{11} 6s^2$ and Er $[Xe]4f^{12} 6s^2$
4. $Eu^{3+} = [Xe]4f^6$, $Yb^{3+} = [Xe]4f^{13}$ and $Ce^{4+} = [Xe]4f^0$
5. +3
6. Difference in the energy of (n-2)f and ns is negligible. So more elements are available for chemical bonding.
7. Yes

313en22

22

COORDINATION COMPOUNDS

You have come across compounds like $Na[Ag(CN)_2]$ and $Na_2[Zn(CN)_4]$. Such compounds are referred to as coordination compounds or complex compounds. Coordination compounds play an important role in the chemical industry and in life itself. For example, the Ziegler-Natta catalyst which is used for polymerization of ethylene, is a complex containing the metals aluminum and titanium. Metal complexes play important role in biological systems. For example, chlorophyll, which is vital for photosynthesis in plants, is a magnesium complex and heamoglobin, which carries oxygen to animal cells, is an iron complex. These are the compounds that contain a central atom or ion, usually a metal, surrounded by a number of ions or molecules. The complexes tend to retain their identity even in solution, although partial dissociation may occur. Complex ion may be cationic, anionic or nonionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.

In this lesson you will study about the complexes including their nomenclature and nature of bonding in them.

OBJECTIVES

After reading this lesson, the learner will be able to,

- state the postulates of Werner's theory;
- define ligands, coordination number and coordination sphere;
- name simple complexes by IUPAC system;
- explain valance bond theory;
- apply VB theory to explain hybridization, shape and magnetic behavior of the following complexes $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ and

- explain Crystal Field Theory (CFT);
- explain the colour and magnetic behaviour of coordination compounds on the basis of CFT.
- explain the isomerism in coordination compounds;
- explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis.

22.1 WERNERS' COORDINATION THEORY

Coordination compounds were known in eighteenth century. It was a mystery for the chemist, of those days to understand as to why a stable salt like $CoCl_3$ reacts with varying number of stable molecules or compounds such as ammonia to give several new compounds: $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$; and what are their structures? These compounds differed from each other in their chloride ion reactivity. Conductivity measurements on solutions of these compounds showed that the number of ions present in solution for each compound are different. Several theories were proposed, but none could satisfactorily explain all the observable properties of these compounds and similar other series of compounds which had been prepared by then. It was only in 1893 that Werner put forward a set of ideas which are known as Werner's coordination theory, to explain the nature of bonding in complexes. His theory has been a guiding principle in inorganic chemistry and in the concept of valence. The important postulates of **Werner's theory** are:

1. Metals exhibit two types of valence:
   (a) Primary valence (ionizable)
   (b) Secondary valence (non-ionizable).

Primary or ionizable valence is satisfied by negative ions and corresponds to oxidation state of the metal. The secondary or non-ionizable valence, which is satisfied by negative, positive or neutral groups, is equal to the coordination number of metal ion.

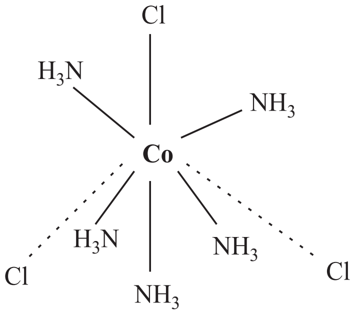
Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence is directed toward fixed positions in space i.e. this has spatial arrangement corresponding to different coordination number.

For the complexes $CoCl_3.6NH_3$ $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$, the number of ionizable ions in these complexes are three, two and one, respectively. It has been proved by precipitation reactions and conductivity measurements. On the basis of Werner's postulate these compounds are formulated as:

$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable ions.

On the basis of Werner's theory the structure of $[Co(NH_3)_5Cl]\ Cl_2$ is:



Primary valance (ionizable)(--------)

Secondary valance (non-ionizable) (———)

One of the three chloride ions satisfy both primary and secondary valence.

He also postulated that octahedral, tetrahedral and square planar shapes are more common for coordination compounds of transition elements. Six coordinated complexes such as $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ are octahedral whereas four coordinated such as $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are tetrahedral and square planar, respectively.

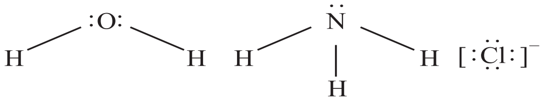
INTEXT QUESTIONS 22.1

1. Explain primary valence.
2. Explain secondary valence.
3. What is the number of the secondary valence in the following: $[Cr(H_2O)_6]$ Cl_3 and $[Co(NH_3)_5Cl]Cl_2$?
4. What is shape associated with a six-coordinated complex?
5. How many types of shapes are possible for four-coordinate complexes?

22.2 DEFINITION OF SOME IMPORTANT TERMS

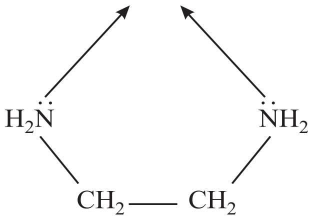
There are certain terms, which are normally used in dealing with coordination compounds. Some of these important terms are defined below:

Ligand: the molecules or ions that are attached to the metal in a complex ion are called ligands. The interaction between a metal atom and the ligands can be thought of as Lewis acid-base reaction. As you know a Lewis base is a substance capable of donating one or more electron pairs, every ligand has at least one unshared pair of valence electron. Few examples are shown below:



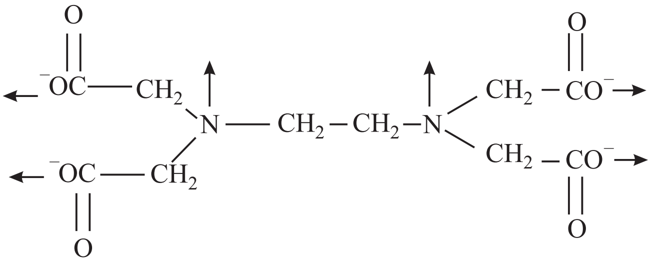
The atom in the ligand that is bound directly to the metal atom is known as the donor atom. For example, nitrogen is the donor atom and Cu^{2+} is the acceptor atom in the $[Cu(NH_3)_4]^{2+}$ complex ion.

Depending on the number of the donor atoms present, ligands are defined as monodentate, bidentate or polydentate. H_2O and NH_3 are monodentate ligands with only one donor atom in each. Ethylenediamine (en) is a bidentate ligand.



Ethylenediamine

The two nitrogen atoms can coordinate with a metal atom. Bidentate and polydentate ligands are also called chelating agents because of their ability to hold the metal atom like a claw (from the Greek Chele, meaning "claw") one example is ethylenediaminetetraacetate ion (EDTA), a polydentate (hexadentate) ligand.



Ethylenediaminetetraccetate ion

Coordination number: The coordination number in coordination compounds is defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in $[Co(NH_3)_6]^{3+}$ is six. Similarly the coordination number of Ag^+ in $[Ag(NH_3)_2]^+$ is 2, that of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is 4, and that of Fe^{3+} in $[Fe(CN)_6]^{3-}$ is 6.

Coordination sphere: The central metal atom and the ligands which are directly attached to it are enclosed in a square bracket and are collectively termed as coordination sphere. The ligands and the metal atom inside the square brackets behave as single constituent unit.

$$\underset{\textbf{Coordination sphere}}{\overbrace{[\mathrm{Cr(NH_3)_4Cl_2}]}}\,\mathrm{Cl}$$

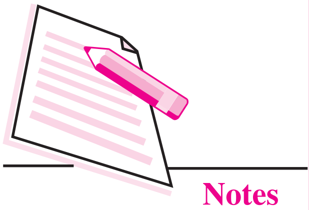
Oxidation number: Another important property of coordination compounds is the oxidation number of the central metal atom. The net charge on a complex ion is the sum of the charges on the central atom and its surrounding ligands. In the $[PtCl_6]^{2-}$ ion for example, each chloride ion has an oxidation number of –1, so the oxidation number of Pt must be +4. If the ligands do not bear net charges the oxidation number of the metal is equal to the charge of the complex ion. Thus in $[Cu(NH_3)_4]^{2+}$ each NH_3 is neutral, so the oxidation number of copper is +2.

INTEXT QUESTIONS 22.2

1. What is the coordination number of the metal ion in the following?
   (i) $[Co(NH_3)_5Cl]^+$
   (ii) $[Cr(en)_2Cl_2]^+$
   (iii) $[NiCl_4]^{2-}$
2. What is the oxidation state of the metal ion in the following?
   (i) $[MnCl_6]^{4-}$
   (ii) $[Fe(CN)_6]^{3-}$
   (iii) $[Cr(NH_3)_6]^{3+}$
   (iv) $[Ni(en)_3]^{2+}$
3. Give an example of a chelate ligand.
4. Give one example of each monodentate, bidentate and polydenatate ligand.
5. What is the oxidation and coordination number of Co in this $[Co(en)_2(H_2O)CN]^{2+}$ complex ion Which ligand is bidentate in the above complex?

22.3 RULES OF NOMENCLATURE OF COORDINATION COMPOUNDS

We have already discussed about the ligands and oxidation number of metal, our next step is, to learn how to name these coordination compounds. The rules for naming coordination compounds as recommended by IUPAC are as follows:



1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in $K_3[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$ compound, we name the K^+ and $[Co(NH_3)_4Cl_2]^+$ first, respectively.
2. Within a complex ligands are named first, in alphabetical order, and the metal ion is named last.
3. The name of anionic ligand ends with the letter 'O', whereas a neutral ligand is usually called by the name of the molecule. The exceptions are H_2O (aqua), CO (carbonyl) and NH_3 (ammine). The table given below lists some common ligands:

Table 22.1: Some Common Ligands

Ligand	Name of the ligand in coordination compounds
Fluoride (F^-)	Fluro
Chloride (Cl^-)	Chloro
Bromide (Br^-)	Bromo
Hydroxide (OH^-)	Hydroxo
Sulphate (SO_4^{2-})	Sulphato
Oxide (O^{2-})	Oxo
Carbonate (CO_3^{2-})	Carbonato
Oxalate ($C_2O_4^{2-}$)	Oxalato
Thiocyanate (SCN^-)	Thiocyanato
Cyanide (CN^-)	Cyano
Isothiocyanate (NCS^-)	Isothiocyanato
Ethylenediamine ($NH_2CH_2CH_2NH_2$)	Etylenediamine
Ammonia (NH_3)	Ammine
Water (H_2O)	Aqua
Carbon monoxide (CO)	Carbonyl
EDTA	Ethylenediamineteracetato

4. When several ligands of a particular kind are present, we use the Greek prefix di, tri- tetra etc to name them. Thus the ligands in cation $[Co(NH_3)_4Cl_2]^+$ are named as "tetraammine dichloro" (note that prefixes are ignored when alphabetizing ligands). If the ligand itself contains a Greek prefix, we use the prefixes *bis,tris and tetrakis* etc to indicate the number of ligands present. For example, the ligand ethylenediamine already contains di, therefore, if two such ligands are present the name is *bis*(ethylenediamine).

5. The oxidation number of the metal is written in roman numerals following the name of the metal. For example, the roman numeral III is used to indicate the +3 oxidation state of chromium in $[Cr(NH_3)_4Cl_2]^+$, which is named as tetraamminedichlorochromium (III) ion.

6. If the complex is an anion, its name ends in –ate. For example, in $K_4[Fe(CN)_6]$ the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the numeral (II) indicate the oxidation state of iron. Table given below gives tha name of anions containing metal atoms (Table 22.2).

7. If the complex is either a cation or is neutral, no change is required in the name of the central metal ion. For example $[Co(NH_3)_6]^{3+}$ and $[Ni(CO)_4]$ are named as hexaamminecobalt(III)ion and tetracarbonyl nickel(0), respectively.

Table 22.2: Some anions containing metal atoms

Metal	Name of metal in anionic state
Copper	Cuperate
Zinc	Zincate
Aluminum	Aluminate
Chromium	Chromate
Tin	Stannate
Cobalt	Cobaltate
Nickel	Nickelate
Gold	Aurate
Silver	Argentate
Lead	Plumbate
Rhodium	Rhodate
Iron	Ferrate
Manganese	Manganate

A. few examples are given below:

$[Co(H_2O)_6]Cl_3$	hexaaquacobalt(III) chloride
$K_2[PtCl_6]$	potassium hexachloroplatinate(IV)
$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
$[Co(en)_2Cl_2]Cl$	dichlorobis (ethylenediamine)cobalt(III) chloride.

INTEXT QUESTIONS 22.3

1. Write down the name of the following complexes:
   - (a) $[Co(NH_3)_4Cl_2]^+$
   - (b) $(NH_4)_3[Cr(NCS)_6]$
   - (c) $Ni(CO)_4$
   - (d) $K_4[Fe(CN)_6]$
   - (e) $[Cr(en)_3]Cl_3$
2. Write down the formula of the following:
   - (a) Tetrachloronickelate(II)
   - (b) Pentaamminenitrocobalt(III) ion
   - (c) Potassium hexacyanoferrate(III)
   - (d) Dichlorobis(ethylenediammine) chromium(III) ion

22.4 VALENCE BOND THEORY

Linus Pauling of the California Institute of Technology developed the valance bond theory. He was awarded the Nobel prize in chemistry in 1954. Pauling's ideas have had an important impact on all areas of chemistry. He applied valence bond theory to coordination compounds. This theory can account reasonably well for the structure and magnetic properties of metal complexes.

The basic principles, which are involved in the valence bond treatment of coordination compounds are:

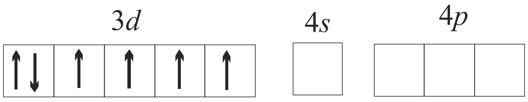
(a) Hybridization of valance orbitals of the central metal/ ion

(b) Bonding between ligand and the metal ion/atom.

(c) Relation between the type of bond and the observed magnetic behaviour.

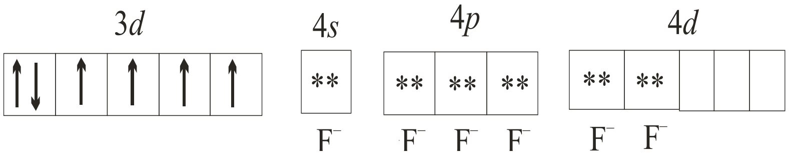
Six Coordinate Complexes

Let us explain by taking simple examples such as $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$. Although in both the complexes, the oxidation state of cobalt is +3, but $[CoF_6]^{3-}$ is paramagnetic and $[Co(NH_3)_6]^{3+}$ is diamagnetic, why? The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken e.g. Co^{3+}. Cobalt atom has the outer electronic configuration $3d^7 4s^2$. Thus Co^{3+} ion will have the configuration $3d^6$ and the electrons will be arranged as:



Co^{+3} ion forms both paramagnetic (outer orbital) and diamagnetic (inner orbital) complexes depending upon the nature of ligands as illustrated below.

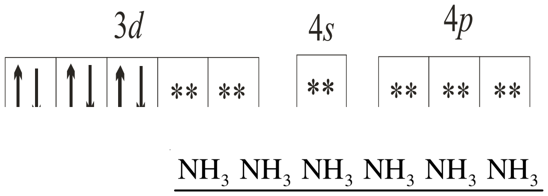
As Co^{3+} ion combines with six fluoride ligands in $[CoF_6]^{3-}$, empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one 4*s*, three 4*p* and two 4*d*. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electron forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ bond is formed with each ligand. The *d*-orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. It is shown below:



sp^3d^2, outer orbital complex

Since the outer 4d orbitals are used for bonding, this is called an outer orbital complex. The energy of these orbitals is quite high, so the complex will be reactive. This complex will be high-spin paramagnetic, because it has four unpaired electrons.

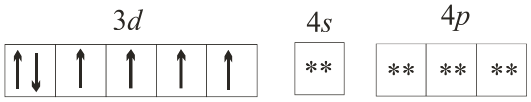
An alternative octahedral arrangement in $[Co(NH_3)_6]^{3+}$ is possible when the electrons on metal ion are rearranged as shown below:



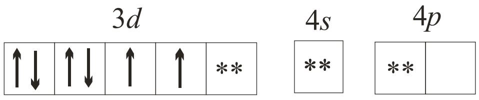
d^2sp^3, inner orbital complex

Since inner *d*-orbitals are used this is called an inner orbital complex. There is no unpaired electron, the complex will be low-spin diamagnetic.

The metal ion can also form 4-coordinate complexes. For such complexes two different arrangements are possible i.e. tetrahedral (sp^3) and square planar (dsp^2):



tetrahedral *sp^3*



square planar *dsp^2*

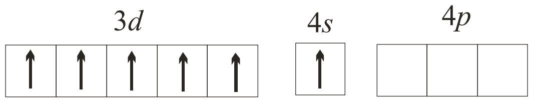
About such complexes you will study later.

Let us illustrate six coordinate complexes with more examples:

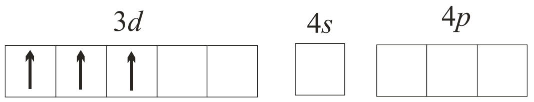
1. $Cr(NH_3)_6]^{3+}$

The electronic configuration of only 3d, 4s and 4p orbitals are taken into account. The following steps are involved. The electronic configuration of Cr atom and Cr^{3+} ion are given in (i) and (ii) below:

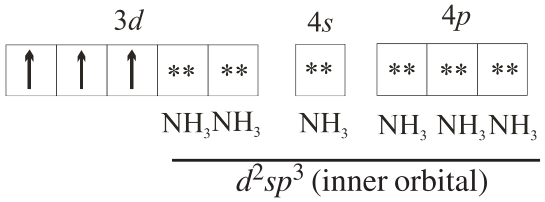
(i) Cr ground state:



(ii) Cr^{3+}



(iii) $[Cr(NH_3)_6]^{3+}$

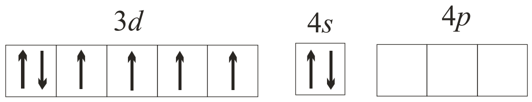


The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be:

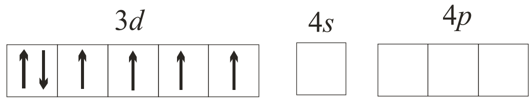
$$\sqrt{n}(n+2) = \sqrt{3}(\sqrt{3+2}) = \sqrt{15} = 3.87\text{B.M}$$

2. $[Fe(CN)_6]^{4-}$

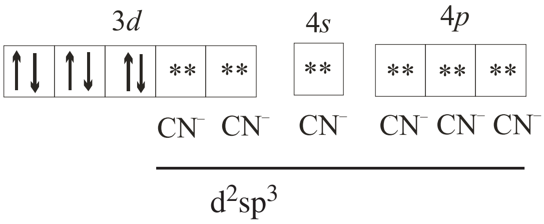
(i) Fe



(ii) Fe^{2+}



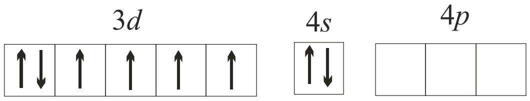
(iii) $[Fe(CN)_6]^{4-}$



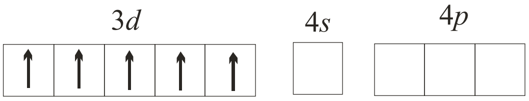
The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diamagnetic.

3. $[Fe(CN)_6]^{3-}$

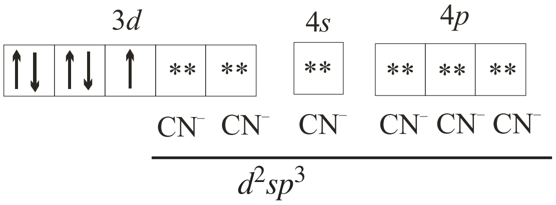
(i) Fe



(ii) Fe^{3+}



(iii) $[Fe(CN)_6]^{3-}$

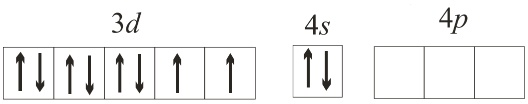


The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

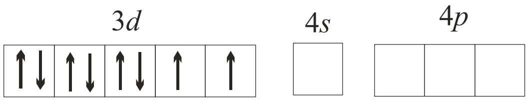
Four coordinate complexes:

1. $[NiCl_4]^{2-}$

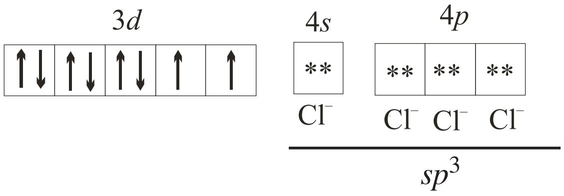
(i) Ni



(ii) Ni^{2+}



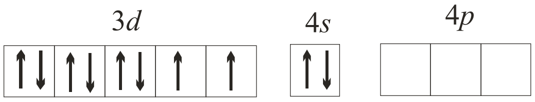
(iii) $[NiCl_4]^{2-}$



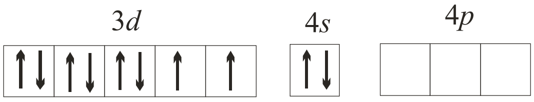
The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.

2. $Ni(CO)_4$

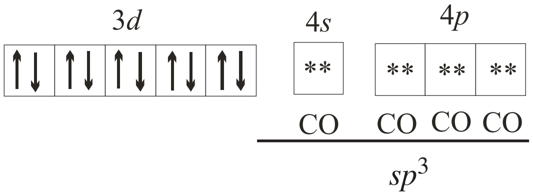
(i) Ni



(ii) Ni(O)



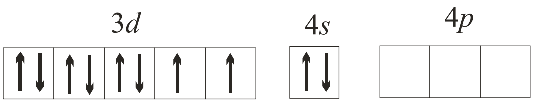
(iii) $Ni(CO)_4$



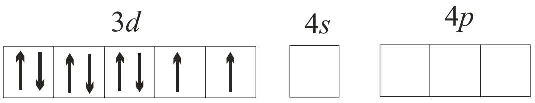
The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.

3. $[Ni(CN)_4]^{2-}$

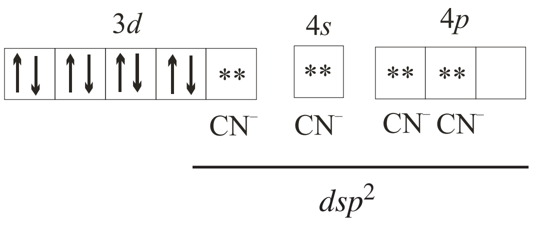
(i) Ni



(ii) Ni^{2+}



(iii) $[Ni(CN)_4]^{2-}$



The resulting complex is square planar and diamagnetic.

22.5 CRYSTAL FIELD THEORY

Although valence bond theory explains the bonding and magnetic properties of complexes, it is limited in two important ways. First, the theory cannot easily explain the color of complexes. Second, the theory is difficult to extend quantitatively. Consequently, another theory—crystal field theory—has emerged as the prevailing view of transition-metal complexes. This theory has been given by Bethe and van Vlack.

Crystal field theory is *a model of the electronic structure of transition-metal complexes that considers how the energies of the d orbitals of a metal ion are affected by the electric field of the ligands.* According to this theory, the ligands in a transition-metal complex are treated as point charges. So a ligand anion becomes simply a point of negative charge. A neutral ligand, with its electron pair that it donates to the metal atom, is replaced by a partial negative charge, representing the negative end of the molecular dipole. In an electric field of these negative charges, the five *d* orbtails of the metal atom no longer have exactly the same energy. The result, as you will see, explains both the paramagnetism and the color observed in certain complexes.

Effect of an Octahedral Field on the *d* Orbitals

All five *d* orbtails of an isolated metal atom have the same energy. But if the atom is brought into the electric field of several point charges, these *d* orbitals may be affected in different ways and therefore may have different energies. To understand how this can happen, you must first see what these *d* orbitals look like. You will then be able to picture what happens to them in the crystal field theory of an octahedral complex.

Figure 22.1 shows the shapes of the five *d* orbitals. The orbital labeled dz^2 has a dumbbell shape along the *z*-axis, with a collar in the *x*–*y* plane surrounding this dumbbell. Remember that this shape represents the volume most likely to be occupied by an electron in this orbital. The other four *d* orbitals have “cloverleaf” shapes, each differing from one another only in the orientation of the lobes in space. The "cloverleaf" orbital $dx^2 - y^2$ has its lobes along the x-axis and the y-axis. Orbitals dxy, dxz, and dyz have their lobes directed between the two sets of axes desinated in the orbital label. Orbital dxy, for example, has its lobes lying between the x- and y-axes.

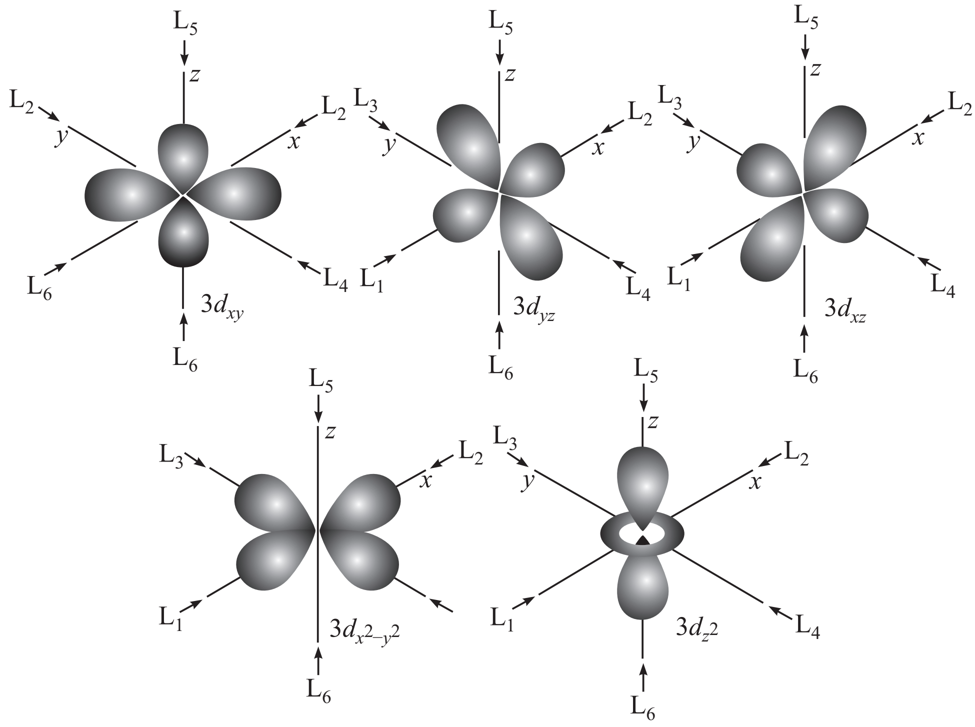


Fig. 22.1: *Shapes of d orbitals*

A complex ion with six ligands will have the ligands arranged octahedrally about the metal atom to reduce mutual repulsion. Imagine that the anionic ligands are replaced by point negative charges and the neutral legands are replaced by the partial negative charge from the molecuar dipoles. The six charges are placed at equal distances from the metal atom, one charge on each of the positive and negative sides of the x-, y-, and z-axes.

Fundamentally, the bonding in this model of a complex is due to the attraction of the positive metal ion for the negative charges of the ligands. However, an electron in a d-orbital of the metal atom is repelled by the negative charge of the ligands.

When ligands approach along the x, y, and z axes, electrons in the 3d orbital will be repelled but as can be seen from above diagrams the effect will be greater for the $3dz^2$ and $3dx^2 - y^2$ orbitals since these two orbitals have lobes lying along the line of approaching ligands. The net result is that the energy of the $3dz^2$ and $3dx^2 - y^2$ orbitals is raised relative to the energy of the $3dxy$, $3dxz$, and $3dyz$ orbitals i.e. the degeneracy of the 3d orbitals is now destroyed.

The 3d levels are split into an upper group of two (doubly degenerate and labeled eg) and a lower group of three (trebly degenerate and labeled t_{2g}), the spilliting of the levels is represented by the symbol Δ. If we reckon the zero of energy as the state of affairs that would obtain if each of the fire 3*d* orbitals had interacted equally with the six ligands, then each of the upper two orbitls is raised by 3/5 Δ while each of the three lower oubitals is lowered by 2/5 Δ (Δ collecdtively). As shown in diagram.

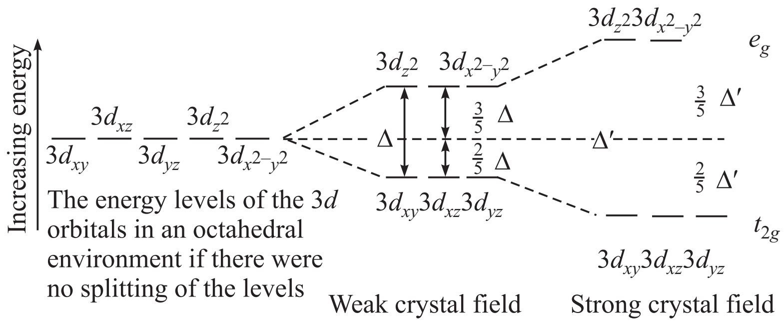


Fig. 22.2: *The splitting of the 3d levels in an octahedral environment of ligands.*

If we now consider the example of a transition metal ion with only one 3d electron surrounded octahedrally by six ligands, e.g. $[Ti\ (H_2O)_6]^{3+}$, then this single 3d electron will normally occupy one of the three degenerate lower levels (t_{2g}). In order to transfer this electron into an upper level (eg) radiation of the appropriate frequency must be supplied. Transition metal ions are coloured because radiation in the visible spectrum is of the right frequency to promote this electronic transition, and in particular $[Ti\ (H_2O)_6]^{3+}$ ions are purple because green light (wavelength about 500 nm) is absorbed, i.e. white light minus green light gives purple light. The relationship between Δ and the frequency of light absorbed is given by the usual expressions-

$$\Delta = h\nu$$

Where h is Planck's constant and ν is the frequency absorbed.

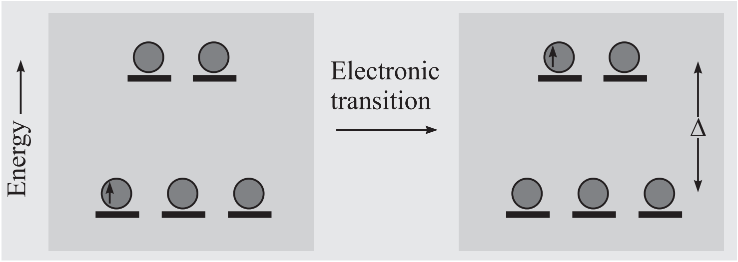


Fig. 22.3: *The electronic tranistion responsible for the visible absorption in $Ti(H_2O)_6^{3+}$. An electron undergoes a transition from a lower-enrgy d orbital to a higher-nergy d orbital. The energy change equals the crystal field splitting Δ.*

Similar considerations apply to complexes in which the central transition metal ion has more than one 3d electrons although needless to say the presence of more than one electron in the 3d orbitals leads to slight complications.

It is found experimentally that for a given transition series (in the case of first transition series) the value of Δ depends upon (a) the charge carried by the central transition metal ion, (b) the nature of the ligand and, (c) the transition metal ion itself. In general, for a given ligand, the crystal field spilitting is greater for M^{3+} octahedral complexes compared to that in Mn^{2+} octahedral complexes, while for transition metal ions carrying the same charge, the value of Δ increase in the order,

$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 <$ ethylenediamine $< NO_2^- < CN^-$,

where the above ions and neutral molecules are the ligands which may surround the transition metal ion. This order is known as the spectro chemical series.

Since small changes in the values of Δ can significantly affect the colour of the light absorbed by transition metal ions, it is not surprising that transition metal ions can show a wide range of colour in different environment.

Magnetic Properties

In order to explain why the same transition metal ion can often display two widely different degrees of paramagnetism in different environments. It is necessary to consider the spectrochemical series. For instance, the CN^- ion produces a greater crystal field spilitting than other ligands.

Consider, for example, the octahderal complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ (Figure). The electron configuration of Fe^{3+} is $[Ar]3d^5$, and there are two possible ways to distribute the five *d* electrons among the *d* orbitals.

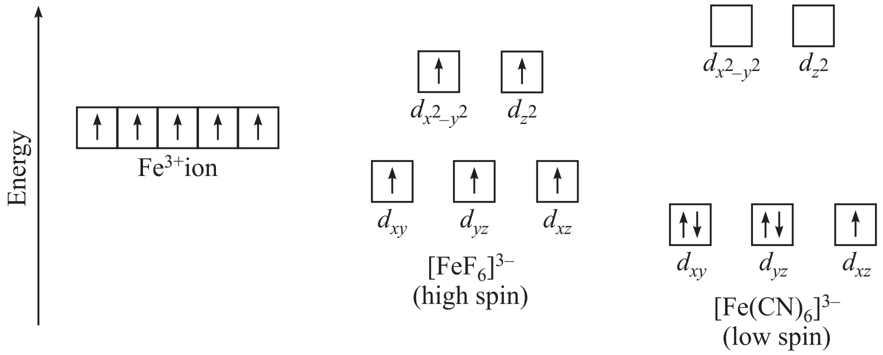


Fig. 22.4: *Energy-level digrams for the Fe^{3+} ion and for the $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$*

As discussed earlier the *d* orbitals are split into two groups i.e. t_{2g} and e_g. If the value of Δ is small then high-spin complex is formed but if value of Δ is large then complex will be of low spin type.

High-spin complexes are more paramegnetic than low-spin complexes. d^4, d^5, d^6 and d^7 electronic configuration form low and high spin complexes. It is not possible to differenciate d^1 d^2 d^3 d^8 and d^9 systems on the basis of magnetic moments.

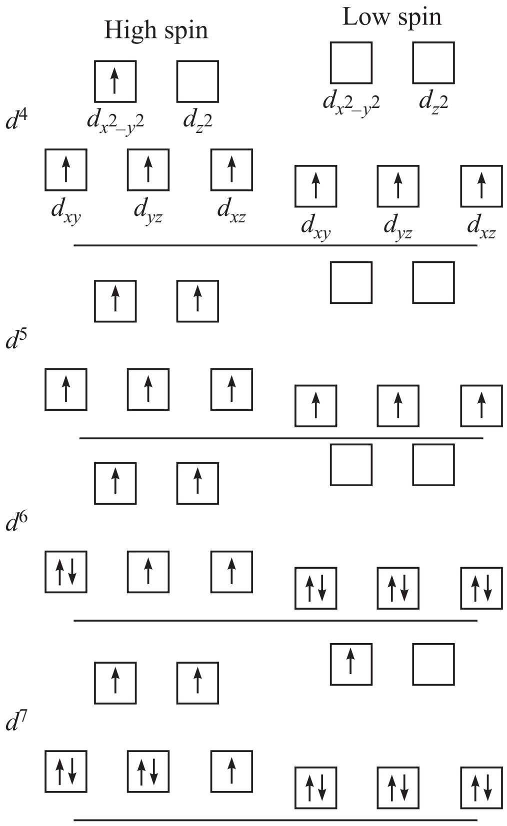


Fig. 22.5: *Orbital diagrams for the high spin and low spin octahedral complexes corresponding to the electron configuration d^4, d^5, d^6, and d^7.*

INTEXT QUESTIONS 22.4

1. Name the type of hybridization present in: $[Co(NH_3)_6]^{3+}$.
2. $[Fe(CN)_6]^{3-}$ is diamagnetic or paramagnetic?
3. $[NiCl_4]^{2-}$ and $Ni(CO)_4$ have sp^3 or dsp^2 hybridization?
4. Which one is diamagnetic: $[Ni(CN)_4]^{2-}$ or $[NiCl_4]^{2-}$?
5. What type of hybridization is shown by (i) inner and (ii) outer orbital complexes?
6. $[FeF_6]^4$ is paramagnetic but $[Fe(CN)_6]^{4-}$ is diamagnetic. explain by CFT.
7. Which is strong field ligand F^- or CN^-.

22.6 ISOMERISM

Compounds which have the same molecular formula, but different structural formulae are said to be isomers. There are many types of isomerism possible The isomerism can be classified as:

Isomerism

Structural isomerism	Stereo isomerism
(a) Ionisation	(a) Geometrical
(b) Hydrate	(b) Optical
(c) Coordination	
(d) Linkage	

1) **Structural isomerism.** This may be subdivided into sub-classes; for example:

   (a) Ionization isomerism, when the compounds yield different ions in solution, e.g. $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$ and $[Co(NH_3)_5SO_4]^{+}$ Br^{-}.

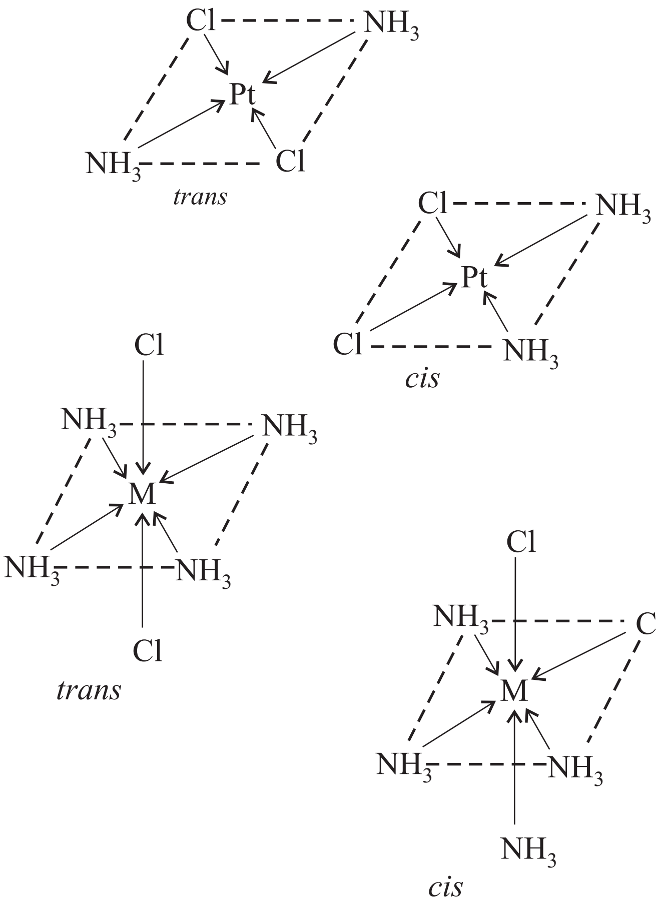
   (b) Hydration isomerism. These compounds show different conductivities in solution, and they precipitate different amounts of silver chloride from cold silver nitrate solution. e.g. $[Cr(H_2O)_6]Cl_3$ (violet), $[Cr(H_2O)_5CI]Cl_2.H_2O$ (light green), and $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$ (dark green).

   (c) Coordination isomerism, when cation and anion both are complexes. e.g. $[Co(NH_3)_6]^{3+}$ $[Cr(C_2O_4)_3]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ $[Co(C_2O_4)_3]^{3-}$.

   (d) Linkage Isomerism: Complexes in which linkages of ligand is different for example $[Co(NH_3)_5\ SCN]]^{2+}$ and $[Co(NH_3)_5NCS]^{2+}$.

2) **Geometrical isomerism.** These are isomers in which the composition of the first coordination sphere is the same, but the geometrical arrangement of the ligands varies. This is often called *cis-trans* isomerism, referring to the relative positions of two selected ligands. This isomerism is only possible for coordination numbers greater than or equal to four, e.g. *cis* and *trans* $PtCl_2(NH_3)_2$.

3) **Optical isomerism**. Any molecule which contains no plane or centre of symmetry may exist in two forms which are non-superiposable mirror images of one another. These have identical chemical and physical properties except that they rotate the plane of plane-polarized light equally but in opposite directions, and they react differently with other optically active compounds. Such compounds are normally obtained as a 50:50 mixture (called a racemic mixture) of the two optical isomers (called enantiomers, or enantiomorphs), which is therefore optically inactive, such as $[Co(en)_3]^{3+}3C1^{-}$.



trans *cis* *trans* *cis*

Two examples of *cis*-*trans* isomers

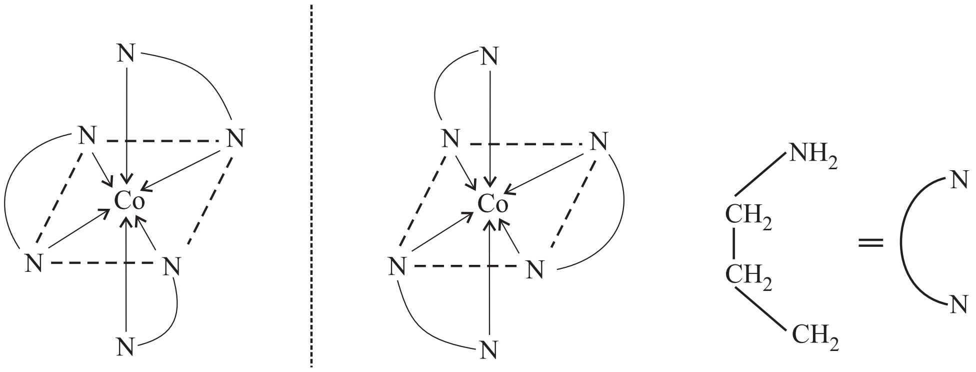


Fig. 22.6: *The enantiomers of* $[Co(en)_3]^{3+}$ *(en = ethylenediamine), also called 1,2-di-aminoethane.*

22.7 APPLICATIONS OF COORDINATION COMPOUNDS

Coordination compounds are found in living systems and have many uses in the home, in industry and in medicines. A few examples are given below:

Extraction of metals: cyanide ions are used for the for the extraction of gold and silver. The crushed ore is heated with an aq. cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion $[Au(CN)_2]^-$.

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^-(aq) + 4\ OH^-(aq)$$

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

Complex formation is also useful for the purification of metals. Nickel is purified by converting the metal to the gaseous compound $Ni(CO)_4$ and then decomposing the latter to pure nickel.

Medicines: EDTA is a chelating agent which is used in the treatment of lead poisoning. Cis platin cis $[Pt(NH_3)_2Cl_2]$ is used in the treatment of cancer. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is used to lower blood pressure during surgery.

Qualitative Analyses: complex formation is useful for qualitative analyses.

(a) Separation of Ag^+ from Pb^{2+} & Hg^{2+}

$$Ag^+ + 2NH_{3(aq.)} \rightarrow [Ag(NH_3)_2]^+$$

Soluble

(b) Separation of IIA and IIB groups: The cations of IIB group form soluble complex with yellow ammonium sulphide.

(c) Cu^{2+} ion forms complex on addition of ammonia $[Cu(NH_3)_4]^{2+}$.

(d) Fe^{2+} forms a blue complex with $K_3Fe(CN)_6$, i.e. $K\ Fe^{II}[Fe^{III}(CN)_6]$.

(f) Cobalt(II) gives color with HCl due to the formation of complex $[CoCl_4]^{2-}$.

(g) Nickel forms a red complex $[Ni(DMG)_2]$ with dimethylglyoxime (H_2DMG).

INTEXT QUESTIONS 22.5

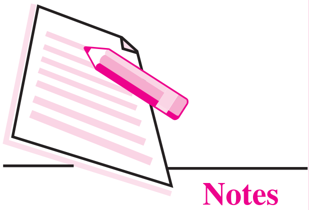
1. Name two elements which are extracted by complexation.
2. What is the use of EDTA in medicine?
3. Name the compound of platinum which is used as anticancer agent?
4. Give two uses of complexes in qualitative analyses
5. Write down geometrical isomers of $Pt(NH_3)Cl_2$.
6. $[Co(NH_3)_5SCN]^{2+}$ and $[Co(NH_3)_5NCS)^{2+}$ is the example of ....

WHAT YOU HAVE LEARNT

- Coordination compounds are compound in which a central metal ion is attached to a group of surrounding ligands by coordinate covalent bond. Ligands can be monodentate or polydentate, depending upon the number of donor atoms attached to the metal. Polydentate ligands are also called chelating agents. They form complexes that have rings of atoms known as chelate rings.
- The number of donor atoms bonded to a metal is called the coordination number of the metal. Common coordination number and geometries are 2 (linear), 4 (tetrahedral and square planar), and 6 (octahedral).
- Systematic names for complexes specify the number of ligands of each particular type, the metal, and its oxidation state.
- Valance Bond Theory describes the bonding in complexes in terms of two-electron, coordinate covalent bonds resulting from the overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands; sp (linear), sp^3 (tetrahedral), dsp^2 (square planar) and d^2sp^3 or sp^3d^2 (octahedral).
- Colour and magnetic behaviour of the complexes by using Crystal Field theory.
- Structural isomension i.e. ionisation, hydrate, coordination and Linkage Stereoisomerism, Geometrical and optical.
- Complexes are very useful in qualitative analyses and in medicine.

TERMINAL EXERCISE

1. Define the following:
   (i) Coordination number
   (ii) Coordination sphere
   (iii) Oxidation number
2. Define ligands. Give one example of each of monodentate, bidentate and polydentate ligands.
3. Write the postulates of Werner's theory of coordination compounds.



4. Write down the name of the following complexes:
   (i) $K_3[Cr(C_2O_4)_3]$
   (ii) $[Co(NH_3)_2(H_2O)_2Cl_2]^+$
   (iii) $[Pt(en)_2]^{2+}$
   (iv) $[NiCl_4]^{2-}$
   (v) $[Fe(CN)_6]^{4-}$
5. Write down the formulae of the following complexes:
   (i) Tris(ethylenediamine)platinum(IV)
   (ii) Tetraaquadibromocobalt(III) ion
   (iii) Sodium tetraiodozincate(II)
   (iv) Tetracyanonickelate(II) ion
   (v) Dichlorotetrathiocyanatochromium(III) ion
6. Give the salient features of VB theory for complexes. What do you mean by inner and outer orbital complexes?
7. $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are tetrahedral but differ in magnetic behaviour, explain.
8. $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic but have different geometry, explain.
9. $[NiCl_4]^{2-}$ is paramagnetic whereas $[Ni(CN)_4]^{2-}$ is diamagnetic, explain.
10. Explain the types of hybridization and magnetic behaviour of the following complexes on the basis of VB theory:
    (i) $[Fe(CN)_6]^{4-}$
    (ii) $[Cr(NH_3)_6]^{2+}$
    (iii) $[Fe(CN)_6]^{3-}$
    (iv) $[NiCl_4]^{2-}$
    (v) $Ni(CO)_4$
11. Explain the application of complexes in extraction of elements, medicines and qualitative analyses.
12. Write down geometrical and optical isomeric of $[Co(Cu)_2Cl_2]^+$.
13. $[Co(NH_3)_6]^{3+}$ is yellow in colour but $[CoF_6]^{3-}$ is blue. Why?
14. $\{Fe(H_2O)_6]^{3+}$ shows magnetic moment is 5.9 BM but magnetic mement of $[Fe(CN)_6]^{3+}$ is 1.82 BM. Explain on the basis of CFT.

ANWERS TO INTEXT QUESTIONS

22.1

1. Primary valence corresponds to the oxidation state of the central metal ion. It is satisfied by negative ions only.
2. Secondary valence of the metal corresponds to coordination number and is satisfied by negative ions or neutral molecules.
3. In both secondary valance is 6.
4. Octahedral.
5. Two i.e. Tetrahedral or square planar.

22.2

1. (i) 6
   (ii) 6
   (iii) 4
2. (i) +2
   (ii) +3
   (iii) +3
   (iv) +2
3. EDTA
4. NH_3, ethylenediammine and EDTA
5. +3, 6, Ethylenediammine.

22.3

1. (i) Tetraamminedichlorocobalt (III) ion
   (ii) Ammonium-hexaisothiocyanatochromate (III)
   (iii) Tetracarbonylnickel (0)
   (iv) Potassium-hexacyanoferrate (II)
   (v) Tris(ethylenediamine) chromium (III) chloride
2. (i) $[NiCl_4]^{2-}$
   (ii) $[Co(NH_3)_5NO_2]^{2+}$

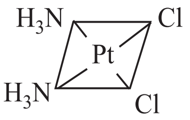
(iii) $K_3[Fe(CN)_6]^-$

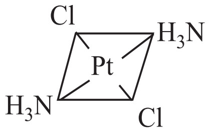
(iv) $[Cr(en)_2Cl_2]^+$

22.4

1. d^2sp^3
2. $[Fe(CN)_6]^{3-}$ is paramagnetic because it has one unpaired electron.
3. Both the complexes have sp^3 (tetrahedral) hybridization.
4. $[Ni(CN)_4]^{2-}$ is diamagnetic because it is square planar (dsp^2 hybridization). It has no unpaired electron.
5. Inner – d^2sp^3, outer – sp^3d^2
6. F^- is weak field ligand therefore electron will be filled $t_{2g}{}^4eg^{02}$ (i.e. four unpaired electron) therefore paramagnetic but CN^- is strong field ligand so electronic configuration will be $t_{2g}{}^6eg^0$ (no unpaired electron)
7. F^- weak field CN^- strong field ligand.

22.5

1. Gold and silver are extracted by cyanide process.
2. EDTA forms soluble complex with elements. It is used in the treatment of lead poisoning.
3. Cis-platin
4. $[Cu(NH_3)_4]^{2+}$ & $[Ni(DMG)_2]$
5. 

(Cis)


(Trans)
6. Linkage isomerism

   $Fe^{2+} = 3d^6$

313en23

23

NOMENCLATURE AND GENERAL PRINCIPLES

Organic compounds are all around us in several forms. They are present in a vast range of substances like fuels, foods, polymers and plastics, textiles, dyes, drugs, medicines, explosives, cosmetics, paints and pesticides. The word organic is derived from the word organism because the body of living things is composed mainly of organic compounds. In addition to the organic compounds of animals and plants origin, a large number of them have been synthesized in the laboratory. All organic compounds are known to contain carbon. The carbon atoms have a unique property called 'catenation' which is the ability to form long chains, rings and networks of carbon atoms resulting into the formation of large number of carbon compounds.

The basic organic compounds are *hydrocarbons* (compounds of carbon and hydrogen) which can be converted to different types of organic compounds by performing different reactions. The *organic chemistry* is the branch of chemistry which deals with the study of compounds of carbon. Some compounds containing carbon are not studied in this branch of chemistry such as oxides of carbon, metal carbides, metal cyanides, and metal carbonates and these come under 'Inorganic Chemistry'.

This lesson describes various rules for naming of organic compounds based upon IUPAC system. A distinction between different types of bond fission in organic compounds is also explained. Various types of reactions and electronic effects are discussed with examples. This lesson also covers different types of isomerism.

OBJECTIVES

After reading this lesson, you will be able to:

- name various types of organic compounds according to IUPAC system;
- distinguish between different types of bond fission;

- explain different types of reactions: substitution, addition, elimination and molecular rearrangements;
- identify nuclophiles and electrophiles;
- explain electronic effects in a covalent bond such as inductive effect; electromeric effect, resonance, hyperconjugation and steric hindrance;
- explain structural isomerism and stereoisomerism.
- define absolute configuration;
- assign absolute configuration (R-S and D-L) to a chiral centre; and
- qualitative and quantitative analysis of organic compound.

23.1 CLASSIFICATION OF HYDROCARBONS

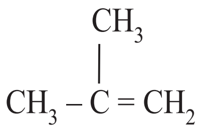
All organic compounds may be divided into two broad classes based upon the pattern of chain of carbon atoms. Let us now understand these classes of compounds.

1. **Open-chain or Aliphatic compounds:** This class includes all hydrocarbons (saturated and unsaturated) and their derivatives which have open-chain structures. Saturated hydrocarbons are those which contain single bonds between all carbon atoms such as

   $CH_3 - CH_3$ and $CH_3 - CH_2 - CH_3$

   On the other hand, unsaturated compounds contain a double (–C = C–) or a triple (–C ≡ C–) bond between two carbon atoms.

   For example :

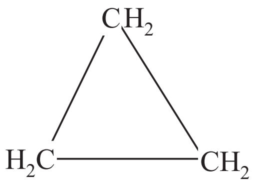
   
   $$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$$

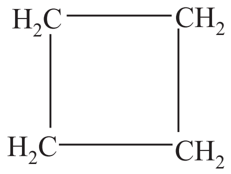
   $CH_3 - CH = CH_2$ $CH_3 - C{\equiv}CH$

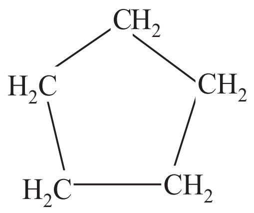
2. **Closed-chain or cyclic compounds:** These compounds have atleast one ring (cyclic) system. These are further divided into two sub-classes: **homocyclic** and **heterocyclic** based on the atoms present in the ring. They are called **homocyclic** or **carbocyclic** when the ring is formed by carbon atoms only.

   Homocyclic (carbocyclic) compounds may again be divided into two groups namely **alicyclic** and **aromatic** compounds.

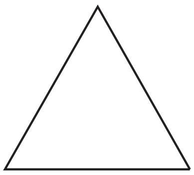
(i) **Alicyclic compounds:** This group includes saturated and unsaturated cyclic hydrocarbons which resemble with the aliphatic hydrocarbons in properties. Some examples are given below:

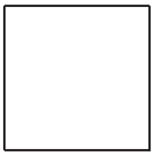


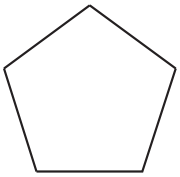




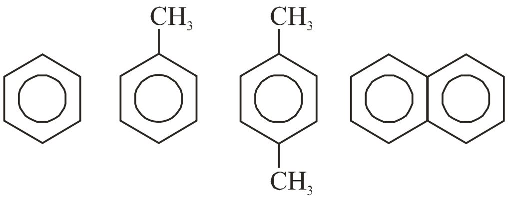
The above compounds can be represented in the form of condensed structures as shown below where each corner represents a –CH_2–group.



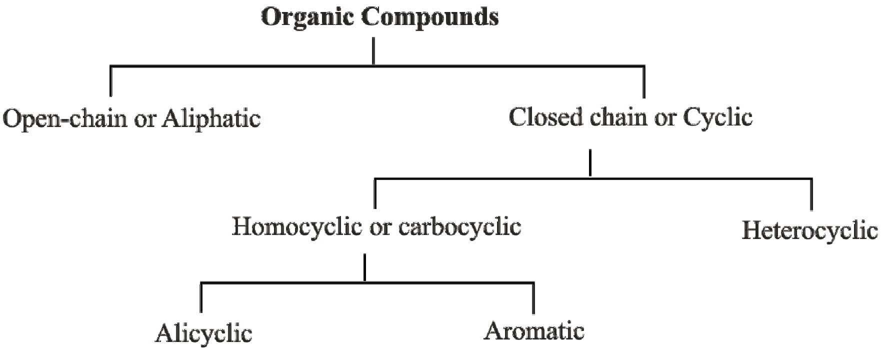




(ii) Aromatic compounds: The group of homocyclic compounds having special set of properties are called aromatic compounds which will be discussed in Lesson 24. They also have characteristic smell or *aroma* and hence called *aromatic*. These include aromatic hydrocarbons and their derivatives are examples of such compounds are as follows :

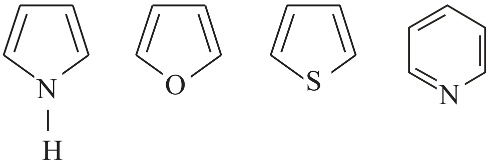


The above classification of the organic compounds can be summarised as below:



On the other hand, **heterocyclic compounds** contain one or more atom (usually O, N or S atom) other than the carbon atoms.

Some examples of heterocyclic compounds are as follows:



23.2 NOMENCLATURE OF ORGANIC COMPOUNDS

In the beginning, the organic compounds were named after the source from which they were obtained e.g. methane was named as marsh gas as well as damp fire because it was obtained from marshy places. Similarly, formic was named so because it was obtained from red ants (Latin name *formica*). These names of organic compounds are called common names or trivial names. There was no systematic basis for naming them and it was very difficult task to remember the names of so many organic compounds. Even the same compound was known by different names. In order to bring uniformity and rationality in naming the organic compounds throughout the world, International Union of Chemistry (in 1958) came out with a system of nomenclature later known as IUPAC (International Union of Pure and Applied Chemistry) system. Before explaining IUPAC system of nomenclature, we shall discuss about homologous series.

Homologous Series: A series of compounds in which the molecular formula of a compound differs from those of its neighbouring compounds by the CH_2 group, is known as a **homologous series**. Each of such homologous series is given a general name. For example, homologous series of open chain saturated hydrocarbons is known as **alkanes** and open chain unsaturated hydrocarbons form *two* series of compounds namely **alkenes** and **alkynes,** which contain carbon - carbon double bond and triple bond, respectively. Some members of homologous series of aliphatic hydrocarbons are listed in the Table 23.1.

Table 23.1: Homologous series of hydrocarbons

Satuarated		**Unsaturated**			
General Name : *Alkanes* **General Formula : C_nH_{2n+2}**		***Alkenes*** C_nH_{2n}			***Alkynes*** C_nH_{2n-2}
CH_4	Methane				
C_2H_6	Ethane	C_2H_4	Ethene	C_2H_2	Ethyne
C_3H_8	Propane	C_3H_6	Propene	C_3H_4	Propyne
C_4H_{10}	Butane	C_4H_8	Butene	C_4H_6	Butyne
C_5H_{12}	Pentane	C_5H_{10}	Pentene	C_5H_8	Pentyne
C_6H_{14}	Hexane	C_6H_{12}	Hexene	C_6H_{10}	Hexyne
...	...	...	...	...	...
...	...	...	...	...	...
...	...	...	...	...	...

23.2.1 IUPAC Nomenclature of Acyclic Hydrocarbons

Acyclic hydrocarbons include straight chain as well as branched chain compounds.

(a) Straight chain Hydrocarbons: The names of these hydrocarbons consist of two parts. The first one is word **root** and second one is **suffix**. The word root designates the number of carbon atoms in the chain. Special word roots (*Meth-, Eth-, Prop-, But-,* etc.) are used for chains containing *one to four carbon atoms* but for chains of *five and more carbon atoms,* Greek number roots such as Pent-, Hex - etc. are used the in IUPAC word roots for a few carbon chains are given below in Table 23.2.

Table 23.2 : Some Word Roots and corresponding number of carbon atoms

Number of C- Atoms	Word root	Number of C- Atoms	Word root
1	Meth -	6	Hex -
2	Eth -	7	Hept-
3	Prop -	8	Oct-
4	But -	9	Non-
5	Pent-	10	Dec-

The general word root for any carbon chain is **alk.**

In order to write the IUPAC name, a suffix is added to the word root to indicate saturation or unsaturation in the hydrocarbons. These suffixes are listed below in the Table 23.3.

Table 23.3 : Types of hydrocarbons and suffixes in their name

Class of compound	Suffix	General name
Saturated	-ane	Alkane
Unsaturated ($>C=C<$)	-ene	Alkene
Unsaturated ($-C\equiv C-$)	-yne	Alkyne

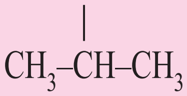
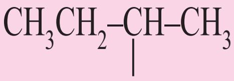
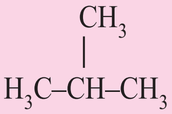
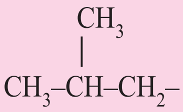
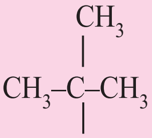
Let us consider some examples:

Compound	IUPAC Name	Word root	Suffix
$CH_3CH_2CH_3$	Propane	Prop-	ane
$CH_3CH_2CH_2CH_2CH_3$	Pentane	Pent-	ane
$CH_2 = CH_2$	Ethene	Eth-	ene
$CH_3-C\equiv CH$	Propyne	Prop-	yne

b) Branched chain Hydrocarbons

In branched chain hydrocarbons, one or more alkyl groups are present as side chain attached to the main straight chain of carbon atoms. The carbon atoms of the side chain constitute **alkyl groups.** These alkyl groups are written as prefixes in the IUPAC name. An alkyl group is obtained from an alkane by removing one hydrogen atom. Since the general formula of alkane is C_nH_{2n+2}, the general formula of alkyl group is C_nH_{2n+1}. The alkyl groups are generally represented by R– and named by replacing the suffix **ane** of the corresponding alkane by **yl**. Let us see some examples of the alkyl groups given in the Table 23.4.

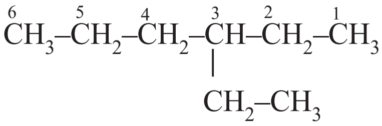
Table 23.4: Some alkyl groups

Parent Chain	Formula R-H	Alkyl group R-	Name
Methane	CH_4	CH_3-	Methyl
Ethane	CH_3CH_3	CH_3CH_2-	Ethyl
Propane	$CH_3CH_2CH_3$	$CH_3CH_2CH_2-$	Propyl
		 $CH_3-\overset{\vert}{C}H-CH_3$	Isopropyl
Butane	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2-$	Butyl
		 $CH_3CH_2-\underset{\vert}{C}H-CH_3$	*sec*-butyl
Isobutane	 $H_3C-\overset{CH_3}{\overset{\vert}{C}H}-CH_3$	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-$	Isobutyl
		 $CH_3-\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}-CH_3$	*tert*-butyl

Branched chain hydrocarbons are named using the following rules in IUPAC system.

Rule 1. Longest chain Rule: According to this rule, the longest possible chain of carbon atoms is considered and the compound is named as the derivative of the corresponding alkane. *If some multiple bond is present, the selected chain must contain the carbon atoms of the multiple bond.* The number of carbon atoms in the selected chain determines the *word root* and the saturation or unsaturation will determine the *suffix*.

Let us consider the following example:

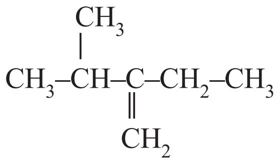


$$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-\underset{CH_2-CH_3}{\underset{\vert}{\overset{3}{C}H}}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

Word root **-Hex** + Suffix **-ane**

Since it has a main chain of *six* carbon atoms; hence, it will be named as a derivative of **hexane**.

Similarly,

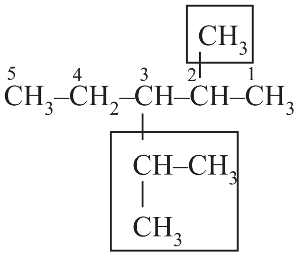


$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{CH_2}{\underset{||}{C}}-CH_2-CH_3$

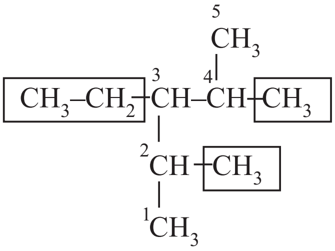
Wordroot - **But** + Suffix - **ene**

The main chain of carbon atoms containing double bond consists of *four* carbon atoms. Therefore, the compound will be a derivative of butene.

If two equally long chains are possible, the chain with maximum number of side chains is selected as the main chain.



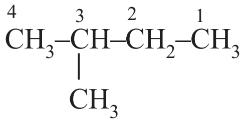
***Main chain has 2 branches* (Wrong)**



***Main chain has 3 branches* (Correct)**

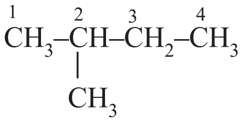
Rule 2: Lowest number or lowest sum rule: The longest carbon chain is numbered from one end to another and the positions of the side chain are indicated by the number of carbon atoms to which these are attached. The numbering is done in such a way that :

a) The substituted carbon atoms have the lowest possible numbers.



$\overset{4}{CH_3}-\underset{CH_3}{\underset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{CH_3}$

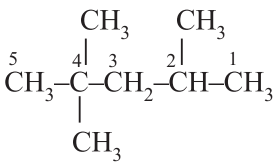
Wrong numbering



$\overset{1}{CH_3}-\underset{CH_3}{\underset{|}{\overset{2}{CH}}}-\overset{3}{CH_2}-\overset{4}{CH_3}$

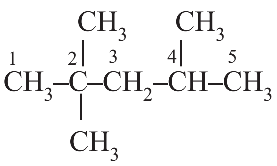
Correct numbering

b) The sum of numbers used to indicate the positions of various alkyl groups must be the lowest.



$\overset{5}{CH_3}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{4|}{C}}}}-\overset{3}{CH_2}-\overset{CH_3}{\overset{2|}{CH}}-\overset{1}{CH_3}$

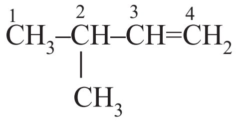
Sum of positions = 2+4+4 = 10
(Wrong)



$\overset{1}{CH_3}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{2|}{C}}}}-\overset{3}{CH_2}-\overset{CH_3}{\overset{4|}{CH}}-\overset{5}{CH_3}$

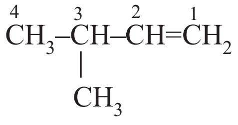
Sum of positions = 2+ 2+4 = 8
(Correct)

Rule 3 : If some multiple bond is present in the chain the carbon atoms involved in the multiple bond should get the lowest possible numbers. For example :



$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{2}{C}H}}-\overset{3}{C}H=\overset{4}{C}H_2$

Wrong numbering



$\overset{4}{C}H_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{2}{C}H=\overset{1}{C}H_2$

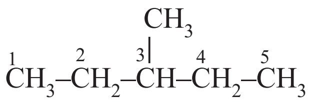
Correct numbering

Rule 4 : Naming of compounds with one alkyl group as the substituent (side chain)

The name of a substituted hydrocarbon consists of the following parts.

Position of substituent - Name of *substituent,* Word *root, Suffix.*

Let us consider a compound represented by the following structure:

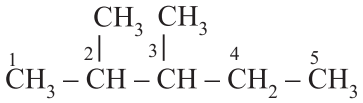


$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{\displaystyle CH_3}{\overset{|}{\overset{3}{C}H}}-\overset{4}{C}H_2-\overset{5}{C}H_3$

In the given structure, we find that the longest chain consists of *five* carbon atoms and the substituent is ***methyl*** group at position number 3. The word root is **Pent** and suffix is **ane.** Hence, the name is 3-methylpentane.

Rule 5 : Naming the same alkyl groups at different positions or more than one alkyl groups

If the compound contains more than one identical alkyl groups, their positions are indicated separately and the prefixes *di* (for two), *tri* (for three) etc. are attached to the name of the substituents. The positions of the substituents are separated by commas (,). In the following structure, two methyl groups are attached to the main chain of five carbon atoms.



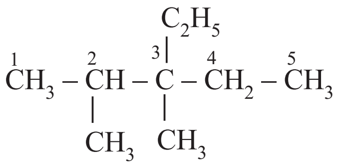
$\overset{1}{C}H_3-\overset{\displaystyle CH_3}{\overset{|}{\overset{2}{C}H}}-\overset{\displaystyle CH_3}{\overset{|}{\overset{3}{C}H}}-\overset{4}{C}H_2-\overset{5}{C}H_3$

You can see that they are attached to the positions 2 and 3 of the main chain. Hence, the name of the compound is 2,3-dimethylpentane.

Rule 6: Naming different alkyl substituents

If there are different alkyl substituents present in the compound, their names are written in the alphabetical order. However, the prefixes *di, tri,* etc. are not considered in deciding the alphabetical order.

For example, in the compound shown below the longest chain consists of **five carbon atoms;** hence, the parent hydrocarbon is pentane. The main chain has two methyl groups at C_2 and C_3 and one ethyl group at C_3 as substituents. The names of these alkyl



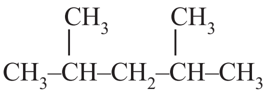
$$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\underset{\displaystyle CH_3}{\overset{\displaystyle C_2H_5}{\overset{3|}{C}}}-\overset{4}{C}H_2-\overset{5}{C}H_3$$

groups are written before the name of parent alkane and their positions are indicated by number of carbon atom to which they are attached. Thus, the name of the compound will be 3-ethyl-2, 3-dimethylpentane.

INTEXT QUESTIONS 23.1

1. Identify word *root* and *suffix* for the following :
   (i) $CH_3CH_2CH_2CH_2CH_2CH_3$
   (ii) $CH_3CH_2CH = CHCH_2$
   (iii) $CH_3C \equiv CH$
2. Give IUPAC name to the following compounds

(i) $CH_3–CH=CH–CH_2–CH_2–CH_2–CH_2–CH_3$

(ii) 

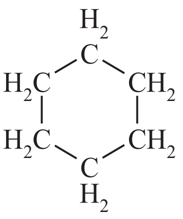
$$CH_3–\underset{}{\overset{\displaystyle CH_3}{CH}}–CH_2–\overset{\displaystyle CH_3}{CH}–CH_3$$

23.2.2 Nomenclature of Cyclic Hydrocarbons

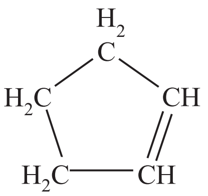
We already know that cyclic hydrocarbons can be divided into alicyclic and aromatic compounds. Now let us learn the nomenclature of these compounds.

a) Alicyclic Compounds

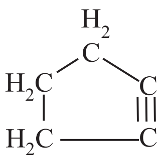
As we have already discussed (in Section 23.3) that alicyclic compounds have closed chain i.e. cyclic structures, hence their names are derived by putting *prefix* **'cyclo'** before the *word root*. The suffix **ane, ene** or **yne** are written according to the saturation or unsaturation in the ring structure. Given below are some examples of alicyclic compounds.



Cyclohexane

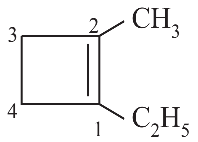


Cyclopentene

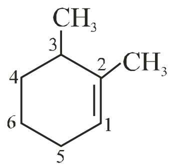


Cyclopentyne

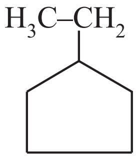
If an alkyl substituent is present, it is indicated by the appropriate *prefix* and its position is indicated by numbering the carbon atoms of the ring in such a way so as to assign the least possible number to the substituent. For example:



1-Ethyl-2-methylcyclobutene



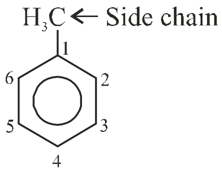
2,3-Dimethylcyclohexene



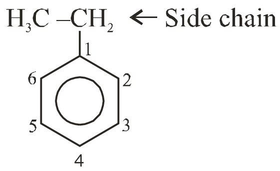
Ethylcyclopentane

b) Aromatic Compounds

The most important members of this class are benzene and its derivatives. For naming an alkyl substituted benzene, the carbon atoms of benzene are numbered from 1 to 6 by giving the lowest possible number to the position of the side chain or substituent. This is shown below.

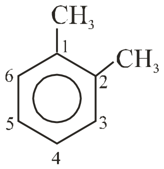


Methylbenzene
(Toluene)

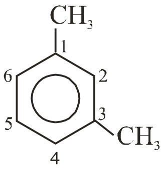


Ethylbenzene

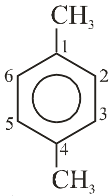
Benzene forms only one monosubstituted derivatives like methylbenzene or ethylbenzene. However, it can form three disubstituted compounds namely 1,2; 1,3 and 1, 4 derivatives. These are also known as *ortho*- (or *o*–), *meta*- (or *m*-) and *para*- (or *p*-) substituted compounds, respectively.



1, 2-Dimethylbenzene
(*ortho*-Xylene)



1, 3-Dimethylbenzene
(*meta*-Xylene)



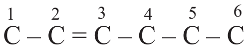
1, 4-Dimethylbenzene
(*para*-Xylene)

23.2.3 Writing Structure of Hydrocarbons from their IUPAC Names

Till now, we have named hydrocarbons from their structures using IUPAC nomenclature. Let us now do the reverse exercise i.e. writing structure of hydrocarbons when their IUPAC names are given. Let us take some examples to write structures for given IUPAC names.

Example 1. Writing the structure of **4-Ethyl-5-methylhex-2-ene**

Step 1 The skeleton of parent hydrocarbon chain of six carbon atoms with C=C at C_2 is drawn.

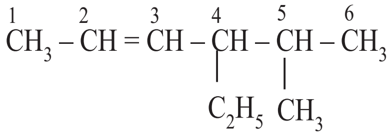


$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

Step 2 Attach ethyl group at C_4 and methyl group at C_5.

Step 3 Attach H-atoms to the C-atoms of main chain to satisfy tetravalency of all the carbon atoms.

Thus, the correct structure of the compound is as given below:



$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{\substack{|\\C_2H_5}}{\overset{4}{CH}}-\underset{\substack{|\\CH_3}}{\overset{5}{CH}}-\overset{6}{CH_3}$$

Example 2. Writing the structure of **Octa-3,5-diene**

Step 1- The skeleton of parent hydrocarbon chain of **eight** carbon atoms is drawn.

Step 2- Make C=C at C_3 and at C_5.

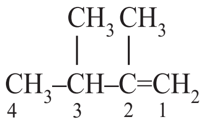
Step 3- Attach hydrogen atoms to the carbon atoms of main chain to satisfy tetravalency of all the carbon atoms.

The correct structure of the compund is as follows :

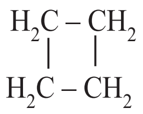
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH}=\overset{6}{CH}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

The following compounds illustrate some more examples:

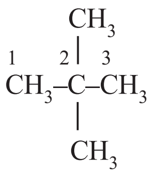
(i) 2,3-Dimethylbut-1-ene (ii) Cyclobutane (iii) 2,2-Dimethylpropane



$$\underset{4}{CH_3}-\underset{3}{\overset{\substack{CH_3\\|}}{CH}}-\underset{2}{\overset{\substack{CH_3\\|}}{C}}=\underset{1}{CH_2}$$



$$\begin{array}{c}H_2C-CH_2\\ |\qquad\ \ |\\ H_2C-CH_2\end{array}$$



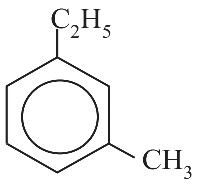
$$\overset{1}{CH_3}-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|\\2}}{C}}-\overset{3}{CH_3}$$

After this reverse exercise, you would have definitely gained confidence in naming and writing structures of various hydrocarbons.

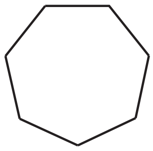
INTEXT QUESTIONS 23.2

1. Write IUPAC names for the following compounds :

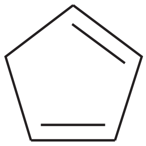
(i)



(ii)



(iii)



2. Write the structural formula for the following compounds:

(i) 1,3-Dimethylcyclohexane (ii) Ethylcyclobutane (iii) *n*-Propylbenzene

23.2.4 IUPAC Nomenclature of Aliphatic Organic Compounds Containing Functional Groups

A **functional group** is an atom or group of atoms which is responsible for characteristic properties of a compound. For example :

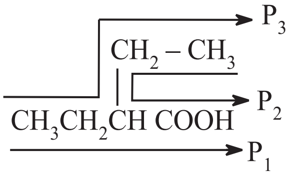
–Cl, –Br, –I, –COOH, –OH, $–NH_2$ etc.

a) Compounds with one functional group (monofunctional Derivatives): The derivatives of hydrocarbons containing only one functional group are called monofunctional derivatives.

Most of the IUPAC names of functional derivatives of hydrocarbons are derived by replacing the suffix **ane** of the parent alkane (corresponding to the number of carbon-atoms in the longest chain) by a specific *suffix* for the functional groups, (see Table 23.5). There are some derivatives in which a particular *prefix* is added to the parent alkane name as in *nitroalkanes, haloalkanes,* and *haloarenes etc*. Given below are some rules for the IUPAC nomenclature of organic compounds containing functional groups. In addition to the *rules listed below,* all the general rules discussed earlier for naming of hydrocarbons are also applicable to such compounds.

Rule1: First of all the longest chain of carbon atoms containing the functional group is identified. In case of carbon containing functional group, (–CHO, –COOH) the main chain must include the carbon atom of the group.

For Example :



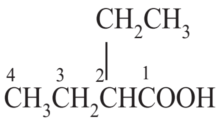
(Structure –I)

P_1 or P_2 are correct selections of chain of carbon atoms whereas P_3 is wrong selection as it does not include the carbon atom of the functional group.

Rule 2: The longest continuous carbon atom chain is numbered from that end which will give the lowest number to the carbon atom bearing the functional group.

Rule 3: There is a specific **suffix** for each functional group that replaces the ending **-e** in the name of the corresponding parent alkane.

Rule 4: If the carbon chain is branched, then the attached alkyl groups are named and numbered as in Structure I (rule 1) main chain contain a branch of two carbon atoms i.e., ethyl group at position 2.



$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{\underset{}{C}}H(CH_2CH_3)\overset{1}{C}OOH$$

(Structure I)

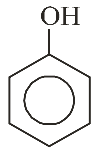
Rule 5: While writing the name of the compound, place the substituents in the alphabetical order.

Table 23.5 lists some examples of the functional groups present in the organic compounds together with the names of the class of compounds they belong to.

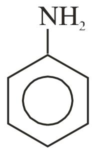
Table 23.5: Some Common Functional Groups and their Aliphatic Derivatives

Functional Group	Suffix/ Prefix	General name	Example (IUPAC name)
–OH (Hydroxy)	–ol	Alkanol (Alcohols)	CH_3CH_2OH (Ethanol)
–COOH (Carboxyl)	–oic acid	Alkanoic acid	CH_3COOH (Ethanoic acid)
$–SO_3H$ (Sulphonic)	–	Alkylsulphonic acid	$CH_3CH_2SO_3H$ (Ethyl sulphonic acid)
–CHO (Aldehydic)	–al	Alkanal	CH_3CHO (Ethanal)
>CO (Ketonic)	–one	Alkanone	CH_3COCH_3 (Propanone)
$–CONH_2$ (Amide)	–amide	Alkanamide	CH_3CONH_2 (Ethanamide)
–COX (Carboxyl halide)	–oyl halide	Alkanoyl halide	CH_3COCl (Ethanoyl chloride)
–COO– (Ester)	–oate	Alkyl alkanoate	CH_3COOCH_3 (Methyl ethanoate)
–CN(Cyano	–nitrile	Alkanenitrile	CH_3CH_2CN (Propanenitrile)
–SH (Thiol)	–thiol	Alkanethiols	CH_3CH_2SH (Ethanethiol)
$–NH_2$ (Amino)	–amine	Alkanamine	$CH_3CH_2NH_2$ (Ethanamine)
–O – (Ether)	–oxy	Alkoxyalkane	$CH_3–O–CH_3$ (Methoxymethane)
–C≡C– (Yne)	–yne	Alkyne	$CH_3C{\equiv}CCH_3$ (But-2-yne)
–C=C– (Ene)	–ene	Alkene	$CH_3CH{=}CHCH_3$ (But-2-ene)
–X = –F,–Cl, –Br, –I	–Halo **(Prefix)**	Haloalkane	$CH_3CH_2–X$ (Haloethane)
$–NO_2$ (Nitro)	–Nitro **(Prefix)**	Nitroalkane	$CH_3CH_2NO_2$ (Nitroethane)

Certain derivatives have some specific general names e.g. monohydroxybenzene is called **phenol** and monoaminobenzene as **aniline.**

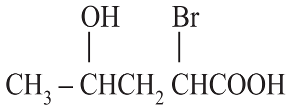


Phenol



Aniline

b) Naming of Organic compounds with more than one functional group: In case of organic compounds containging more than one functional group, one group is given preference over the other(s) in deciding the parent compound. The priority order of the various functional groups is as follows; –COOH, –COOR, $-SO_3H$, –COX, $-CONH_2$, –CHO, –CO–, –CN, –OH, –SH, –O–, $-NH_2$, –X (halogen), $-NO_2$, –C=C–, and –C≡C–. Let us try to name a polyfunctional compound by following the priority of the functional groups.


$$CH_3-\overset{\overset{OH}{|}}{C}HCH_2\overset{\overset{Br}{|}}{C}HCOOH$$

2-Bromo-4-hydroxypentanoic acid

In the above example, –COOH group is given priority over the –OH and –Br (halo) groups.

23.3 TYPES OF REACTIONS IN ORGANIC COMPOUNDS

You are aware that a chemical reaction occurs when one substance is converted into another substance(s). A chemical reaction is accompained by breaking of some bonds and by making of some others. In organic chemistry, this can happen in more than one way involving a variety of reactions. The different types of reactions in organic compounds are: (i)Substitution (ii) Elimination (iii) Addition and (iv)Molecular Rearrangements.

These different ways of occurrence of organic reactions can be understood by the study of reaction mechanisms. A **reaction mechanism** is defined as the detailed knowledge of the steps involved in a process in which the reactant molecules change into products. Let us explain first some of the terms used in reaction mechanism.

23.3.1 Breaking of a Covalent Bond - Types of Bond Fission

Chemical reactions involve breaking of one or more of the existing chemical bonds in reactant molecule(s) and formation of new bonds leading to products. *The breaking of a covalent bond is known as bond fission.* We know that a covalent bond is formed by the sharing of two electrons from two atoms. During bond breaking or bond fission, the two shared electrons can be distributed equally or unequally between the two bonded atoms. There are **two types of bond fission.**

1. **Homolytic fission:** *The fission of a covalent bond with equal sharing of bonding electrons is known as homolytic fission.*
   Homolytic fission in a hypothetical molecule: $A{-}B \longrightarrow \underset{\text{(Free radicals)}}{A\bullet + B\bullet}$

   Now consider the following C-C bond fission:

$$H_3C - CH_3 \xrightarrow[\text{Light}]{\text{Heat}} \bullet CH_3 + \bullet CH_3$$

(Free radicals)

The neutral species so formed are known as **free radicals.**

Free radicals are neutral but reactive species having an unpaired electron and these can also initiate a chemical reactiion.

2. **Heterolytic fission :** *The fission of a covalent bond involving unequal sharing of bonding electrons is known as heterolytic fission.* The heterolytic fission of a hypothetical molecule is shown below.

$$A : B \rightarrow \underset{\textbf{Carbocation}}{A^+} + \underset{\textbf{Carbanion}}{B^-}$$

This type of bond fission results in the formation of *ions*. The ion which has a *positive charge on the carbon atom,* is known as the **carbonium ion** or a **carbocation.** For example,

$$CH_3\overset{+}{C}H_2 \text{ (Ethyl carbocation) and } CH_3\overset{+}{C}HCH_3 \text{ (Isopropyl carbocation)}$$

On the other hand, an ion with a *negative charge* on the carbon atom is known as the **carbanion.**

For example,

$$CH_3\bar{C}H_2 \text{ (Ethyl carbanion), } \bar{C}H_3 \text{ (Methyl carbanion)}$$

The charged species obtained by the heterolytic fission initiate chemical reactions and they are classified as electrophiles and nucleophiles.

Electrophiles: An electrophile is an electron deficient species and it may be positively charged or neutral. Examples are H^+, NO_2^+, Br^+, Cl^+, Ag^+, $CH_3\overset{+}{C}O$, BF_3 etc. Thus, an electrophile is an electron seeking species and hence, it attacks at a position of high electron density.

Nucleophiles : A nucleophile is negatively charged or electron rich neutral species. Examples of nucleophiles are OH^-, NO_2^-, H_2O, $:NH_3$ etc. Nucleophiles attacks a position of low electron density.

23.3.2 Electron Displacements in a Covalent Bond

For a reaction to take place by breaking of a covalent bond, with the attack of a nucleophile or electrophile, the molecule or bond under attack must develop polarity on some of its carbon atoms. This polarity can only be developed by the displacement (partial or complete) of bonding electrons due to certain effects. Some of these electronic effects are permanent (e.g. inductive) and others are temporary (e.g. electromeric) in nature. Such changes or effects involving displacement of electrons in the substrate molecules (molecule under attack of a reagent) are known as electron displacement or **electronic effects**. Some of these effects are discussed below.

(a) Inductive effect: In a covalent bond between the two dissimilar atoms, the shared electron pair is attracted more towards the atom having greater electronegativity. Let us consider the case of a haloalkane (higher than halomethane). The halogen atom (X) being more electronegative than carbon atom, pulls the bonded electrons of the C–X bond. Thus, the C–X bond is polarised as shown below.

$$C^{\delta+} \rightarrow C^{\delta-}$$

The carbon atom gets a partial + ve charge (δ +) and halogen atom a partial negative charge (δ–). This positively charged C_1 attracts bonded electrons of $C_1 – C_2$ bond, thus making C_2 atom a little less positive than C_1. Similarly, this +ve charge is shifted to C_3 but to a very less magnitude (nearly zero +ve charge is present after third atom)

$$\underset{3}{\overset{\delta\delta\delta+}{C}} \rightarrow \underset{2}{\overset{\delta\delta+}{C}} \rightarrow \underset{1}{\overset{\delta+}{C}} \rightarrow \overset{\delta-}{X} \text{ (where X = F, Cl, Br).}$$

This transmission of induced charges along a chain of σ bonded carbon atoms is known as ***inductive effect***. The inductive effect is a permanent polarisation in the molecule and it decreases as we move along a chain of carbon atoms, away from the electronegative atom. Many of the properties of organic compounds such as acidic strength of carboxylic acids are explained on the basis of inductive effect.

Groups with – I Effect (Electron Withdrawing Groups) :

Any atom or group of atoms that withdraws electrons more strongly than the H-atom, is said to have – I effect. Following are various groups arranged in the decreasing order of their –I effect.

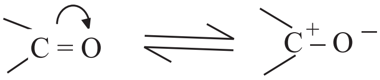
$(CH_3)_3 N^+ > –NO_2 > –CN > –F > –Cl > –Br > –I > –OH > –OCH_3 > –C_6H_5 > –H$

Groups with + I Effect (Electron Releasing Groups) :

Any atom or group of atoms that repels electrons more strongly than hydrogen, is said to have +I effect.Following are the various groups in the decreasing order of +I effect.

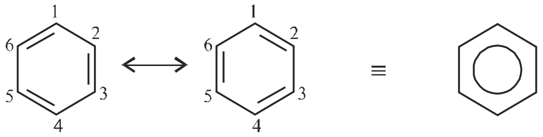
$$(CH_3)_3C– > (CH_3)_2CH– > CH_3CH_2– > –CH_3 > –H$$

(b) Electromeric effect : This type of temporary electron displacement takes place in compounds containing multiple covalent bonds (e.g. $>C=C<$, $>C=O$, $>C=N$ etc.). It involves the complete transfer of electrons resulting into the development of + ve and – ve charges within the molecule. The electromeric effect takes place in the direction of more electronegative atom and is generally shown by an arrow starting from the original position of the electron pair and ending at the new position of the electron pair. In a carbonyl group it operates as follows :



The electromeric effect is represented by the symbol **E**. It is known as **+E effect** when displacement of electron pair is away from the atom or group, or **– E effect** when the displacement is towards the atom or group. As in above example it is +E effect for C and –E effect for O.

(c) Resonance : This phenomenon is exhibited by a number of organic molecules, which can be represented by two or more structures which are called resonating or canonical structures. However, none of those structures explains all the properties of the compound. All the possible structures of a compound are arrived at by the redistribution of valence electrons. The true structure of the compound is an intermediate of all the possible resonating structures or canonical structures and thus called *a resonance hybrid*. For example, the benzene molecule (C_6H_6) may be represented by the following two structures, I and II.

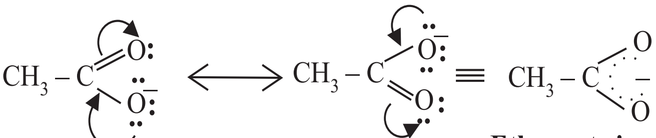


I II III

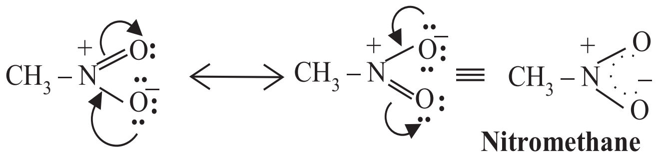
Resonating or canonical structures Resonance hybrid

The evidence in support of the hybrid structure (III) of 'benzene' is available from the bond length data. Equal bond lengths of all C–C bonds (139 pm), which is an intermediate value of C–C single bond (154 pm) and C=C double bond (130 pm) lengths, indicates that each C–C bond in benzene (structure III) has a partial double bond character. Hence, structure III, a resonance hybrid, represents the benzene molecule.

Some more examples of resonance structures are as follows:

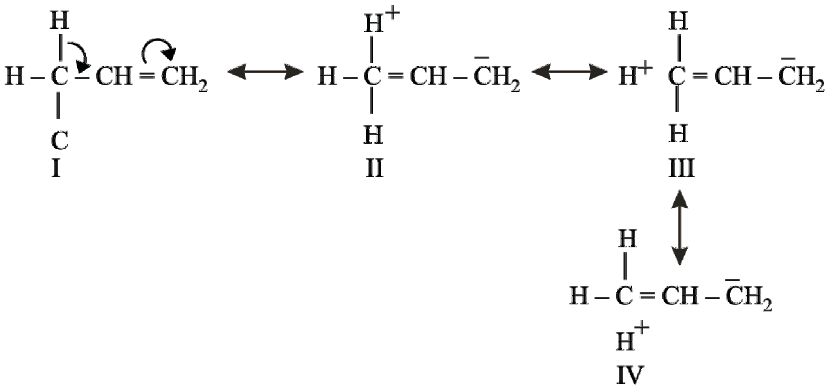


Ethanoate ion



Nitromethane

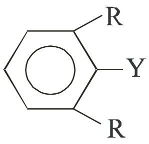
d) Hyperconjugation : Hyperconjugation is also known as *no-bond resonance*. It involves the conjugation of σ (sigma) bond with π (pi) bond. For example, hyperconjugation in propene can be represented as follows.



The structures II to IV have no bond between one of the H-atom and the C-atom.

23.3.3 Steric Hinderance

The effect is caused by the large bulky groups present in the vicinity of the reaction centre. This effect was first observed by Hofmann (1872) and Meyer (1874). They regarded it as mechanical hinderance for the attacking species to approach the reaction site. Hofmann (1872) observed that when a compound of the type



Y (where, Y = – COOH, – CONH$_2$, – CHO, – NH$_2$ etc. and R = –CH$_3$, –C$_2$H$_5$ etc) is treated with the reagents such as Cl$^-$, Br$^-$, I$^-$, OH$^-$, etc., the reaction is hindered or retarded by the substituents at 'R'. The magnitude of hinderance is proportional to the size and number of substituents present in the vicinity of reaction site. Meyer (1874) observed that rate of esterification of aliphatic carboxylic acids and found that their activity was decreased by increasing the number of substituents at the carbon atom adjacent to the COOH group.

$$\underline{CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOC}$$

decreasing order of reactivity with alcohols

INTEXT QUESTIONS 23.3

1. What is the condition of polarity for a covalent bond?
2. Identify the groups with –I and +I effect from the following species :

   $-NO_2$, $-CH_3$, $-CN$, $-C_2H_5$, $-C_6H_5$ and $CH_3-\underset{|}{C}H-CH_3$
3. What is the difference between electromeric and inductive effects?
4. Classify the following species as electrophiles or nucleophiles :

   (i) H_3O^+ (ii) NO_2^+ (iii) Br^- (iv) $C_2H_5O^-$

   (v) CH_3COO^- (vi) SO_3 (vii) CN^- (viii) $^+CH_3$ (ix) $:NH_3$

With the above general background, let us study various types of reactions in a little more details.

23.3.5 Substitution Reactions

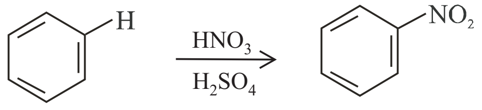
A substitution reaction involves the displacement of one atom or group in a molecule by another atom or group. Aliphatic compounds undergo **nucleophilic substitution** reactions. For example, a haloalkane can be converted to a wide variety of compounds by replacing halogen atom (X) with different nucleophiles as shown below.

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Nu\!: \longrightarrow R-Nu + X^-$$

Haloalkane

(where R- is an alkyl group and $Nu:= -OH, -NH_2, -CN, -SH, -OR', -NHR'$ etc.)

There is yet another type of substitution reaction which takes place in an aromatic hydrocarbons. In this case, an **electrophilic reagent** attacks the aromatic ring because the latter is electron rich. The leaving group, in this case, is always one of the hydrogen atom of the ring.

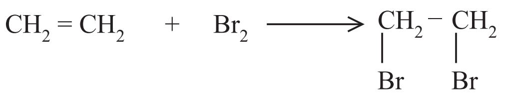


Nitrobenzene

For example, in case of nitration the $-NO_2$ group replaces one hydrogen atom of benzene.

23.3.6 Addition Reactions

Unsaturated hydrocarbons such as alkenes and alkynes are extremely reactive towards a wide variety of reagents. The carbon-carbon double bond (–C=C–) of an alkene contains two types of bonds; one σ (sigma) bond and another π (pi) bond. In alkynes, out of the three carbon-carbon bonds, one is σ (sigma) bond and the other two are π (pi) bonds. The π (pi) bond is weaker than the σ (sigma) bond and breaks easily. For example, the colour of bromine solution disappears when added to the unsaturated hydrocarbons. This is due to the following addition reaction.



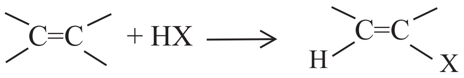
$$CH_2=CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}-\underset{Br}{CH_2}$$

1, 2-Dibromoethane
(Colourless)

Similarly, hydrogen, halogen acids and chlorine add on to a –C=C– double bond, as shown below.

$$CH_3-CH=CH_2+H_2 \xrightarrow{(Ni/Pt\ as\ catalyst)} CH_3\,CH_2\,CH_3$$

The multiple bond of an alkene or alkyne is a region of high electron density. Therefore, it is easily attacked by the electrophilic reagents. One of the most thoroughly studied addition reactions is that of halogen acids.



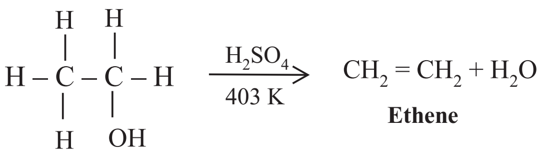
In alkynes (–C≡C–), two molecules of hydrogen add; first to give an alkene and finally the corresponding alkane, as shown below:

$$CH_3C\equiv CH \xrightarrow{+H_2/Ni-Pt} CH_2CH=CH_2 \xrightarrow{+H_2/Ni-Pt} CH_3CH$$

Propyne **Propene** **Propane**

23.3.7 Elimination Reactions

From the above discussion, you know that we get a saturated compound by the addition reaction of an alkene. The reverse reaction i.e. the formation of an alkene from a saturated compound, can also be carried out and is called an **elimination reaction.** An elimination reaction is characterized by the removal of a small molecule from adjacent carbon atoms and the formation of a double bond. For example, when alcohols are heated with a strong acid as the catalyst, a molecule of water is removed and a double bond is formed.



$$H_3C{-}CH_2OH \xrightarrow[403\ K]{H_2SO_4} CH_2=CH_2 + H_2O$$

Ethanol **Ethene**

23.3.8 Molecular Rearrangements

A molecular rearrangement proceeds with a fundamental change in the hydrocarbon skeleton of the molecule. During this reaction, an atom or group migrates from one position to another. For instance, 1-chlorobutane in the presence of a Lewis acid ($AlCl_3$) rearranges to 2-chlorobutane.

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3} CH_3CH_2CHClCH_3$$

1- Chlorobutane **2 - Chlorobutane**

INTEXT QUESTIONS 23.4

1. Write the products of each of the following reactions:

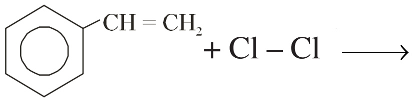
   (i) $CH_3CH_2Br + CN^- \longrightarrow$

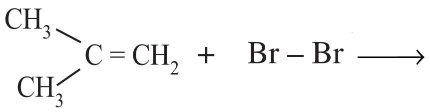
   (ii) $CH_3Cl + RNH_2 \longrightarrow$

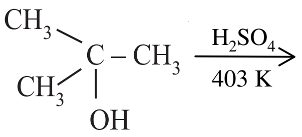
2. Write the conditions for nitration of benzene.

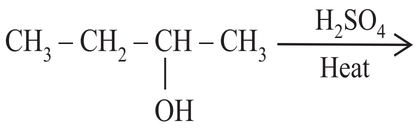
3. Predict the products of the following reactions :

   (i) $CH_2 = CH_2 \xrightarrow{+HBr}$

   (ii) 

   (iii) 

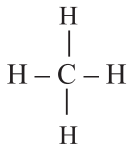
   (iv) 

   (v) 

$$CH_3-CH_2-CH(OH)-CH_3 \xrightarrow[Heat]{H_2SO_4}$$

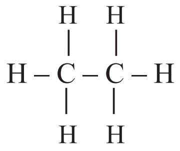
23.4 ISOMERISM

The simple alkanes containing upto three carbon atoms, i.e. methane, ethane and propane have only one possible structure. There is only one way in which the carbon atoms can be linked together as shown below :



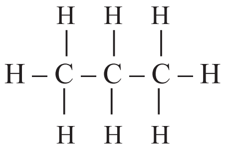
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Methane



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

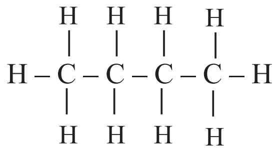
Ethane



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

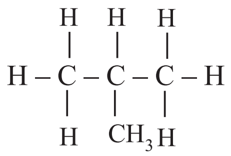
Propane

But for next higher hydrocarbon i.e. butane (C_4H_{10}), there are two possible ways in which the carbon atoms can be linked together. They may be linked to form a **straight chain** or a **branched chain.**



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

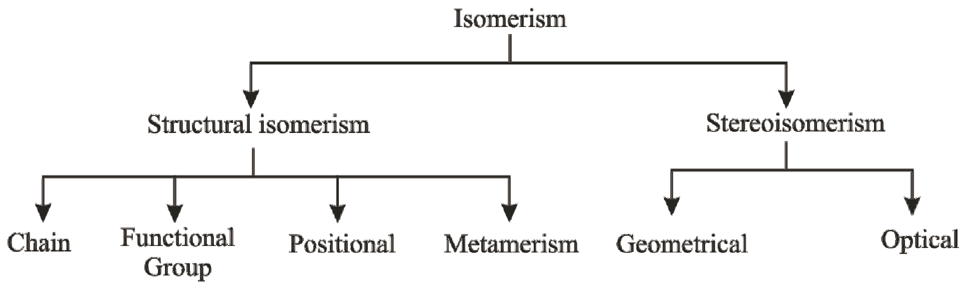
Butane (b.p.- –5 °C) 268 K



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & CH_3 & & H & & \end{array}$$

(2-Methylpropane) (b.p.- 12 °C) 261 K

Thus, there are two types of butane which are different compounds and they show different properties. *Different substances which have the same molecular formula but differ in their structures, physical or chemical properties are called* ***isomers*** and this phenomenon is known as **isomerism.** The isomerism can be of various types as shown below :

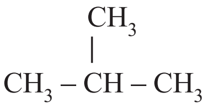


1. Structural Isomerism : Compounds which have the same molecular formula but differ in their structure are called **structural isomers** and the phenomenon is called **structural isomerism**. This is further subdivided into four types; **chain**, **functional, positional isomerism**, and **metamerism**.

(i) **Chain isomerism :** These isomers differ in the chain of the carbon atoms, for instance, *n*-butane and isobutane are two isomers of C_4H_{10}.

$CH_3 - CH_2 - CH_2 - CH_3$

n-Butane



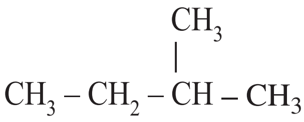
$CH_3 - \overset{\overset{\large CH_3}{|}}{CH} - CH_3$

Isobutane

Similarly, pentane (C_5H_{12}) has the following three isomers :

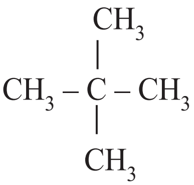
$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-Pentane



$CH_3 - CH_2 - \overset{\overset{\large CH_3}{|}}{CH} - CH_3$

2-Methylbutane
(Isopentane)



$CH_3 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - CH_3$

2,2- Dimethylpropane
(Neopentane)

Similarily, hexane (molecular formula C_6H_{14}) can have five chain isomers.

(ii) **Functional isomerism :** These isomers differ in the type of functional group. For example; *ethanol* and *ether* the two isomers having molecular formula C_2H_6O, belong to two different classes of organic compounds. Similarly, the two isomers corresponding to molecular formula $C_3H_6O_2$ are, an acid and an ester having quite distinct structures and properties.

(Molecular Formula: C_2H_6O) C_2H_5OH and $CH_3 - O - CH_3$

Ethanol (alcohol) **Methoxymethane (ether)**

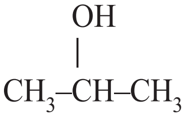
(Molecular Formula: $C_3H_6O_2$) CH_3CH_2COOH and $CH_3 - COOCH_3$

Propanoic acid **Methyl ethanoate**

(iii) **Positional isomerism:** These isomers differ in the attachment of the functional group to the chain at different positions. Examples are as follows :

$CH_3CH_2CH_2OH$ and

Propan-1-ol

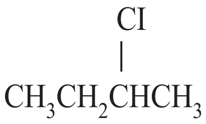


$CH_3 - \overset{\overset{\large OH}{|}}{CH} - CH_3$

Propan-2-ol

$CH_3CH_2CH_2CH_2Cl$ and

1-Chlorobutane



$CH_3CH_2\overset{\overset{\large Cl}{|}}{CH}CH_3$

2-Chlorobutane

(iv) **Metamerism** is exhibited by those compounds in which functional group comes in between the carbon chain and breaks the continuity of the chain. This breaking occurs at different positions and different isomers are formed which are called Metamers. For example, 1-methoxypropane and ethoxyethane are two metamers differing in chain length (size of alkyl groups) on the two sides of oxygen atom as shown below.

$CH_3 - O - CH_2CH_2CH_3$ and $CH_3\,CH_2 - O - CH_2CH_3$

1-Methoxypropane **Ethoxyethane**

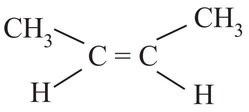
2. Stereoisomerism : Steroisomerism is exhibited by the compounds which have the same structural formula i.e. their atoms are connected in the same order, but they differ from each other in the way these atoms (or groups) are arranged in space.

Stereoisomerism can be further divided into **conformational isomerism** and **Configurational isomerism**.

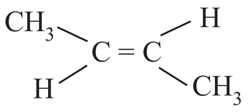
The **absolute configuration** of a compound *is the actual three dimensional arrangement of the groups or atoms in space*. Thus, *configurational isomers* have uique configuration. These isomers *cannot* be converted to each other *without breaking of bonds*. The configurational isomerism could be further sub-divided into **geometrical** and **optical isomerisms**. These are explained below.

Conformational isomerism is exhibited by those isomers which can be interconverted **without breaking of bonds**. Thus, conformational isomers are obtained by **rotation** about single bonds. The conformational isomerism is explained using ethane as the example, see section 24.13.

(i) **Geometrical Isomerism:** Consider two isomers of 2-butene as shown below.

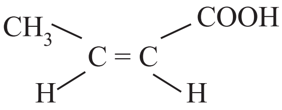


cis– **But-2-ene**

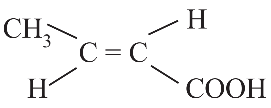


trans– **But-2-ene**

A *cis*- **isomer** is the one having identical groups on same side of double bond. On the other hand, a *trans*-**isomer** has identical groups on opposite side. In the above structures, *cis*-2- butene (two $-CH_3$ groups on the same side) and *trans*-2-butene (two $-CH_3$ groups on different sides) are two geometrical isomers (stereoisomers) as they differ in the geometries of the groups around the double bond. Another example of *cis*-and *trans*-isomerism is **2-butenoic acid** or **But-2-enoic acid.**



cis- **But-2-enoic acid**



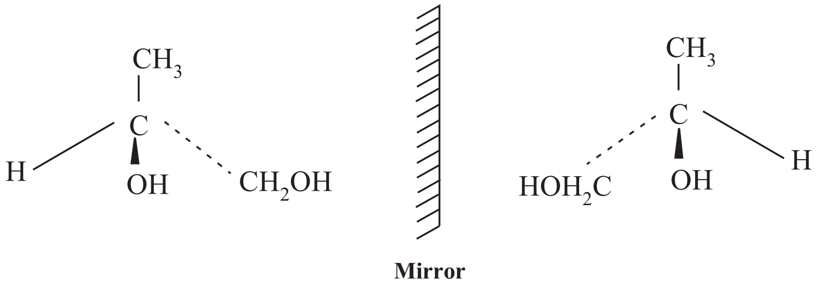
trans-**But-2-enoic acid**

Note that in the above examples, the two isomers exist because the rotation of groups across C=C bond is not possible (it is also called as restricted rotation).

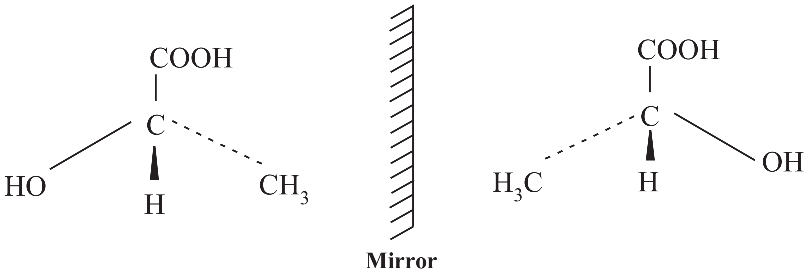
Geometrical isomerisms is also shown by cyclic compounds and compounds containing –C=N– bond, about which you will study at higher level.

(ii) **Optical Isomerism:** The optical isomerism is shown by the compounds having at least one carbon atom joined to four different atoms or groups. Such a carbon atom is called **asymmetric** or **chiral** carbon atom; and those which are not chiral (do not have four different groups) are called **achiral.** A chiral compound can have two different arrangements of groups attached to the chiral carbon as shown below for 1,2-dihydroxypropane.

The wedge sign (▲) shows that the direction of the bonds is towards the viewer and dotted line (.....) indicates backward direction of the bonds.



The resulting isomers are non-superimposable mirror images of each other and are called enantiomers. Thus, the enantiomers differ in the three-dimensional arrangement of atoms or groups. Another example of enantiomers is that of lactieacid as shown below:



Enantiomers of Lactic acid

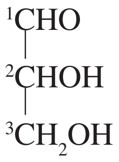
The optical isomers have idenical physical properties except optical activity. They rotate the plane of plain polarized light in opposite directions. The **plain polarized light** is defined as the light that vibrates in one plane only. *The rotation of the plane of polarized light is called* ***optical activity.*** Those substances that can rotate the plane of polarized light are said to be **optically active.** Compounds that rotate the plane of plane polarized light to the right (clockwise) are said to be **dextrorotatory.** The dextrorotatory is denoted by **'*d*' or (+)** before the name of the compound. Similarly, compounds that rotate the plane to the left (anticlockwise) are called **laevorotatory** and this is denoted by placing **'*l*'** or **(-)** before the name of the compound. A mixture containing equal amounts of ***d*- and *l*- isomers** is called a **recemic mixture** and is optically inactive denoted by ***dl*** or ±.

Assignment of Configuration

The nature of rotation whether *laevo* or *dextro*, i.e. *l*- or *d*- does not indicate the actual arrangement of atoms or groups of a molecule in space. In other words, by knowing the optical activity, one cannot tell about the *absolute configuration* of a compound. The absolute configuration in case of geometrical isomers is indicated by the designations *cis*- or *trans*- followed by the name of the compounds.

However, in case of optical isomers, the absolute configuration is given by D, L system and *R*, *S* system. For assiging the absolute configuration of a compound as *D* or *L* **or** *R* or *S*, the structure of a compound has to be written in a particular way.

One such way was given by Emil Fischer and the structure represented in such a way is called **Fischer projection**. For drawing such projections, a molecule is oriented vertically so that the carbon atom number 1 which is most highly oxidised is placed at the top in the chain. For example, in case of glyceraldehyde, the carbon atom carrying carbonyl group is placed at the top in the vertical chian as shown below:

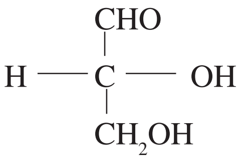


$$\begin{array}{l} {}^{1}CHO \\ \;| \\ {}^{2}CHOH \\ \;| \\ {}^{3}CH_2OH \end{array}$$

Glyceraldehyde

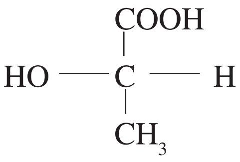
Then, the main substituent attached to the carbon, for the configuration to be arranged is looked for. Here, in case of glyceraldehyde, the configuration is to be assigned to C-2 atom and the main substituent attached to C-2 atoms is an –OH group. Please note that, here, C-2 atom is attached to 4 different substituents and such a centre (atom) in the molecule is called a **chiral centre.** It is also represented by an asterisk (*) mark in the structure.

If, in a Fischer projection, the main substituent appears on the *right*, then the particular molecule is said to have **D configuration.** In the other situation, if the main substituent in the molecule appears on the *left side* in the Fischer projection, then that compound said to have **L configuration**. The structures of D-glyceraldehyde and L-lactic acid are shown below:



$$\begin{array}{ccc} & CHO & \\ & | & \\ H - & C & - OH \\ & | & \\ & CH_2OH & \end{array}$$

D-(+)-Glyceraldehyde



$$\begin{array}{ccc} & COOH & \\ & | & \\ HO - & C & - H \\ & | & \\ & CH_3 & \end{array}$$

L(+)-Lactic acid

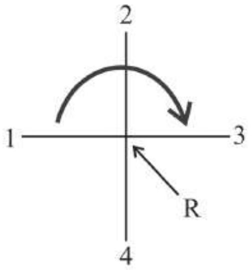
Note that in addition to configuration as D or L, the signs of rotation (i.e. + or –) are also given in the names of the compounds above. You can see that both the compounds are dextrorotatory though one is having D configuration while other has L configuration. Thus, the configurations are not related to the directions (or signs) of the rotation of plane polarized light. The D, L system of assigning configurations is widely used for carbohydrates and amino acids.

However, this system can not be applied equally well to all compounds because sometimes it is not easy to identify the main chain and the main substituent in the structure of the compound. In such situations, another system called, ***R*, *S* convention** is used to assign the absolute configuration of a chiral centre in a compound.

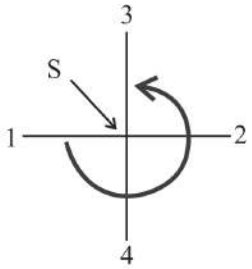
Assignment of Absolute Configuration as *R* or *S*

First of all, the Fischer projection of a particular given optical isomer is written. Then, the four substituents attached to the chiral carbon, for which the absolute configuration is to be assigned, are identified. These substituents are then assigned a priority order as 1, 2, 3 and 4 according to certain rules which were given by Cohn-Ingold and Prelog.

The Fischer projection of the molecule is then rearranged, if required, so as to place the substituent of lowest priority, *i.e.* substituent number 4, at the bottom of the Fischer projection. There are also certain rules to convert one fisher projection to another about which you will study in higher classes. When we place the substituent of lowest priority at the bottom in the Fischer projection, there are two ways in which the other substituents (1, 2 and 3) appear depending upon the actual position of these groups in the molecules. These are shown below.

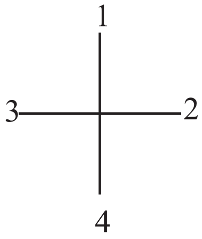


I

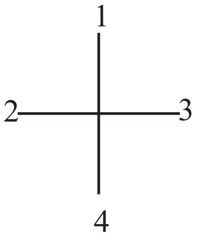


II

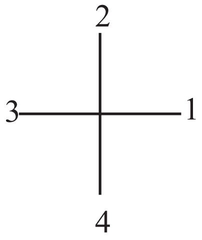
Now, it we ignore 4 and trace a path from 1 → 2 → 3, it will be *clockwise* in I while *anticlockwise* in II. The isomer I is said to have *R* configuration at chiral centre while in isomer II, the chiral centre is said to have *S* configuration.
You may also be thinking that the following arrangements of 1, 2, 3 are also possible.



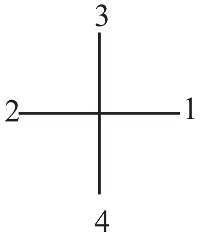
III



IV

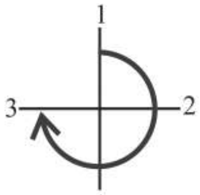


V



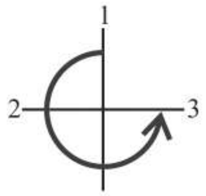
VI

But again, to assign the configuration we have to follow the same rules. *i.e.* trace the path from 1 → 2 → 3 and see it is *clockwise* or *anticlockwise*. Accordingly, the configuration is given as *R* or *S*. This is illustrated below for the representations II to VI alongiwth their absolute configurations R or S:



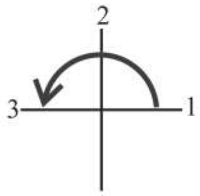
R

III



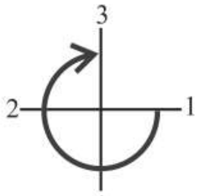
S

IV



S

V

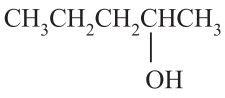


R

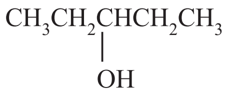
VI

INTEXT QUESTIONS 23.5

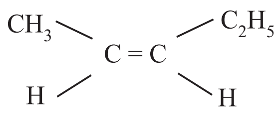
1. Is 1-butene a structural isomer of **cis-** or **trans**-2-butene?
2. Identify the type of isomerism exhibited by the following pairs of compounds:

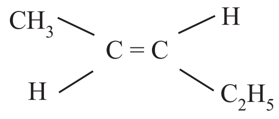
(i) 

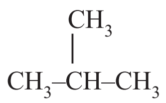
$\mathrm{CH_3CH_2CH_2\underset{OH}{\underset{|}{C}}HCH_3}$

and 

$\mathrm{CH_3CH_2\underset{OH}{\underset{|}{C}}HCH_2CH_3}$

(ii) 

and 

(iii) $CH_3CH_2CH_2CH_3$ and 

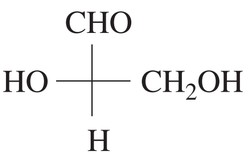
$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_3}$

(iv) $CH_3CH_2CH_2OH$ and $CH_3CH_2 - O - CH_3$

3. Write the structures of all the isomers of hexane (C_6H_{14}).
4. Which one of the following compounds would show geometrical isomerism?

(i) $CH_3CH_2CH = CHCH_2CH_3$ (ii) $CHF = CHF$ (iii) $CH_2 = CHCH_2CH_3$

5. Assign the configuration as R or S to the following compound



23.5 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Organic compounds contain C and H; in addition to these, they may also contain O, N, S, halogens, and phosphorous.

23.5.1. Detection of C and H

Many organic compounds burn with a sooty flame or char when strongly heated. C and H are detected by heating the compound with CuO (copper oxide) in a dry test tube. They are oxidised to CO_2 and H_2O, respectively. CO_2 turns lime water milky and H_2O turns anhydrous $CuSO_4$ to hydrated $CuSO_4$ which is blue in colour.

(i) $C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

(ii) $H + CuO \xrightarrow{\Delta} Cu + H_2O$

(iii) $CO_2 + Ca\,(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$

(iv) $\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4{\cdot}5H_2O}$

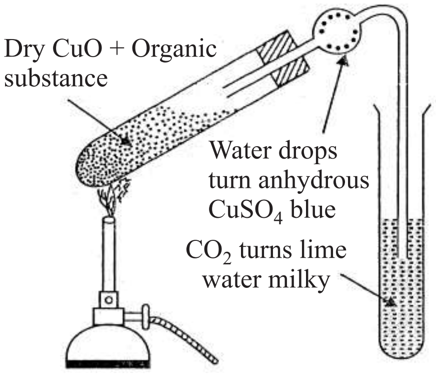


Fig. 23.1 *Detection of carbon and hydrogen*

23.5.2 Detection of Other Elements

N, S, halogens, and phosphorus present in an organic compound are detected by **Lassaigne's test**, by fusing the compound with sodium metal, which converts the elements present in the compound from covalent to ionic form. The following reactions occur:

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX\ (X = Cl, Br, \text{or } I)$$

C, N, S, and X come from organic compound.

NaCN, Na_2S, and NaX so formed are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract or Lassaigne's extract (L.E.).

(a) **Test for nitrogen:** The sodium fusion extract or L.E. is boiled with $FeSO_4$ and then acidified with conc. H_2SO_4. The appearance of Prussian blue colour confirms the presence of N. The following reactions occur:

(i) $$Fe^{2+} + 6CN \longrightarrow \left[Fe^{2+}(\overset{6-}{CN})_6\right]^{4-}$$

Hexa cyanoferrate (II)

(ii) $$Fe^{2+} \xrightarrow[H_2SO_4]{Conc.} Fe^{3+} + \bar{e}$$

(iii) $$\left[Fe^{2+}(\overset{6-}{CN})_6\right]^{4-} + 4Fe^{3+} \longrightarrow Fe_4^{3+}\left[Fe^{2+}(\overset{6-}{CN})_6\right]_3^{4-} \cdot H_2O$$

Ferriferro cyanide (Prussian blue)

(iv) This test is not given by compounds which do not contain C atoms but contain N atoms, for example, NH_2NH_2 (hydrazine), NH_2OH (hydroxylamine). Since these compounds do not contain C atoms, so in sodium fusion extract, CN ion is not formed and Prussian blue colour is not observed.

(v) This test is also not given by diazonium salts (e.g, Ph N≡N–X), although they contain both C and N elements, because they decompose and lose N_2 on heating much before they have a chance to react with the fused sodium metal.

(vi) If S is present along with N, the appearance of blood red colour confirms the presence of both.

$$Na + N + C + S \longrightarrow NaCNS \text{ (Sodium thiocyanate)}$$

$$3\ CNS^{\ominus} + Fe^{+3} \longrightarrow Fe(CNS)_3$$

Thiocyanatc ion **Ferric thiocyanate (Blood-red colour)**

(vii) If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to give cyanide and sulphide. These ions give usual tests.

$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$

(b) **Test for sulphur:** The sodium fusion extract or L.E: is treated with sodium nitroprusside. The appearance of violet colour indicates the presence of S.

(i) $$\underset{\text{Sulphide ion}}{S^{2-}} + \left[Fe^{2+}\overset{5-}{(CN)_5}\ \overset{1+}{NO}\right]^{2-} \longrightarrow \underset{\text{Violet colour}}{\left[Fe^{2+}\overset{5-}{(CN)_5}\ \overset{1-}{NOS}\right]^{-4}}$$

(ii) The L.E. is acidified with acetic acid and lead acetate is added to it. The appearance of black precipitate of lead sulphide indicates the presence of S.

$$Pb^{2+} + S^{2-} \longrightarrow \underset{\text{black ppt.}}{PbS}$$

(c) Test for halogens

(i) L.E. is acidified with HNO_3 and then treated with $AgNO_3$. A white precipitate soluble in NH_4OH indicates the presence of Cl, a pale yellow precipitate partiatly soluble in NH_4OH indicates the presence of Br, and a yellow precipitate insoluble in NH_4OH shows the presence of I.

$$AgNO_3 + NaCl \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{soluble in (NH}_4\text{OH)}}}{AgCl\downarrow} + NaNO_3$$

$$AgNO_3 + NaBr \longrightarrow \underset{\substack{\text{Pale-yellow ppt.}\\ \text{partly soluble in NH}_4\text{OH}}}{AgBr\downarrow} + NaNO_3$$

$$AgNO_3 + NaI \longrightarrow \underset{\substack{\text{Dark-yellow ppt.}\\ \text{insoluble in NH}_4\text{OH}}}{AgI\downarrow} + NaNO_3$$

(ii) If N and S are also present in the compound, the L.E. is first boiled with conc. HNO_3 to decompose the NaCN or Na_2S formed during Lassaigne's test. These ions would otherwise interfere with the $AgNO_3$ test for halogens. If these ions are not removed, they would give a white precipitate of AgCN or Ag_2S with $AgNO_3$ and will confuse it for AgCl.

(iii) **Organic layer test:** Add CS_2 or $CC1_4$ to the L.E. and then add Cl_2 water or $KMnO_4$, shake, and keep it for some time. The appearance of orange colour in organic layer confirms the presence of Br, while violet colour confirms iodine.

$$2Br^{\ominus} + 2Cl_2 \longrightarrow \underset{\text{Orange colour}}{Br_2} + 2Cl^{\ominus}$$

$$2I^{\ominus} + 2Cl_2 \longrightarrow \underset{\text{Violet colour}}{I_2} + 2Cl^{\ominus}$$

$$16H^{\oplus} + 2MnO_4^{\ominus} + 10Br^{\ominus} \longrightarrow 5Br_2 + 2Mn^{2+} + 8H_2O$$

$$16H^{\oplus} + 2MnO_4^{\ominus} + 10I^{\ominus} \longrightarrow 5I_2 + 2Mn^{2+} + 8H_2O$$

(iv) **Beilstein test:** The organic compound is heated on a clean copper wire in Bunsen flame. A green or blue colour due to the formation of volatile copper halides confirms the presence of halogens. This test is not satisfactory as some compounds which do not contain halogens also give this test, for example urea and thiourea. Moreover, this test does not tell which halogen is present in the compound.

(d) Test for phosphorus: The organic compound is heated with an oxidising agent (sodium peroxide). Phosphorus is oxidised to phosphate. The solution is then boiled with conc. HNO_3 and treated with ammonium molybdate. A yellow precipitate confirms the presence of phosphorous.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow$$

$$\underset{\text{Ammonium phosoph molybdate}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2$$

23.6 QUANTITATIVE ANALYSIS

(a) Estimation of C and H: The percentage composition of elements present in an organic compound is determined by the methods based on the following principle:

Liebig's combustion method: A known mass of compound is heated with CuO. The carbon present is oxidised to CO_2 and hydrogen to H_2O. The CO_2 is absorbed in KOH solution, while H_2O vapours are absorbed in anhydrous $CaC1_2$ and weighed (Fig. 23.2).

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O}{\text{Mass of compound}} \times 100$$

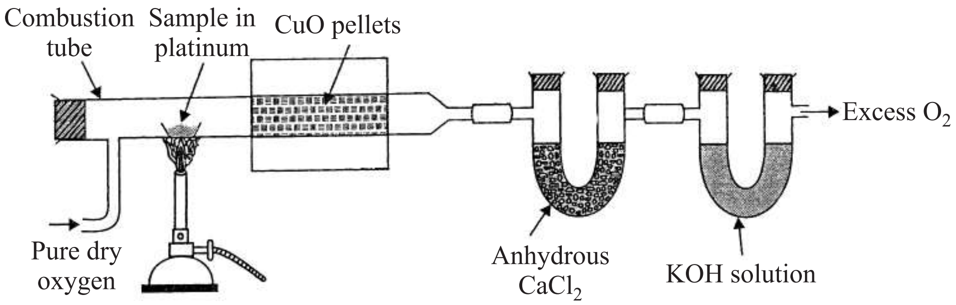


Fig. 23.2 *Estimation of carbon and hydrogen*

b. Estimation of halogens:

Carius method: A known mass of compound is heated with conc. HNO_3 in the presence of $AgNO_3$ contained in a hard glass tube known as Carius tube (Fig. 23.3 in a furnance. C and H are oxidised to CO_2 and H_2O. The halogen forms the corresponding AgX. It is filtered, dried, and weighed.

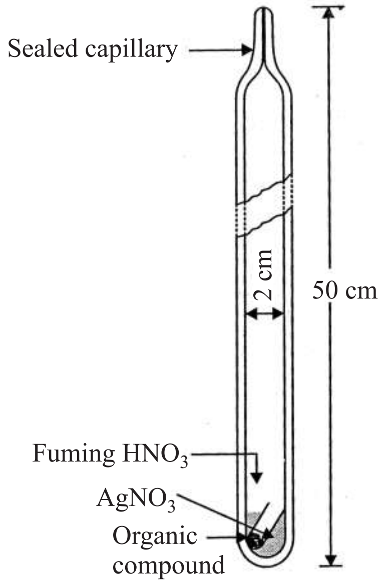


Fig. 23.3 *Carius method*

i. Percentage of X $= \dfrac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \dfrac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$

ii. Percentage of Cl $= \dfrac{35.5}{143.5} \times \dfrac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$

iii. Percentage of Br $= \dfrac{80}{188} \times \dfrac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$

iv. Percentage of I $= \dfrac{127}{235} \times \dfrac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$

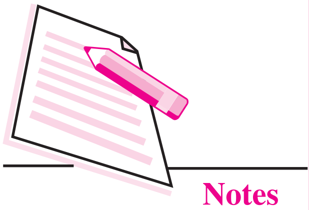
(c) Estimation of sulphur: A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in the presence of $BaCl_2$ solution in Carius tube. Sulphur is oxidised to H_2SO_4 and precipitated as $BaSO_4$. It is filtered, dried, and weighed.

$$\text{Percentage of S} = \frac{\text{Atomic mass of S}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}}$$

$$= \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}}$$

(d) Estimation of phosphorus

First method: A known mass of compound is heated with fuming HNO_3 in Carius tube which converts phosphorus to H_3PO_4 (phosphoric acid). It is precipitated as ammonium phosphomolybdate $[(NH_4)_3PO_4.12MoO_3]$ by adding NH_3 and ammonium molybdate $(NH_4)_2MoO_4]$. It is filtered, dried, and weighed.



Percentage of P

$$= \frac{\text{Atomic mass of P}}{\text{Molecular mass of ammonium phospho molybdate}} \times \frac{\text{Mass of ammonium phospho molybdate} \times 100}{\text{Mass of compound}}$$

$$= \frac{31}{1877} \times \frac{\text{Mass of } (NH_4)_3 \cdot PO_4 \cdot 12MoO_3 \times 100}{\text{Mass of compound}}$$

Second method: A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2) in Carius tube which converts phosphorous to H_3PO_4. Magnesia mixture ($MgC1_2$ + NH_4C1) is then added, which gives the precipitate of magnesium ammonium phosphate ($MgNH_4.PO_4$) which on heating gives magnesium pyrophosphate ($Mg_2P_2O_7$), which is weighed.

Percentage of P

$$= \frac{\text{Atomic mass of P}}{\text{Molecular mass of } Mg_2P_2O_7} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$$

$$= \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$$

(e) Estimation of nitrogen: There are two methods for the estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

(i) **Dumas method:** A known mass of compound is heated with copper oxide (CuO),in an atmosphere of CO_2, which gives free nitrogen along with CO_2 and H_2O.

$$C_xH_yN_z + (2x + y/2)CuO \longrightarrow xCO_2 + y/2(H_2O) + z/2(N_2) + (2x + y/2)Cu$$

The gaseous mixture is passed over a heated copper gauze which converts traces of nitrogen oxides formed to N_2. The gaseous mixture is collected over an aqueous solution of KOH which absorbs CO_2, and nitrogen is collected in the upper part of the graduated tube (Fig. 23.4).

Let the volume of N_2 collected be V_1 ml

$$\text{Volume of } N_2 \text{ at STP} = \frac{p_1V_1 \times 273}{760 \times T_1} = V \text{ ml}$$

where p_1 and V_1 are the pressure and volume of N_2, and p_1 = atmospheric pressure – aqueous tension. 22400 ml of N_2 at STP weighs 28 g

$$V \text{ ml of } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

Percentage of N is

$$\frac{\text{Molecular mass of } N_2}{22400 \text{ ml}} \times \frac{\text{Volume of } N_2 \text{ at STP } \times 100}{\text{Mass of compound}}$$

$$= \frac{28}{22400} \times \frac{\text{V ml} \times 100}{\text{Mass of compound}}$$

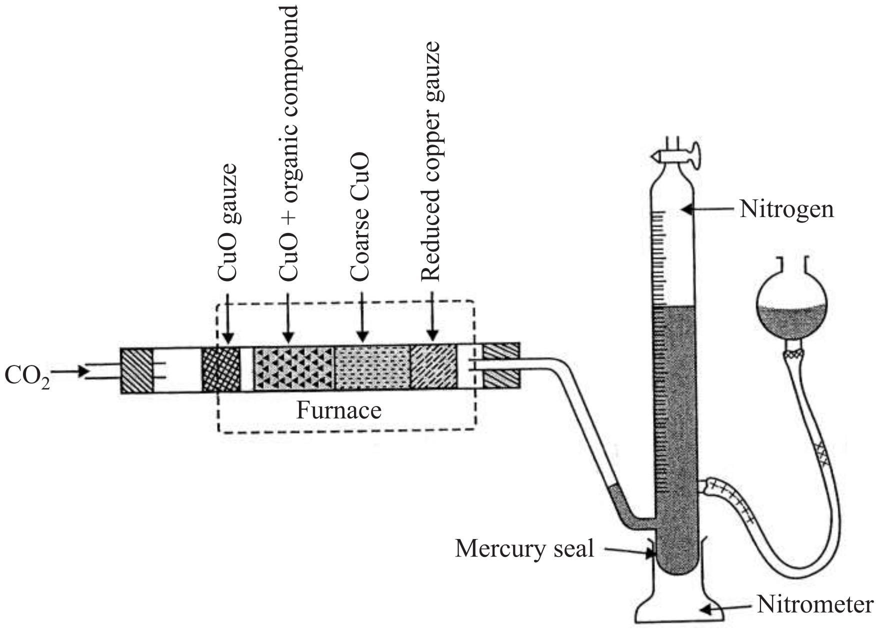
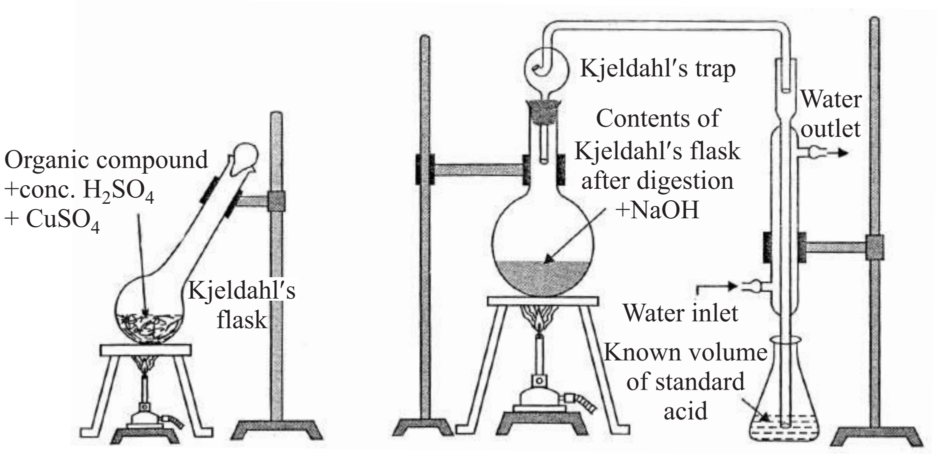


Fig. 23.4 *Dumas method*



Digestion (heating in Kjeldahl's flask)

Kjeldahl's distillation

Fig. 23.5 *Kjeldahl's method*

(ii) **Kjeldahl's method:** A known mass of organic compound (0.5 g) is mixed with K_2SO_4 (10 g) and $CuSO_4$ (1.0 g) or a drop of mercury (Hg) and conc. H_2SO_4 (25 ml), and heated in Kjeldahl's flask. $CuSO_4$ or Hg acts as a catalyst, while K_2SO_4 raises the boiling point of H_2SO_4

(Fig. 23.5). The nitrogen in the organic compound is quantitatively converted to ammonium sulphate. The resulting mixture is then distilled with excess of NaOH solution and the NH_3 evolved is passed into a known but excess volume of standard HCI or H_2SO_4. The acid left unused is estimated by titration with some standard alkali. The amount of acid used against NH_3 can thus be known and from this the percentage of nitrogen is calculated.

1. $C + H + S \xrightarrow[H_2SO_4]{\text{Conc.}} CO_2 + H_2O + SO_2$
2. $N \xrightarrow[H_2SO_4]{\text{Conc.}} (NH_4)_2SO_4$
3. $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$
4. $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Calculation of percentage of N

Let the mass of organic compound *m* g.

Volume of H_2SO_4 of molarity M [or (2M) normality] taken = V ml

Volume of NaOH of molarity M (or M normality)

used for titration excess of H_2SO_4 = V_1 ml

mEq. of excess H_2SO_4 = mEq. of NaOH = M V_1 mEq.

Total mEq. of H_2SO_4 taken = 2 MV

mEq. of H_2SO_4 used for neutralisation of NH_3 = (2 MV – MV_1)

∴ mEq. of NH_3 = (2 MV – MV_1)

1000 mEq. or 1000 ml of *M* NH_3 solution contains = 17 g of NH_3 = 14 g of N

∴ (2 MV – MV_1) mEq. of NH_3 solution contains

$$= \frac{14 \times (2MV - MV_1)}{1000} \text{ g of N}$$

$$\text{Percentage of N} = \frac{14 \times (2MV - MV_1) \times 100}{1000 \times m}$$

$$= \frac{1.4 \times 2M(V - V_1/2)}{m}$$

$$\text{Percentage of N} = \frac{1.4 \times \text{ mEq. of } H_2SO_4 \text{ used to neutralise } NH_3}{\text{Mass of the compound}}$$

(iii) This method is not applicable to compounds containing N in nitro and azo groups, and N present in the ring (e.g., pyridine) as N of these compounds does not change to $(NH_4)_2SO_4$ (ammonium sulphate) under these reaction conditions.

(f) Estimation of oxygen

First method: It is usually found by the difference between the total percentage composition (100) and sum of the percentages of all the other elements, e.g.,

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N)

Second method (Aluise's method): A known mass of compound is decomposed by heating it in the presence of N_2 gas. The mixture of gaseous products containing O_2 is passed over red hot coke when all the O_2 is converted to CO. This mixture is heated with I_2O_5 (iodine pentaoxide) in which CO is oxidised to CO_2 liberating I_2. Organic compound $\xrightarrow{\Delta}$ Other gaseous product + O_2

$$2C + O_2 \xrightarrow{1373\text{ K}} 2CO$$

$$I_2O_5 + 5CO \longrightarrow 5CO_2 + I_2$$

Percentage of O

$$= \frac{\text{Molecular mass of } O_2}{\text{Molecular mass of } CO_2} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compouund}}$$

$$= \frac{32}{44} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compound}}$$

(g) CHN elemental analyser: Nowadays, the estimation of elements in an organic compound is carried out with automatic experimental techniques using micro quantities of the compound. The elements C, H, and N present in an organic compound are determined by an automatic instrument called CHN elemental analyser using a very small amount of the compound (1-3 mg), which displays the result within a very short time.

WHAT YOU HAVE LEARNT

- Organic compounds are classified into **aliphatic** (open-chain), **homocyclic** (closed ring) or **carbocyclic (alicyclic and aromatic)** hydrocarbons and their derivatives, and **heterocyclic** compounds (contain at least one heteroatom i.e., N,S,O in the ring).

- **Homologous series** of organic copmounds and IUPAC naming of different classes.
- The substitution, elimination, additions reactions and molecular rearrangements.
- **Homolytic** fission of a covalent bond produces free radicals because each of the parting away atoms takes away its shared electron.
- **Heterolytic fission** of a covalent bond produces ions because one of the atoms takes away both the shared electrons.
- **Electrophiles** are positively charged or electron deficient species.
- **Nucleophiles** are negatively charged or electron rich species.
- Benzene ring undergoes aromatic substitution reactions.
- A **functional group** is an atom or group responsible for specific properties of a compound.
- The compounds which have the same molecular formula but different structure are called structural **isomers.**
- Isomerism is classified into **structural isomerism** and **stereoisomerism**.
- A carbon atom attached to four different groups is called **chiral** atom or **asymmetric** carbon atom.
- The non-superimposable mirror image isomers of a compound are called enantiomers. They are optically active and rotate the plain of plain polarized light in opposite directions.
- The absolute configuration of a chirol carbon can be specified as *R* or *S*.

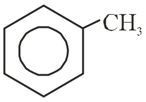
TERMINAL EXERCISE

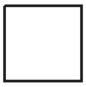
1. What are hydrocarbons? Explain giving two examples.
2. Give two examples of aromatic hydrocarbons.
3. Classify the following hydrocarbons as alkanes, alkenes or alkynes and write their IUPAC names.

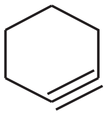
(i) $(CH_3)_3CH$ (ii) $CH_3CH = CH_2$

(iii) $(CH_3)_4C$ (iv) $CH_3\ C \equiv CH$

(v) $CH_3\ C \equiv CCH_3$ (vi) $CH_2 = CH_2$

(vii) 

(viii 

(ix) 

4. Write structures of the possible isomers and their IUPAC names of compounds having the following molecular formula:

   (i) C_5H_{10} and (ii) C_5H_8.

5. Write the structures of the following compounds :

   (i) Isobutylbenzene
   (ii) 4-Methyl-2-pentene
   (iii) Hepta-1,6-diene
   (iv) Cyclobutene

6. Write the structures for the following compounds:

   (i) 1-Bromo-3-methylhexane
   (ii) 3-Chloro-2,4-dimethylpentane
   (iii) 3-Methylbutanal
   (iv) Ethyl propanoate
   (v) 2-Methylbutanenitrile
   (vi) Cyclohexene
   (vii) 3-Methylhexan-2-one

7. What are electrophilic aromatic substitution reactions? How will you prepare nitrobenzene from benzene?

8. Draw all the possible structural isomers having the molecular formula C_4H_9Cl and give their IUPAC names.

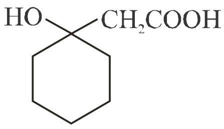
9. What is a nucleophilic aliphatic substitution reaction? Give one example.

10. Describe the electrophilic addition reaction of an alkene. Write the product obtained by the addition of Br_2 to propene.

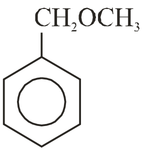
11. Write a short note on the following; (i) Structural isomerism (ii) Stereo-isomerism

12. Define a functional group. Identify the functional group(s) present in following compounds :

(i)

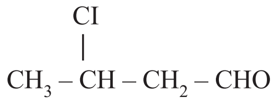


(ii)



(iii) $CH_3COCH_2C \equiv CH$

(iv) $CH_3CH_2CH_2 - O–CH_3$

(v) 

$CH_3-\underset{}{\overset{\overset{CI}{|}}{C}H}-CH_2-CHO$

(vi) CH_3CONH_2

15. Describe hyperconjugation in terms of resonance.

ANSWERS TO INTEXT QUESTIONS

23.1

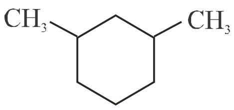
1.

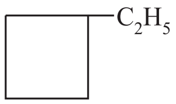
Word root	**Suffix**
(i) Hex	ane
(ii) Pent	2–ene
(iii) Prop	yne

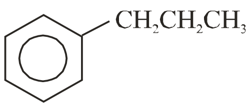
2. (i) Oct-2-ene (ii) 2, 4-Dimethylpentane

23.2

1. (i) 1-ethyl-3-methylbenzene
   (ii) Cycloheptane
   (iii) Cyclopenta-1,3-diene

2. (i) 

(ii) 

(iii) 

23.3

1. Covalent bond between two different atoms having large difference in their electronegativities.

2. **–I effect groups** $-NO_2$, $-CN$, $-C_6H_5$ **+**
   I effect groups $-CH_3$, $-C_2H_5$, $CH_3\underset{|}{C}HCH_3$.

3. Electromeric effect is temporary polarization, whereas inductive effect is permanent polarisation of a covalent bond.

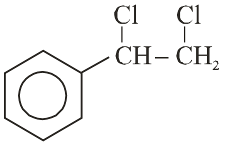
4. (i) Electrophile (ii) Electrophile
   (iii) Nucleophile (iv) Nucleophile
   (v) Nucleophile (vi) Nucleophile

(vii) Nucleophile (viii) electrophile

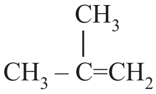
(ix) Nucleophile

23.4

1. (i) CH_3CH_2CN (ii) CH_3NHR
2. HNO_3 in presence of H_2SO_4.
3. (i) CH_3CH_2Br

(ii) 

(iii) $(CH_3)_2\ CBr - CH_2Br$ (major product)

(iv) 
$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$

(v) $CH_3{-}CH{=}CHCH_3$ (major product)

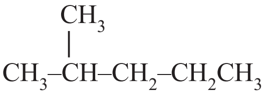
23.5

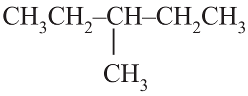
1. Yes
2. (i) Positional isomerism

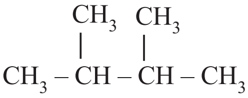
   (ii) Geometrical isomerism

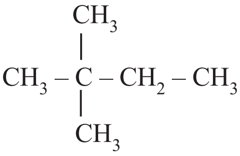
   (iii) Chain isomerism

   (iv) Functional group isomerism
3. (i) $CH_3CH_2CH_2CH_2CH_2CH_3$

(ii) 
$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CH_2CH_3$

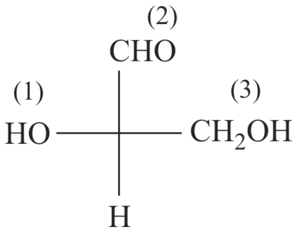
(iii) 
$CH_3CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}CH_2CH_3$

(iv) 
$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3$

(v) 
$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_3$

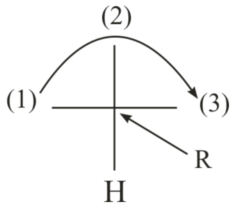
4. (i) Yes
   (ii) Yes
   (iii) No

5.



(i) Priority of groups is shwon as (1), (2) and (3)

(ii) path from (1) → 2 → 3 is clockwise, therefore, the absolute configuration of chiral chain is R.



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24

HYDROCARBONS

You have studied in the previous lesson that hydrocarbons are the compounds containing carbon and hydrogen. You also know that they are classified as aliphatic, alicyclic and aromatic hydrocarbons. They constitute a very important class of organic compounds and are widely used as fuels, lubricants and dry cleaning agents. They are also used as important ingredients in medicines and in dyes. Petroleum and coal are the major sources of various types of hydrocarbons. The products obtained from fractional distillation of petroleum and destructive distillation of coal are used almost in every sphere of life. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with different functional groups. In this lesson, you will study about the preparation, important physical and chemical properties of hydrocarbons.

OBJECTIVES

After reading this lesson, you will be able to :

- list different methods of preparation of alkanes;
- explain the reasons for variation in physical properties of alkanes;
- draw the conformations of ethane and compare their relative stability;
- describe different chemical properties of alkanes;
- list different methods of preparation of alkenes;
- explain the physical properties of alkenes;
- describe the chemical properties of alkenes;
- list different methods of preparation of alkynes;
- explain physical and chemical properties of alkynes;
- discuss the cause of greater reactivity of alkenes and alkynes over alkanes;

- distinguish alkanes, alkenes and alkynes;
- list various fractions obtained by destructive distillation of coal;
- explain the stability of various aromatic compounds using resonance;
- state Huckel rule and its use;
- describe methods of preparation, physical properties and chemical properties of benzene;
- list various uses of hydrocarbons; and
- explain the term carcinogenicity and Toxicity.

24.1 ALKANES (PARAFFINS)

Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as *paraffins* (*parum* means little, *affins* means affinity).

24.1.1 Methods of Preparation

Some important methods of preparation of alkanes are as follows:

1. **From Haloalkanes (Alkyl Halides):** Monohaloalkanes can be converted to alkanes by following three methods :

   a) **By reduction of haloalkanes:** The replacement of halogen atom of haloalkanes with hydrogen is called the reduction and can be carried out by the following reagents :

   (i) Zinc and dilute HCl

$$\underset{\textbf{Bromomethane}}{CH_3Br} + Zn + 2\,HCl \longrightarrow \underset{\textbf{Methane}}{CH_4} + ZnCl_2 + HBr$$

   (ii) HI in the presence of red phosphorus

$$\underset{\textbf{Iodoethane}}{C_2H_5I} + HI \xrightarrow[423\text{ K}]{\text{red phosphorus}} \underset{\textbf{Methane}}{C_2H_6} + ZnCl_2 + HBr$$

   (iii) Catalytic reduction

$$\underset{\textbf{Chloromethane}}{CH_3Cl} + H_2 \xrightarrow{\text{Pt (catalyst)}} \underset{\textbf{Methane}}{CH_4} + HCl$$

   b) **By using Grignard's Reagent :** A Grignard reagent is a compund of the type RMgX which is prepared by reacting a haloalkane with magnesium metal in the presence of dry ether.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br + Mg} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethyl Magnesium Bromide}}{C_2H_5MgBr}$$

The Grignard's reagents are used to prepare various compounds like hydrocarbons, ethers, alcohols and carboxylic acids. It reacts with the compounds containing active hydrogen and forms alkanes. An easily replaceable hydrogen atom present in the compounds is called *active hydrogen*. An active hydrogen is present in (i) alcohols and (ii) water and (iii) acids.

$$CH_3MgBr + C_2H_5OH \rightarrow CH_4 + Mg(OC_2H_5)Br$$

$$C_2H_5MgBr + H_2O \rightarrow C_2H_6 + Mg(OH)Br$$

c) **By Wurtz Reaction :** In this reaction, an alkyl halide reacts with sodium metal in the presence of dry ether and forms the higher alkanes.

$$\underset{\textbf{Bromoethane}}{CH_3-Br + 2\,Na + Br-CH_3} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethane}}{CH_3-CH_3} + 2\,NaBr$$

2. **From Unsaturated Hydrocarbons :** The unsaturated hydrocarbons (i.e. alkenes and alkynes) can be converted to alkanes by the addition of hydrogen in the presence of a catalyst like nickel, platinum or palladium.

$$CH_2=CH_2 + H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3-CH_3$$

$$CH\equiv CH + 2H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3-CH_3$$

This reaction is also called **hydrogenation** and is used to prepare vegetable ghee from edible oils (by converting unsaturated fats to saturated ones.)

3. **From Alcohols, Aldehydes and Ketones :** Alcohols, aldehydes and ketones on reduction with HI, in presence of red phosphorus, give alkanes.The general reactions are as shown below.

$$\underset{\textbf{Alcohol}}{ROH} + 2HI \xrightarrow{\text{red P/423K}} \underset{\textbf{Alkane}}{RH} + I_2 + H_2O$$

$$\underset{\textbf{Aldehyde}}{RCHO} + 4HI \xrightarrow{\text{red P/423K}} \underset{\textbf{Alkane}}{RCH_3} + 2\,I_2 + H_2O$$

$$\underset{\textbf{Ketone}}{RCOR'} + 4HI \xrightarrow{\text{red P/423K}} \underset{\textbf{Alkane}}{RCH_2R'} + 2\,I_2 + H_2O$$

4. **From Carboxylic Acids :** Carboxylic acids can produce alkanes in a number of ways as shown below :

i) **Heating with soda lime :** $RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$

In this reaction, an alkane with one carbon less than those present in the parent carboxylic acid is obtained.

ii) By Reduction of carboxylic acid:

$$\mathrm{RCOOH} + 6\,\mathrm{HI} \xrightarrow{\text{red P}/423\,\mathrm{K}} \mathrm{RCH_3} + 3\,\mathrm{I_2} + 2\mathrm{H_2O}$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe's Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The reaction takes place as follows.

$$\underset{\textbf{Sodium salt of carboxylic acid}}{\mathrm{RCOONa}} \xrightarrow{\text{electrolysis}} \underset{\textbf{Anion}}{\mathrm{RCOO^-}} + \underset{\textbf{Cation}}{\mathrm{Na^+}}$$

At Anode :

$$\mathrm{RCOO^-} \longrightarrow \mathrm{RCOO^\bullet} + e^-$$

$$\mathrm{RCOO^\bullet} \longrightarrow \mathrm{R^\bullet} + \mathrm{CO_2}$$

$$\mathrm{R^\bullet} + \mathrm{R^\bullet} \longrightarrow \mathrm{R-R}$$

Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\textbf{Sodium ethanote}}{2\,\mathrm{CH_3COONa}} \longrightarrow \underset{\textbf{Ethane (at anode)}}{\mathrm{CH_3-CH_3}}$$

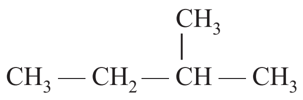
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

24.1.2 Physical Properties of Alkanes

Physical State: The physical state of alkanes depends upon the intermolecular forces of attraction present between molecules which in turn, depend upon the surface area of the molecules. *As the molecular mass of the alkanes increases, their surface area also increases, which in turn, increases the intermolecular forces of attraction, and accordingly, the physical state of alkanes changes from gaseous to liquid, and then to solid.* The alkanes containing 1 to 4 carbon atoms are gases, whereas those containing 5 to 17 carbon atoms are liquids, and the still higher ones are solids. In the case of isomeric alkanes, the straight chain alkanes will have maximum surface area, and hence, stronger intermolecular force of attraction. As the branching increases, surface area decreases. Hence the intermolecular forces of attraction decrease. Let us consider the isomers of pentane (C_5H_{12}).

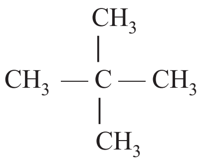
$$\mathrm{CH_3 - CH_2 - CH_2 - CH_2 - CH_3}$$

***n*-Pentane**



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2-Methylbutane (Isopentane)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2,2-Dimethylpropane (Neopentane)

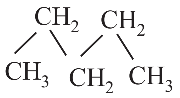
Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

Density: *The density of alkanes increases with the increase in molecular mass which increases with the increase in the number of carbon atoms.* All alkanes are lighter than water i.e. their density is less than 1.0 g/cm^3. The maximum density in the case of alkanes is 0.89 g cm^3. The lower density of alkanes than water is due to the absence of strong intermolecular attractions in alkanes.

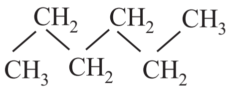
Boiling Point: *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. Thus, in the above example, isopentane and neopantane have a lower boiling point than pentane.

Melting Point: Similar to the boiling points, the melting points of alkanes also increase with the increase in their molecular mass, but there is no regular variation in melting point. The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (i.e. the packing) of the molecules in the crystal lattice.

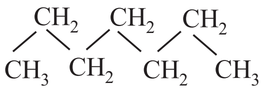
In alkanes, each carbon atom is sp^3 hybridized which results in a bond angle of 109°28′. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the interaction between the alkane molecules, with odd number of carbon atoms, is less than the molecule with even number of carbon atoms, in which terminal methyl groups lie on the opposite sides.



n-Pentane



n-Hexane



n-Heptane

(Carbon atoms = 5, m.p.142 K) (Carbon atoms =6, m.p. = 179 K)(carbon atoms = 7, m.p. = 183 K)

In the above structures, we find that alkanes containing even number of carbon atoms are more symmertical and can be more closely packed as compared with alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, due to which they have higher melting points. *Therefore, the alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms.*

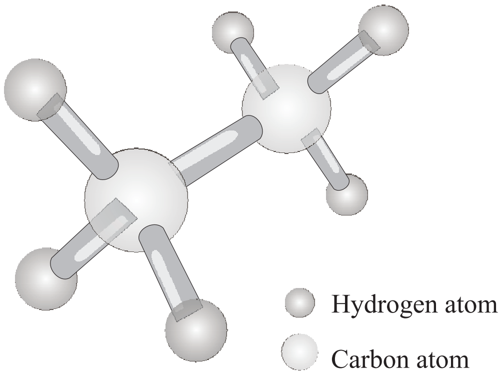
24.1.3 Conformations of Ethane

You have studied section 25.3.2 that electronic displacements affect the physical and chemical properties of organic compounds. You will now study how the forces present within the molecules affect their structures and stabilities. In fact, these interactions make some geometric arrangements of atoms energetically *more favorable* than others.

In ethane molecule, C_2H_6, the two carbon atoms are linked together by a single bond called *sigma* (σ) bond.

$$\underset{\text{ethane}}{\overset{\text{sigma }(\sigma)\text{ bond}}{\overset{\downarrow}{H_3C — CH_3}}}$$

If we make a model of ethane molecule showing the C — C bond and the hydrogens attached to carbon atoms, it will look like as follows :



Model of ethane molecule

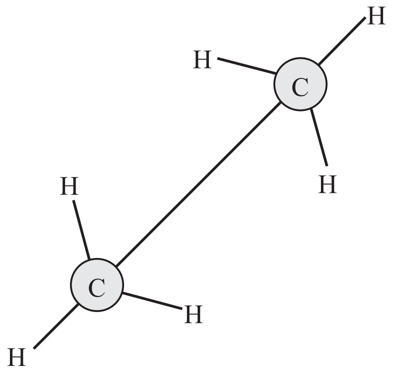
The groups bonded through a sigma bond can easily rotate with respect to each other. *i.e.* the two — CH_3 groups in ethane can rotate with respect to each other. The different arrangement of atoms resulting from such a rotation are called **conformations** and each such specific conformation is called a **conformer** (from *confor*mational iso*mer*).

The conformational isomers can be represented in the following two ways:

(i) Sawhorse representations

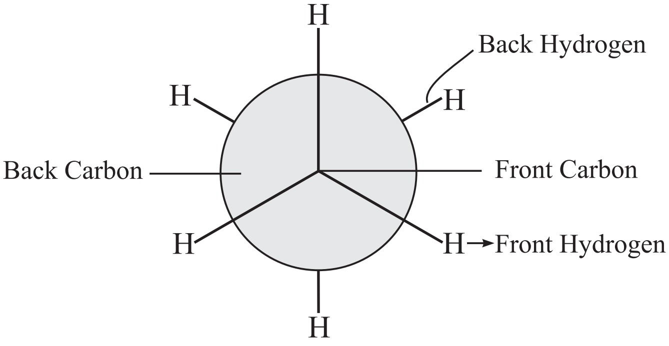
(ii) Newman projections

The **Sawhorse representations** show the carbon–carbon bond from an oblique angle and indicate the spatial arrangement of all C — H bonds.



Sawhorse Projections

In **Newman projections** the two carbon atoms are viewed along the C — C bond axis. The front carbon and its bonds are represented as  whereas the back carbon and its bonds are represented as .

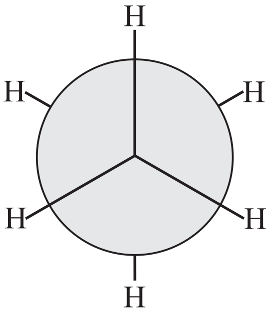


Newman Projection

The Newman projections are easier to draw and in such drawings, the relative positions of atoms are easily visualised. Therefore, we will use Newman projections to study the conformations of ethane.

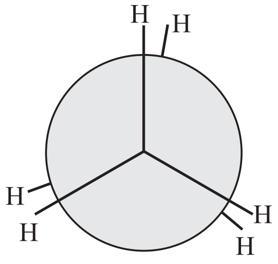
Several conformations of ethane are possible. But, there are two extreme possibilities. These are discussed below:

(i) In this conformation all the six C — H bonds are *as far away as possible*. This conformation is called **staggered conformation** and is shown below:



Staggered conformation of ethane

(ii) Another conformation in which all the six C — H bonds *are as close as possible is* shown below:



Eclipsed conformation of ethane

This is called **eclipsed conformation.** The three rear hydrogens are drawn little more rotated than the perfectly eclipsed positions to make them visible in the structure.

Remember that there are infinite number of possible conformations in between the staggered and the eclipsed conformations. All these conformations originate by the rotation of the C — C bond.

The *staggered conformation* is the **most slable** conformation whereas the *eclipsed conformation* is the **least stable** conformation of ethane. The eclipsed conformation has about 12 kJ mol^{-1} higher energy than the staggered conformation.

24.1.4 Chemical Properties of Alkanes

1. Halogenation reactions: The chemical reactions in which a hydrogen atom of an alkane is replaced by a halogen atom are known as *halogenation*. Alkanes react with chlorine in the following way.

$$CH_4 + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} CH_3Cl$$

Methane **Chloromethane**

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} CH_2Cl_2$$

Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} CHCl_3$$

Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} CCl_4$$

Tetrachloromethane

Chlorination of methane takes place via the **free radical mechanism**. When the reaction mixture is exposed to sunlight, chlorine molecules absorb energy from sunlight and get converted to free radicals i.e. chlorine atoms with an unpaired electron $(\dot{C}l)$. The chlorine radicals then combine with methane and form methyl radical $[\dot{C}H_3]$. The methyl radical further reacts with chlorine molecule and produces chloromethane. This reaction continuously takes place till it is stopped or the reactants completely react to form the products. The free radical mechanism involves the following three steps.

(i) **Chain Initiation Step:** It involves the formation of free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet} \qquad (h\nu = \text{energy of light})$$

(ii) **Chain Propagation Step :** The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$$

(iii) **Chain Termination Step :** In this step, free radicals combine with one another and the further reaction stops.

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

The reactivity of halogens is in the order of $F_2 > Cl_2 > Br_2 > I_2$.

2. **Oxidation:** Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature.For example :

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \;+\; 890\text{ KJ mol}^{-1}$$

If the combustion is carried out in the presence of an insufficient supply of air or O_2, then *incomplete combustion takes place forming carbon monoxide* instead of carbon dioxide.

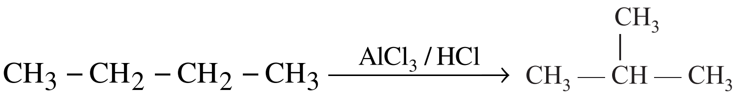
$$2C_2H_6 + 5O_2 \xrightarrow{\text{heat}} 4CO + 6H_2O$$

3. **Cracking or Pyrolysis:** At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873\text{ K}} CH_3CH = CH_2 + H_2$$

or $$CH_2 = CH_2 + CH_4$$

4. **Isomerisation :** *n*-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.



$$\underset{n\text{-butane}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{AlCl_3/HCl} \underset{\text{isobutane}}{CH_3 - \overset{\overset{\large CH_3}{|}}{C}H - CH_3}$$

n-**butane** **isobutane**

24.1.4 Uses of Alkanes

Alkanes are used as fuel gases, solvents, drycleaning agents, lubricants and in ointments (paraffin wax). Methane is used for illuminating and domestic fuel and also for the production of other organic compounds such as haloalkanes, methanol, formaldehyde and acetylene. Propane is used as a fuel, refrigerant and as raw material in the petrochemical industry. Butane and its isomer–isobutane, are the major constituents of LPG .

INTEXT QUESTIONS 24.1

1. List four important uses of hydrocarbons.
2. What is Grignard's reagent in a molecule?
3. What is an active hydrogen in a molecule?
4. What makes the physical properties of various hydrocarbons different?
5. Name two alkanes which are gases and two alkanes which are liquids at room temperature.
6. Name three isomers of pentane.
7. Which one has higher b.p. *n*-butane or *n*-pentane? Explain.
8. Write the balanced chemical equation for the complete combustion of propane.

24.2 Alkenes

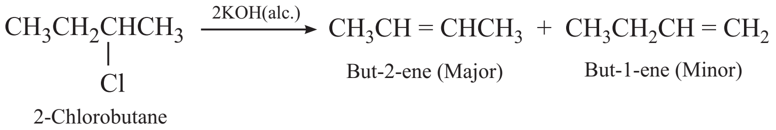
These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called **olefines** (*olefiant* = oil forming).

24.2.1 Methods of Preparation

In the laboratory, alkenes are generally prepared either from haloalkanes (alkyl halides) or alcohols.

1. From Haloalkanes: Halaoalkanes are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCl, HBr or HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called *dehydrohalogenation*.

$$\underset{\textbf{Chloroethane}}{CH_3 - CH_2 - Cl} + KOH(alc.) \rightarrow \underset{\textbf{Ethene}}{CH_2 = CH_2} + KCl + H_2O$$



$$\underset{\text{2-Chlorobutane}}{CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3} \xrightarrow{2KOH(alc.)} \underset{\text{But-2-ene (Major)}}{CH_3CH=CHCH_3} + \underset{\text{But-1-ene (Minor)}}{CH_3CH_2CH=CH_2}$$

The major product is formed according to the Saytzeff's Rule.

Saytzeff's Rule : ***It states that when an alkyl halide reacts with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more substituted, will be the major product.*** In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the –C=C– group.

2. From Alcohols : Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as (i) Al_2O_3 or (ii) concentrated H_2SO_4.

$$\underset{\textbf{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[623-633K]{Al_2O_3} \underset{\textbf{Ethene}}{CH_2=CH_2} + H_2O$$

$$\underset{\textbf{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[433K]{\text{conc. } H_2SO_4} \underset{\textbf{Ethene}}{CH_2=CH_2} + H_2O$$

In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule.

24.2.2 Physical Properties of Alkenes

Some important physical properties of alkanes are as follows:

Physical State : Unbranched alkenes containing upto four carbon atoms are gases and containing five to sixteen carbon atoms are liquids while those with more than 16 carbon atoms are solids.

Boiling Points : The boiling points of alkenes increase with molecular mass as is shown in Table 24.1.

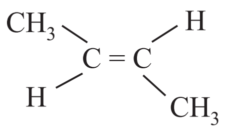
Table 24.1 : Boiling points of Alkenes

Alkene	Ethene	Propene	But-1-ene	Pent-1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

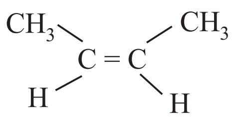
The increase in boiling point can be attributed to the van der Waals forces which increases with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

Melting Point : In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the ***cis*** and ***trans*** isomers have different melting points.

For example



***trans*-But-2-ene**
(m.p. 167 K)



***cis*-But-2-ene**
(m.p. = 134 K)

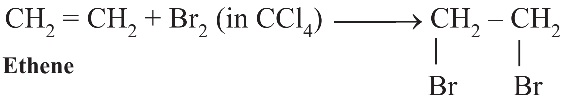
24.2.3 Chemical Properties of Alkenes

1. **Addition Reactions :** The chemical reactions in which a molecule adds to another molecule are called an *addition reaction*. These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

   (i) Addition of Hydrogen : Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[573K]{Ni\ (Pt\ or\ Pd)} \underset{\textbf{Ethane}}{CH_3 - CH_3}$$

   (ii) Addition of Halogens : Halogens on addition to alkenes, form 1,2-dihaloalkanes.



$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + Br_2\ (in\ CCl_4) \longrightarrow \underset{\textbf{1, 2-Dibromoethane}}{\underset{Br\qquad Br}{\overset{}{CH_2 - CH_2}}}$$

   As a result of this addition reaction, the reddish-brown colour of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

   (iii) Addition of Halogen Acids (HX) : When halogen acids are added to alkenes , hydrogen adds to one carbon atom whereas halogen atom adds to the second carbon atom of the double bond.

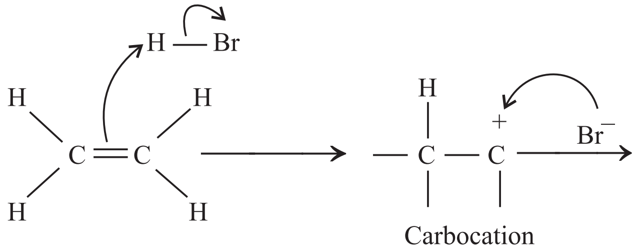
$$\underset{\textbf{Ethene}}{CH_2 = CH_2} \quad + \quad HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3 - CH_2 - Br}$$

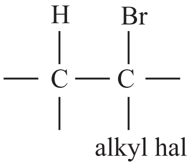
   In case of unsymmetrical alkenes (which contain unequal number of H-atoms attached to the carbon atoms of the double bonds), the addition of HX takes place according to the **Markownikoff's rule. This rule states that in the addition of halogen acids to unsymmetrical alkenes, the halogen of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it.** In other words, hydrogen atom of HX goes to the carbon atom with more number of H-atoms attached to it.

$$CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBr\,CH_3$$

Propene **2-Bromopropane**

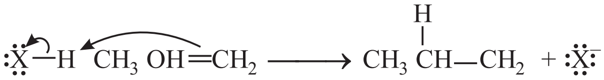
Mechanism of Electrophilic Addition: You have studied earlier that the electron cloud of the pi bond is present above and below the plane of the molecule in alkenes. Various electron seeking species and reagents thus react with the alkenes. For example, H^+ of HX(HBr) can add to the double bond to yield a carbocation.



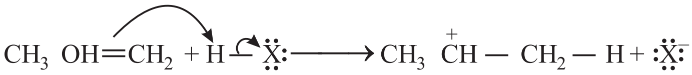


The carbocation being highly reactive reacts with the halide ion in the second step to yield an alkyl halide (alkyl bromide).

In case, the starting alkene is unsymmetrical *e.g.* propene, then in the first step of formation of a carbocation, there are two possibilities of attachment of H^+ of HX which are shown below:



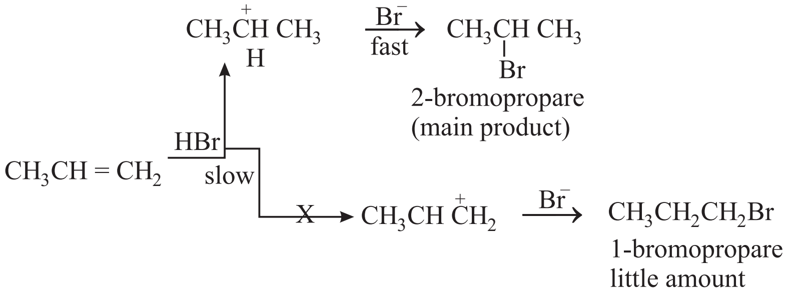
(I) primayr carbocation (less stable)



(II) secondary carbocation more stable

This would lead to the formation of two carbocations as shown above.

The two possible carbocations have different stabilities *i.e.* the secondary carbocation (II) is more stable than the primary carbocation (I). Therefore, the secondary carbocation (II) is formed preferentially in the first step. Further reaction, *i.e.* attack of Br^- on the carbocation, thus yields 2-bromopropane as the major product.



Thus, the above explanation describes for the formation of 2-bromopropane as the major product as per the Markownikoff's rule.

If the addition of HBr is carried out in the presence of peroxides such as benzoyl peroxide, then the reaction takes place contrary to Markownikoff's rule. This is also known as **Anti-Markownikoff's addition** or **peroxide effect**.

$$\underset{\textbf{Propene}}{CH_3CH = CH_2 + HBr} \xrightarrow{\text{benzoyl peroxide}} \underset{\textbf{1 – Bromopropane}}{CH_3CH_2 - CH_2 - Br}$$

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2 + H_2O} \xrightarrow[\text{Heat}]{H_2SO_4} \underset{\textbf{Ethanol}}{CH_3 - CH_2 - OH}$$

(v) Addition of H_2SO_4

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + \text{conc. } H_2SO_4 \longrightarrow \underset{\textbf{Ethyl hydrogen sulphate}}{CH_3 - CH_2 - HSO_4}$$

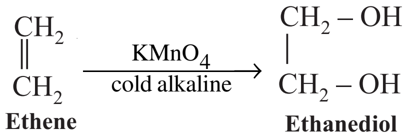
(vi) Addition Polymerization : The process in which many molecules of an alkene add together to form a larger molecule is called **addition polymerization.**

$$\underset{\textbf{Ethene}}{n\,(CH_2{=}CH_2)} \xrightarrow[\text{heat, pressure}]{} \underset{\textbf{Polyethene}}{(-CH_2-CH_2-)_n}$$

2. **Oxidation :** The oxidation of alkenes can be done by using different oxidizing agents like $KMnO_4$, oxygen and ozone.

(i) Oxidation with $KMnO_4$

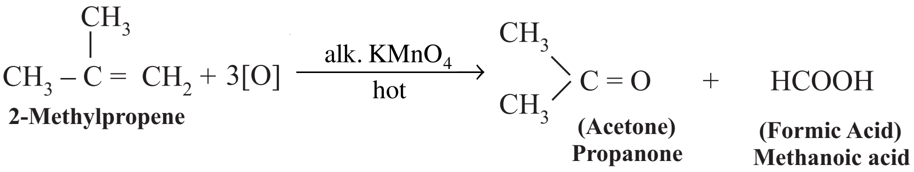
Alkenes are unsaturated hydrocarbons having Pi (π)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.



$$CH_2{=}CH_2 \xrightarrow[\text{cold alkaline}]{KMnO_4} CH_2(OH){-}CH_2(OH)$$

Ethene Ethanediol

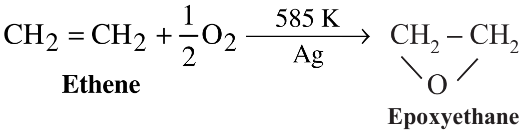
When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + 3[O] \xrightarrow[\text{hot}]{\text{alk. }KMnO_4} (CH_3)_2C=O + HCOOH$$

2-Methylpropene (Acetone) Propanone (Formic Acid) Methanoic acid

(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:



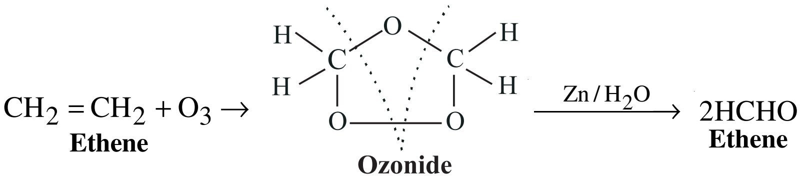
$$CH_2=CH_2+\frac{1}{2}O_2 \xrightarrow[Ag]{585\ K} CH_2-CH_2 \text{ (bridged by O)}$$

Ethene Epoxyethane

(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called **combustion.**

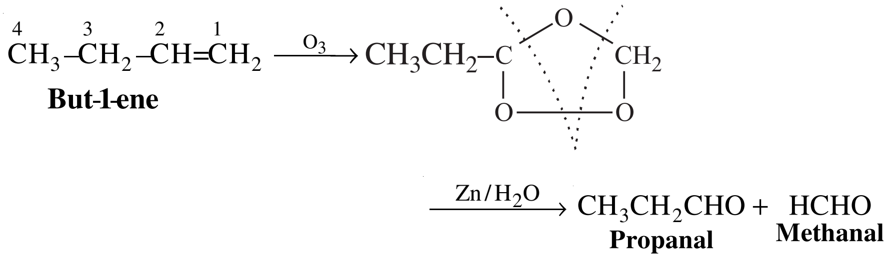
$$CH_2=CH_2+3\ O_2 \xrightarrow{\text{heat}} 2\ CO_2+2\ H_2O \quad \Delta H = -1411\ KJ\ mol^{-1}$$

(iv) Oxidation with Ozone : Ozone adds to the alkene forming ozonide. The ozonide when further reacted with water in the presence of zinc dust, forms aldehydes or ketones, or both.

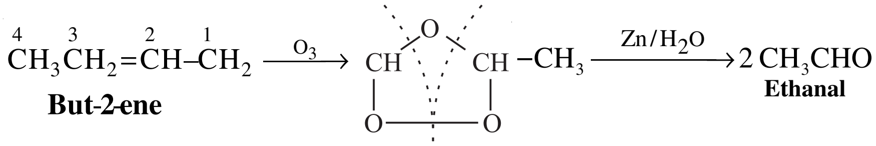


This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis.**

Ozonolysis can be used for the determination of the position of double bonds in alkenes by analysing the products formed i.e. aldehydes and ketones. This is explained below.



When but-1-ene is oxidized with ozone and the ozonide formed is hydrolysed, we get one mole of propanal and one mole of methanal, showing that the double bond is between carbon atom 1 and 2. Whereas but-2-ene on oxidation with ozone, followed by hydrolysis, gives two moles of ethanal, showing that the double bond is present between carbon atoms 2 and 3 as shown below.



24.2.4 Uses of Alkenes

Ethene is used for making mustard gas, which is a poisonous gas used in warfare. It is also used for artificial ripening of fruits, as a general anaesthetic and for producing other useful materials such as polythene, ethanal, ethylene glycol (antifreeze), ethylene oxide (fumigant) etc.

INTEXT QUESTIONS 24.2

1. Which one has higher boiling point: *cis* but-2-ene or *trans* but-2-ene?
2. Name the products formed when ethene is oxidized with cold alkaline solution of $KMnO_4$.
3. Write the conditions for hydrogenation of alkenes.
4. What happens when ethene reacts with oxygen at 575 K in presence of Ag?

24.3 ALKYNES

These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$$\underset{\textbf{Ethyne}}{CH \equiv CH}, \quad \underset{\textbf{Propyne}}{CH_3 - C \equiv CH}, \quad \underset{\textbf{But-2-yne}}{CH_3 - C \equiv C - CH_3}$$

24.3.1 Preparation of Ethyne (Acetylene)

Some important methods for preparation of ethyne are explained below.

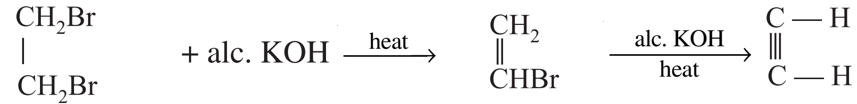
1. From Calcium Carbide: Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

$$\underset{\textbf{Calcium carbide}}{CaC_2} + \underset{\textbf{Water}}{2\,H_2O} \longrightarrow \underset{\textbf{Ethyne}}{H-C\equiv C-H} + Ca(OH)_2$$

Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

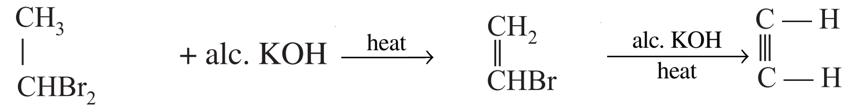
2. Preparation of Ethyne from Dihaloalkanes

Ethyne can be prepared by refluxing *geminal* dihaloalkanes (having both halogens attached to the same carbon atom) or *vicinal* dihaloalkanes (having halogen atoms attached to the adjacent carbon atoms) with alcoholic solution of KOH.



$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + \text{alc. KOH} \xrightarrow{\text{heat}} \begin{matrix}CH_2\\\parallel\\CHBr\end{matrix} \xrightarrow[\text{heat}]{\text{alc. KOH}} \begin{matrix}C-H\\|||\\C-H\end{matrix}$$

1,2-Dibromoethane **Vinyl Bromide** **Ethyne**



$$\begin{matrix}CH_3\\|\\CHBr_2\end{matrix} + \text{alc. KOH} \xrightarrow{\text{heat}} \begin{matrix}CH_2\\\parallel\\CHBr\end{matrix} \xrightarrow[\text{heat}]{\text{alc. KOH}} \begin{matrix}C-H\\|||\\C-H\end{matrix}$$

1,1-Dibromoethane **Vinyl Bromide** **Ethyne**

3. Preparation of higher alkynes : Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R-C\equiv CH + Na \xrightarrow{\text{liq. }NH_3} R-C\equiv C^-Na^+$$

$$R-C\equiv C^-Na^+ + CH_3I \longrightarrow R-C\equiv C-CH_3 + NaI$$

24.3.2 Physical Properties of Alkynes

1. First three members of alkynes are gases, the next eight members are liquids and members having more than twelve carbon atoms are solids.
2. They are colourless and odourless, except ethyne which has a garlic odour.
3. The melting points, boiling points and densities of alkynes increase with the increasing molar mass. In alkynes, there are π(pi)-electrons due to which these molecules are slightly polar. So charge separation takes place in alkynes, and hence dipoles are formed. The presence of dipoles increases the inter molecular force of attraction, and hence the boiling points of alkynes are higher than those of the corresponding alkanes.
4. Alkynes are very slightly soluble in water and soluble in acetone.

24.3.3 Chemical Properties of Alkynes

1. **Addition Reactions** : Some of the addition reactions of alkynes are as follows.

(i) **Addition of Hydrogen :** Addition of hydrogen to alkynes takes place in the presence of a catalyst like Ni, Pt or Pd.

$$CH \equiv CH + H_2 \xrightarrow[573\ K]{Ni\ or\ Pt\ or\ Pd} CH_2 = CH_2 \xrightarrow{H_2\ +\ Ni\ or\ Pt\ or\ Pd} CH_3 - CH_3$$

(ii) **Addition of Halogens :** When halogens are added to alkynes, they form 1,2-dihaloalkenes and 1,1,2,2-tetrahaloalkanes.

$$CH \equiv CH \xrightarrow{Br_2\ in\ CCl_4} CHBr = CHBr \xrightarrow{Br_2\ in\ CCl_4} CHBr_2 - CHBr_2$$

Ethyne **1,2-Dibromoethene** **1,1,2,2-Tetrabromoethane**

(iii) **Addition of Halogen Acids (HX) :** Addition of HBr to ethyne is as follows :

$$CH \equiv CH \xrightarrow{HBr} CH_2 = CHBr \xrightarrow{HBr} CH_3 - CHBr_2$$

Ethyne **Bromoethene** **1,1–Dibromoethane**

(iv) **Addition of Water :** Addition of water takes place in the presence of mineral acids like H_2SO_4 and in the presence of Hg^{2+} as the catalyst.

$$CH \equiv CH + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} [CH_2 = CHOH] \xrightleftharpoons{Rearrangement} CH_3CHO$$

Ethyne **Vinyl Alcohol (Unstable)** **Ethanal**

(v) **Addition of H_2SO_4:** Conc. H_2SO_4 adds to ethyne as shown below.

$$CH \equiv CH \xrightarrow{conc.\ H_2SO_4} CH_2 = CHHSO_4 \xrightarrow{H_2SO_4} CH_3 - CH\ (HSO_4)_2$$

Vinyl hydrogen sulphate **Ethylidene hydrogen sulphate**

2. **Oxidation** : Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

(i) **Oxidation with $KMnO_4$**

$$CH \equiv CH + 4\,[O] \xrightarrow{Cold\ alkaline\ KMnO_4} \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Ethyne **Ethanedioic acid**

The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

$$R - C \equiv C - R' \xrightarrow[heat]{KMnO_4\ +\ KOH} RCOOH + R'\,COOH$$

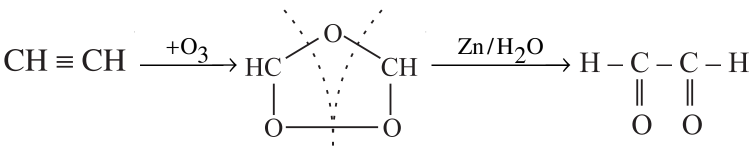
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH \equiv CH + 4\,[O] \xrightarrow[\text{heat}]{KMnO_4\ +\ KOH} (COOH)_2 \xrightarrow[\text{Heat}]{[O]} 2\,CO_2 + H_2O$$

Combustion : Combustion of ethyne in excess of oxygen or air gives carbon dioxide and water as shown below :

$$2\,C_2H_2 + 5\,O_2 \xrightarrow{\text{heat}} 4\,CO_2 + 2\,H_2O \quad \Delta H = -1300\ \text{KJ mol}^{-1}$$

Ozonolysis : On ozonolysis, alkynes give dicarbonyl compounds at the position of C≡C without breaking the chain of carbon atoms as shown below:



3. **Formation of Acetylides :** Ethyne forms precipitates of copper and silver acetylides when passed through ammonical solution of cuprous chloride and ammonical silver nitrate, respectively.

$$\underset{}{CH \equiv CH + 2Cu(NH_3)_2 \longrightarrow \underset{\textbf{Cuprous acetylide (red)}}{CuC \equiv CCu} + 2\,NH^+_4 + 2\,NH_3}$$

$$CH \equiv CH + 2Ag(NH_3)_2 \longrightarrow \underset{\textbf{Silver acetylide (white)}}{AgC \equiv CAg} + 2\,NH^+_4 + 2\,NH_3$$

24.3.4 Acidic Nature of Ethyne

The acidic nature of hydrocarbons can be determined with the help of the percentage (%) of *s*-character of the hydrocarbon. The greater the percentage of *s*-character of a hydrocarbon, the more will be its acidic nature.

Table 24.2 : % *s*-Character of hyrid orbitals in Hydrocarbons

Hydrocarbon	Type of hybridization	(%) s-character
Alkanes	sp^3	25%
Alkenes	sp^2	33.3%
Alkynes	sp	50%

As alkynes have 50% *s*- character, they are the most acidic in nature. An *sp*-hybridized carbon atom is more electronegative than sp^2 or sp^3 carbon atoms. Due to greater electronegativity of *sp* hybridized carbon atom in ethyne, hydrogen atom is less tightly held by the carbon and hence, it can be removed as a proton (H^+) by a strong base like sodium metal and sodamide. **The following reactions**

of ethyne with sodium and sodamide confirm its acidic nature. In these reactions, disodium acetylide is formed.

$$H-C\equiv C-H + 2\,Na \xrightarrow{\text{Heat}} Na-C\equiv C-Na + H_2$$

Ethyne (Acetylene) **Disodium Acetylide**

$$H-C\equiv C-H + 2\,NaNH_2 \xrightarrow{\text{Heat}} Na-C\equiv C-Na + 2\,NH_3$$

Ethyne **Sodamide** **Disodium Acetylide**

24.3.5 Uses of Alkynes

Ethyne (acetylene) is used for producing oxyacetylene flame (2800°C) which is used for for welding and cutting of iron and steel. It is also used for artificial ripening of fruits and vegetables. It also finds use in the production of a number of other organic compounds such as ethanal, ethanoic acid, ethanol, synthetic rubbers and synthetic fibre *orlon*.

24.3.6 Distinction Between Alkanes, Alkenes and Alkynes

The folloiwng table shows different tests for distinction between alkanes, alkenes and alkynes :

Table 24.3 : Tests for identification of alkanes, alkenes and alkynes

S.No	Test	Alkanes	Alkenes	Alkynes
1.	Add bromine dissolved in carbon tetrachloride.	No change	Reddish brown colour of Br_2 is discharged	Reddish brown colour of Br_2 is discharged
2.	Add alkaline solution of $KMnO_4$ (Baeyer's reagent)	No change	Purple colour of $KMnO_4$ is discharged	Purple colour of $KMnO_4$ is discharged
3.	Add ammonical solution of silver nitrate	No change	No change	White ppt. of silver acetylide is formed
4.	Add ammonical solution of cuprous chloride (Cu_2Cl_2)	No change	No change	Red ppt. of cuprous acetylide is formed

INTEXT QUESTIONS 24.3

1. How is ethyne prepared from calcium carbide?
2. Give one reaction to confirm the acidic nature of ethyne.
3. What is the percentage of *s*-character in ethane, ethene and ethyne?

24.4 AROMATIC HYDROCARBONS

Till now, we have explained various methods of preparation of aliphatic hydrocarbons. Now, we shall deal with an aromatic hydrocarbon (benzene) in detail. It is one of the major components obtained by the destructive distillation of coal as shown in Fig. 24.1

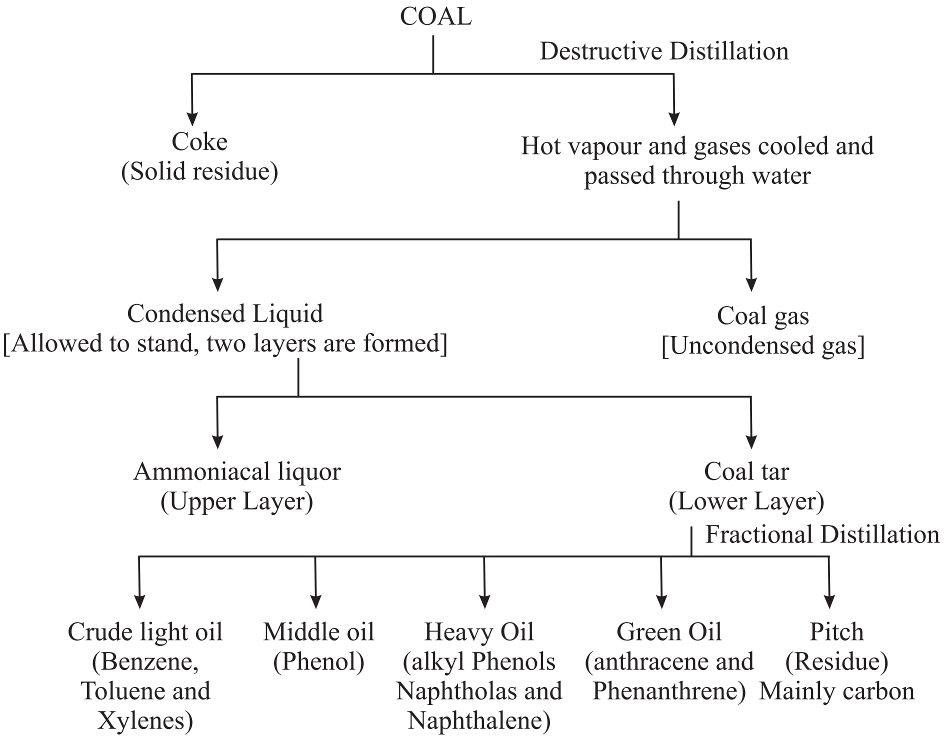


Fig. 24.1 : *Destructive Distillation of coal*

24.4.1 Structure of Benzene

The molecular formula of benzene is C_6H_6 which indicates that benzene is an unsaturated hydrocarbon. The unsaturation in benzene can be verified by the following reactions.

(i) Benzene undergoes the addition of H_2 in the presence of Ni or Pt as catalyst.

$$\underset{\textbf{Benzene}}{C_6H_6 + 3H_2} \xrightarrow{\text{Ni or Pt}} \underset{\textbf{Cyclohexane}}{C_6H_{12}}$$

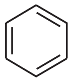
(ii) Benzene undergoes the addition of chlorine in the presence of sunlight.

$$\underset{\textbf{Benzene}}{C_6H_6 + 3\,Cl_2} \xrightarrow{h\nu} \underset{\textbf{Benzene hexachloride (B.H.C.)}}{C_6H_6Cl_6}$$

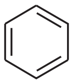
Benzene does not respond to the tests of unsaturation which are shown by alkenes and alkynes i.e., both the alkenes and the alkynes decolourize bromine water and alkaline solution of potassium permanganate (Bayer's Reagent). However, benzene undergoes substitution reactions.

e.g. $$\underset{\textbf{Benzene}}{C_6H_6} + Br_2 \xrightarrow{\text{Fe or FeCl}_3} \underset{\textbf{Bromobenzene}}{C_6H_5Br} + HBr$$

Kekule Structure : A ring structure for benzene was proposed by Kekule in 1865. According to him, six carbon atoms are joined to each other by alternate single and double bonds to form a hexagon ring. As the proposed structure of benzene has three double bonds, so its properties should resemble with the properties of alkenes. But the chemical properties of benzene are different from alkenes.

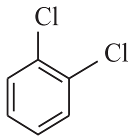


or

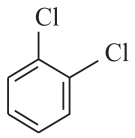


As Kekule's structure contains three single bonds and three double bonds, one may expect that in benzene there should be two different bond lengths i.e. 154 pm for C-C single bond and 134 pm for C=C double bond. But the experimental studies show that benzene is regular hexagon with an angle of 120^0 and all the carbon-carbon bond lengths are equal i.e. 139 pm.

If Kekule's structure is to be taken as a true structure, then benzene should form only one monosubstitution product and two ortho distubstitution products, shown below as (a) and (b).

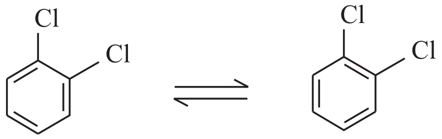


(a)



(b)

In structure (a), the two halogen atoms are on the doubly bonded carbon atoms, whereas in structure (b), the two halogen atoms are on singly bonded carbon atoms. As per the Kekule's structure these two isomers (a and b) should exist and show different properties. But, in reality, only one ortho disubstituted product exists. In order to explain this, Kekule proposed a dynamic equilibrium between the two structures.



Kekule's structure does not explain the stability of benzene and its some unusual reactions. Resonance can explain the unusual behaviour of benzene. Let us now study about resonance.

Resonance : ***The phenomenon by virtue of which a single molecule can be represented in two or more structures is called resonance.*** The actual structure is the resonance hybrid of all the canonical or resonating structure. (see lesson 25)

Heat of hydrogenation data provides proof for resonance stabalization in benzene. **The heat of hydrogenation is the amount of heat liberated when hydrogen is added to one mole of an unsaturated compound in the presence of a catalyst.**

$$\text{Cyclohexene} + H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 119.5 \text{ KJ mol}^{-1}$$

(One – C = C– bond)

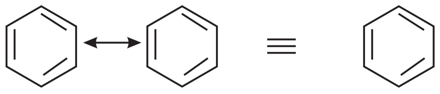
If the three double bonds in benzene do not interact, then it should behave like cyclohexatriene and the amount of heat liberated on adding there molecules of hydrogen should be 358.5 KJ mol^{-1}. But, the actual heat of hydrogenation of benzene is 208.2 kJ mol^{-1}.

$$\text{Benzene} + 3H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 208.2 \text{ kJ mol}^{-1}$$

(Three – C = C– bond)

This difference of (358.5 – 208.2) 150.3 kJ mol^{-1} in the heat of hydrogenation is the measure of stability of benzene. Benzene acquires stability due to resonance and hence, this energy is called resonance energy of benzene.

Thus, the structure of benzene can be described as a resonance hybrid of two equivalent forms, (I) and (II). None of these two forms is correct by itself.

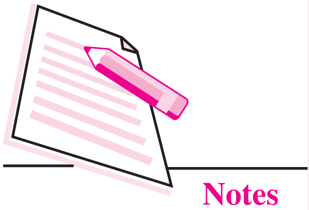


I II III

Resonance forms of benzene

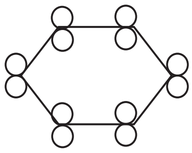
Resonance hybrid structure showing delocalisation of electrons

and the actual structure is intermediate of these two forms. This can be represented as III where the circle inside the ring indicates the equivalence of the carbon-carbon bonds. The carbon-carbon bond length has been found to be 139 pm. which is same for all the carbon-carbon bonds in benzene. Also, this value of bond length is intermediate between the typical C—C single (154 pm) and C=C double bond (134 pm) lengths.

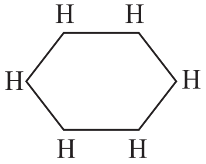


Molecular Orbital Picture of Benzene

All the six carbon atoms of benzene are sp^2 hybridised. All C—C—C bond angles are 120° and there is a *p* orbital on each carbon atom. All the six *p*-orbitals are perpendicular to the plane of the six-membered carbon ring. The overlap of these *p* orbitals leads to a delocalised electron cloud above and below the place of the carbon ring. This is shown below in IV and V.



IV



V

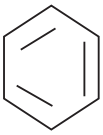
24.4.2 Aromaticity

So far you have studied that benzene

- is a cyclic conjugated molecule.
- is unusually stable.
- is planar in nature and its all C — C bond lengths are equal.
- can be represented as a resonance hybrid of two structures.
- undergoes substitution reactions rather than addition reactions.

Though the above properties indicate that benzene is *aromatic* in nature. But to complete the argument for its aromatic nature, we have to check whether it follows **Huckel's rule** or not. According to **Huckel rule** – a molecule is aromatic only if it has a planar, monocyclic system of conjugated 4n + 2 π electrons where *n* = 0, 1, 2, 3, …. Thus, molecules with 2, 6, 10, 14 π … electrons can be aromatic.

For example, in Benzene, C_6H_6



Benzene

No. of π electrons = $6e^-$ (3π bonds × $2e^-$ = $6e^-$)

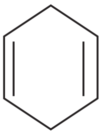
Using formula,

4n + 2 = No. of π electrons

4n + 2 = 6 gives n = 1

Hence, benzene is aromatic.

Let us take another example, i.e. 1,4-hexadiene



Hex-1, 4-diene

For this compound, No. of π electron = $4e^-$ (2π bond × $2e^-$)

Using formula,

4n + 2 = No. of π electrons

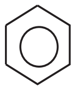
$4n + 2 = 4$

$$n = \frac{\cancel{2}}{\cancel{4}} = 0.5$$

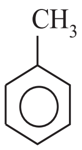
Hence, the value of n is 0.5. So, it does not obey Huckel rule and is non aromatic.

24.4.3 Physical Properties of Aromatic Hydrocarbons

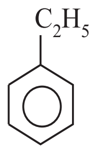
1. Benzene and its homologues are colourless liquids having a characteristic odour.
2. They are immiscible in water but are miscible in all proportions with organic solvents such as alcohol, ether, petrol, etc. They dissolve fats and many other organic substances.
3. Most of the aromatic hydrocarbons are lighter than water.
4. Their boiling points show a gradual increase with increasing molecular mass e.g. benzene (b.p. 353 K), toluene (b.p. 383 K) and ethylbenzene (b.p. 409 K) and so on.



Benzene
(b.p. 353 K)



Toluene
(b.p. 383 K)

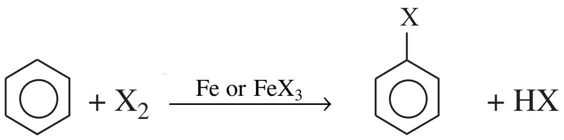


Ethylbenzene
(b.p. 409 K)

24.4.4 Chemical Properties of Aromatic Hydrocarbons

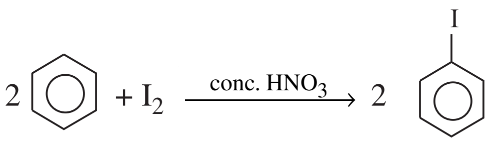
Aromatic hydrocarbons generally undergo electrophilic substitution reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile. Such reactions are discussed below in detail taking benzene as an example.

(i) Halogenation : The reaction in which a hydrogen atom of benzene is replaced by a halogen atom is called halogenation of benzene. Halogenation takes place in the presence of iron, or ferric halides (FeX_3, where X = Cl or Br).



Halobenzene

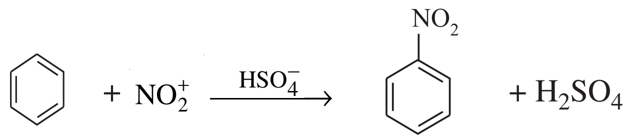
In case of iodination the HI formed can reduce iodobenzene back to be benzene which is prevented by carrying out this reaction in the presence of HNO_3 or HIO_3. These acids react with HI as soon as it is formed.



Iodobenzene

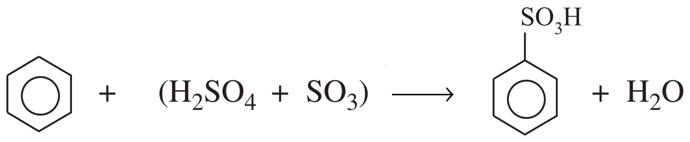
(ii) **Nitration :** The chemical reaction in which a hydrogen atom of benzene ring is replaced by $-NO_2$ group, is called nitration. It is carried out in the presence of nitrating mixture, i.e. a mixture of conc. HNO_3 and conc. H_2SO_4. Nitronium ion (NO_2^+) so formed acts as an electrophile.

$$2\,H_2SO_4 + HNO_3 \longrightarrow 2\,HSO_4^- + NO_2^+ + H_3O^+$$



Nitrobenzene

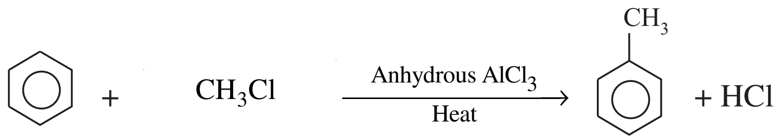
(iii) **Sulphonation :** The chemical reaction in which the hydrogen atom of benzene is replaced by $-SO_3H$ group when benzene is heated with fuming sulphuric acid (oleum), is called sulphonation.



Fuming sulphuric acid **Benzenesulphonic acid**

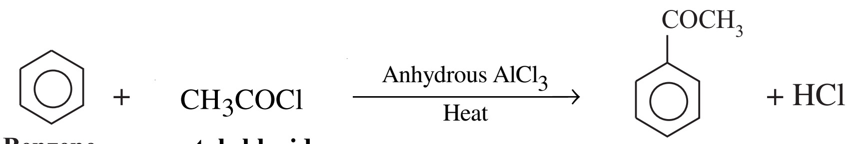
(iv) **Friedel–Craft's Reactions :** In Friedel-Craft's reaction, benzene is heated either with alkyl halide **(alkylation)** or acyl halide **(acylation)** in the presence of a catalyst (anhydrous $AlCl_3$). The products formed are alkyl or acyl derivatives of benzene.

Alkylation



Benzene **Chloromethane** **Toluene**

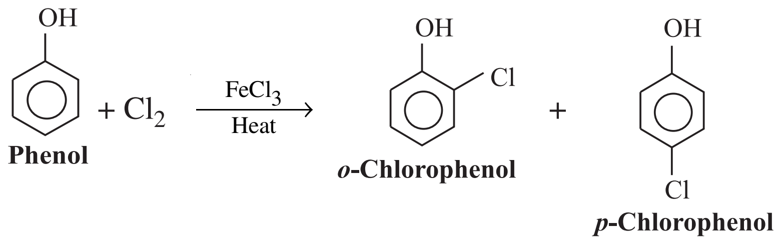
Acylation



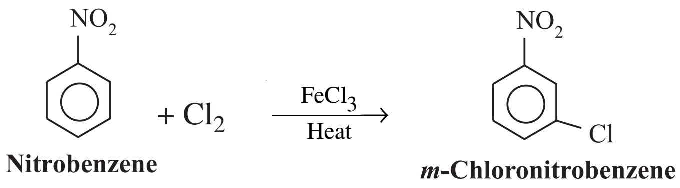
Benzene **acetyl chloride** **Acetophenone**

24.4.5 Directive Influence of Functional Groups

In case of substituted aromatic compounds, the functional group(s) already present directs the next incoming group to a particular position in the aromatic ring.. It is called directive influence of the group already attached to the benzene ring. For example, phenol on chlorination gives a mixture of *ortho* – chlorophenol and *para*– chlorophenol as – OH groups is an *ortho* and *para* directing group.



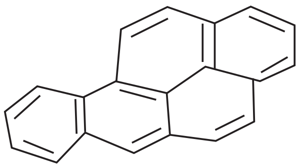
In case of nitrobenzene, we find that –NO_2 group is a *meta* directing group and hence, the product obtained on chlorination is *meta*-chloronitrobenzene.



24.4.6 Carcinogenicity & Toxicity

There exist several aromatic compounds-many of them being very important for the life while there are some others which are harmful. A large number of them are toxic in nature. For example benzene is carcinogenic in nature.

Another such hydrocarbon, is benzo[α] pyrene which has been found in cigarette smoke and in the exhaust from automobiles. This compound is also carcinogenic and can cause skin cancer in mice.



Benzo [a] pyrene

24.4.7 Uses of Aromatic Hydrocarbons

Benzene is used as a solvent for several organic compounds and thus, acts as a medium for carrying out synthetic reactions. It is the basic aromatic hydrocarbon and can be converted to other organic compounds by carrying out substitution in the benzene ring. **Toluene,** a higher homologue of the benzene, finds its uses for dry-cleaning, as a solvent, and as a starting material for the manufacture of dyes, drugs, explosive (trinitrotoluene, T.N.T.), benzaldehyde, benzoic acid etc.

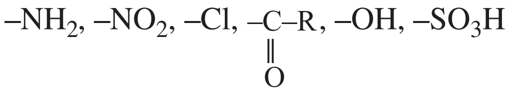
INTEXT QUESTIONS 24.4

1. What is the value of resonance energy of benzene?
2. Name the product formed when :

   (i) benzene reacts with chlorine in the presence of light.

   (ii) phenol reacts with chlorine in the presence of $FeCl_3$.

   (iii) nitrobenzene reacts with chlorine in the presence of $FeCl_3$.
3. Classify the following into *o*-and *p*- or *m*-directing groups :



$$-NH_2,\ -NO_2,\ -Cl,\ -\underset{\underset{O}{\|}}{C}-R,\ -OH,\ -SO_3H$$

WHAT YOU HAVE LEARNT

- Alkanes can be prepared by (i) the reduction of haloalkanes, (ii) action of water or alcohol on Grignard's reagent, (iii) Wurtz reaction and (iv) hydrogenation of unsaturated hydrocarbons.
- Physical properties of hydrocarbons depend on the intermolecular forces of attraction. which in turn depend upon the shapes of molecules and their surface area.
- The melting points of hydrocarbons depends upon the symmetry of the molecules i.e. hydrocarbons with even number of carbon atoms are more symmetrical and have higher melting points.
- Rotation about carbon-carbon single bond leads to various conformations of a molecule. Ethane has many conformations out of which the staggered conformation is the most stable one and the eclipsed conformation is the least stable one.
- Alkenes can be prepared by dehydrohalogenation of alkyl halides and by dehydration of alcohols.
- Alkenes and alkynes undergo addition reactions e.g. addition of hydrogen, halogens, halogen acids, water, sulphuric acid etc. due to the presence of carbon-carbon double or triple bonds.
- Addition of halogen acids and other unsymmetrical reagents to unsymmetrical alkenes and alkynes takes place according to the Markownikoff's rule.
- Alkenes undergo polymerization on heating under pressure.

- All hydrocarbons (saturated as well as unsaturated) form CO_2 and H_2O on combustion and liberate energy.
- An alkaline solution of $KMnO_4$ can oxidize alkenes and alkynes forming different products such as carboxylic acids, aldehydes and/or ketones and carbon dioxide.
- Ozone can oxidize unsaturated hydrocarbons (alkenes and alkynes) forming ozonides which when further reacted with water in the presence of zinc dust either form aldehydes or ketones or both.
- Reaction of ozone with alkenes can be used to determine the position of double bond.
- Ethyne can be prepared by the action of water on calcium carbide and by dehydrogenation of dihaloalkanes.
- Alkynes are acidic in nature due to *sp*-hybridization of carbon atoms. Because *sp* hybridized carbon atoms are more electronegative than sp^2 and sp^3, and the bond between C—H is weakened. Hence, hydrogen atoms in alkynes can be replaced by certain metal atoms.
- Alkanes, alkenes and alkynes can be distinguished by using:
  - a) Br_2 dissolved in carbon tetrachloride.
  - b) Ammoniacal solution of $AgNO_3$
  - c) Ammoniacal solution of Cu_2Cl_2
  - d) Alkaline solution of $KMnO_4$
- Benzene is obtained by destructive distillation of coal.
- A ring structure of benzene was suggested by Kekule. Actual structure of benzene is the resonance hybrid of the canonical structures.
- Aromatic hydrocarbons undergo substitution reactions i.e. the reactions in which hydrogen atom of hydrocarbons is replaced by another atom or group of atoms. Halogenation, sulphonation, nitration and Friedel Craft’s reaction are substitution reactions of benzene.
- The position of second substituent on a benzene ring depends upon the nature of the group already present.

TERMINAL EXERCISE

1. What happens when : (Write chemical equations)
   - (i) Iodoethane is heated with HI in the presence of red phosphorus.
   - (ii) 2-Chlorobutane reacts with sodium metal.

(iii) Ethyl magnesium bromide is reacted with methyl alcohol (methanol).

(iv) 2-Chloropropane reacts with alcoholic solution of KOH.

(v) 1,1-Dichloroethane reacts with alcoholic solution of KOH.

2. Give reasons for the following :

   (i) The boiling point of neopentane is less than that of n-pentane.

   (ii) Stability of benzene ring

   (iii) Boiling points of hydrocarbons decrease with the increase in branching.

3. How will you prepare the following?

   (i) Ethane from ethene

   (ii) Ethene from ethanol

   (iii) Cyclohexane from benzene

   (iv) Methane from sodium acetate

   (v) Butane from bromoethane

4. What happens when (write balanced chemical equations):

   (i) Hydrochloric acid is added to ethene.

   (ii) Hydrobromic acid (HBr) is added to propene in the presence of benzoyl peroxide.

   (iii) Benzene reacts with chloromethane in the presence of anhydrous $AlCl_3$.

   (iv) Br_2 is added to ethyne.

   (v) Methane is oxidized with oxygen in the presence of copper at 475K and a high pressure of 120 atm.

5. How are the following conversions carried out?

   (i) Ethyne to ethane

   (ii) Benzene to nitrobenzene

   (iii) Ethyl alcohol (ethanol) to ethene

   (iv) Ethyne to ethanedioic acid

   (v) Benzene to *o*-nitrochlorobenzene.

6. You are provided with three gas jars containing ethane, ethene and ethyne. Give the suitable chemical tests to identify the three hydrocarbons.

7. What is ozonolysis? How is it used to determine the position of a double bond?

8. Give reasons for the following :

   (i) Alkanes do not undergo addition reactions like alkenes and alkynes.

   (ii) Ethyne is more acidic than ethane.

(iii) Ethene undergoes polymerization but not ethane.

(iv) Benzene undergoes electrophilic substitution reactions.

ANSWERS TO INTEXT QUESTIONS

24.1

1. They are used as fuels and to prepare detergents, dyes, drugs, explosives etc. Hydrocarbons are used to prepare some important organic compounds like alcohols, aldehydes, carboxylic acids etc.
2. The alkyl magnesium halides (R-MgX) are called Grignard's reagent.
3. Easily replaceable hydrogen present in a molecule is called active hydrogen.
4. The physical properties of hydrocarbons differ from one another due to difference in molecular mass, surface area, intermolecular force of attraction.
5. Methane and ethane are gases, pentane and hexane are liquids.
6. Three isomers of pentane are : *n*-pentane, isopentane and neopentane.
7. *n*-pentane has higher boiling point than n-butane.
8. $C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$

24.2

1. *Trans*-2-butene has higher boiling point than *cis*-isomer.
2. Ethane-1, 2-diol
3. Hydrogen in presence of catalist Ni, Pt or Pd
4. Epoxyethane is produced.

24.3

1. Calcium carbide is reacted with water to prepare ethyne.

   $CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

2. Reaction with sodium metal confirms the acidic nature of ethyne.

   $$\underset{\textbf{Ethyne}}{H-C\equiv C-H} + 2\,Na \longrightarrow \underset{\textbf{Disodium acetylide}}{Na-C\equiv C-Na} + H_2$$

3. The *s*-character in : Ethane = 25%,
   Ethene = 33%,
   Ethyne = 50%

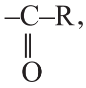
24.4

1. The resonance energy of benzene is 150.3 KJ mol^{-1}.

2. (i) Benzene hexachloride (BHC).

   (ii) *o*-Chlorophenol and *p*-chlorophenol.

   (iii) *m*-Chloronitrobenzene.

3. *o* – and *p* – directing groups : $-NH_2$, $-Cl$, $-OH$
   m-directing groups : NO_2,  $-\underset{\underset{O}{\|}}{C}-R$, $-SO_3H$

313en25

25

COMPOUNDS OF CARBON CONTAINING HALOGENS

(HALOALKANES AND HALOARENES)

You have studied about the hydrocarbons in the previous lesson.When a hydrogen attached to a carbon atom in the hydrocarbons is replaced by a halogen atom (i.e. F,C1,Br or I), the compounds formed are called **haloalkanes or haloarenes.**The halogen derivatives do not occur in nature and they are synthesized in the laboratory. These compounds have wide applications in industry and domestic uses. They are used as industrial solvents, in the manufacture of pharmaceuticals, as dry cleaning agents, as pesticides, as anesthetics in medicine, as refrigerants, as fire extinguishers and as antiseptics. In this lesson, you will study the nomenclature, methods of preparation and properties of this important class of carbon compounds.

OBJECTIVES

After reading this lesson, you will be able to :

- define haloalkanes and haloarenes;
- name haloalkanes and haloarenes according to IUPAC rules;
- explain methods of preparation, physical properties, chemical properties and uses of haloalkanes and haloarenes;
- distinguish between haloalkanes and haloarenes, and
- explain the preparation, properties and uses of some important polyhalogen compounds.

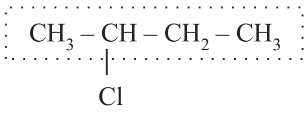
25.1 NOMENCLATURE OF HALOALKANES AND HALOARENES

You have learnt the nomenclature of hydrocarbons in lesson 25. In this section, you will learn the nomenclature of halogen derivatives of both aliphatic and aromatic hydrocarbons i.e. haloalkanes and haloarenes.

Nomenclature of Haloalkanes

The following rules are used for naming haloalkanes according to the IUPAC system.

1. The longest chain of the carbon atoms bearing the halogen atom is selected.

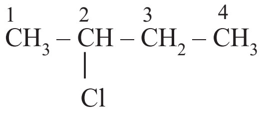


$$\boxed{CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3}$$

   The longest chain of carbon atoms in the above example is shown in the box.

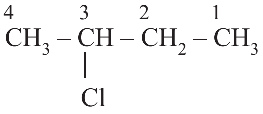
2. Numbering of the carbon atoms in the chain is done in such a way that the carbon atom bearing the halogen atom gets the lowest number.

   For example.



$$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

(Correct) I



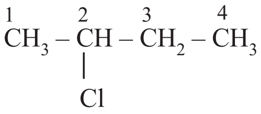
$$\overset{4}{CH_3}-\underset{\underset{Cl}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

(Incorrect) II

   In the above example, numbering shown in (I) is correct while in (II), it is incorrect since the carbon atom bearing halogen atom gets lower number in I than in II.

3. The word chloro, is prefixed to the parent hydrocarbon name.

   So, the correct name for the above halocompound is

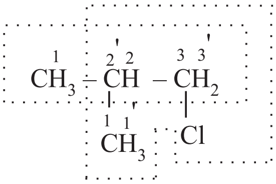


$$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

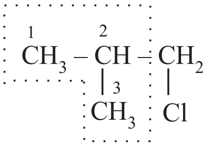
2-Chlorobutane

4. In case of alkyl substituted haloalkanes, the longest chain containing halogen atom is selected for numbering.

   For example :



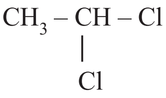
I



II

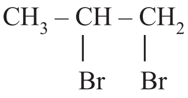
In structure I, the selection of chain is shown by two different ways. Both the ways of selection are correct since they include chloro group. In structure II numbering shown is not correct since it does not include chloro group.

5. When two or more halogen atoms are present in a compound, the longest chain selected must contain the maximum number of halogen atoms. The multiplicative prefixes (*di, tri, tetra,* etc.) are added before the name of halogen atom to indicate the number of halogen atoms. The following examples illustrate this rule.



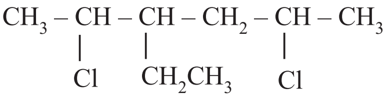
$CH_3-\underset{Cl}{CH}-Cl$

1, 1 - Dichloroethane



$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}$

1, 2 - Dibromopropane

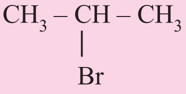
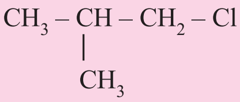


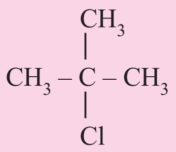
$CH_3-\underset{Cl}{CH}-\underset{CH_2CH_3}{CH}-CH_2-\underset{Cl}{CH}-CH_3$

2,5 - Dichloro - 3 - etylhexane

Some more examples are given in Table 25.1 to illustrate the above rules.

Table 25.1: Names of Some Haloalkanes

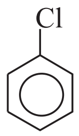
Compound	IUPAC name	Common name
CH_3CH_2Br	Bromoethane	Ethyl bromide
$CH_3CH_2CH_2Br$	1-Bromopropane	*n*-Propyl bromide
 $CH_3-\underset{Br}{CH}-CH_3$	2-Bromopropane	*iso*-Propyl bromide
 $CH_3-\underset{CH_3}{CH}-CH_2-Cl$	1-Chloro-2-methylpropane	*iso*-Butyl chloride

 $CH_3-\underset{\underset{Cl}{\mid}}{CH}-CH_2-CH_3$	2-Chlorobutane	*sec*- Butyl chloride
 $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{Cl}{\mid}}{C}}-CH_3$	2-Chloro-2-methylpropane	*tert*-Butyl chloride

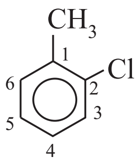
* All compounds essentially do not have common names.

Nomenclature of Haloarenes

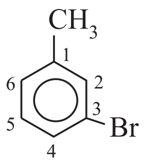
Haloarenes are those aromatic halogen compounds in which the halogen atom is directly linked to an aromatic ring. Their general formula is Ar-X where Ar- represents an aromatic ring and X denotes the halogen. In naming a haloarene, the prefix *chloro, bromo-or iodo-* etc. is are added to name of arene according to halogen(s) present. The relative positions of halogen atoms are indicated by appropriate numbers. The prefixes *ortho (o-), meta(m-) and para (p-)* are also commonly used respectively to indicate the relative positions i.e. 1,2- ;1,3 – and 1,4- of substituents in a benzene ring. Following examples illustrate the nomenclature of some haloarenes.



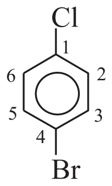
Chlorobenzene



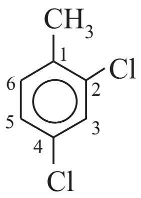
2-Chlorotoluene
(*o*-Chlorotoluene)



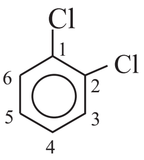
3-Bromotoluene
(*m*-Bromotoluene)



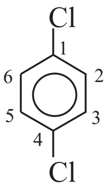
4-Bromochlorobenzene
(*p*-bromochlorobenzene)



2, 4-Dichlorotoluene



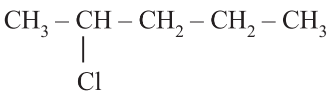
1, 2-Dichlorbenzene
(*o*-Dichlorobenzene)



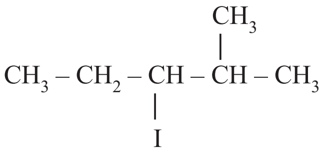
1, 4-Dichlorobenzene
(*p*-Dichlorobenzene)

INTEXT QUESTIONS 25.1

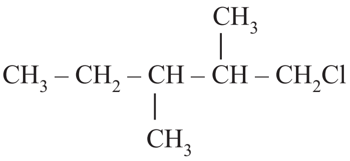
1. Write the IUPAC names of each of the following compounds :

(i) 

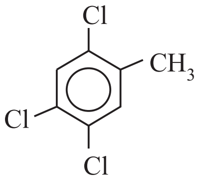
$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-CH_3$

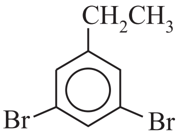
(ii) 

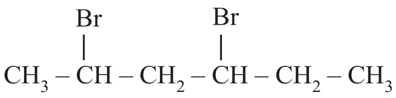
$CH_3-CH_2-\underset{\underset{I}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(iii) 

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2Cl$

(iv) 

(v) 

(vi) 

$CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-\overset{\overset{Br}{|}}{CH}-CH_2-CH_3$

2. Draw structural formulae of the following compounds:

(i) 2-Bromo-3-methylbutane

(ii) 3-Chloro-4-methylhexane

(iii) 3-Bromochlorobenzene

(iv) 2,4-Dibromotoluene

25.2 PREPARATION OF HALOALKANES AND HALOARENES

25.2.1 Preparation of Haloalkanes

(i) **From Hydrocarbons :** Direct halogenation of hydrocarbons takes place in the presence of sunlight or at high temperature in dark. For example, chloroethane is prepared by monochlorination of ethane.

$$\underset{\textbf{Ethane}}{CH_3-CH_3}+Cl_2 \xrightarrow{\text{Sunlight}} \underset{\textbf{Chloroethane}}{CH_3-CH_2Cl}+HCl$$

This reaction follows a free radical mechanism. You have already learnt the mechanism of chlorination of methane in lesson 26.

Bromo derivatives of alkanes are also prepared by direct bromination.

$$\underset{\textbf{Ethane}}{CH_3-CH_3}+Br_2 \xrightarrow{\text{Sunlight}} \underset{\textbf{Bromoethane}}{CH_3-CH_2-Br}+HBr$$

Direct iodination is not possible with iodine as the reaction is reversible. Direct fluorination is also not possible because due to the high reactivity of the fluorine, the reaction cannot be controlled.

(ii) **From Alcohols :** Alcohols are converted into haloalkanes by treating with (a) hydrogen halides (b) phosphorus halides or (c) thionyl chloride.

(a) **Reaction with Hydrogen Halides :** Hydrogen halides react with an alcohol in presence of a dehydrating agent such as anhydrous zinc chloride to produce a haloalkane.

Chloroethane is conveniently prepared by the reaction of ethanol with concentrated hydrochloric acid in presence of anhydrous zinc chloride.

$$\underset{\textbf{Ethanol}}{CH_3CH_2OH}+HCl \xrightarrow{\text{anhy.}ZnCl_2} \underset{\textbf{Chloroethane}}{CH_3-CH_2Cl}+H_2O$$

Zinc chloride absorbs water from the reaction mixture and thus prevents the reverse reaction.

Bromoethane is obtained by refluxing ethanol with HBr in presence of little concentrated H_2SO_4 as the catalyst.

$$\underset{\textbf{Ethanol}}{CH_3CH_2OH}+HBr \xrightarrow[\Delta]{\text{conc. }H_2SO_4} \underset{\textbf{Bromoethane}}{CH_3CH_2Br}+H_2O$$

(b) **Reaction with Phosphorus Halides :** Haloalkanes are conveniently prepared by the reaction of an alcohol with a phosphorus halide $\left(PCl_3, PCl_5 \text{ or } PBr_3\right)$ according to the following equations.

$$3\,C_2H_5OH + PCl_3 \longrightarrow 3\,C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$3\,C_2H_5OH + PBr_3 \longrightarrow 3\,C_2H_5Br + H_3PO_3$$

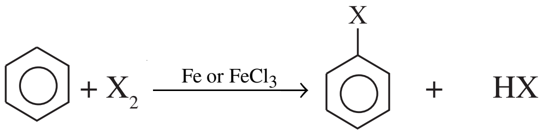
(c) **Reaction with Thionyl Cholride :** Thionyl chloride ($SOCl_2$) is another reagent which reacts with an alcohol to yield a chloroalkane.

$$\underset{\textbf{Ethanol}}{C_2H_5OH} + SOCl_2 \longrightarrow \underset{\textbf{Chloroethane}}{C_2H_5Cl} + SO_2\uparrow + HCl\uparrow$$

As both the byproducts, SO_2 and HC1 are gases, the purification of final product is not required.

25.2.2 Preparation of Haloarenes

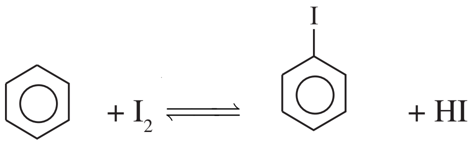
(i) **From Aromatic Hydrocarbons :** Haloarenes are obtained by direct halogenation of aromatic hydrocarbons in the presence of a catalyst. Usually iron filings or iron (III) halide is used as the catalyst.



Benzene **Halobenzene (Haloarene)**

where X = Cl or Br

The direct iodination of aromatic hydrocarbons is not a useful reaction since the HI produced reduces the aryl iodide back to the aromatic hydrocarbon.



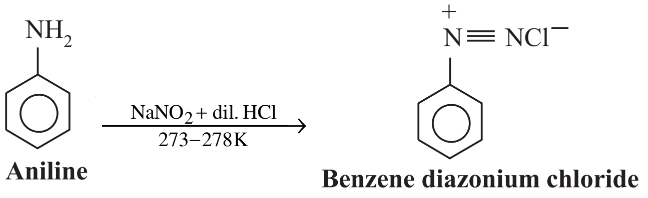
Benzene **Iodobenzene**

However, in the presence of an oxidizing agent such as nitric acid, iodic acid (HIO_3), mercury oxide, the HI produced is either oxidized to iodine or is eliminated as mercuric iodide and, thus, iodobenzene is obtained.

$$5\,HI + HIO_3 \longrightarrow 3\,I_2 + 3H_2O$$

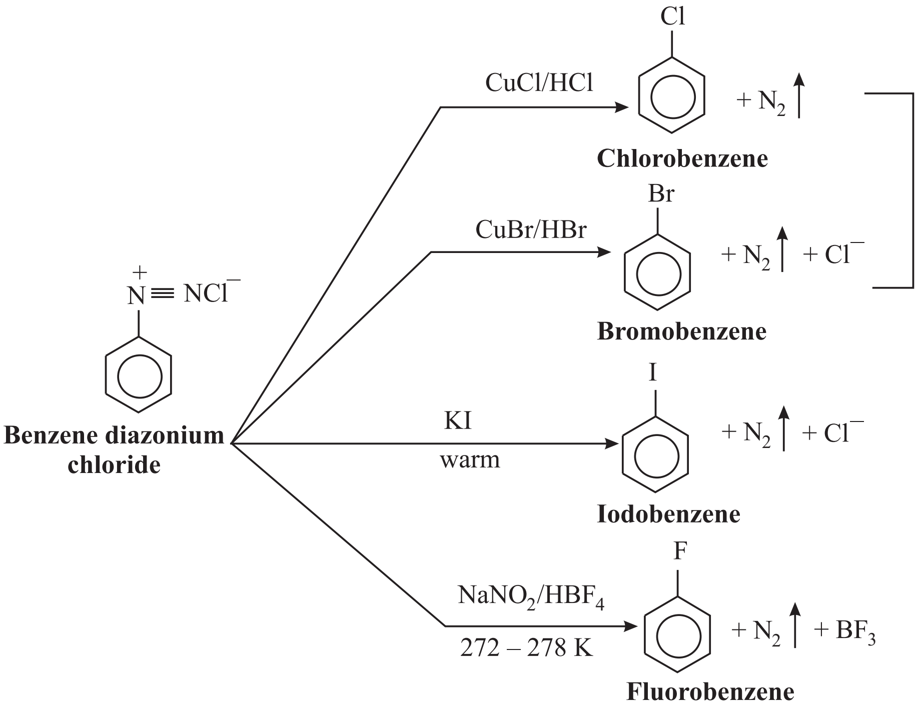
Fluorobenzene cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is very violent and cannot be controlled.

(ii) **From Diazonium Salts :** Benzene diazonium salt is formed by treating an aromatic primary amine with $NaNO_2$ and dil. HCl at low temperature. The process is known as **diazotisation**.

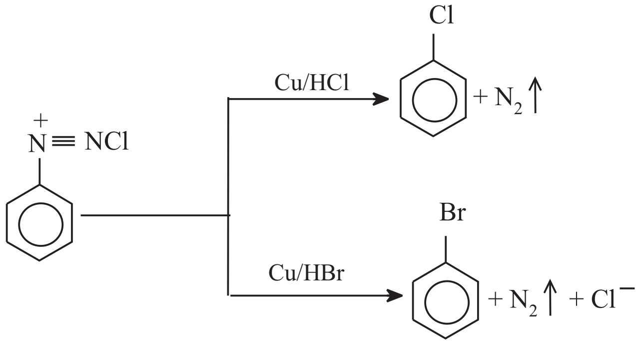


Diazonium salts are highly reactive compounds. They are used in the preparation of a large number of arene derivatives. When a diazonium salt is treated with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2), the corresponding haloarene is formed.

This reaction is known as **Sandmeyer reaction**. It is used for introducing a chloro or bromo group in the benzene ring.

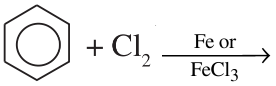


Haloarenes can also be prepared by reacting benzene diazonium chloride with copper powder in presence of corresponding halogen acid. This reaction is called **Gattermann reaction** and is shown below :



INTEXT QUESTIONS 25.2

1. Write the structure of the main product obtained by treating 1-propanol with excess of hydrogen chloride in the presence of anhydrous zinc chloride.
2. What will be the product obtained on treatment of 1-propanol with thionyl chloride?
3. Give one example of preparation of chlorbenzene using Sandmeyer reaction?
4. Complete the following reaction :

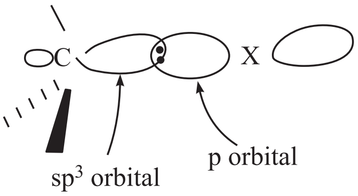


25.3 PROPERTIES OF HALOALKANES AND HALOARENES

Before we discuss the important physical and chemical properties of alkylhalides and aryl halides, let us consider the nature of C—X bond.

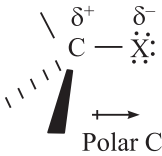
25.3.1 The Nature of C–X Bond

In alkyl halides, the carbon – halogen bond is formed by the overlap of the sp^3 hybrid orbital of carbon atom with the *p*-orbital of the halogen atom.



As one moves from fluorine to iodine, the size of the halogen atom increases and hence the overlap decreases. Hence, the C–X bond becomes longer and weaker on going from alkyl fluorides to alkyl iodides.

Also, the halogens are more electronegative than carbon. Thus, the electron density along the C–X bond is displaced in the direction of the halogen. Thus, *the C–X bond in polar in nature*. The carbon atom bears a partial positive charge (δ^+) and the halogen atoms bears a partial negative charge (δ^-).



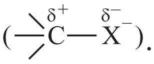
Polar C–X bond

You will now study that this bond polarity has important impact on the physical and chemical properties of alkyl halides.

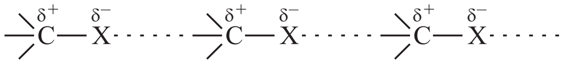
The partially positively charged carbon in haloalkanes can be easily attached by anions and electron rich species which are called *nucleophiles*. On the other hand, the partially negatively charged halogen atom can be attacked by the cations and electron deficient species.

25.3.2 Physical Properties

1. The lower alkyl halides (CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl) are gases at room temperature. The other alkyl halides containing upto C_{18} are liquids having high boiling points.

2. Haloalkanes and haloarenes are moderately polar molecules . Still they are immiscible in water. It is due to their inability to form hydrogen bonds with water molecules.

3. The melting and boiling points of haloalkanes and haloarenes are higher than those of their parent hydrocarbons (Table 25.2) This is due to (i) the greater molecular mass and hence greater magnitude of van der Waals forces of attraction in halocompounds than in the parent hydrocarbons and (ii) the existence of intermolecular dipole-dipole interaction, as shown below:

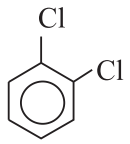


For a given alkyl or aryl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 25.2 to show this variation.

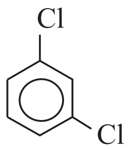
Table 25.2 : Boiling Points of Haloalkanes and Haloarenes

Compound	Boiling Point (K)				
	X=H	X=F	X=Cl	X=Br	X=I
CH_3-X	111.5	194.6	248.8	276.6	315.4
C_2H_5-X	184.3	241	285	311.4	345
C_6H_5-X	351	358	405	429	461

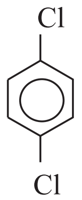
4. All monohalobenzenes are liquids at room temperature. Among dihalobenzenes, the *para* isomers have the highest melting points. It is due to the greater symmetry that causes a better packing of molecule in the *para* isomer.



256 K



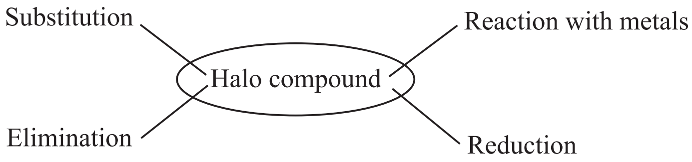
249 K



325 K

25.3.4 Chemical Properties

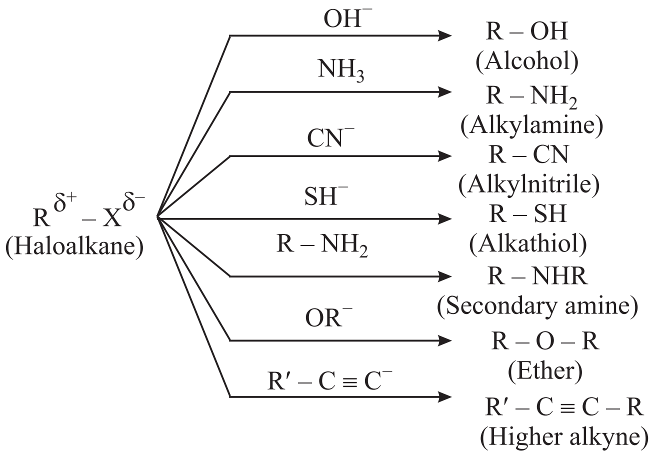
Halo compounds can undergo the following types of reactions :



1. Substitution : Substitution reactions are those in which an atom or a group of atoms from the reactant molecule is displaced by another atom or a group of atoms. For example, on treating chloroethane with sodium hydroxide, the chlorine atom of chloroethane is substituted by the hydroxyl group and ethanol is formed as the reaction product.

$$C_2H_5-Cl+OH^- \longrightarrow C_2H_5OH+Cl^-$$

In this reaction, it is to be noted that the hydroxide ion (nucleophile) displaces the chlorine atom from C_2H_5Cl as chloride ion (another nucleophile). Such reactions which are initiated by the attack of a nucleophile are known as **nucleophilic reactions**. In haloalkanes, the carbon atom carrying the halogen atom is electron deficient due to – I effect of halogen atom. This electron deficient carbon atom is susceptible to attack by a nucleophile. Thus, you may conclude that haloalkanes undergo **nucleophillic substitution reactions**. Following are a few examples of nucleophilic substitution reactions of haloalkanes.



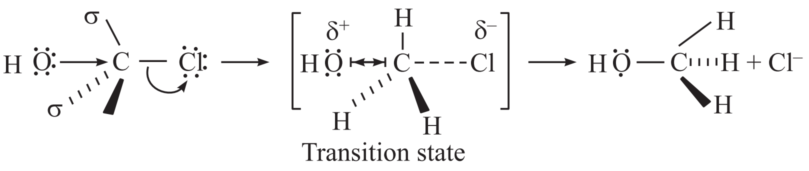
In all the above reactions, the stronger nucleophile $\left(HO^-, C_2H_5O^-, CN^- \text{ or } NH_3 \text{ etc.}\right)$ displaces a weaker nucleophile X^- as

$$\underset{\textbf{Stronger nucleophile}}{\bar{N}u:} + R^{\delta+}-X^{\delta-} \longrightarrow R-Nu + \underset{\textbf{Weaker nucleophile}}{:X^-}$$

25.3.3 Mechanism of Nucleophilic Substitution Reactions

The nucleophilic substitution reactions could be either S_N1 or S_N2 type.

When the nucleophilic attacks the haloalkane, and simultaneously the leaving groups leaves then, the reaction is called **nucleophilic substitution bimolecular** i.e. S_N2.

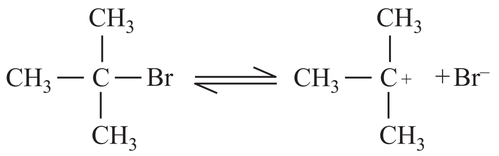


Also, note that it is a one step process and the transition state involves *two* species. The formation of this transition state is the rate determining step in this mechanism.

Here, the bond making and the bond breaking takes place simultaneously. The nucleophilie (^-OH) attacks from one side of the carbon atom whereas the leaving group (Cl^-) leaves from the opposite direction. Hence, there is an *inversion* of configuration at the carbon atom.

Primary alkyl halides undergo substitution by S_N2 mechanism.

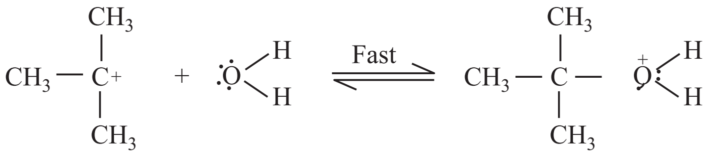
However, in case of tertiary alkyl halides, the substitution takes place by an alternative mechanism, i.e. *substitution nucleophilic*, unimolecular or SN^1 mechanism. For example, in the hydrolysis of 2-bromo-2-methylpropane, any one molecule participates in the rate determining step which is the dissociation of the alkyl halide to alkyl cation and bromide ion.



Carbocatiron

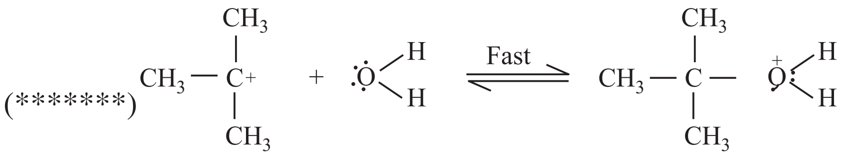
This alkyl cation is a carbocation and its formation is a slow and rate determining step.

After this, as soon as this carbocation is formed, the nucleophile, which is water (solvent) molecule, attacks on it which is a fast step.



alkyl oxonium

Finally, the alkyl oxonium ion loses a proton to give the alcohol as the product.

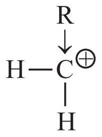


alkyl oxonium

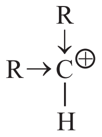
Since, the S_N1 reactions proceed via the formation of carbocations, the stability of the carbocation formed is an important factor in the S_N1 reactions.

Stability of Carbocations

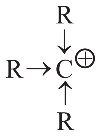
Let us consider the following carbocations.



I
A primary carbocation



II
A secondary carbocation



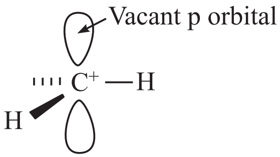
III
A tertiary carbocation

A carbocation is classified as *primary, secondary* or *tertiary* depending upon whether the positively charged carbon atom is linked to *one, two or three* carbon atoms, respectively.

Here, as the *number of alkyl groups* attached to the positively charged carbon atoms increases, the stability of the carbocation *also increases*. This is because alkyl groups are electron releasing in nature and help in the stabilization of the positive charge on the carbon atom of the carbonation.

Thus, a tertiary carbocation is more stable than a secondary carbocation which, in turn, is more stable than a primary carbonation.

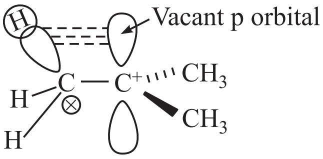
The above order of stability of carbocations is also explained on the basis of ***hyperconjugation***. Hyperconjugation results from the overlap of a *p* orbital with a neighbouring bonding molecular orbital. In a carbocation, the *p* orbital on the carbon carrying positive charge is vacant.



Carbocation

This vacant *p* orbital can overlap with the neighboring orbital of C–H bond and stabilize the charge. The more the number of such neighboring orbitals, the move will be the stabilization.

If we see the extent of hyper conjugation possible in primary, secondary and tertiory carbocation we can observe that in a primary carbocation cation 3 C–H bonds are available for hyperconjugation and in secondary carbocation 6 C–H bonds are available for hyperconjugation. Similarly, in a tertiary carbocation, 9 C–H bonds are available for hyperconjugation.

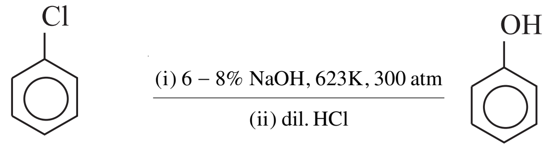


Hyper conjugation

Hence, a tertiary carbocation is more stable than a secondary carbocation which is, in turn, more stable than a primary carbocation.

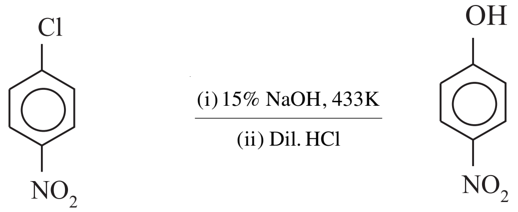
Thus, this also explains why tertiary halides undergo nucleophilic substitution reactions by S_N1 mechanism.

Haloarenes are almost unreactive to reagents such as NaOH, C_2H_5ONa, NaCN and NH_3 under ordinary laboratory conditions but can show nucleophillic substitution reactions under drastic conditions.



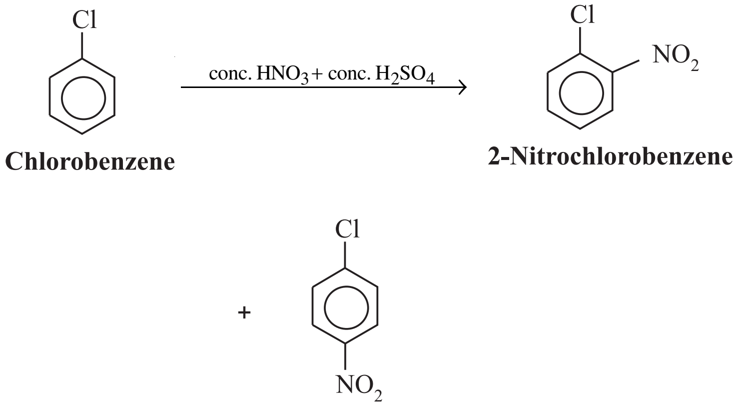
Chlorobenzene **Phenol**

It is also observed that the presence of electron withdrawing groups such as $-NO_2$ groups at *o*- and *p*-position (but not a *m*-position) with respect to halogen activates the halogens towards nucleophillic displacement.For example:



4-Nitrochlorobenzene **4-Nitrophenol**

Haloarenes can also readily undergo substitution reactions in benzene ring. The benzene ring is an electron rich species. Therefore, it is attacked by an electron deficient species such as NO_2^+. As *ortho* and *para* positions in haloarenes are electron rich due to resonance (Fig. 25.1), the electrophilic substitution takes place mainly at these positions. For example, the nitration of chlorobenzene, with a mixture of concentrated HNO_3 and H_2SO_4, gives a mixture of 2-nitrochlorobenzene and 4-nitrochlorobenzene.



4-Nitrochlorobenzene

Haloalkanes are highly reactive compounds due to the presence of a polar carbon-halogen bond in their molecules. The bond energy values of C–X bonds in haloalkanes and haloarenes are given in Table 25.3.

Table 25.3 : C–X bond energy Values

Bond	Bond Energy/kJ mol^{-1}
C–F	485
C–C1	339
C–Br	284
C–I	213

These bond energy values show that C-I bond is the weakest bond and C-F bond is the strongest bond. Therefore, the order of reactivity of haloalkanes is iodoalkane >bromoalkane > chloroalkane> fluoroalkane.

Comparing the haloalkanes and haloarenes, haloalkanes are found to more reactive than haloarenes in reactions involving the breaking of C–X bond (X = F,C1,Br, or I). It is due to the existernce of the phenomenon of resonance which cause carbon–halogen bond to acquire double bond character in haloarenes. The resonating structures of chlorobenzene are shown below :

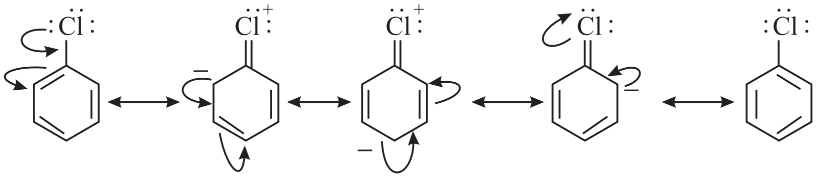


Fig. 25.1 : *Resonance Structures of Chlorobenzene*

2. Elimination reactions : When haloalkanes are heated with aqueous solution of potassium or sodium hydroxide, the major product formed is the alcohol, produced by nucleophilic displacement of the halogen atom by HO^-.

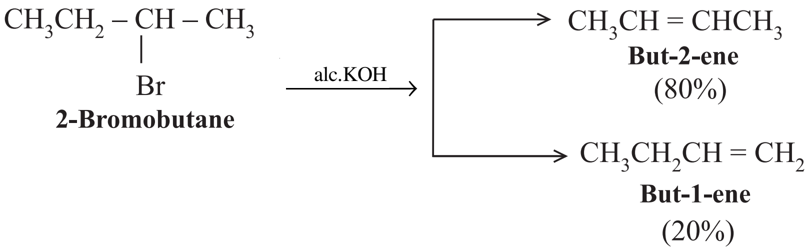
$$\underset{\textbf{Chloroethane}}{C_2H_5Cl} \xrightarrow{\text{aq. KOH}} \underset{\textbf{Ethanol}}{C_2H_5OH} + Cl^-$$

If a haloalkane is heated with concentrated alcoholic potassium hydroxide, the major product formed is an alkene due to the elimination of hydrogen halide. This is called β-elimination or dehydrohalogenation.

$$\underset{\textbf{Chloroethane}}{C_2H_5Cl} \xrightarrow{\text{alc.KOH}} \underset{\textbf{Ethene}}{CH_2 = CH_2}$$

In this reaction, the OH^- ion acts and a base removes a proton from the molecule.

If the structure of alkyl halide is such that it can undergo elimination in two different ways, then the more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of elimination. This is known as **Saytzeff's rule**. For example, elimination reaction of 2-bromobutane gives 2-butene as major product according to the Saytzeff's rule, (refer lesson 26).



$$CH_3CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{alc.KOH}} CH_3CH=CHCH_3 \; (80\%) + CH_3CH_2CH=CH_2 \; (20\%)$$

2-Bromobutane **But-2-ene** (80%) **But-1-ene** (20%)

3. Reactions with metals : Haloalkanes and haloarenes react with a variety of metals (zinc, magnesium and lithium).The compounds so obtained have a metal atom directly bonded to a carbon atom. Such compounds in which the metal atom is directly bonded to a carbon atom are known as **organometallic compounds**. The organometallic compounds of magnesium with alkyl and aryl halides are known as **Grignard reagents.**

$$C_2H_5-Cl + Mg \xrightarrow{\text{dry ether}} C_2H_5-Mg-Cl$$

Chloroethane **Ethyl magnesium chloride**

These are named after the French chemist Victor Grignard.

French Chemist

Victor Grignard was awarded Nobel Prize in 1912. He introduced **organomagnesium halide as a** common synthetic reagent.

Alkyl halides react with metallic sodium in presence of dry ether to form symmetrical higher alkanes. This reaction is called **Wurtz reaction.**

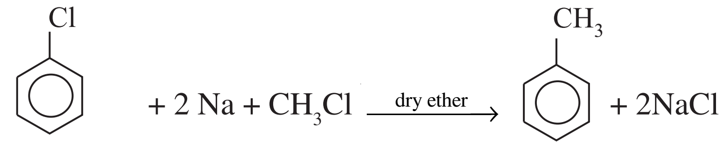
$$2\,R-X + 2\,Na \xrightarrow{\text{dry ether}} R-R + 2\,Na^+X^-$$

Ethyl bromide can react with lead in presence of dry ether to form tetraethyl lead (TEL) which is used as antiknocking agent in gasoline used for running automobilies.

$$4\,CH_3CH_2Br + 4\,Pb \xrightarrow{\text{dry ether}} (CH_3CH_2)_4\,Pb$$

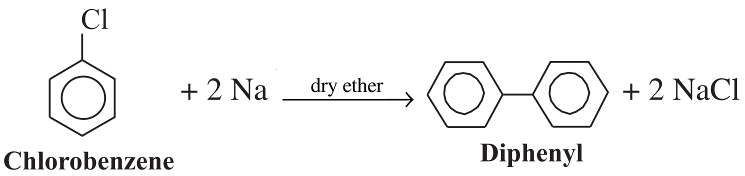
Bromethane **Tetraethyl lead**

When haloarenes react with alkyl halides in presence of sodium and dry ether, the alkyl derivatives of benzene are formed. This reaction is called **Wurtz-Fittig reaction.**



Chlorobenzene **Toluene**

When haloarenes are treated with sodium, diaryls are produced. This reaction is called **Fittig reaction.**



4. Reduction : Haloalkanes can be reduced to the corresponding alkanes. For example, bromoethane can be reduced to ethane by using metal catalyst such as nickel or palladium or platinum or by using hydroiodic acid (HI) in presence of red phosphorus.

$$CH_3CH_2Br + H_2 \xrightarrow[\text{or Pd}]{\text{Ni or Pt}} CH_3 - CH_3 + HBr$$

Bromethane **Ethane**

$$CH_3CH_2I + HI \xrightarrow{\text{red P}} CH_3 - CH_3 + I_2$$

Iodoethane **Ethane**

Distinction between haloalkanes and haloarene

Haloalkane and haloarenes can be distinguished by silver nitrate ($AgNO_3$). Haloalkanes react with $AgNO_3$ to give white precipitate of AgCl while haloarenes do not react.

$$RCl + NaOH \longrightarrow NaCl + ROH$$

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow NaNO_3$$

INTEXT QUESTIONS 25.3

1. Although haloalkanes are polar in nature, they are immiscible in water. Explain.
2. Which one of the following isomers has the higher boiling point and why?
   (i) *o*-dichlorobenzene (ii) *p*-dichlorobenzene
3. What will be the products of nitration of chlorobenzene?
4. What products will obtained when ethylbromide reacts with
   (i) aq. KOH and (ii) alc. KOH
5. What is the major product of elimination reactions of 2- bromobutane?

25.4 SOME USEFUL POLY HALOGEN COMPOUNDS

A large number of polyhalogen aliphatic and aromatic halogen compounds are known. These are extensively used as solvents, pesticides, anaesthetics etc. Some of the important compounds are chloroform ($CHCl_3$), iodoform (CHI_3), carbon tetrachloride (CCl_4), benzene hexachloride (BHC), DDT, etc.

Let us now study some of these compounds.

25.4.1 Chloroform

Chlorofom is a derivative of the simplest hydrocarbon, methane. Its IUPAC name is trichloromethane.

1. From Ethanol

Chlorofom is prepared in the laboratory by treating ethanol or propanone with chlorine gas in the presence of an alkali :

$$\underset{\textbf{Ethanol}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\textbf{Ethanal}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\substack{\textbf{Trichloroethanal}\\ \textbf{(Chloral)}}}{Cl_3CCHO}$$

$$Ca(OH)_2 + 2Cl_3C-CHO \longrightarrow \underset{\substack{\textbf{Calcium}\\ \textbf{formate}}}{(HCOO)_2Ca} + \underset{\textbf{chloroform}}{2\,CHCl_3}$$

$$\underset{\textbf{Propanone}}{CH_3COCH_3} \xrightarrow[-3HCl]{3Cl_2} Cl_3C-CO-CH_3$$

$$Ca(OH)_2 + 2\,CCl_3CO-CH_3 \longrightarrow \underset{\substack{\textbf{Calcium}\\ \textbf{acetate}}}{(CH_3COO)_2Ca} + \underset{\textbf{chloroform}}{2\,CHCl_3}$$

Chlorofom is a colourless sweet smelling liquid (b.p. 334K). It is slowly oxidized by air in the presence of light to a poisonous gas, phosgene. Chemically phosgene is carbonyl chloride, ($COCl_2$). Therefore, chloroform is stored in dark coloured bottles to protect it from light. The bottle are completely filled so that the air is kept out. A small amount of ethanol is added to chloroform to convert toxic phosgene, if formed, into a nontoxic compound, ethyl carbonate.

$$CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\textbf{Phosgene}}{COCl_2} + 2\,HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\textbf{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2HCl$$

Chloroform is used in isocyanide test for the detection of primary amines. In this test, a mixture of amine and chloroform is heated with alcoholic NaOH. A foul smelling isocyanide is obtained. This test is also known as **carbylamine test.** It can be used to test aliphatic and aromatic primary amines.

$$\underset{\textbf{Ethylamine}}{C_2H_5NH_2} + CHCl_3 + 3\,NaOH \longrightarrow \underset{\textbf{Ethyl isocynanide}}{C_2H_5NC} + 3\,NaCl + 3\,H_2O$$

25.4.2 Iodoform

Iodoform is a pale yellow solid with a distinct smell. Its IUPAC name is triiodomethane.

Preparation

Iodoform is prepared by heating ethanol or acetone with iodine in the presence of alkali.

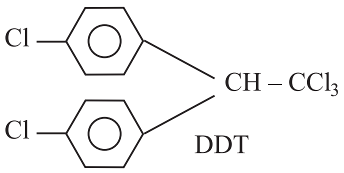
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3CONa + 3NaI + 3H_2O$$

Yellow crystals of iodoform can easily be recognized by the characteristic smell. Formation of iodoform is used to test compounds containing $CH_3-\underset{|}{C}=O$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group. This test is known as **iodoform test**. Iodoform is used as an antiseptic.

25.4.3 Dichlorodiphenyltrichloroethane (DDT)

It is available in several different forms : powder, aerosols, granules, etc.



DDT

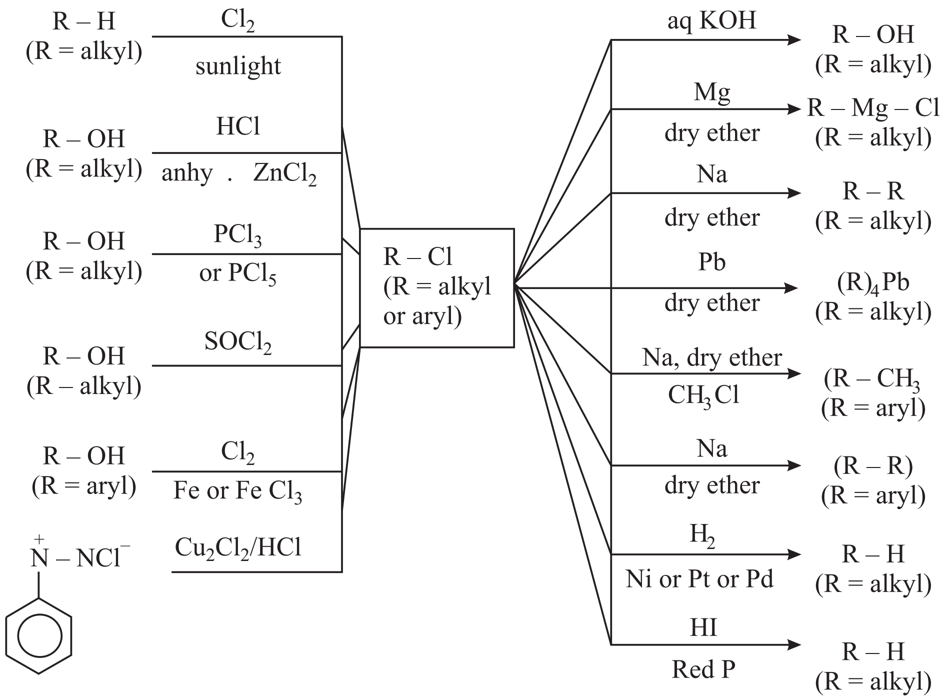
Uses : It is used mainly to control mosquito-borne malaria. It is also used as an argicultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.

INTEXT QUESTIONS 25.4

1. Write IUPAC names of chloroform and iodoform.
2. Why is chloroform stored in dark coloured bottles?
3. What type of of compounds will give a positive iodoform test?
4. Name two commonly used polyhalogen compounds.

WHAT YOU HAVE LEARNT

- Haloalkanes and haloarenes are important organic compounds having wide industrial and household applications.
- Various rules for IUPAC naming of haloalkanes and haloarenes.
- Methods of preparation and chemical properties of haloalkanes and haloarenes which are summarized below :

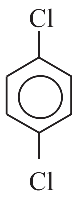


- Due to the polar nature, halo compounds have higher melting and boiling points than the corresponding hydrocarbons.
- Chemically, fluoro compounds are comparatively least reactive and iodo compounds are the most reactive. Also, haloalkanes are more reactive than haloarenes in reactions involving cleavage of C–X bond.

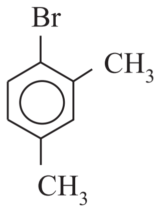
- Haloalkanes undergo nucleophilic substitution reactions. But in haloarenes, the substitution in the benzene ring is an electrophilic substitution reaction.
- Grignard reagents are produced by the reaction of a haloarene or haloalkane with magnesium metal.
- Chloroform and idoform are useful trihalo derivatives of methane. Chloroform is prepared in the laboratory from ethanol or propanone by reacting with chlorine in presence of alkali.
- Iodoform test is given by compounds containing either $CH_3–\overset{|}{C}O = O$or $CH_3–\overset{|}{C}H–OH$ group.

TERMINAL EXERCISE

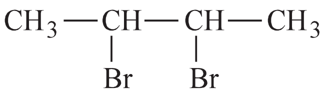
1. Give IUPAC names of the following compounds:
   (i) *sec*-butyl chloride
   (ii) *iso*- propyl bromide
   (iii)



   (iv)



   (v)



$$CH_3—\underset{Br}{\underset{|}{CH}}—\underset{Br}{\underset{|}{CH}}—CH_3$$

2. Name the product obtained by treating 2-propanol with hydrogen chloride in presence of anhydrous zinc chloride. Also write reaction involved.
3. Alkyl halides are more reactive towards nucleophilic reagents than aryl halides. Discuss briefly.
4. Write chemical equations for the reactionss of :
   (i) *n*-propanol with PCl_5.
   (ii) chlorine gas with benzene in presence of $FeCl_3$ as catalyst.

(iii) bromoethane with aqueous KOH solution.

(iv) nitrous acid with aniline at 278 K.

(v) chlorobenzene with magnesium.

(vi) chlorobenzene with a mixture of conc. HNO_3 and H_2SO_4.

5. Give reason for the following :
   (i) Haloalkanes undergo nucleophilic substitution reactions.
   (ii) Haloarenes undergo electrophilic substitution reactions.

6. What is a Grignard reagent ? How is it prepared?

7. Disucss briefly the following :
   (i) Iodoform test
   (ii) Carbylamine test
   (iii) Diazotization
   (iv) Releative reactivities of chloroethane and bromoethane

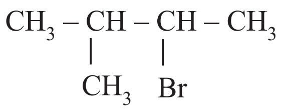
8. How is chloroform prepared in the laboratory? Write the reaction for its prepartion from ethanal.

ANSWERS TO INTEXT QUESTIONS

25.1

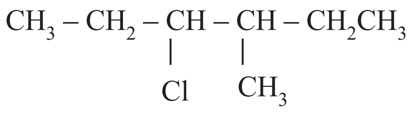
1. (i) 2-Chloropentane
   (ii) 3-Iodo-2-methylpentane
   (iii) l-Chloro-2,3-dimethylpentane
   (iv) 1,3,4-Trichloro-6-methylbenzene or 2,4,5 - Trichlorotoluene
   (v) 1,3-Dibromo-5-ethylbenzene
   (vi) 2,4-Dibromohexane

2. (i)

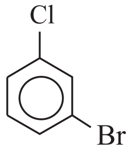


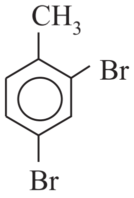
$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{Br}{|}}{CH} - CH_3$$

(ii)



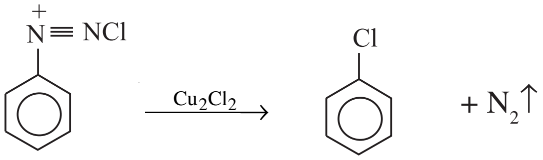
$$CH_3 - CH_2 - \underset{\underset{Cl}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_2CH_3$$

(iii) 

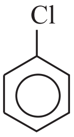
(iv) 

25.2

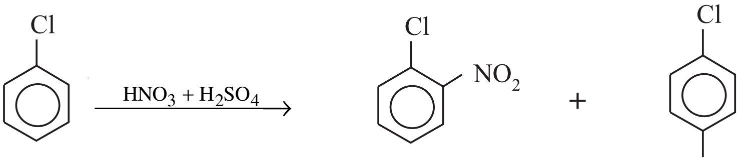
1. $CH_3CH_2CH_2Cl$
2. 1-chloropropane
3. The Diazonium salt on treatment with copper (I) chloride Cu_2Cl_2 gives chlorobenzene.



Chlorobenzene

4. 

25.3

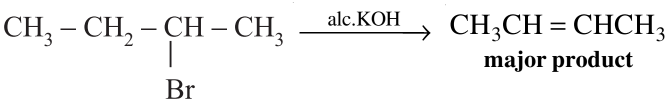
1. Due to their inability to form hydrogen bonds.
2. *Para* dichlorobenzene; due to greater symmetry and hence a better packing.
3. 

***o*-Nitrochlorobenzene**

***p*-Nitrochlorobenzene**

4. (i) $C_2H_5Cl \xrightarrow{\text{aq.KOH}} C_2H_5OH$

   (ii) $C_2H_5Cl \xrightarrow{\text{alc.KOH}} CH_2 = CH_2$

5. 

$$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{alc.KOH}} \underset{\textbf{major product}}{CH_3CH = CHCH_3}$$

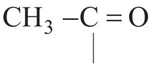
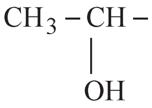
25.4

1. (i) Trichloromethane

   (ii) Triiodomethane

2. Chloroform oxidises to phosgene in the presence of air and sunlight. Dark coloured bottles reduce formation of poisionous phosgene

$$CHCl_3 + O_2 \xrightarrow{\text{sunlight}} COCl_2 + HCl$$

3. Compounds having  $CH_3-\underset{|}{C}=O$ or  $CH_3-\underset{\underset{OH}{|}}{CH}-$ units in their structure.

   Dark coloured bottles reduce formation of poisonous phosgene.

4. DDT, BHC, $CHCl_3$ and CHI_3.

313en26

26

ALCOHOLS, PHENOLS AND ETHERS

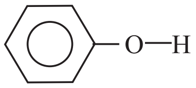
So far you have learnt the chemistry of hydrocarbons which serve as basic skeleton for the attachment of various functional groups to give a large number of their derivatives. In the last lesson, we discussed one such class of compounds *viz halogen derivatives of hydrocarbons*. Another very useful and important catagory of hydrocarbon derivatives is that of compounds containing functional groups in which the carbon atom is linked to an oxygen atom.

We have devoted two lessons for the study of these compounds. In this lesson, you will study about compounds containing carbon-oxygen single bond (–C–O) whereas the next lesson deals with compounds containing carbon-oxygen double-bond ($>C{=}O$).

Among the compounds with carbon-oxygen single bond are the classes of *alcohols, phenols* and *ethers* having the following general structures.

R—O—H

Alcohol



Phenol

R—O—R′

Ether
R/R′ can also be aromatic

These are very important categories of compounds both in the industry and in the synthesis of other organic compounds. You will study each of these classes of compounds in this Lesson.

OBJECTIVES

After reading this lesson, you should be able to

- classify alcohols as primary, secondary or tertiary;
- name simple alcohols according to IUPAC system of nomenclature;
- list general methods of preparation of alcohols;
- discuss the properties of alcohols in the light of their structure;
- explain various reactions exhibited by alcohols to give other categories of organic compounds;
- describe important uses of alcohols;
- give the names of common phenolic compounds;
- describe the laboratory and industrial methods of preparation of phenols;
- explain the greater acidity of phenols as compared to alcohols;
- discuss the reactions of phenols;
- name ethers according to the IUPAC system of nomenclature;
- describe the general methods of preparation of ethers and
- explain the important reactions of ethers.

26.1 ALCOHOLS

Alcohols are organic compounds that have one or more hydroxy (-OH) groups bonded to the *carbon atoms in aliphatic compounds*. They occur widely in nature and have many industrial and pharmaceutical applications. For example, methanol and ethanol are two industrially important alcohols.

$CH_3{-}OH$

Methanol

(Methyl alcohol)

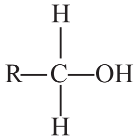
$CH_3CH_2{-}OH$

Ethanol

(Ethyl alcohol)

26.1.1 Classification and Nomenclature of Alcohols

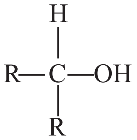
Alcohols are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) depending upon whether the number of alkyl groups bonded to the carbon atom bearing the hydroxy group is one, two or three, respectively.



$$R{-}\underset{H}{\overset{H}{C}}{-}OH$$

primary alcohol

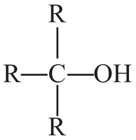
1°



$$R{-}\underset{R}{\overset{H}{C}}{-}OH$$

secondary alcohol

2°



$$R{-}\underset{R}{\overset{R}{C}}{-}OH$$

tertiary alcohol

3°

According to the IUPAC system of nomenclature, alcohols are called **alkanols**. They are named as the derivatives of the corresponding alkane in which the -*e* of the alkane is replaced by *-ol* .

The procedure for nomenclature involves the following steps:

Step 1: Select the longest carbon chain which contains the carbon atom bearing the –OH group. Count the number of carbon atoms and identify the corresponding alkane. From the name of this alkane, drop the final *e* and suffix *-ol* in its place. This gives the root name or the parent name.

Step 2: Number the carbon chain starting from the end nearest to the hydroxy group. The number of the carbon atom bearing the hydroxy group is indicated before *-ol* in the name.

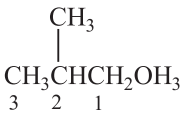
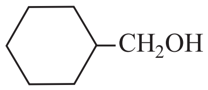
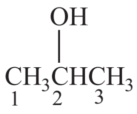
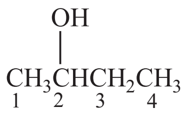
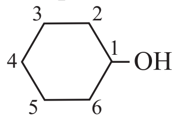
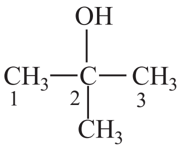
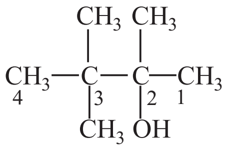
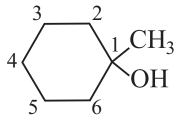
Step 3: Number the other substituents according to their position on the chain.

Step 4: Write the name of the alcohol by listing the substituents in the alphabetical order alongwith their position.

You may remember from Lesson 25 that the hydroxyl group takes precedence over double and triple bonds.

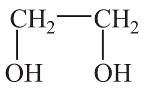
Table 26.1 illustrates some common alcohols and their IUPAC and common names. Go through them in light of the steps given above for nomenclature.

Table 26.1 : Some common Alcohols and their Names

Primary Alcohol	 $\underset{3\quad 2\quad 1}{CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_2OH_3}$ **2-Methyl propan-l-ol** **(Isobutyl alcohol)$^+$**	 **Pheaylmethanol** **(Benzyl alcohol)**	CH_3CHCH_2OH 3 2 1 **1-Propanol** **(n-Propyl alcohol)** $H_2C{=}CHCH_2OH$ 3 2 1 **Prop-2-en-1-ol**
Secondary Alcohol	 $\underset{1\quad 2\quad 3}{CH_3\overset{\overset{OH}{\vert}}{C}HCH_3}$ **Propan-2-ol** **(Isobutyl alcohol)$^+$**	 $\underset{1\quad 2\quad 3\quad 4}{CH_3\overset{\overset{OH}{\vert}}{C}HCH_2CH_3}$ **Butan-2-ol** **(*sec* Benzyl alcohol)**	 **Cyclohexanol** **(Cyclohexyl alcohol)**
Tertiary Alcohol	 $\underset{1\qquad 2\qquad 3}{CH_3-\overset{\overset{OH}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3}$ **2-Methyl propan-2-ol** **(*tert*-Benzyl alcohol)**	 $\underset{4\qquad 3\qquad 2\qquad 1}{CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-\overset{\overset{CH_3}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CH_3}$ **2,3,3-Trimethylbutan-2-ol**	 **1-Methyloyclohex-1-ol**

* The names given in the brackets are common names.

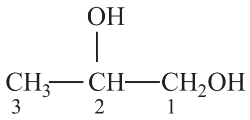
In the above examples, only one –OH group is present in the molecule. These alcohols are called **monohydric** alcohols. Alcohols having **two hydroxyl** groups in a molecule are known as **dihydric alcohols** or **diols** or **glycols**. Examples of some diols are shown below :



$$\underset{OH}{CH_2}-\underset{OH}{CH_2}$$

Ethane-1,2-diol

(Ethylene glycol)



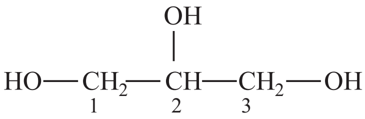
$$\underset{3}{CH_3}-\underset{2}{\overset{OH}{CH}}-\underset{1}{CH_2OH}$$

Propane-1,2-diol

(Propylene glycol)

Note that the term *glycol* generally means 1,2-diol or a **vicinal** diol. In these diols, the two hydroxyl groups are present on the adjacent carbon atoms.

Similarly, alcohols having *three* hydroxyl groups are called *trihydric* alcohols. 1,2,3-propanetriol which is commanly known as *glycerol*, is a trihydric alcohol.



$$HO-\underset{1}{CH_2}-\underset{2}{\overset{OH}{CH}}-\underset{3}{CH_2}-OH$$

1,2,3-Propanetriol

(Glycerol)

26.1.2 General Methods of Preparation

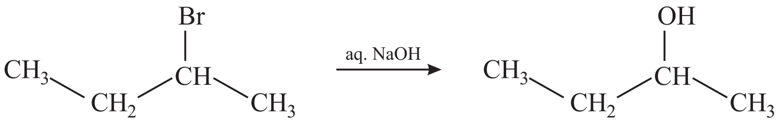
Alcohols are synthesized by the following general methods. You might have come across some of these methods in previous lessons. Let us now study these methods.

1. Hydrolysis of Haloalkanes

Haloalkanes can be converted to corresponding alcohols using aqueous sodium or potassium hydroxide or water as nucleophiles.

$$CH_3CH_2Cl + NaOH(aq.) \longrightarrow CH_3CH_2OH + NaCl$$

Chloroethane **Ethanol**



2-Bromobutane

Butan-2-ol
(90%)

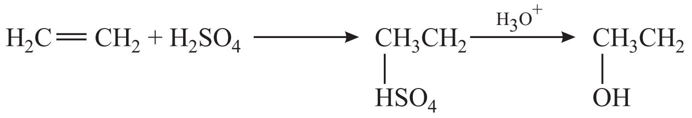
2. From hydration of Alkenes

Hydration means addition of water molecule. In case of alkenes, hydration is the addition of H^+ and OH^- across the double bond to give alcohols.

Alkenes can be hydrated by the following methods:

(i) Acid-catalysed Hydration

Alkenes can be hydrated to yield alcohols in the presence of acid catalysts.

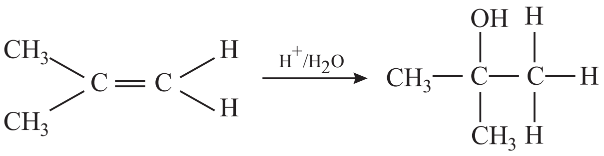


$$H_2C{=}CH_2 + H_2SO_4 \longrightarrow \underset{\displaystyle HSO_4}{\underset{|}{CH_3CH_2}} \xrightarrow{H_3O^+} \underset{\displaystyle OH}{\underset{|}{CH_3CH_2}}$$

Ethene **Ethyl hydrogen sulphate** **Ethanol**

The reaction proceeds via alkyl hydrogen sulphate and this method is used for the industrial preparation of ethanol.

In case of unsymmetric alkenes, the addition follows Markovniokov's rule.

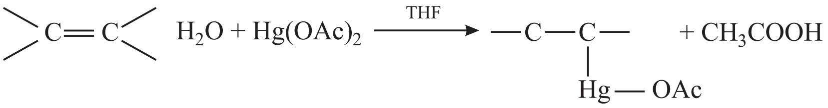


2-Methylpropene **2-Methyl-2-propanol**

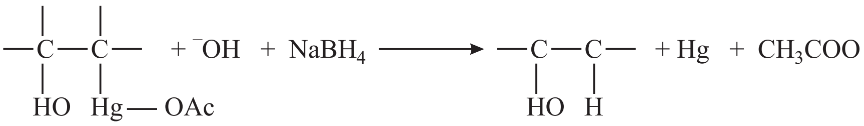
(ii) Oxymercuration-demercuration

Alkenes react with mercury (II) acetate, i.e. mercuric acetate $[Hg(O\overset{\overset{\displaystyle O}{\|}}{C}CH_3)_2$ also represented as $Hg(OAc)_2]$ in aqueous tetrahydrofuran (THF) solvent to give hydroxyalkyl mercury compounds which are reduced to alcohols by sodium borohydride.

Step 1: Oxymercuration

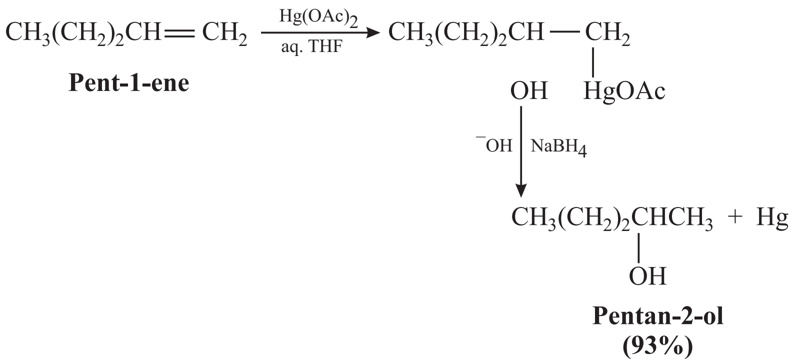


Step 2: Demercuration



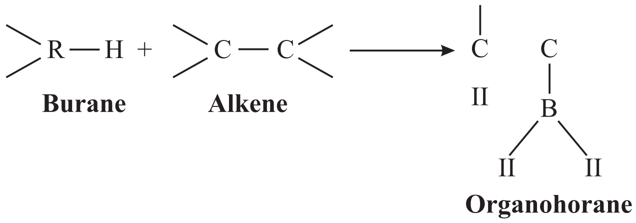
$$\underset{HO\ \ \ Hg-OAc}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-} + {}^-OH + NaBH_4 \longrightarrow \underset{HO\ \ \ H}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-} + Hg + CH_3COO$$

This method gives very good yield of alcohols and here also, the addition takes place in Markovnikov's fashion.

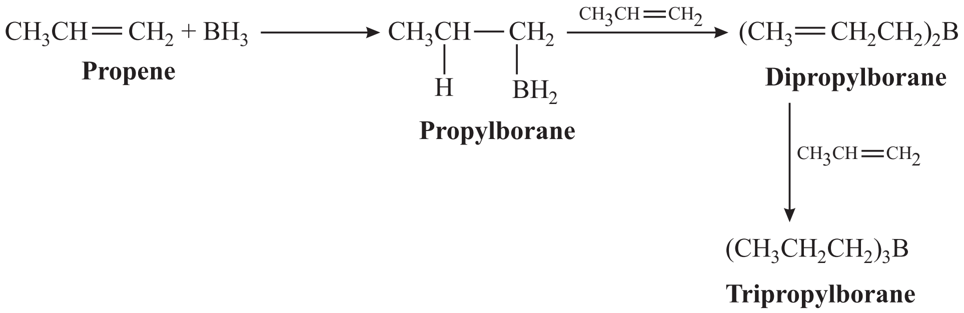


(iii) Hydroboration - Oxidation

When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained.



Since BH_3 has three hydrogens, above addition can occur three times to give trialkylborane (R_3B). This is shown below for propene.



The trialkylborane so obtained is oxidised using alkaline hydrogen peroxide solution to give three molecules of alcohols and boric acid.

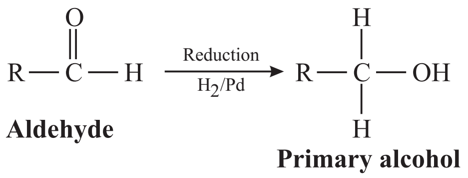
$$\underset{\textbf{Tripropylborane}}{(CH_3CH_2CH_2)_3\,B} \xrightarrow{H_2O_2/^-OH} \underset{\textbf{Propanol}}{3CH_3CH_2CH_2OH} + \underset{\textbf{Boric acid}}{B(OH)_3}$$

Note that hydroboration-oxidation yields the anti-Markovnikov addition of water although the reaction proceeds according to Markonikov's rule.

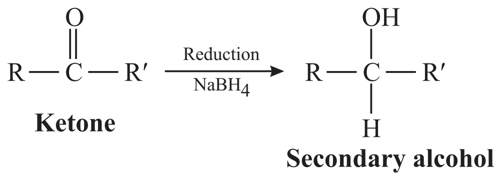
3. Reduction of Carbonyl Compounds

Carbonyl compounds (which contain $\overset{\overset{\text{O}}{\|}}{\text{—C—}}$ group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols.

Aldehydes give primary alcohols while ketones yield secondary alcohols on reduction.

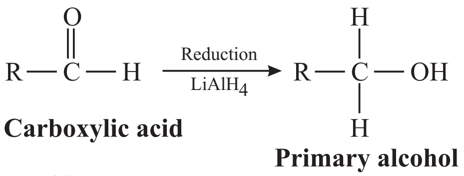


$$\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{H} \xrightarrow[\text{H}_2/\text{Pd}]{\text{Reduction}} \text{R}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{OH}$$



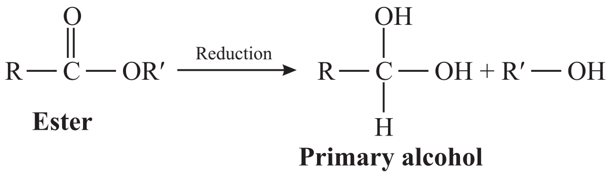
$$\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}' \xrightarrow[\text{NaBH}_4]{\text{Reduction}} \text{R}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{OH}}{|}}{\text{C}}}-\text{R}'$$

Carboxylic acids and esters also give primary alcohols on reduction.



$$\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{H} \xrightarrow[\text{LiAlH}_4]{\text{Reduction}} \text{R}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{OH}$$

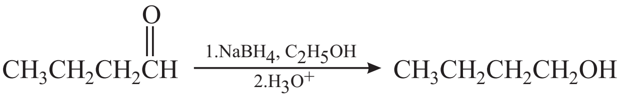
or



$$\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OR}' \xrightarrow{\text{Reduction}} \text{R}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{OH}}{|}}{\text{C}}}-\text{OH} + \text{R}'-\text{OH}$$

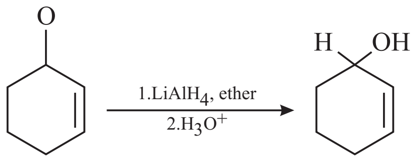
The reduction is carried out using hydride reagents such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). $LiAlH_4$ is stronger and reacts explosively with water while $NaBH_4$ is convenient to handle and reacts slowly.

Lithium aluminium hydride reduces all of the above classes of compounds while sodium borohydride reduces only aldehydes and ketones and does not reduce carboxylic acids and esters. Hence, it can be used to selectively reduce aldehydic/ketonic carbonyl group in presence of carboxylic acid/ester function. Some examples below illustrate the use of these reagents.



$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[2.H_3O^+]{1.NaBH_4,\ C_2H_5OH} CH_3CH_2CH_2CH_2OH$$

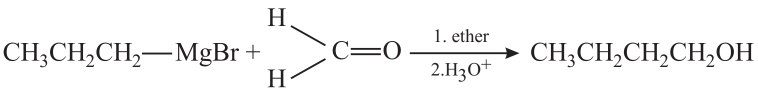
Butan-1-ol



Cyclohex-2-enone **Cyclohex-2-enol**

4. From Aldehydes and Ketones using Grignard Regents

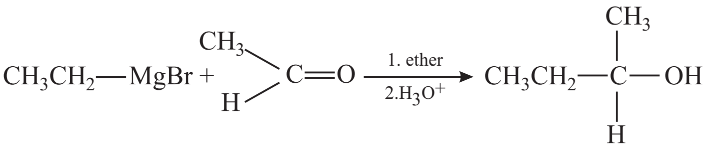
Grignard reagents react with methanal (or formaldehyde) to give a *primary alcohol*.



$$CH_3CH_2CH_2{-}MgBr + \begin{matrix}H\\ \\ H\end{matrix}\!>C{=}O \xrightarrow[2.H_3O^+]{1.\ ether} CH_3CH_2CH_2CH_2OH$$

Propyl magnesium bromide **Methanal** **Butan-1-ol (Primary alcohol)**

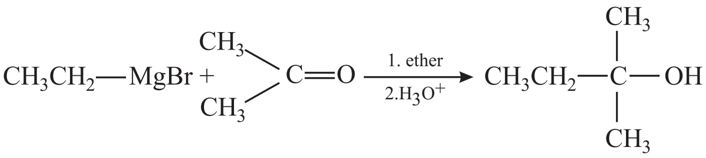
All other aldehydes yield *secondary alcohols* on reaction with Grignard reagents.



$$CH_3CH_2{-}MgBr + \begin{matrix}CH_3\\ \\ H\end{matrix}\!>C{=}O \xrightarrow[2.H_3O^+]{1.\ ether} CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH$$

Ethyl magnesium bromide **Ethanal (Acetaldehyde)** **Butan-2-ol (Secondary alcohol)**

With ketones, Grignard reagents give *tertiary alcohols*.



$$CH_3CH_2{-}MgBr + \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!>C{=}O \xrightarrow[2.H_3O^+]{1.\ ether} CH_3CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH$$

Ethyl magnesium bromide **Propanone** **2-Methylbutan-2-ol**

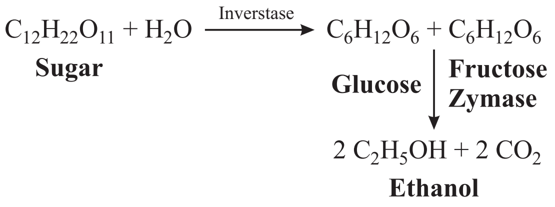
5. Diazotization of Primary Aliphatic Amines

This reaction also yields alchols and will be discussed in Lesson 30.

6. Fermentation

Ethanol is prepared on a large scale using fermentation. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes.

The fermentation of sugar is shown below :



$$\underset{\textbf{Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Inverstase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose **Fructose** **Zymase**

$$\underset{\textbf{Ethanol}}{2\ C_2H_5OH} + 2\ CO_2$$

26.1.3 Structure and Physical Properties

The structure of alcohols is similar to that of water. The structures of water and methanol molecules are shown in Fig. 26.1.

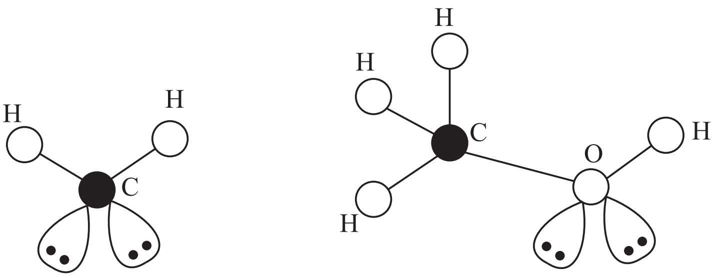


Fig. 26.1: *Water and Methanol molecule*

You know that the electronegativity of oxygen is more than that of hydrogen. Therefore, in alcohols, the O–H bond is polar in nature. In other words, oxygen has a slight negative charge on it whereas hydrogen has a slight positive charge. This bond polarity alone cannot explain the higher boiling points of alcohols as compared to hydrocarbons or similar haloalkanes, as listed in Table 26.2.

Normally, hydrogen bonding is responsible for higher boiling points of alcohols. Hydrogen bonding amongst alcohol molecules is depicted in Fig. 26.2.

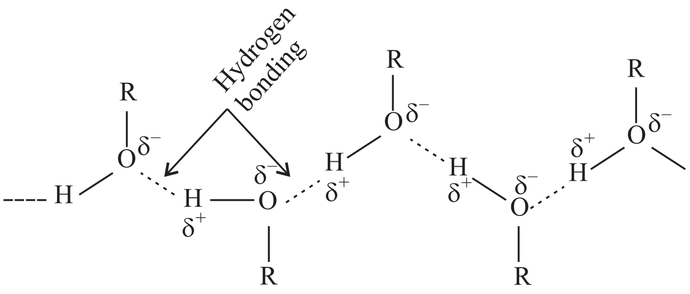
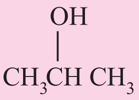
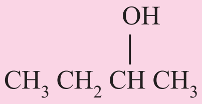


Fig. 26.2: *Hydrogen bonding in alcohol molecules*

You can see that the negatively polarised oxygen atom of one alcohol molecule attracts the positively polarised hydrogen atom of the other molecule. Thus, alcohol molecules are associated or are held together. This force of attraction is to be overcome before a molecule is set free from the liquid state and vaporises. Thus, more heat energy is required to break the hydrogen bonds and hence, the boiling points of alcohols are higher than alkanes and haloalkanes of comparable molecular mass.

Table 26.2: Physical Properties of some Alcohols, Hydrocarbons and related Haloalkanes

Compound	IUPAC Name	Melting Point (K)	Boiling Point (K)	Solubility g/100 mL of water
CH_3OH	Methanol	175.2	322.8	∞
CH_4	Methane	90.5	181.13	–
CH_3Cl	Chloromethane	175.3	248.8	–
CH_3CH_2OH	Ethanol	158.3	351.5	∞
CH_3CH_3	Ethane	189.7	184.4	–
CH_3CH_2Cl	Chloroethane	136.6	285.3	–
$CH_3CH_2CH_2OH$	Propan-1-ol		378.04	∞
$CH_3CH_2CH_3$	Propane	85.3	230.9	–
 $CH_3\underset{}{\overset{OH}{\overset{\vert}{C}}}H\,CH_3$	Propan-2-ol	184	355	∞
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol	183	391	8.3
 $CH_3\,CH_2\,\overset{OH}{\overset{\vert}{C}}H\,CH_3$	Butan-2-ol	159	373	10.0

From the last column of Table 26.2, you must have noticed that alcohols have high solubilities in water. The lower alcohols are completely miscible and their solubilities decrease as the hydrocarbon portion of the molecule becomes larger. The higher solubility of alcohols can be again attributed to the hydrogen bonding. In this case, hydrogen bonding takes place between the alcohol and water molecules as is shown below in Fig. 26.3.

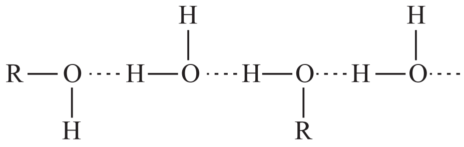


Fig. 26.3: *Hydrogen bonding in a solution of methanol and water*

26.1.5 Reactions of Alcohols

Alcohols exhibit the following reactions:

1. Acidic and Basic behaviour

Alcohol behave both as acids and bases. They are weakly acidic. A strong base such as a hydride ion (H^-) in sodium hydride (NaH), can remove the proton from the alcohol molecule and an alkoxide ion results.

$$R-\ddot{\underset{..}{O}}-H + B\!:^- \rightleftharpoons R-\ddot{\underset{..}{O}}\!:^- + B-H$$

Alcohol **Base** **Alkoxide ion** **Protonated base**

$$CH_3CH_2-\ddot{\underset{..}{O}}-H + B\!:^- \rightleftharpoons CH_3CH_2\ddot{\underset{..}{O}}\!:^- + BH$$

Ethanol **Base** **Ethoxide ion** **Protonated base**

When water is used as a base, the *acid dissociation constant* (K_a) and pK_a can be written as follows:

$$R-O-H + H_2O \overset{K_a}{\rightleftharpoons} R-O^- + H_3O^+$$

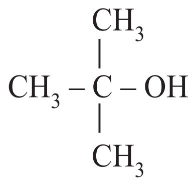
$$K_a = \frac{[H_3O^+][RO^-]}{[ROH]}$$

$$pK_a = -\log K_a$$

Some pK_a values are listed in Table 26.3.

Table 26.3: ***pK_a* values of some compounds**

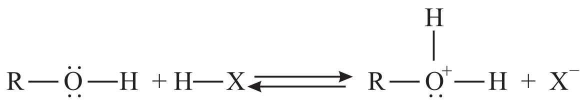
Compound	pK_a
CH_3OH	15.5
H_2O	15.74
CH_3CH_2OH	15.9
$CH_3\underset{\underset{OH}{\vert}}{C}HCH_3$	16.5



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

Remember that the lower the pK_a value, higher is the acidity of the compound.

Alcohols can behave as weak bases also. They have lone pair of electrons on oxygen atom and hence they can be protonated by strong acids to give oxonium ions as shown below:



$$R-\ddot{O}-H + H-X \rightleftharpoons R-\overset{\displaystyle H}{\overset{|}{\overset{+}{O}}}-H + X^-$$

Alcohol **Acid** **Oxonium ion**

2. Formation of Alkoxides

Alcohols react with sodium or potassium metals to give the respective alkoxides.

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2(g)$$

Ethanol **Sodium metal** **Sodium ethoxide**

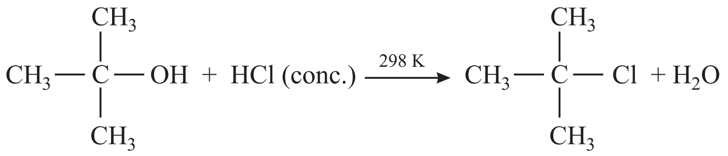
$$(CH_3)_3C-OH + K \longrightarrow (CH_3)_3C-O^-K^+ + \frac{1}{2}H_2(g)$$

***tert*-Butyl alcohol** **Potassium metal** **Potassium *tert*-butoxide**

Alkoxides are used in the synthesis of organic compounds.

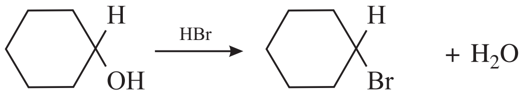
3. Conversion to Alkyl Halides

You have already studied in Lesson 27 that alcohols react with a variety of reagents to form alkyl halides. These are hydrogen halides (such as HCl, HBr or HI), phosphorus tribromide (PBr_3) and thionyl chloride ($SOCl_2$). The reaction involves the breaking of R–OH bond of alcohol molecule.

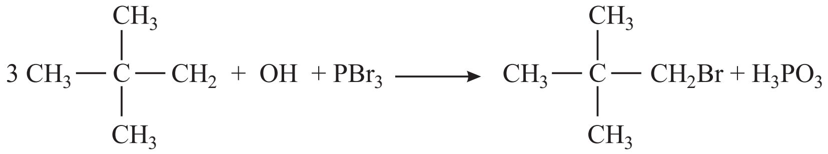


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH + HCl\,(conc.) \xrightarrow{298\ K} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl + H_2O$$

2-Methyl propan-2-ol **2-chloro-2-methyl propan**



Cyclohexanol **Bromocyclohexane**



$$3\,CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2 + OH + PBr_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br + H_3PO_3$$

2, 2-Dimethylpropan-1-ol **1-Bromo-2, 2-Dimethylpropane**

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2(g) + HCl(g)$$

Propan-1-ol **1-Chloropropane**

Tertiary alcohols are readily converted to alkyl halides by HCl or HBr while the best method with primary and secondary alcohols is by using PBr_3 or $SOCl_2$ as the reagents. Another advantage of using $SOCl_2$ is that both the by-products in this reaction, i.e. SO_2 and HCl are gases and hence can be easily eliminated to yield pure alkyl halide.

Lucas Test

The formation of alkyl halides from alcohols is the basis of this test. In involves the reaction of the alcohol with Lucas reagent (i.e. anhyd. $ZnCl_2$ + conc. HCl). Since the reactivity of alcohols is in the following order :

primary alcohols < secondary alcohols < tertiary alcohols

With primary alcohols turbidity does not appear. In case of secondary alcohols, turbidity appears within 5 mintues whereas it appears immediately with tertiary alcohols. The turbidity is due to the formation of alkyl chlorides from the corresponding alcohols.

4. Formation of Alkenes

Alcohols can be dehydrated to alkenes. This reaction requires an acidic catalyst and is favoured at higher tempratures. Usually sulphuric and phosphoric acid are used as acidic catalysts. You have come across this reaction in Lesson 26 also. The ease of dehydration follows the following order amongst alcohols.

tertiary alcohols > secondary alcohols > primary alcohols

26.1.4 Mechanism of Dehydrations of Alcohols

The dehydration of alcohols to give alkenes follows an E1 mechanism. The reaction is acid catalysed. Here, E stands for dimination and 1 denotes that it is unimolecular in nature which means only one molecule is involved in the rate determining step.

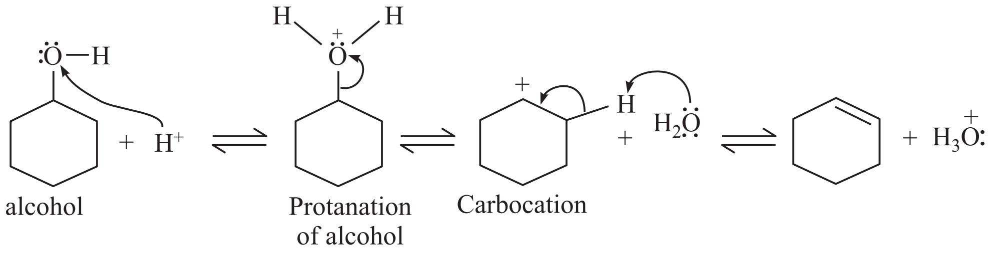
The reaction occurs in three steps :

(i) Protonation of the oxygen of OH group

(ii) Loss of water to give a carbocation

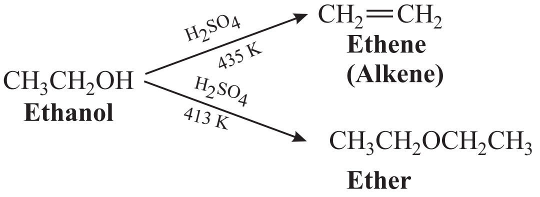
(iii) Loss of a proton from a neighboring carbon atom which produces an alkene

This is shown below:



5. Dehydration to form Ethers

Intermolecular dehydration of alcohols yields ethers. This reaction takes place at a lower temperature than that for dehydration to give alkenes.



The formation of ethers by dehydration is a substitution type of reaction and gives only symmetrical ethers. You will study a better method of synthesis of ethers later under the section of ethers in this lesson.

6. Oxidation

Alcohols can be oxidised to carbonyl compounds. Primary alcohols give aldehydes or carboxylic acids on oxidation while secondary alcohols yield ketones. The tertiary alcohols do not usually undergo oxidation. Normally $KMnO_4$, CrO_3 and $Na_2Cr_2O_7$ or $K_2Cr_2O_7$ are used as oxidising agents.

$$\underset{\textbf{Propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow[H_2O]{K_2Cr_2O_7, H_2SO_4} \underset{\textbf{Propanal}}{CH_3CH_2CHO}$$

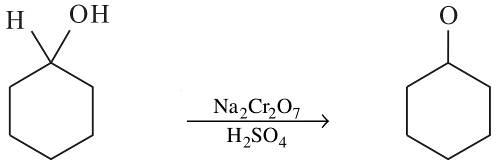
$$\xrightarrow{\text{Further oxidation}} \underset{\textbf{Propanoic acid}}{CH_3CH_2COOH}$$

The aldehydes obtained by oxidation of the primary alcohols get further oxidised to carboxylic acids as shown above. You will study more about these classes of compounds in the next lesson.

The oxidation can be controlled and aldehydes are obtained as the products by using pyridium chlorochromate (PCC) which is a mild reagent.

$$\underset{\textbf{Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{PCC} \underset{\textbf{Decanal}}{CH_3(CH_2)_8CHO}$$

Secondary alcohols can be oxidised to ketones as shown below :



Cyclohexanol **Cyclohexanone**

7. Formation of Esters

Alcohols react with carboxylic acids to form esters. This reaction is discussed in the next lesson.

$$\underset{\textbf{Ethanoic acid}}{CH_3COOH} + \underset{\textbf{Ethanol}}{CH_3CH_2OH} \overset{H+}{\rightleftharpoons} \underset{\textbf{Ethyl ethanoate}}{CH_3COOCH_2CH_3} + \underset{\textbf{Water}}{H_2O}$$

This reaction is called **esterification reaction** and is reversible in nature.

Uses

Alcohols find a large variety of uses as follows :

1. As solvents
2. As laboratory reagents
3. In medicines
4. As thinners in paints, varnishes, etc.

Uses of Methanol and Ethanol

Methanol is toxic to humans and even its small quantities can cause blindness. In larger quantities, its consumptions can cause death. However, it is useful industrially both as a solvent and in the production of formaldehyde and acetic acid, as a starting material. It is also used in the synthesis of which is used as an to gosoline MTBE

$$CH_3OC(CH_3)_3$$

Methyl tert-butyl ether
(MTBE)

Ethanol, obtained by the fermentation of sugars is present in all alcoholic beverages.

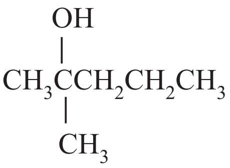
It is also an important industrial chemical. Thus, ethanol used for scientific and industrial purposes is made purposely toxic to prohibit people from consuming it.

Ethanol can be used as a fuel and as a fuel additive. It is also used as a solvent in the manufacture of varnishes and perfumes.

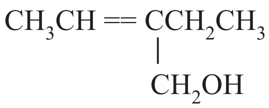
It is also used in hand sanitizers as an antiseptic.

INTEXT QUESTIONS 26.1

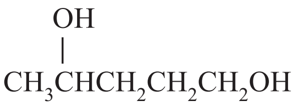
1. Give the IUPAC names of the following alcohols :

(i) 

$$CH_3\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_3$$

(ii) 

$$CH_3CH{=\!=}\underset{\underset{CH_2OH}{|}}{C}CH_2CH_3$$

(iii) 

$$CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2OH$$

2. How will you prepare propan-1-ol from propanal?
3. Give the synthesis of 2-methylpropan-2-ol using Grignard reagent.
4. Give the product of the following reactions:

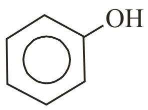
(i) Hexan-1-ol $\xrightarrow[H_3O,H^+]{CrO_3}$

(ii) Hexan-1-ol $\xrightarrow[\text{Chlorochromate}]{\text{Pyridium}}$

5. What is MTBE? GIve its use.
6. What is the product obtained when alcohols are dehydrated?

26.2 PHENOLS

The name phenol is specifically used for the following compound (hydroxybenzene) in which one hydroxyl group is attached to the benzene ring.

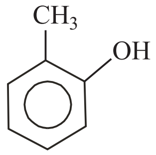


Phenol

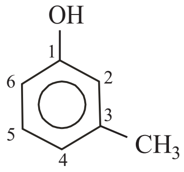
It is also used as a general name for the class of compounds derived from the above compound. Phenol is a disinfactant. Phenols are widely distributed in nature. They are also important in the synthesis of organic compounds such as aspirin and in the preparation of dyes. Phenol is also used in the manufacture of bakelite which is a very useful polymer.

26.2.1 Nomenclature of Phenols

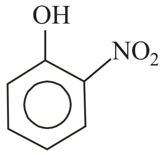
Some representative examples of phenolic compounds are given below:



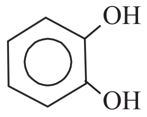
2-Methylphenol
(*o*-Cresol)



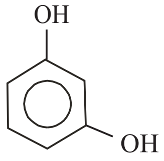
3-Methylphenol
(*m*-Cresol)



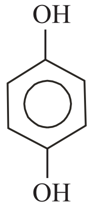
2-Nitrophenol
(*o*-Nitrophenol)



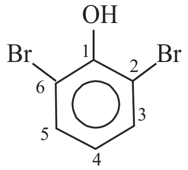
1,2-Benzenediol
(Catechol)



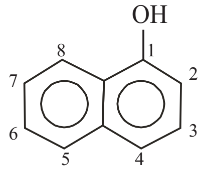
1,3-Benzenediol
(Resorcinol)



1,4-Benzenediol
(Hydroquinone)



2,6-Dibromophenol



1-Naphthol
(α-Naphthol)

Note that the term *phenol* is used as a parent name and the other substituents present in the compound are given a specific number according to their position on the aromatic ring. As done before the common names of the above compounds are given in the brackets below their IUPAC names.

26.2.2 General Methods of Preparation

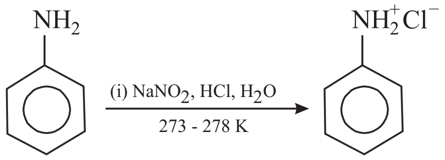
We can categorise the methods of preparation as methods of *laboratory synthesis* and *industrial synthesis* of phenols.

A. Laboratory Synthesis of Phenols

1. From Arenediazonium Salts

It is the most general method of preparation of phenols and requires mild conditions.

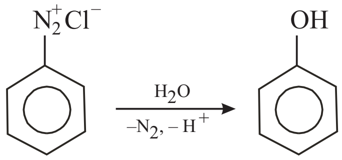
Arenediazonium salts or aromatic diazonium salts are obtained by the *diazotization* of primary aromatic amines as given below :



Benzenamine
(Aniline)
(an aromatic amine)

Benzenediazonium chloride

The arenediazonium salt on hydrolysis yields phenol.

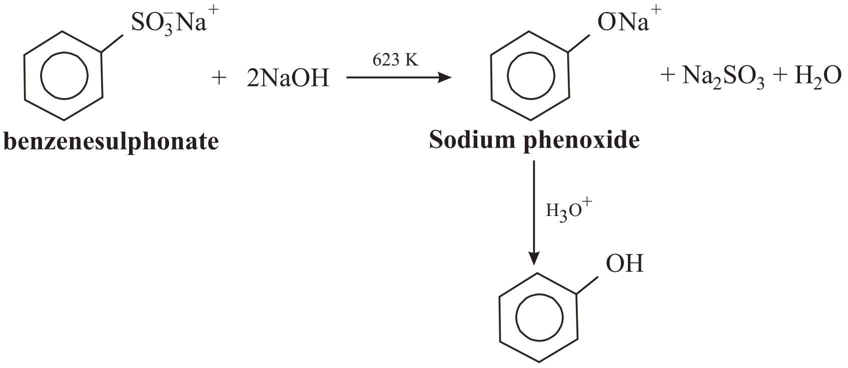


Benzenediazonium chloride **Phenol**

2. Alkali Fusion of Sodium Benzenesulphonate

This was the first commercial synthesis of phenol developed in Germany in 1890. It can also be used as a laboratory method for synthesis of phenol.

Sodium benzenesulphonate is fused with sodium hydroxide to give sodium phenoxide which on acidification yields phenol.

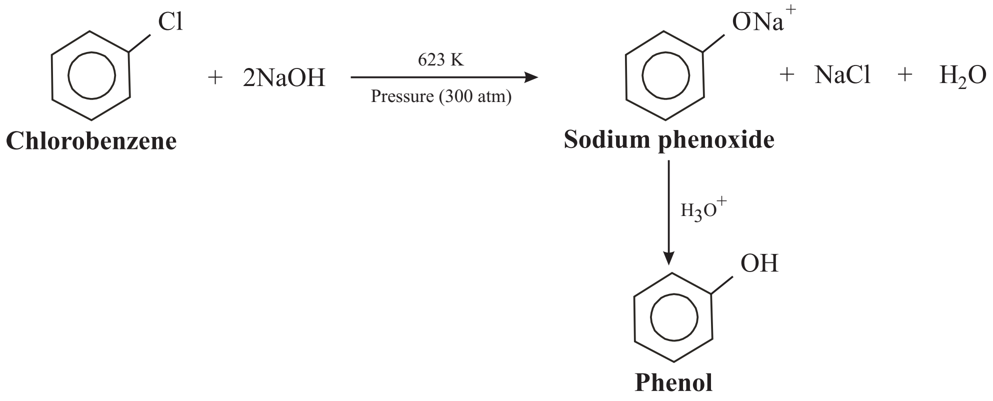


Phenol

B. Industrial Synthesis of Phenols

1. Dow Process

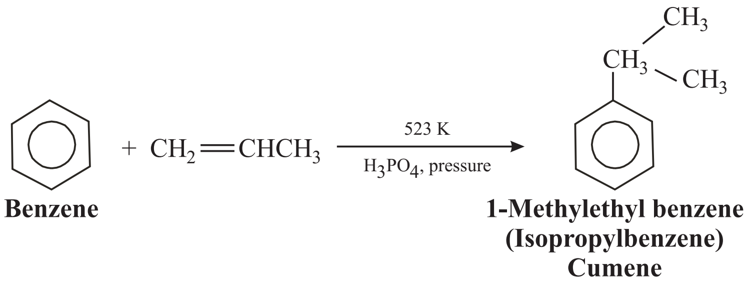
In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.



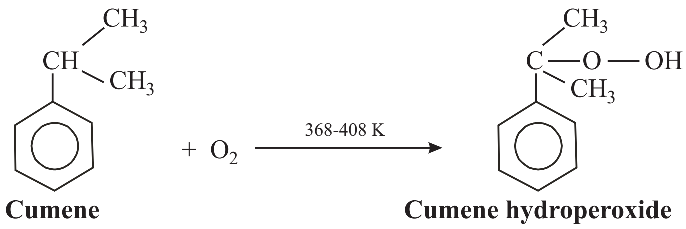
This method was in use for many years but now phenol is synthesised via cumene hydroperoxide which is discussed below.

2. From Cumene Hydroperoxide

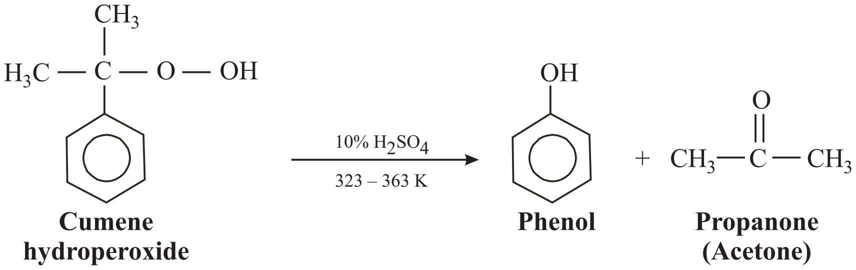
The reaction between benzene and propene in presence of phosphoric acid yields cumene.



Cumene is then oxidised to cumene hydroperoxide by air.



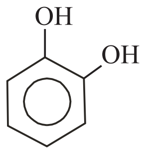
In the final step, cumene hydroperoxide is treated with 10% sulphuric acid to give phenol and acetone on hydrolytic rearrangement.



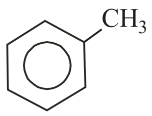
Note that propanone is obtained as a valuable byproduct in this reaction.

26.2.3 Physical Properties

Similar to alcohols, phenols also have hydrogen atom linked to the electronegative oxygen atom. Thus, phenols also exhibit hydrogen bonding and hence have higher boiling points as compared to the hydrocarbons of similar molecular weight.



b.p. – 454.7 K
Phenol



b.p. = 383.6 K
Methylbenzene]
(Toluene)

Due to their ability to form hydrogen bonds, phenols show some water solubility. For example, the solubility of phenol is 9.3 g per 100 mL of water.

26.2.4 Reactions of Phenols

Let us now study the reactions exhibited by phenols.

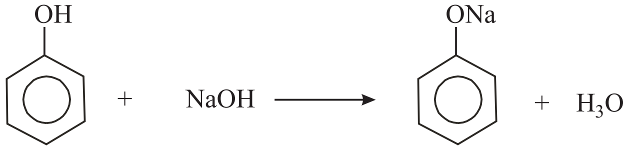
1. Acidic and Basic Nature

Phenols are much more acidic than alcohols. pK_a values of some phenols are listed in Table 26.4.

Table 26.4: pK_a values of phenols

Name	pK_a
Phenol	9.89
2- Methylphenol	10.20
2-Chlorophenopl	8.11
3-Chlorophenol	8.80
2-Nitrophenol	7.17
3-Nitrophenol	8.28
4-Nitrophenol	7.15
2,4,6-Trinitrophenol (Picric acid)	0.38

Since phenols are acidic in nature, they are soluble in dilute sodium hydroxide.



Phenol **Sodium phenoxide**

The greater acidity of phenols can be attributed to the resonance stablisation of the phenoxide ion. The resonance structures of pheoxide ion are shown in Fig. 26.4.

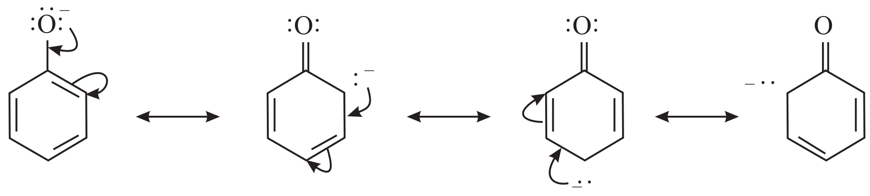


Fig. 26.4: *Resonance structures of phenoxide ion*

The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of alkoxide ions.

Similar resonance is also shown in phenol itself, see Fig 26.5. But the resonance structures of phenol are less stable as compared to those of phenoxide ion as they involve the separation of charge.

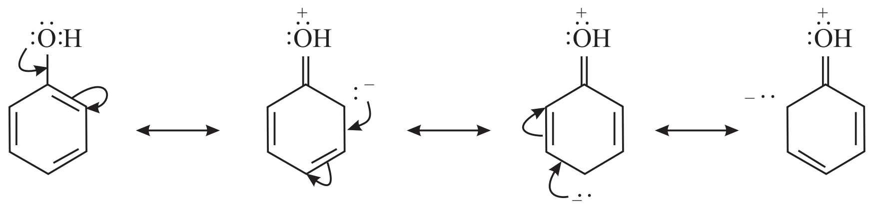
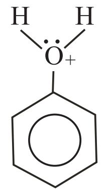


Fig. 26.5: *Resonance structures of phenol*

If you carefully go through the pK_a values given in Table 26.4, you would see that the electron donating substituents such as methyl group decrease the acidity of phenol and hence alkylphenols have greater pK_a values as compared to phenol itself. On the other hand, electron withdrawing substituents increase the acidity and phenols having these substituents (–Cl, –NO_2, etc.) have lower pK_a values than phenol. In fact, 2,4,6-trinitrophenol is more acidic than many carboxylic acids.

Phenols behave as weak bases also. Similar to alcohols, they can also be protonated to give phenyloxonium ion.

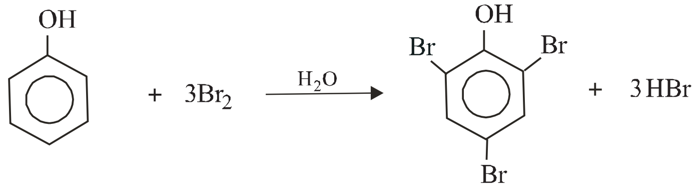


Phenyloxonium ion

2. Electrophilic Substitution Reactions

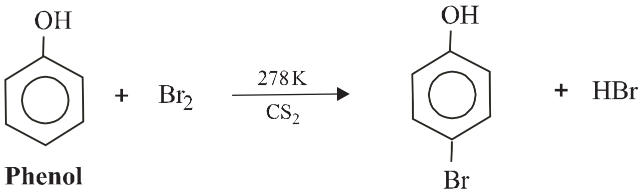
The hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. In this reaction, an **electrophile** (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho* and *para* positions of the phenol are electron rich, the substitution takes place at these positions. Two such reactions are **halogenation** and **nitration** reactions. Let us now study them in details.

(i) Halogenation: Phenol reacts with bromine in aqueous solution to give 2,4,6-tribromophenol in about 100% yield.



Phenol **2,4,6-Tribromophenol**

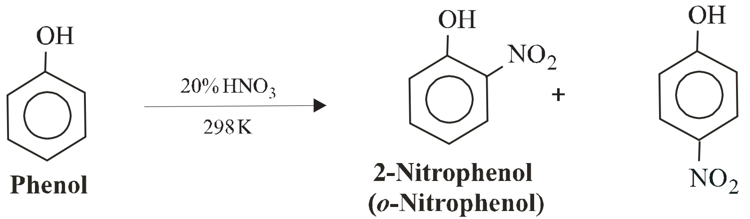
Bromination can be limited to monobromination to give mainly 4-bromophenol using low temprature and less polar solvent such as carbon disulphide. The other product formed in minor quantity is 2-bromophenol.



Phenol

4-Bromophenol

(ii) Nitration: Phenol gives a mixture of 2-nitro and 4-nitrophenols on nitration with dilute nitric acid.

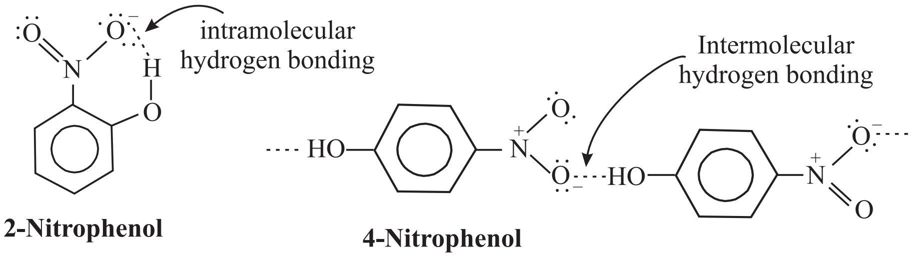


Phenol

2-Nitrophenol
(*o*-Nitrophenol)
(30-40%)

4-Nitrophenol
(*p*-Nitrophenol)
(15%)

The mixture of nitrophenols so obtained is separated using steam distillation. Both these products show hydrogen bonding. In case of 2-nitrophenol, the hydrogen bonding is **intramolecular** (in the same molecule) whereas in case of 4-nitrophenol, it is **intermolecular** (between different molecules). These are depicted in Fig. 26.5.



2-Nitrophenol **4-Nitrophenol**

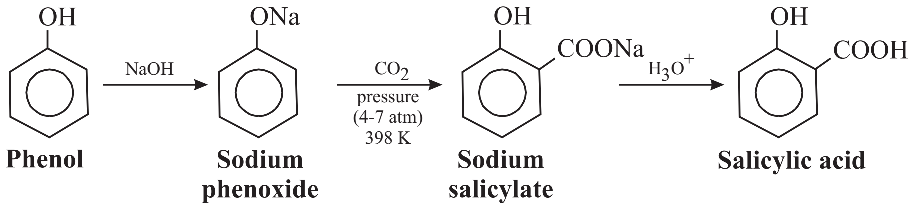
Fig. 26.5 : *Intramolecular and intermolecular hydrogen bonding in nitrophenols*

2-Nitrophenol is steam volatile and distills out on passing steam whereas 4-nitrophenol is less volatile due to intermolecular hydrogen bonding.

Treatment of phenol with a mixture of conc. nitric acid and conc. sulphuric acid at 323K yields 2,4,6-trinitrophenol also known as picric acid.

3. Kolbe Reaction

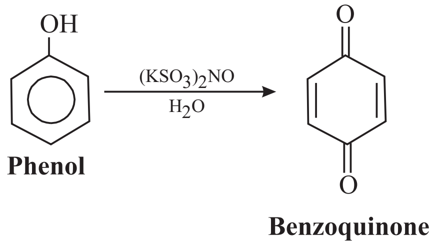
It involves sodium phenoxide which is allowed to absorb carbon dioxide and then heated under a pressure of CO_2 to 398 K. Sodium salicylate so obtained on acidification yields salicylic acid.



By reaction with acetic anhydride, salicylic acid yields *aspirin*, which is the common pain reliever.

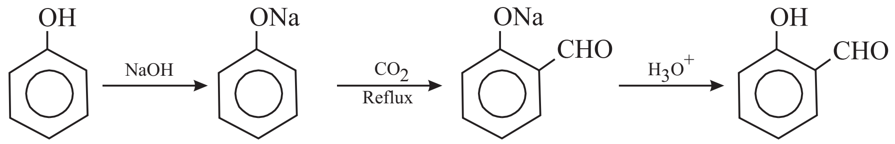
4. Oxidation

Phenols undergo oxidation reactions to give products which are diffrent from those obtained by alcohols. They can be oxidised using a variety of oxidising agents such as sodium dichromate or silver oxide to give quinones. These days Fremy's salt $[(KSO_3)_2NO]$ is preferred for oxidation.



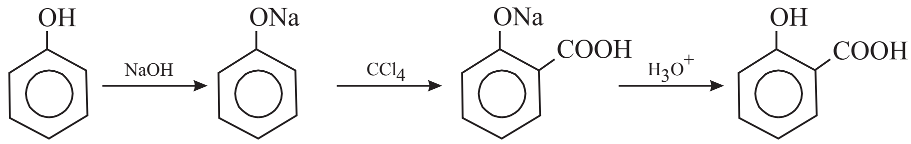
5. Reimer Tiemann Reaction

Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.



Phenol **Sodium phenoxide** **Salicyldehyde**

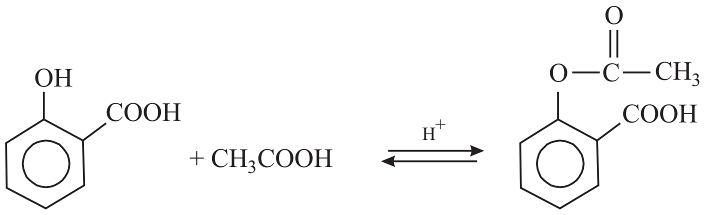
Use of carbon tetrachloride in place of chloroform gives salicylic acid.



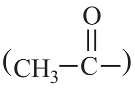
Phenol **Sodium phenoxide** **Salicyldehyde**

6. Esterification

Similar to alcohols, phenols react with carboxylic acids to give esters.

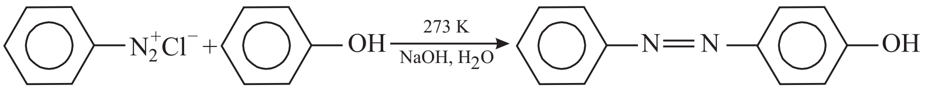


2-Hydroxybenzoic acid **Ethanoic acid** **Acetyl salicylic acid**

This reaction is an acetylation reaction as the H of –OH the phenol is replaced by the acetyl  $(CH_3-\overset{\overset{O}{\|}}{C}-)$ group.

7. Coupling Reaction

Phenols react with aromatic diazonium salts in slightly alkaline conditions to give *azo* compounds. These *azo* compounds are brightly coloured and are used as *azo dyes*.



Benzenediazonium chloride **Phenol** **orange solid *p*-Phenylazophenol (*p*-Hydroxyazobenzene)**

Uses

1. Phenol is used as a disinfectant.
2. It is also used in the synthesis of polymers.
3. Phenols are used in the synthesis of many organic compounds.
4. Substituted phenols are used in dyeing and tanning industries.

INTEXT QUESTIONS 26.2

1. How will you convert aniline to phenol?
2. What is the starting material in Dow's process?
3. Arrange the following in the increasing order of their acidity:
   Phenol, 2-Methylphenol, 2-Chlorophenol
4. How will you prepare salicylic acid from phenol?
5. What is an azo dye?

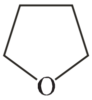
26.3 ETHERS

Ethers are organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups. Thus, ethers can be represented as $R-O-R'$ where R and R' may be alkyl or aryl groups. When the two substituent groups (R and R') are identical, then the ether is called a **symmetrical ether,** otherwise if these two groups are different, then the ether is known as an **unsymmetrical ether.**

$CH_3CH_2 - O - CH_2CH_3$ $CH_3 - O - CH_2CH_3$

A symmetricalether **An unsymmetrical ether**

The oxygen atom of the ether can also be part of a ring, in which case the ether is known as a **cyclic ether**. Tetrahydrofuran is one such cyclic ether which is used as a solvent.



Tetrahydrofuran (THF)

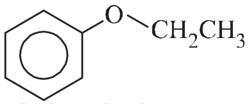
Ethers are commonly used as solvents for organic reactions. The symmetrical ether shown above is diethyl ether and is commonly also referred to simply as *ether* because of its wide use as a solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years.

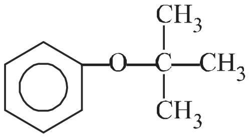
26.3.1 Nomenclature of Ethers

Common names of ethers are arrived by alphabetically naming the two groups attached to the oxygen followed by the word ether. The common names for some ethers are given below :

$CH_3OCH_2CH_3$
Ethyl methyl ether

$CH_3CH_2OCH_2CH_3$
Diethyl ether


Ethyl phenyl ether


***tert*-Butyl phenyl ether**

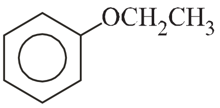
$Cl-CH_2-O-CH_3$
Chloromethyl methyl ether

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane* and the smaller alkyl group is treated as an *alkoxy* substituent on this alkane. For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.

$CH_3OCH_2CH_3$
Ethyl methyl ether

The remaining portion , *i.e.*, $-OCH_3$ part in this case, is called the methoxy substituent. Hence, the above ether is called **methoxyethane.** Some more examples of IUPAC names of ethers are given below :

$CH_3CH_2OCH_2CH_3$
Ethoxy ethane


Ethoxybenzene

$CH_3O\overset{1}{C}H_2\overset{2}{C}H_2OCH_3$
1,2-Dimethoxyethane

26.3.2 General Methods of Preparation

You have already studied under the reactions of alcohols that ethers can be obtained by the dehydration of alcohols. Ethers can also be prepared by Williamson synthesis which is explained below :

Williamson Synthesis : It involves the reaction of a metal alkoxide with a primary alkyl halide. The metal alkoxide is prepared by adding sodium or potassium metal or sodium hydride (NaH) to the alcohol.

$$< ROH + Na \longrightarrow RO^-Na^+ + \frac{1}{2}H_2 >$$

Metal alkoxide

$< ROH + NaH \longrightarrow RO^{-}Na^{+} + H_2 >$

Metal alkoxide

$< RO^{-}Na^{+} + R'-X \longrightarrow R-O-R' + NaX >$

Metal alkoxide **Alkyl halide** **Ether**

$CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2ONa \xrightarrow{CH_3CH_2I}$
propan-1-ol **Sodium propoxide**

$CH_3CH_2CH_2OCH_2CH_3 + NaI$
1-Ethoxypropane
(Ethyl propyl ether)

Williamson synthesis involves the displacement of the halide ion by the alkoxide ion.

26.3.3 Sturcture and Properties of Ethers

Ethers have geometry similar to water and alcohols. The oxygen atom is sp^3 hybridised. There are two lone pairs of electrons present on the oxygen atom as is shown in Fig. 26.6.

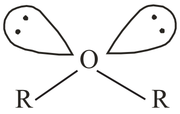


Fig. 26.6 : *Geometry of an ether molecule*

Note that the ether molecule has a bent structure. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar is nature (Fig. 26.7). Ethers, thus, act as polar solvents.

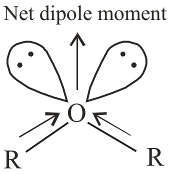
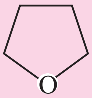
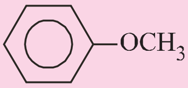


Fig. 26.7 : *Polar ether molecule*

Since ethers do not have a hydrogen atom linked to the oxygen atom, they cannot form hydrogen bonds amongst their own molecules. Due to the absence of hydrogen bonding, they have lower boiling points as compared to alcohols having similar molecular masses. The boiling boints of some ethers are listed in Table 26.5.

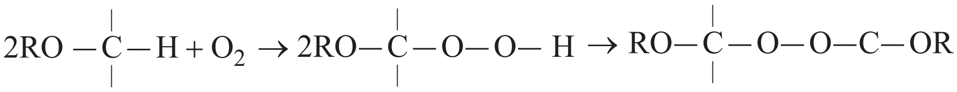
Table 26.5 : Boiling points of some common ethers

Ether	Boiling point (K)
CH_3OCH_3	248.1
$CH_3OCH_2CH_3$	283.8
$CH_3CH_2OCH_2CH_3$	307.6
$CH_3OCH_2CH_2OCH_3$	356
	338.4
	431.3

26.3.4 Reactions of Ethers

Ethers are normally unreactive in nature. Their unreactivity makes them good solvents. However, they show some reactions which are discussed below :

1. Reaction with Oxygen : Ethers slowly react with oxygen to form hydroperoxides and peroxides.



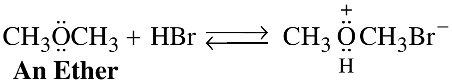
$$2RO-\underset{|}{\overset{|}{C}}-H + O_2 \rightarrow 2RO-\underset{|}{\overset{|}{C}}-O-O-H \rightarrow RO-\underset{|}{\overset{|}{C}}-O-O-C-OR$$

Ether **Ahydroperoxideofether** **Aperoxide of ether**

Peroxides have a tendency to explode. Therefore, one should be very careful in handling ethers which may have been stored for sometime because they may contain some peroxide.

2. Reaction wtih Acids

Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature.



$$CH_3\ddot{\underset{..}{O}}CH_3 + HBr \rightleftharpoons CH_3\underset{H}{\overset{+}{\ddot{O}}}CH_3Br^-$$

An Ether **An oxonium salt**

3. Acidic Cleavage

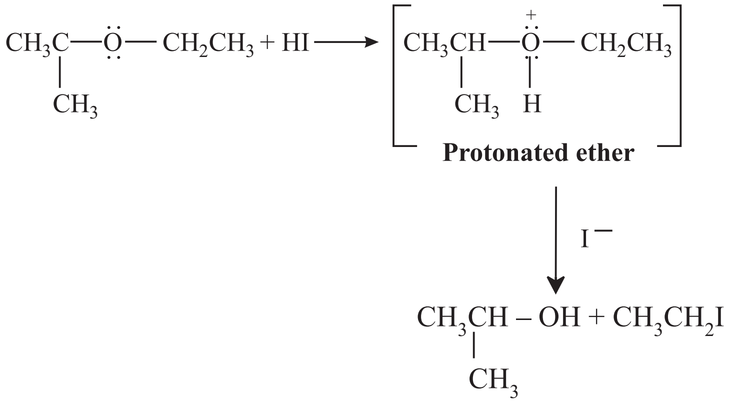
Heating dialkyl ethers with strong acids such as HI, HBr or H_2SO_4 leads to their cleavage.

$$\underset{\textbf{Ethoxyethane}}{CH_3CH_2OCH_2CH_3} + HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3CH_2Br} + \underset{\textbf{Ethanol}}{CH_3CH_2OH}$$

The alcohol formed further reacts with additional HBr to give bromoethane. Hence,

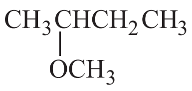
$$CH_3CH_2OCH_2CH_3 + 2HBr \longrightarrow 2CH_3CH_2Br + H_2O$$

In case of ethers having primary or secondary alkyl groups, the nucleophile (Br^- or I^-) attacks the less hindered alkyl group. Thus, in case of the following unsymmetrical ether, the products contain alkyl halide formed by the attack of the halide ion on the less hindered primary alkyl group, *i.e.*, ethyl group.



INTEXT QUESTIONS 26.3

1. What are the IUPAC names of the following ethers ?

   (i) 
   $\underset{\displaystyle OCH_3}{CH_3\underset{|}{C}HCH_2CH_3}$

   (ii) $CH_3–O–CH_3$

2. (i) How will you prepare methyl propyl ether using Williamson synthesis?

   (ii) What is the IUPAC name of methyl propyl ether ?

3. Why should you be careful in using old stock of ethers.

4. Why are ethers good solvents ?

5. What is tetrahydrofuran ? Give its structure and use.

WHAT YOU HAVE LEARNT?

In this lesson, you have learnt that

- Alcohols can be classified as primary, secondary or tertiary.
- Alcohols can be monohydric, dihydric or polyhydric.
- Alcohols can be prepared by the following general methods :

  – Hydrolysis of haloalkanes

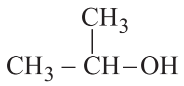
  – Hydration of alkenes

  – Reduction of carbonyl compounds

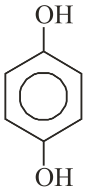
  – From aldehydes and ketones using Grignard reagents
- Alcohols behave both as weak acids and weak bases.
- Alcohols can be converted to alkyl halides, alkenes, ethers, aldehydes, ketones, carboxylic acids and esters.
- In the laboratory, phenols can be prepared from arenediazonium salts and sodium benzene sulphonate. Their industrial preparation is done by Dow's process and from cumene hydroperoxide.
- Similar to alcohols, phenols can also behave both as acids and bases.
- Typical reactions of phenols being electrophilic substitution reactions such as halogenation, sulphonation, nitration, etc.
- Phenols undergo oxidation and also exhibit Reimer Tiemann reaction. They react with aromatic diazonium salts to give azo dyes.
- Ethers can be symmetrical or unsymmetrical.
- Ethers can be prepared by Williamson synthesis.
- Dialkyl ethers are cleaved on heating with strong acids .

TERMINAL EXERCISE

1. Give the IUPAC names of the following compounds :

(i) 
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-OH$

(ii) $C_6H_5OCH_2CH_3$

(iii) 

2. Compare the boiling points of ethyl alcohol and dimethyl ether. Which one has higher boiling point and why ?

3. Which ester would give ethanol and methanol on reduction?

4. Complete the following reactions :

   (i) $CH_3CH_2CH_2Cl$ + NaOH (aq.) $\longrightarrow$ ....

   (ii) $CH_3CHO \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4,\ ether}$ ....

   (iii) CH_3OH + Na $\longrightarrow$ ....

5. How is ethanol prepared using fermentation?

6. What is Lucas test? What is its use?

7. Which reagent is used for oxidising primary alcohols to aldehydes?

8. Why are phenols more acidic than alcohols? Explain.

9. Why are ethers polar in nature?

ANSWERS TO INTEXT QUESTIONS

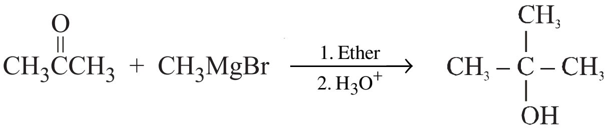
26.1

1. (i) 2-Methylpentan-2-ol

   (ii) 2-Ethylbut-2-en-1-ol

   (iii) 1, 4-Pentanediol

2. By reduction with $NaBH_4$ or $LiAlH_4$

3. 

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ Ether} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

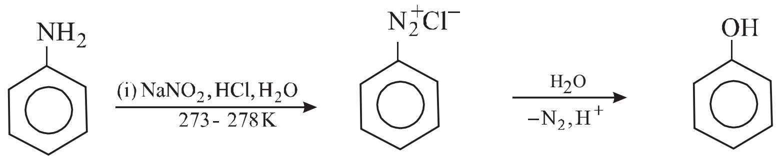
4. (i) Hexanoic Acid

   (ii) Hexanal

5. MTBE is methyl tert-butyl ether. It is used as an additive to gasoline.
6. Alkenes.

26.2

1.



Aniline **Benzenediazonium chloride** **Phenol**

2. Chlorobenzene
3. 2-Methylphenol < Phenol < 2-Chlorophenol
4. By Kolbe reaction
5. Azo dyes are azo compounds formed by the reaction of phenols with aromatic diazonium salts. They are brightly coloured.

26.3

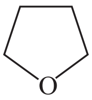
1. (i) 2-Methoxybutane

   (ii) Methoxymethane

2. (i) $CH_3CH_2CH_2O^- + CH_3Br \longrightarrow CH_3CH_2 - O - CH_3 + Br^-$

   (ii) Methoxypropane

3. They may explode due to the presence of peroxides.
4. Because they are unreactive in nature.
5. It is a cyclic ether.



It is used as a solvent.

313en27

27

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

In the last lesson, you studied about organic compounds containing functional groups having carbon-oxygen single bond. There are other classes of organic compounds in which the functional group contains the carbon- oxygen double bond. The examples of these classes of compounds being carbonyl compounds such as *aldehydes* and *ketones* as well as *carboxylic acids* and their *derivatives*. These organic compounds are very important both in the industry and in the synthesis of other organic compounds. Therefore, their study forms an important part of the organic chemistry. Let us study the chemistry of these classes of compounds in detail.

OBJECTIVES

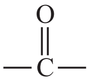
After reading this lesson, you should be able to

- give IUPAC names of aldehydes and ketones;
- describe the general methods of preparation of aldehydes and ketones;
- discuss the trends in physical properties of the aldehydes and ketones in the light of the polar nature of the carbonyl group;
- explain important reactions exhibited by aldehydes and ketones;
- distinguish between aldehydes and ketones on the basis of certain reactions and tests based on them;
- give IUPAC names of carboxylic acids;
- explain general methods of preparation of carboxylic acids;
- discuss the physical properties and their trends for simple monocarboxylic acids;
- describe important reactions exhibited by carboxylic acids;

- explain the preparation and some interconversion reactions of carboxylic acid derivatives, and
- highlight the importance of aldehydes, ketones and carboxylic acids.

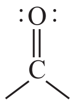
27.1 ALDEHYDES AND KETONES

You have some familiarity with these classes of compounds from previous lessons. These compounds are also referred to as *carbonyl compounds* and have

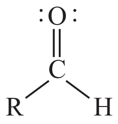


$-\overset{\overset{\displaystyle O}{||}}{C}-$ functionality present in them. These compounds exist widely in nature and are responsible for the flavour and aroma of many foods. They are also important industrially both as reagents in synthesis and as solvents.

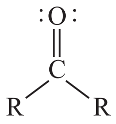
Aldehydes have at least one hydrogen atom bonded to the carbonyl group, the other group may be either a hydrogen or an alkyl (or aryl) group. In *ketones*, the carbonyl group is bonded to two alkyl or aryl groups. The two groups bonded to a ketone may be similar or different resulting in a symmetrical or an unsymmetrical ketone, respectively.



Carbonyl group

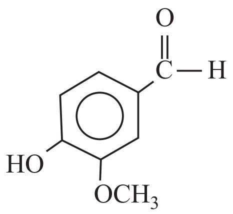


an aldehyde

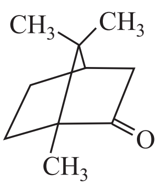


a ketone

You must be familiar with vanilin and camphor. Their structures are given below. You can see that they contain an aldehyde and a keto functional group, respectively.



Vanilin
(used for vanila flavour)

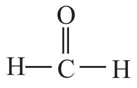


Camphor

27.1.1 Nomenclature of Aldehydes and Ketones

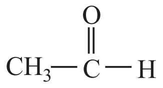
In the IUPAC system of nomenclature, aliphatic *aldehydes* are named as ***alkanals***. The final *-e* in the name of the corresponding alkane is substituted by *-al*.

Some common examples of aldehydes and their names are given below :



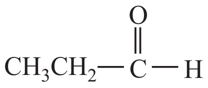
$H-\overset{\overset{O}{\|}}{C}-H$

Methanal
(Formaldehyde)



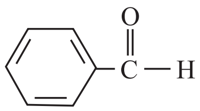
$CH_3-\overset{\overset{O}{\|}}{C}-H$

Ethanal
(Acetaldehyde)



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-H$

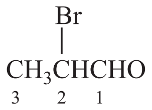
Propanal
(Propionaldehyde)



Benzenecarbaldehyde
(Benzaldehyde)

Note that when the -CHO group is attached to a ring, then the compound is called a *carbaldehyde*.

Remember that the carbonyl carbon of the aldehydes is present at the end of the chain and is assigned 1 position. Therefore, it is not necessory to specify its position in the name of the aldehyde. The examples given below illustrate this point.



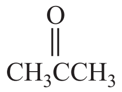
$\underset{3}{CH_3}\overset{\overset{Br}{|}}{\underset{2}{C}}H\underset{1}{C}HO$

2-Bromopropanal

$ClCH_2CH_2CH_2CHO$
4 3 2 1

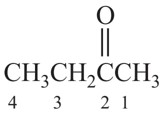
4-Chlorobutanal

Ketones are named as ***alkanones*** in the IUPAC namenclature. Their names are obtained by replacing final -*e* in the name of alkane by -*one*. The carbon chain is numbered in such a way that the carbonyl group gets the lowest number. Some examples of ketones are mentioned below :



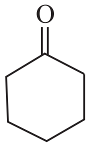
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

Propanone
(Acetone)

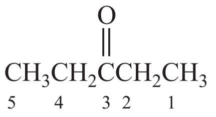


$\underset{4}{CH_3}\underset{3}{CH_2}\overset{\overset{O}{\|}}{\underset{2}{C}}\underset{1}{CH_3}$

Butan-2-one
(Ethyl methyl ketone)

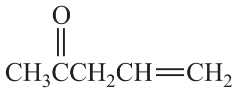


Cyclohexanone



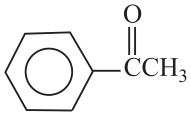
$\underset{5}{CH_3}\underset{4}{CH_2}\overset{\overset{O}{\|}}{\underset{3}{C}}\underset{2}{CH_2}\underset{1}{CH_3}$

Pentan-3-one
(Diethyl ketone)

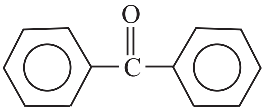


$CH_3\overset{\overset{O}{\|}}{C}CH_2CH{=}CH_2$

Pent-4-en-2-one



1-Phenylethanone
(Acetophenone)



(Benzophenone)

27.1.2 Preparation of Aldehydes and Ketones

You have already studied most of the methods used in the synthesis of aldehydes and ketones in the previous lesson. Let us now refresh them.

1. Oxidation of Primary and Secondary Alcohols

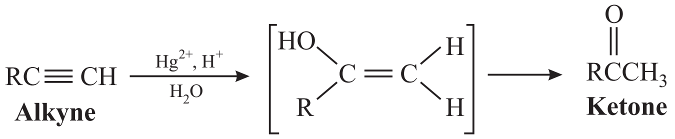
From the last lesson, you know that primary alcohols can be oxidised to aldehydes and secondary alcohols can be oxidised to ketones.

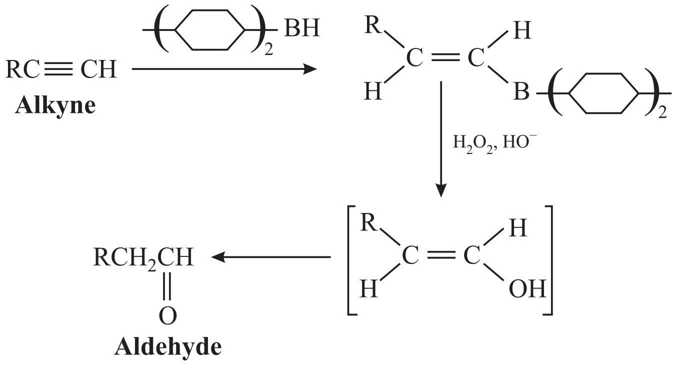
2. Ozonolysis of Alkenes

This reaction has been discussed in lesson 26. The products obtained are aldehydes or ketones depending upon the structure of the starting alkene.

3. Hydration of Alkynes

Hydration of alkynes can give an aldehyde or a ketone. Markovnikov's hydration yields ketones whereas anti-Markovnikov's hydration gives aldehydes.

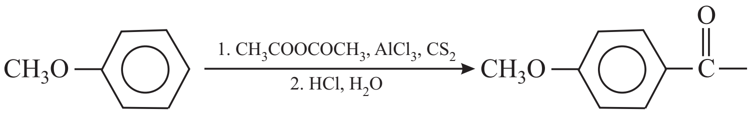




You can go through the details of these reactions as discussed in lesson 26.

4. Friedal-Crafts Acylation

Aromatic ketones can be prepared by Friedel-Crafts acylation (alkanoylation) reaction. One example of this reaction is given below:



Similar acylation reaction using ethanoyl chloride was also discussed in lesson 26 under the **electrophilic substitution** reactions of aromatic hydrocarbons.

27.1.3 Structure and Physical Properties

In both aldehydes and ketones, the carbonyl carbon and oxygen atoms are sp^2 hybridised. Therefore, the groups attached to the carbon atom and oxygen are present in a plane. This is shown in Fig. 27.1.

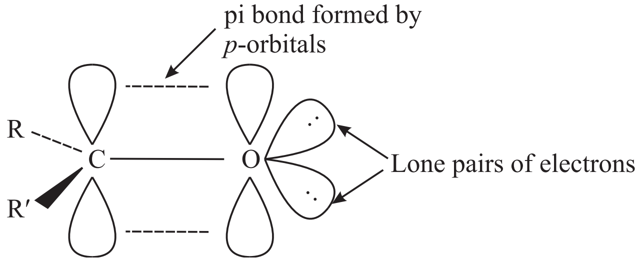
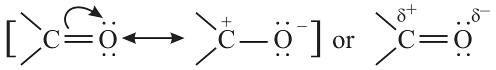


Fig. 27.1 : *The structure of the carbonyl functional group*

You can see in the figure that a π-bond is formed by the overlap of *p*-orbitals of carbon and oxygen atoms. The *p*-orbitals are present in a plane perpendicular to the plane of the molecule. Note the presence of two lone pairs of electrons on oxygen atom.

You also know that oxygen is more electronegative than carbon. Hence, it attracts the electrons of the carbon-oxygen double bond ($>C=O$ bond) resulting in its appriciable polarisation.



The oxygen atom, thus, acquires a partial negative charge (δ^-) whereas the carbon atom gets a partial positive charge (δ^+). This polar nature of the carbonyl group makes the oxygen atom ***nucleophilic*** and **basic** while the carbon atom becomes ***electrophilic***. The physical properties and chemical reactions of aldehydes and ketones are a direct consequence of this polarisation.

The dipole-dipole attraction between the molecules of aldehydes and ketones results in their higher boiling points as compared to the hydrocarbons of similar molecular weight. The physical properties of some aldehydes and ketones are given in Table 27.1.

Table 27.1 Physical properties of some representative aldehydes and ketones

Compound	m.p. (K)	b.p. (K)	Water Solubility (%)
Methanal	181	252	55
Ethanal	150	294	∞
Propanal	192	322	20

Butanal	166	348	7.1
Benzaldehyde	217	452	0.3
Propan-2-one	178	329	∞
Butan-2-one	187	353	25.6
Pentan-2-one	195	375	5.5
Pentan-3-one	232	374	4.8
Acetophenone	294	475	15
Benzophenone	321	578	–

You can see from Table 27.1 that these compounds have appriciable water solubility. This is because of the hydrogen bonding possible between the oxygen atom of the aldehyde (or the ketone) with hydrogen atom of water molecule, as shown in Fig 27.2.

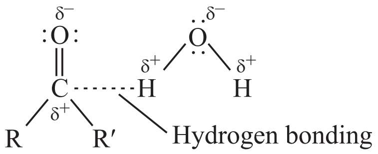
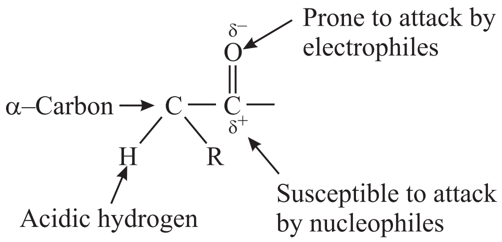


Fig. 27.2 : *Hydrogen bonding between carbonyl compound and water molecule*

27.1.4 Reactions of Aldehydes and Ketones

If you examine the structure of a molecule of the carbonyl compound, you will find that there are three centres of reactivity in it as shown below :



Since the oxygen atom is *nucleophilic* in nature, it is attacked by the *electrophiles*, whereas the carbonyl carbon is *electrophilic* in nature and hence is attacked by *nucleophiles*. The third site of reactivity is hydrogen atom present at the α- carbon atom. It is *acidic* in nature and gives typical reactions which you will study in this section.

It is also important to know here that aldehydes are more reactive than ketones. This is because of the following two reasons :

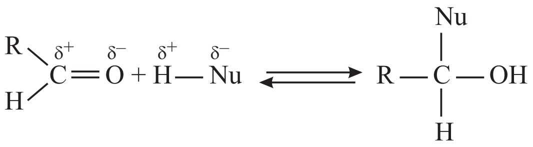
(i) Aldehydes have only one alkyl group whereas ketones have two. Since the alkyl groups are electron donating in nature, the carbonyl carbon in ketones which is bonded to two alkyl groups, is less positive (electrophilic) as compared to the aldehydic carbonyl carbon. Hence, it is less susceptible to attack by nucleophiles.

(ii) The two alkyl groups in ketones also make the carbonyl carbon more crowded as compared to carbonyl carbon in aldehydes. This factor also makes the aldehydic carbonyl carbon more accessible for attack by the nucleophiles as compared to carbonyl carbon of the ketone.

With this background in mind, let us now study the reactions of aldehydes and ketones.

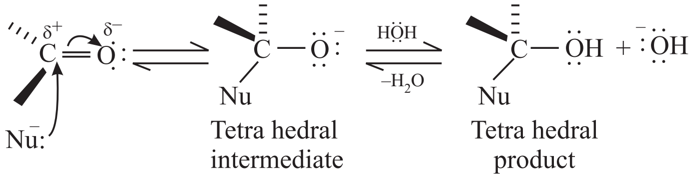
A. Nucleophilic Addition Reactions

The general reaction of addition of nucleophiles on the carbonyl group can be represented as follows :

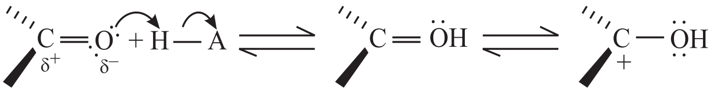


Mechanism of Nucleophilic Addition

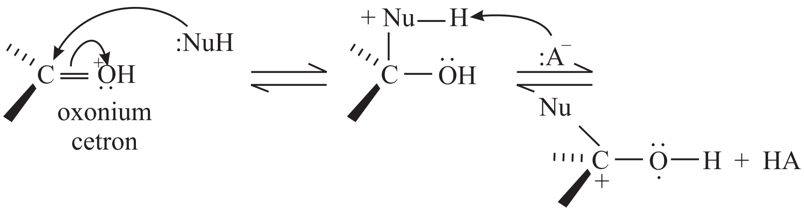
Under basic conditions, the nucleophile attacks at the carbonyl group yields a tetrahedral intermediate. Subsequent to this, the protonation from a solvent (H_2O or alcohol) takes place. This is shown below:



However, in acidic additions, in the first step the protonation of the carbonyl oxygen takes place.



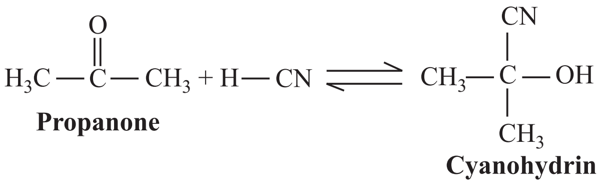
The nucleophile then attacks in the second step to carbonyl carbon and the addition process is completed.



Some specific reactions of this category are discussed below :

1. Formation of Cyanohydrins

Carbonyl compounds react with hydrogen cyanide to yield *cyanohydrins*.



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + H-CN \rightleftharpoons CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}}-OH$$

Propanone **Cyanohydrin**

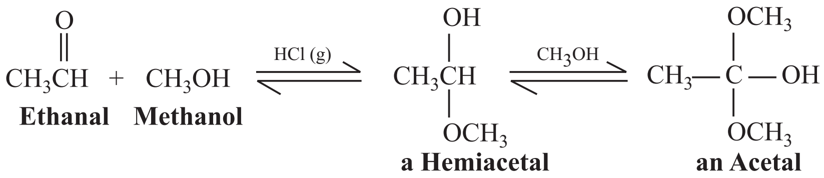
Note that one more carbon atom is present in the cyanohydrin as compared to the starting carbonyl compound.

Cyanohydrins are useful in the synthesis of carboxylic acids about you will study in the next section.

2. Formation of Hemiacetals

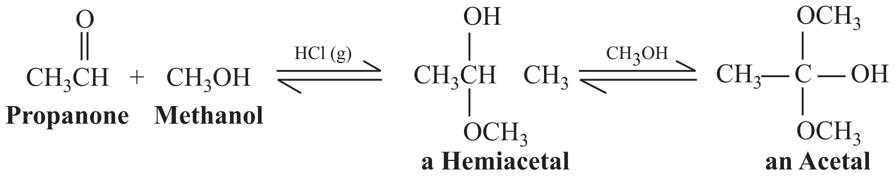
Aldehydes and ketones react with alcohols to give *hemiacetals*. *Hemi* in Greek means *half*. Hemiacetals have an –OH and an –OR group attached to the same carbon atom in their molecules.

When an excess of the alcohol is used, a second molecule of the alcohol reacts to give an *acetal.*



$$CH_3\overset{\overset{O}{\|}}{C}H + CH_3OH \xrightleftharpoons{HCl\,(g)} CH_3\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{C}}H \xrightleftharpoons{CH_3OH} CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-OH$$

Ethanal **Methanol** **a Hemiacetal** **an Acetal**



$$CH_3\overset{\overset{O}{\|}}{C}H + CH_3OH \xrightleftharpoons{HCl\,(g)} CH_3\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{C}}H\ \ CH_3 \xrightleftharpoons{CH_3OH} CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-OH$$

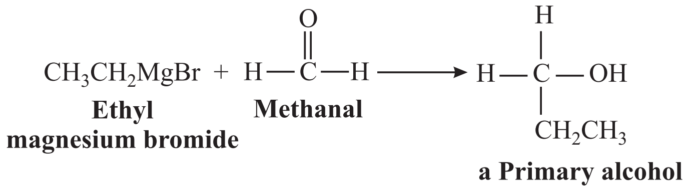
Propanone **Methanol** **a Hemiacetal** **an Acetal**

Note that an acetal has two —OR groups attached to the same carbon atom.

Acetals are stable in basic solutions and are 'therefore' used as protecting groups for aldehydes and ketones. Acetals can be converted back to the carbonyl compounds by treating them with dilute acids because of the reversible nature of the above reaction.

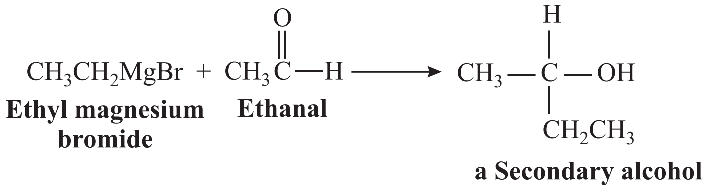
3. Formation of Alcohols

Grignard reagents (RMgX) react with aldehydes and ketones to give alcohols as shown below :



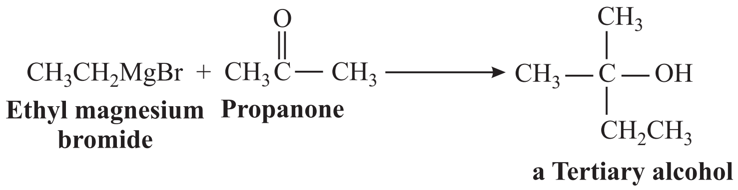
$$CH_3CH_2MgBr + H-\overset{\overset{O}{\|}}{C}-H \longrightarrow H-\underset{CH_2CH_3}{\overset{H}{C}}-OH$$

Ethyl magnesium bromide **Methanal** **a Primary alcohol**



$$CH_3CH_2MgBr + CH_3\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-\underset{CH_2CH_3}{\overset{H}{C}}-OH$$

Ethyl magnesium bromide **Ethanal** **a Secondary alcohol**



$$CH_3CH_2MgBr + CH_3\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{CH_2CH_3}{\overset{CH_3}{C}}-OH$$

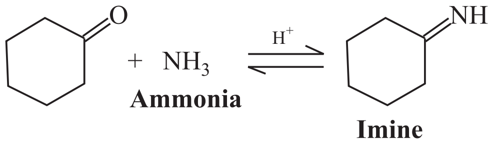
Ethyl magnesium bromide **Propanone** **a Tertiary alcohol**

You have already studied these reactions under the preparation of alcohols in lesson 28.

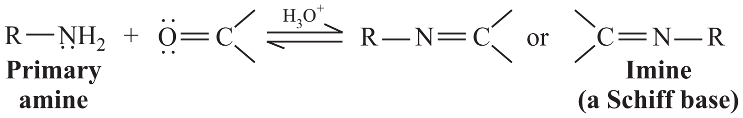
B. Addition-Elimination or Condensation Reactions

1. Reaction with Ammonia and its Derivatives

Aldehydes and ketones react with ammonia and primary amines to give **imines** which are compounds having carbon-nitrogen double bond.

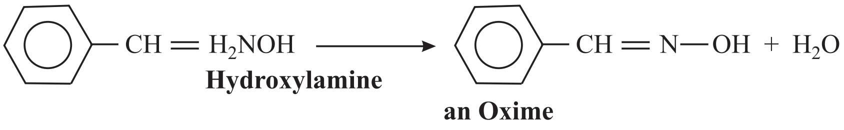


Ammonia **Imine**

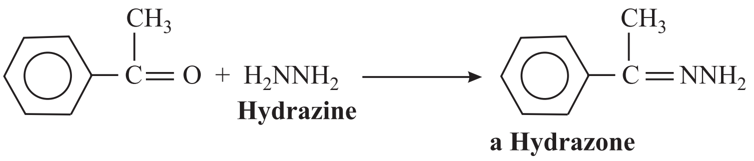


Primary amine **Imine (a Schiff base)**

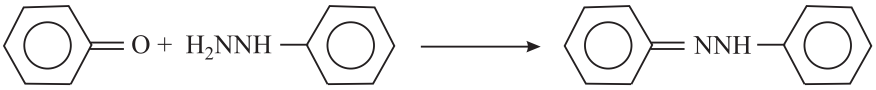
It appears that during the above reaction a molecule of water is lost from the primary amine and the carbonyl compound. The reactions with other derivatives of ammonia are given below:



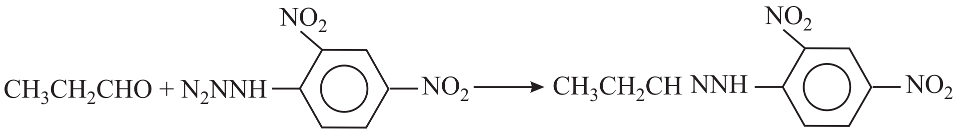
Hydroxylamine **an Oxime**



Hydrazine **a Hydrazone**



Phenylhydrazine **a Phenylhydrazone**



2, 4-Dinitrophenzylhydrazine **2, 4-Dinitrophenzylhydrazone**

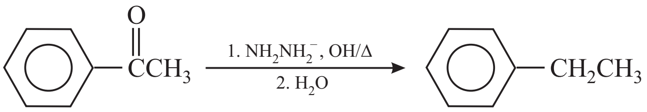
The compounds formed above are relatively insoluble solids and have characteristic melting points. These compounds can be prepared for the unknown aldehyde or ketone and their melting points can be determined. These melting points are matched with the derivatives of already known aldehydes and ketones listed in standard tables and the carbonyl compound is thus identified.

C. De-oxygenation Reactions

De-oxygenation reactions are reactions involving removal of oxygen. Aldehydes and ketones can be reduced to the corresponding alkanes by the following two reactions:

1. Wolff-Kishner Reduction

When an aldehyde or a ketone is heated in a basic solution of hydrazine in a high-boiling alcohol, then the carbonyl group gets converted to a methylene ($>CH_2$) group.



Ethylbenzene

2. Clemmensen Reduction

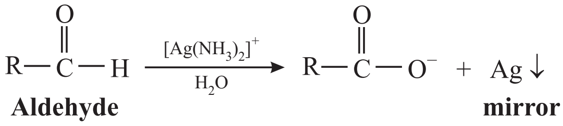
It is carried out in acidic medium using amalgamated zinc and hydrochloric acid.

$$CH_3(CH_2)_5CHO \xrightarrow[HCl,\ H_2O]{Zn(Hg)} CH_3(CH_2)_5-CH_3$$

Heptanal **Heptane**

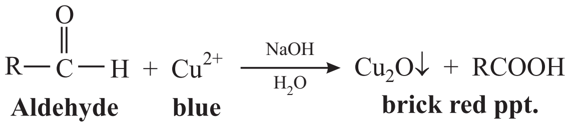
D. Oxidation of Aldehydes

Unlike ketones, aldehydes can be easily oxidised to carboxylic acids using a variety of oxidising agents. These reagents can be chromic acid, chromium trioxide, permanaganate or silver oxide. You have already read about oxidation with some of these reagents. *Silver ions selectively oxidise —CHO group*. This forms the basis of *Tollen's test*. It involves the addition of a mixture of aqueous silver nitrate and aqueous ammonia which is known as *Tollen's reagent* to the carbonyl compound. Tollen's reagent contains $[Ag(NH_3)_2]^+$ complex ion. If an aldehyde is present, it gets oxidised to the carboxylic acid whereas the Ag^+ ions are reduced to form silver metal which gets deposited on the walls of the test tube and this gives a mirror like shining appearance.



$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow[H_2O]{[Ag(NH_3)_2]^+} R-\overset{\overset{O}{\|}}{C}-O^- + Ag\downarrow$$

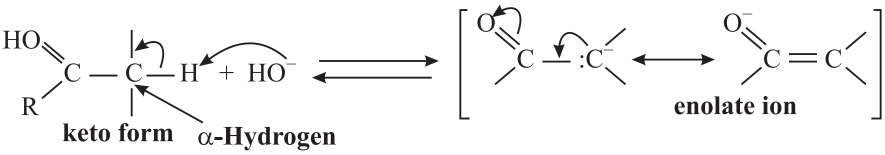
Aldehydes are also oxidised by *Fehling solution*, which contain Cu^{2+} (cupric) ions complexed with tartarate ions as the oxidant. These Cu^{2+} ions are reduced by the aldehydes in alkaline medium to give a brick red precipitate of cuprous oxide.



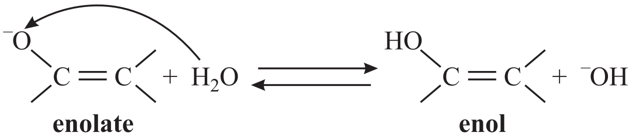
$$R-\overset{\overset{O}{\|}}{C}-H + Cu^{2+} \xrightarrow[H_2O]{NaOH} Cu_2O\downarrow + RCOOH$$

E. Reactions at α-carbon

The $\alpha-$hydrogen in aldehydes and ketones is quite acidic and can be easily abstracted by a strong base.



The resulting anion can stabilise by resonance as shown above. It is called an *enolate ion*. On protonation, it gives an *enol*.

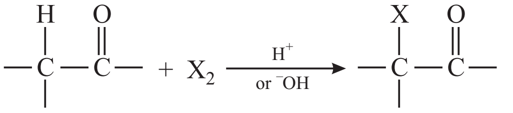


Thus, keto form and enol form are in equilibrium. This is also known as ***keto-enol tautomerism.***

Other reactions feasible due to the presence of α-hydrogen are as follows:

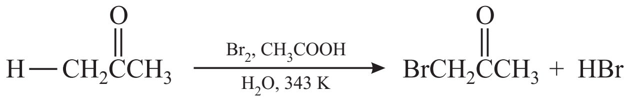
1. Halogenation

Ketones having an α-hydrogen atom react readily with halogens and α-haloketones are obtained as the product. The reaction is promoted both by acids and bases.



α-halo product

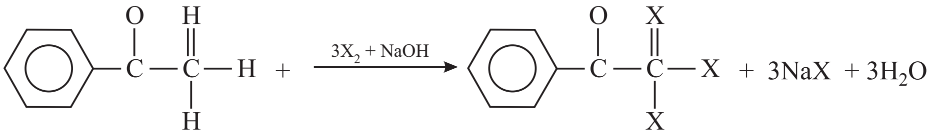
$(X_2 = Cl_2, Br_2 \text{ or } I_2)$



$$H-CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[H_2O,\ 343\ K]{Br_2,\ CH_3COOH} BrCH_2\overset{O}{\overset{\|}{C}}CH_3 + HBr$$

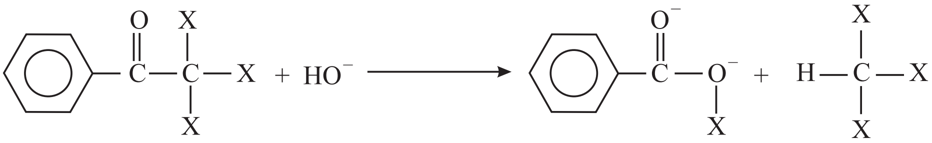
Propanone **Bromopropanone**

In presence of the base, multiple halogenation occurs to give the trihalo product.



trihaloketone

The trihalo group is a good leaving group and the trihalo ketone reacts with OH^- which finally gives a carboxylate ion and a *haloform*.



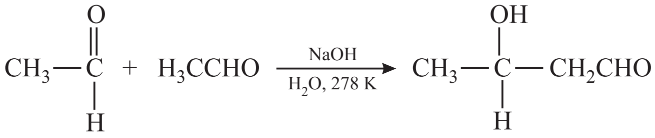
trihaloketone **Carboxylate ion** **Haloform**

This reaction is called the ***haloform reaction*** after the name of the product.

If iodine is used as the halogen, then we get *iodoform* (CHI_3) as the product. The iodoform is a bright yellow solid having a characterstic melting point. This reaction, thus, forms the basis of the *iodoform test.* Thus, methyl ketones give a positive iodoform test. You had studied the iodoform formation in lesson 27 also.

2. Aldol Condensation

Aldehydes having α – hydrogen atom on reaction with dil. NaOH give *aldols*. The reaction is illustrated below by using ethanal as the example.

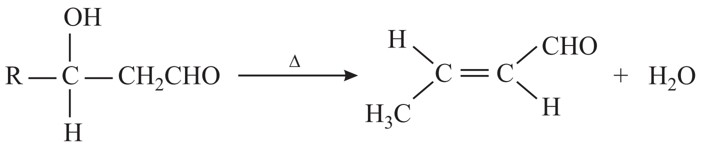


$$CH_3-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}} + H_3CCHO \xrightarrow[H_2O,\ 278\ K]{NaOH} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CHO$$

Ethanal **Ethanal** **3-Hydroxybutanal (an Aldol)**

Note that the product contains both the *aldehyde* and the *alcohol* functional groups and therefore, it is called an *aldol*. The aldol addition product on heating undergoes dehydration to give an α, β– unsaturated aldehyde which is a condensation product.

Notes



Aldol → ***trans*-But-2-enal**

This complete sequence of reactions is called ***aldol condensation.***

Aldol condensation is also possible with ketones. Can you now think of a little more complex situation? What will be the products of aldol condensation when two diffrent aldehydes having $\alpha -$ hydrogen atoms are used as reactants. In this case, the reaction is called a ***crossed-aldol condensation.*** This is left as an exercise for you. There is a hint of course. Suppose, the two aldehyde molecules are represented by A and B; then condensation can occur between two molecules of the same aldehyde or diffrent aldehydes. Thus, the products obtained would be the following types:

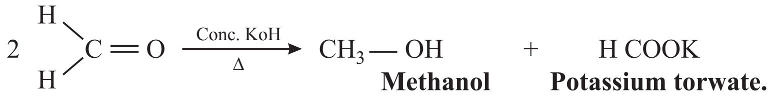
A-A, B-B, A-B and B-A.

With this background in mind, you can now proceed to write the aldol addition products of ethanal and propanal.

3. Cannizzaro Reaction

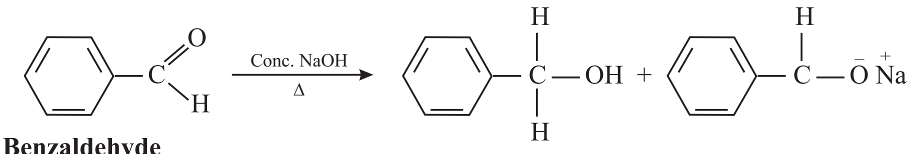
Aromatic or aliphatic aldehydes which do not have α-hydrogen, an reaction with conc. KOH/NaOH give one molecule of and alcohol and sodium salt of the carboxylic acids. This reaction is known as **Carnizzaro reaction.**

In this reaction, one molecule of the aldehyde is oxidised to carboxylic acid salt (sod. or pot. salt) and another molecule of the aldehyde is reduced to alcohol molecule. For example,



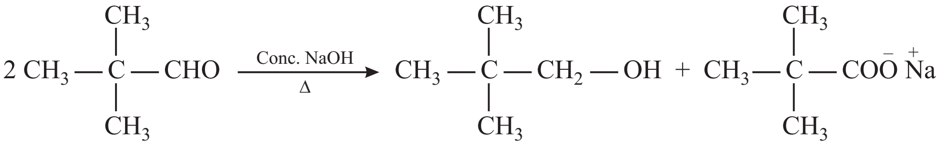
Methanol **Potassium torwate.**

Methanol



Benzaldehyde

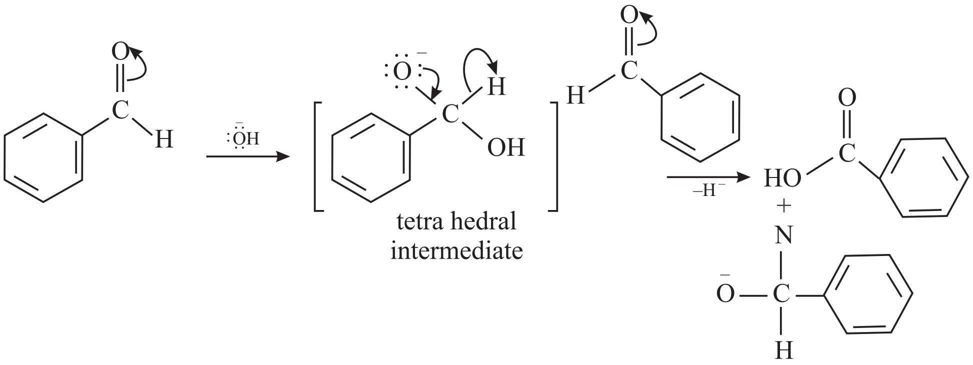
Benzyl alcohol **Sodium benzoate**



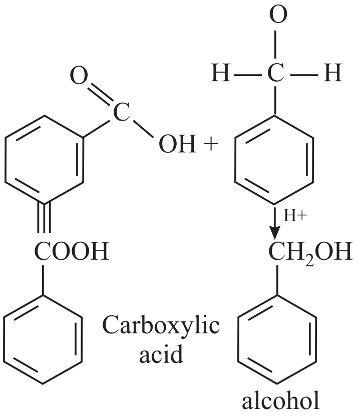
2,2 -dimethyl propanal

2,2 -dimethyl propan-1-01

This reaction takes place by nucleophilic addition of —OH to an aldehyde to give tetrahedral intermediate. This intermediate expels a hydride ion as the leaving group.



This hydride ion is accepted by second molecule of aldehyde

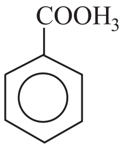


Thus, we can say, that *disproportonation* has occurred and simultaneous *oxidation* and *reduction* has taken place to give one molecule of a carboxylic acid and are molecule of an alcohol from the two molecules of the starting aldehyde. This reaction is limited to those aldehydes only which have no hydrogen on carbon next to the CHO group.

INTEXT QUESTIONS 27.1

1. Classify the following as aldehydes or ketones and give their IUPAC names:

   (i) CH_3CHO (ii) $CH_3COCH_2CH_3$

   (iii)  (iv) $OHCCH_2CH_3$

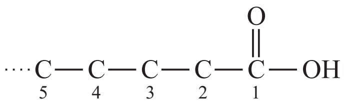
2. How will you prepare propanone from propyne ?
3. Why are aldehydes more reactive than ketones towards nucleophilic addition reactions?
4. Write the general structure for the following :
   (i) a cyanohydrin (ii) an acetal (iii) a hemiacetal
5. How can you convert the carbonyl $\left(>C=O\right)$ group to $\left(>CH_2\right)$ group ?
6. What is an aldol?
7. Write the equation for cannizzaro reaction using a suitable example.

27.2 CARBOXYLIC ACIDS

You already know that carboxylic acids contain a **carboxyl (—COOH)** funtional group. They are most widely distributed in nature and are also industrially important chemicals. *Acetic acid* in the form of vinegar is produced in large quantities. It is also a very important building block in complex biological molecules. You must have also heard about *fatty acids* which are long chain aliphatic acids derived from the hydrolysis of fats and oils. Stearic acid is a fatty acid containing a long chain of eighteen carbon atoms.

27.2.1 Nomenclature

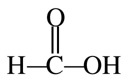
Several carboxylic acids have been known since long and their common names are based on their sources. However, in the IUPAC nomenclature, carboxylic acids are named by choosing the longest carbon chain containing the –COOH group. The final *-e* in the name of the alkane is replaced by *-oic acid.* While numbering the carbon chain, the –COOH carbon is always given number 1 as shown below :



$$\cdots\underset{5}{C}-\underset{4}{C}-\underset{3}{C}-\underset{2}{C}-\underset{1}{\overset{\overset{O}{\|}}{C}}-OH$$

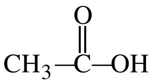
The other groups and substituents are numbered and named according to the usual rules of nomenclature which you have already studied.

Some common carboxylic acids and their names are given below :



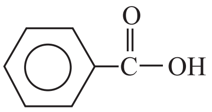
$$H-\overset{\overset{O}{\|}}{C}-OH$$

Methanoic acid
(Formic acid)



$$CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Ethanoic acid
(Acetic acid)



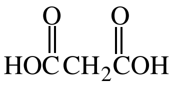
Phenylmethanoic acid
(Benzoic acid)

Carboxylic acids containing two carboxyl groups are called **dicarboxylic acids.**

They are named by adding **dioic acid** as a suffix to the name of the corresponding hydrocarbon. Both the carboxyl carbon atoms are numbered as a part of the main chain. Note that in this case, final-*e* of the alkane is **not** dropped.

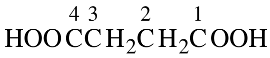
$HO\underset{1}{\overset{\overset{O}{\|}}{C}}\underset{2}{\overset{\overset{O}{\|}}{C}}OH$

Ethanedioic acid
(Oxalic acid)



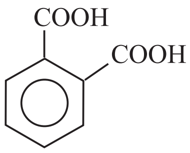
$HO\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OH$

Propanedioic acid
(Malonic acid)

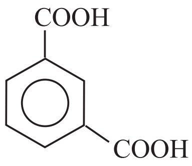


$HOO\overset{4}{C}\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$

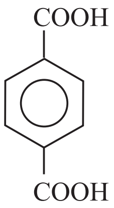
Butane-1,4-dioic acid
(Succinic acid)



***o*-Phthalic acid**
(Phthalic acid)



***m*-Phthalic acid**
(Isophthalic acid)



***o*-Phthalic acid**
(Terephtyhalic acid)

27.2.2 Preparation of Carboxylic Acids

The following methods are generally used for the synthesis of carboxylic acids. You have already studied some of these methods in the earlier lessons.

1. Oxidation of Alkenes

Alkenes on oxidation with hot alkaline $KMnO_4$ yield carboxylic acids.

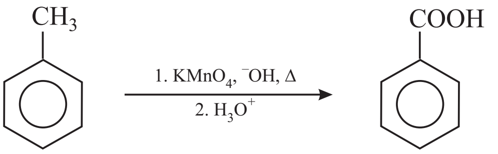
$$RCH{=}CHR' \xrightarrow[2\cdot H_3O^+]{1\cdot KMnO_4,\ {}^-OH} RCOOH + R'COOH$$

2. Oxidation of Alcohols and Aldehydes

You have read in the last lesson and the previous section of this lesson that alcohols and aldehydes can be oxidized to carboxylic acids using a variety of oxidising agent. You can refer back to the details of these reactions.

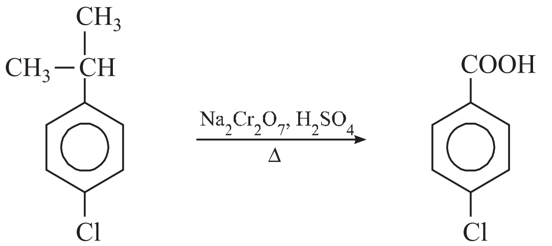
3. Oxidation of Alkylbenzenes

Primary and secondary alkyl groups attached to the benzene ring can be oxidised, using alkaline $KMnO_4$, to the carboxyl group.



Methylbenzene **Benzoic acid**

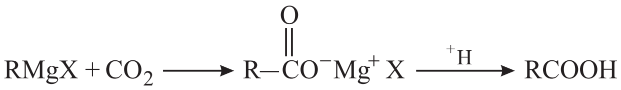
Acidified sodium dichromate can also be used for this oxidation.



***p*-Chlorobenzoic acid**

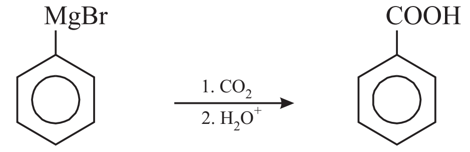
4. Carbonation of Grignard Reagents

Grignard reagents (RMgX) react with carbon dioxide to give magnesium carboxylates which on acidification yield carboxylic acids.



$$RMgX + CO_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}O^-Mg^+X \xrightarrow{^+H} RCOOH$$

$$\underset{\substack{\textbf{Chloroethane}\\\textbf{(an alkyl halide)}}}{CH_3CH_2Cl} \xrightarrow[Et_2O]{Mg} \underset{\textbf{Grignard reagent}}{CH_3CH_2MgCl} \xrightarrow[2\cdot H_3O^+]{1\cdot CO_2} \underset{\textbf{Propanoic acid}}{CH_3CH_2COOH}$$

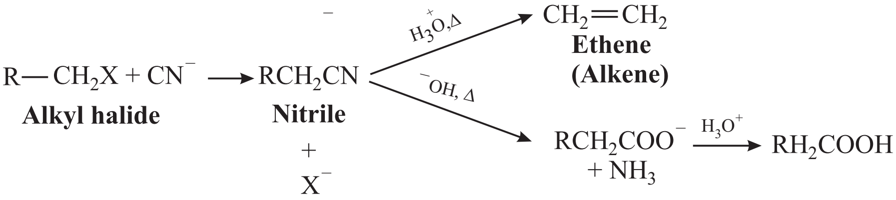


Phenyl magnesium bromide **Benzoic acid**

Note that there is an increase of one carbon atom in the carboxylic acid as compared to the starting alkyl halide.

5. Hydrolysis of Nitriles and Cyanohydrins

Alkyl halides can be converted to *nitriles* which on hydrolysis yield carboxylic acids having *one more carbon atom than the starting alkyl halide.*

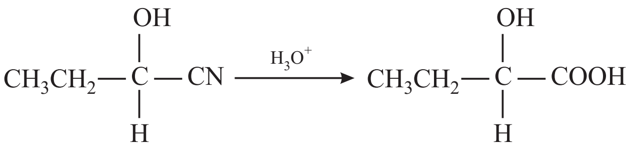


$$\underset{\textbf{Alkyl halide}}{R-CH_2X + CN^-} \longrightarrow \underset{\substack{\textbf{Nitrile}\\+\\X^-}}{RCH_2CN} \xrightarrow{H_3O^+,\Delta} \underset{\substack{\textbf{Ethene}\\\textbf{(Alkene)}}}{CH_2{=}CH_2}$$

$$RCH_2CN \xrightarrow{^-OH,\ \Delta} \underset{+\ NH_3}{RCH_2COO^-} \xrightarrow{H_3O^+} RH_2COOH$$

$$\underset{\textbf{1, 2-Dibromoethane}}{Br-CH_2CH_2-Br} \xrightarrow{NaCN} \underset{\textbf{Butane dinitrile}}{NC-CH_2CH_2-CN} \xrightarrow{H_3O^+} \underset{\textbf{Butanedioic acid}}{HOOCCH_2CH_2COOH}$$

Cyanohydrins obtained from aldehydes also yield 2-hydroxycarboxylic acids on hydrolysis.



$$CH_3CH_2-\overset{OH}{\underset{H}{C}}-CN \xrightarrow{H_3O^+} CH_3CH_2-\overset{OH}{\underset{H}{C}}-COOH$$

2-Hydroxybutanenitrile **2-Hydroxybutanoic acid**

27.2.3 Structure and Physical Properties

Similar to the aldehydes and ketones, the carboxyl carbon atom is sp^2 hybridised. Thus, the three atoms attached to this carbon which lie in the same plane with an approximate bond angle of 120º between them, see Fig. 27.3.

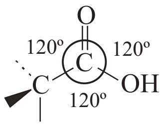
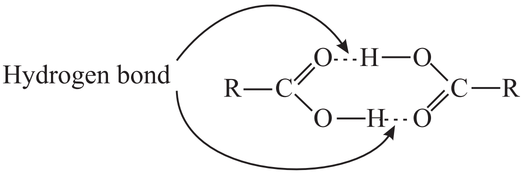


Fig. 27.3 : *Structure of the carboxyl group*

Carboxylic acids form hydrogen bonds because of the presence of polar carbonyl and hydroxyl groups. Most carboxylic acids exist in dimeric form in which two carboxylic acid molecules are held together by two hydrogen bonds. This is shown below :



Dimer of a carboxylic acid

Intermolecular hydrogen bonding is in fact responsible for high melting and boiling points of carboxylic acids. The melting and boiling points of some carboxylic acids are listed in Table 27.2. You can also see in the table that the lower members have appreciable solubility in water. This is also due to the presence of hydrogen bonding between the carboxylic acid molecule and solvent water molecules.

Table 27.2 : Some Physical Properties of Carboxylic Acids

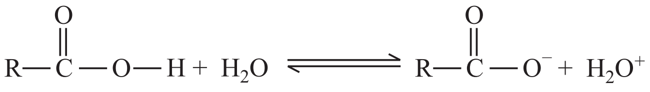
Carboxylic Acid	m. p. (K)	b. p. (K)	Water solubility gmL^{-1} of H_2O at 298K	pK_a
HCOOH	281	373·5	∞	3·75
CH_3COOH	289.6	391	∞	4·76

CH_3CH_2COOH	252	414	∞	4·87
$CH_3CH_2CH_2COOH$	267	437	∞	4·82
$CH_3CH_2CH_2CH_2COOH$	239	460	4·97	4·81
$ClCH_2COOH$	336	462	very soluble	2·86
$Cl_2CHCOOH$	283.8	465	very soluble	1·48
Cl_3CCOOH	329.3	471	very soluble	0·70
C_6H_5COOH	295	523	0·34	4·19
p-$CH_3C_6H_4COOH$	450	548	0·03	4·36
p-ClC_6H_4COOH	515		0.009	3.98
$p-NO_2C_6H_4COOH$	515		0.03	3.41

Do not worry about the pK_a values listed in the last column of the table. We will refer to them when we discuss the acidic nature of carboxylic acids in the following section.

27.2.4 Acidity of Carboxylic Acids

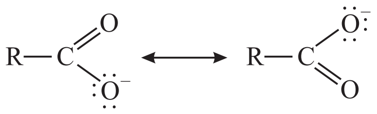
Carboxylic acids are acidic in nature. They dissociate in water according to following equilibrium to give a proton and the carboxylate ion.



$$R-\overset{O}{\overset{\|}{C}}-O-H + H_2O \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O^- + H_2O^+$$

Carboxylic acid **Carboxylate ion**

The pK_a values of some carboxylic acids are given in the last column of Table 27.2. Remember that the *lower* pK_a *indicates greater acidity*. If you compare these pK_a value with those of alcohols, you will note that the carboxylic acids are much more acidic than alcohols. This can be explained on the basis of the anion formed as a result of ionisation. The carboxylate ion obtained by the dissociation of carboxylic acids can be represented as a resonance hybrid of the following two structures:



Resonance structures of Carboxylate Ion

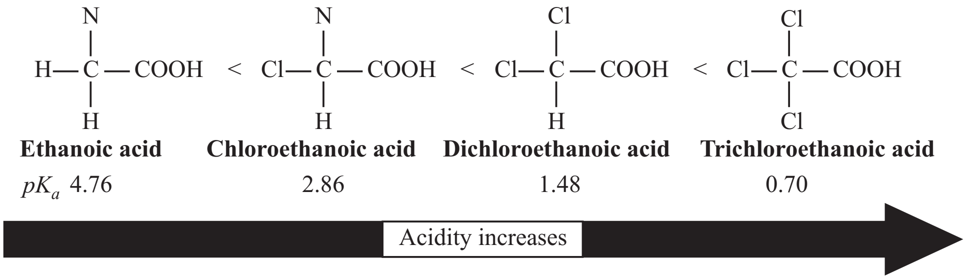
These structures show that the negative charge is delocalised over two oxygen atoms. Thus, the carboxylate ion gets stabilised. The greater stability of carboxylate ion facilitates the release of proton from the –COOH group.

If you compare this situation with the alkoxide ion (RO^-) obtained by the dissociation of an alcohol molecule, you will see that no such resonance stabilisation is possible in the alkoxide ion.

Let us now analyse the acid strength of different acids and correlate them with their structure. If we examine the first five acids listed in table 27.2, we find that their pK_a values keep on increasing which means that as we go down, their acid strength decreases. Since the alkyl groups are electron releasing in nature, they make the release of H^+ difficult and hence decrease the acidity. Thus, ethanoic acid is less acidic than methanoic acid. Therefore, we can say that the **electron-donating substitutents decrease the acidity of carboxylic acids.**

Let us next see what will be the effect of electron withdrawing substituents such as halogens and nitro-group on the acidity. The comparison of pK_a values of ethanoic acid (4·76) and chloroethanoic acid (2·86) suggests that chloroethanoic acid is a stronger acid than ethanoic acid. The chloro substituent has $-I$ effect and pulls the electrons towards itself which facilitates the release of H^+ ions.

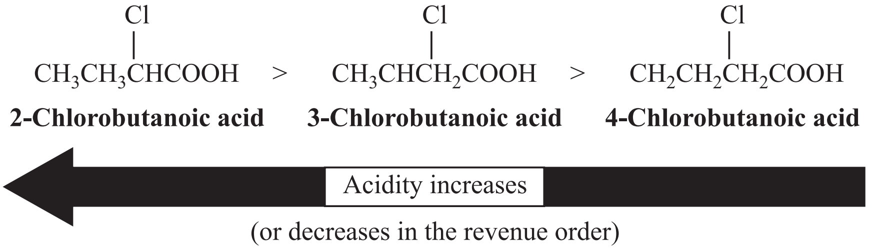
You can also see below that as the number of halogen groups increases in the carboxylic acid, its acidity increases. This is because they make the release of H^+ ion more and more easy.



$$H-\overset{N}{\underset{H}{C}}-COOH < Cl-\overset{N}{\underset{H}{C}}-COOH < Cl-\overset{Cl}{\underset{H}{C}}-COOH < Cl-\overset{Cl}{\underset{Cl}{C}}-COOH$$

Ethanoic acid	**Chloroethanoic acid**	**Dichloroethanoic acid**	**Trichloroethanoic acid**
pK_a 4.76	2.86	1.48	0.70

Since the inductive effect decreases with increase in the distance of the group in the carbon chain, 2-chlorobutanoic acid (pK_a 2·86) is more acidic than 3-chlorobutanoic acid (pK_a 4.05) which is in turn more acidic than 4-chlorobutanoic acid (pK_a 4.50).



$$CH_3CH_3\overset{Cl}{C}HCOOH > CH_3\overset{Cl}{C}HCH_2COOH > \overset{Cl}{C}H_2CH_2CH_2COOH$$

2-Chlorobutanoic acid **3-Chlorobutanoic acid** **4-Chlorobutanoic acid**

(or decreases in the revenue order)

27.2.5 Reactions of Carboxylic Acids

Let us now study the reactions given by carboxylic acids.

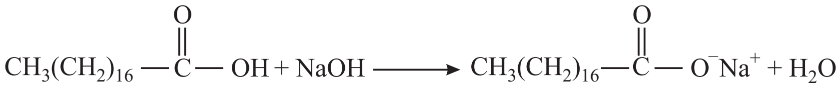
1. Formation of Salts

Carboxylic acids are completely deprotonated by strong bases such as metal hydroxides to give salts.

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O-H + NaOH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + H_2O$$

Ethanoic acid **Sodium ethanoate**

It will be interesting to know that *soaps* are sodium salts of long chain carboxylic acids which are called **fatty acids**.



$$CH_3(CH_2)_{16}-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NaOH \longrightarrow CH_3(CH_2)_{16}-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + H_2O$$

Stearic acid **Sodium stearate (soap)**

Caboxylic acids are also deprotonated by the weak bases such as sodium bicarbonate. In this reaction, they form sodium salt of the acid, carbon dioxide and water.

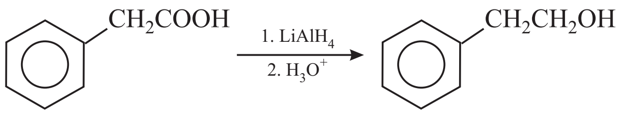
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + NaHCO_3 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ + H_2O + CO_2\uparrow$$

This reaction is also used as a test for carboxylic acids in the laboratory. The liberation of CO_2 in the form of bubbles on treatment with $NaHCO_3$ indicates a carboxyl functional group in the compound.

This test is not given by phenols since they are weaker acids than the carboxylic acids. Hence, the two categories of compounds can be distinguished on the basis of the above test.

2. Reduction of Carboxylic Acids

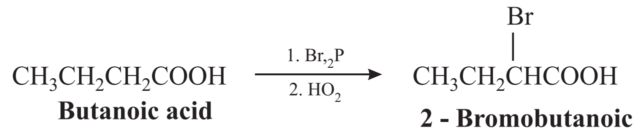
Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride $(LiAlH_4)$.



Phenylethanoic acid **2-Phenylethanol**

3. Hell-Volhard-Zelinski Reaction

Similar to aldehydes and ketones, carboxylic acids undergo halogenation at α-carbon atom using $Br_2(or\,Cl_2)$ in the presence of phosphorus or phosphorus trihalide.



$$\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} \xrightarrow[2.\ HO_2]{1.\ Br_2,P} \underset{\text{2 - Bromobutanoic acid}}{CH_3CH_2\overset{Br}{\overset{|}{C}}HCOOH}$$

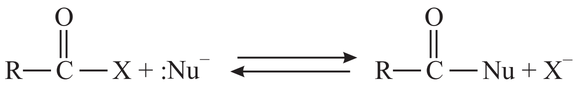
Butanoic acid **2 - Bromobutanoic acid**

α-Haloacids so obtained are useful intermediates in the synthesis of other organic compounds.

4. Synthesis of Acid Derivatives

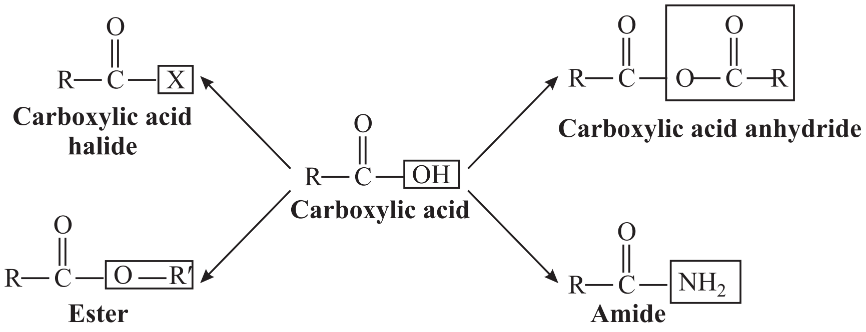
This is one of the very important reactions of carboxylic acids. The nucleophilic addition to the carboxyl carbon of the carboxylic acids is followed by elimination of the leaving group leading to a **substitution product.** If you remember the reactions of aldehydes and ketones, the addition of nucleophile is followed by addition of the proton to give an **addition product.**

In case of carboxylic acids, since the substitution takes place at the acyl carbon atom as shown below. It is also known as **nucleophilic acyl substitution.**



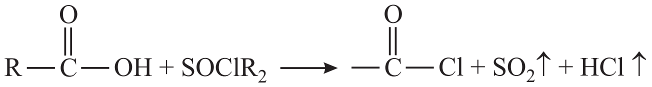
$$R-\overset{O}{\overset{\|}{C}}-X + :Nu^{-} \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-Nu + X^{-}$$

Here, X = OH in case of the carboxylic acids and Nu^{-} can be a halide ion, $^{-}O-\overset{O}{\overset{\|}{C}}-R$, $^{-}O-R'$ or $^{-}NH_2$ group leading, respectively to **carboxyl acid halides, anhydrides, esters** or **amides** as the substitution products which are known as **derivatives of carboxylic acids** because they are derived from carboxylic acids.



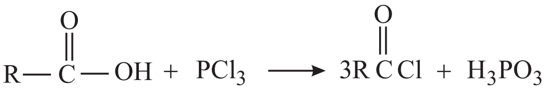
(i) Formation of Acid Chlorides

Carboxylic acids react with $SOCl_2, PCl_3$ or PCl_5 to give carboxylic acid chlorides also known as **acyl chlorides,** as shown below :



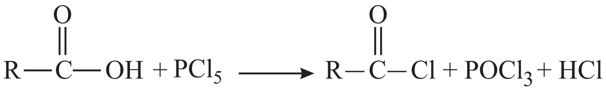
$$R-\overset{O}{\overset{\|}{C}}-OH + SOClR_2 \longrightarrow -\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$$

Carboxylic acid **Thionyl chloride** **an acid chloride**



$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \longrightarrow 3R\overset{O}{\overset{\|}{C}}Cl + H_3PO_3$$

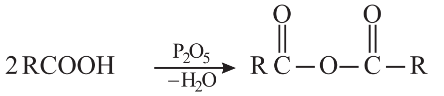
Phosphorus trichloride



$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

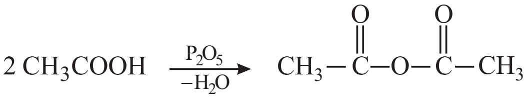
Phosphorus pentachloride

(ii) Formation of Acid Anhydrides



$$2\,RCOOH \xrightarrow[-H_2O]{P_2O_5} R\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

aCarboxylicacid **an Acid Anhydride**



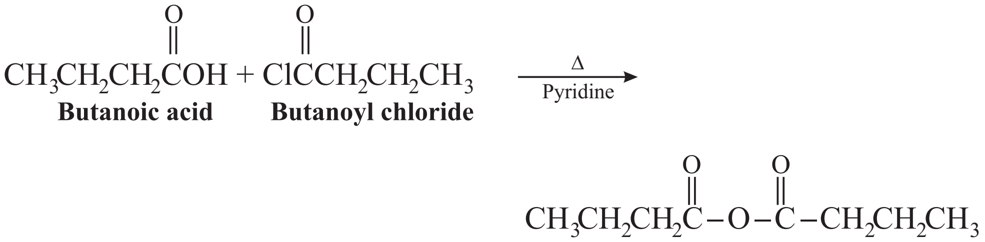
$$2\,CH_3COOH \xrightarrow[-H_2O]{P_2O_5} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

Ethanoicanhydride

Since the carboxylic acid anhydrides are formally derived from carboxylic acids by loss of water, their names are derived from the corresponding acids by using the word *anhydride* in place of the acid. As the anhydride formed in the above reaction is derived from ethanoic acid, it is called ethanoic anhydride.

This method is used for the *preparation of symmetrical anhydrides.*

Carboxylic acid also react with acyl chlorides in the presence of pyridine to give carboxylic acid anhydrides.



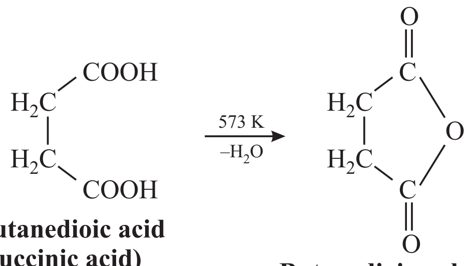
$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OH + Cl\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow[\text{Pyridine}]{\Delta} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$$

Butanoic acid **Butanoyl chloride**

Butanoicanhydride

We can prepare unsymmetrical anhydrides by this method.

Cylic anhydrides are obtained by the dehydration of dicarboxylic acids at higher temperature.

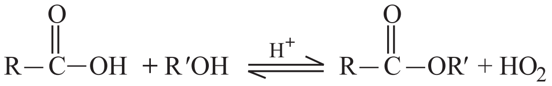


Butanedioic acid
(Succinic acid)

Butanedioic anhydride
(Succinic anhydride)

(iii) Formation of Esters

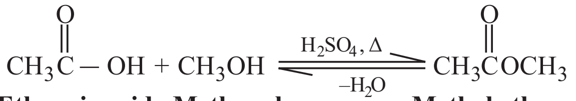
Carboxylic acids react with alcohols to form esters.



$$R-\overset{\overset{\large O}{\|}}{C}-OH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{\overset{\large O}{\|}}{C}-OR' + HO_2$$

Carboxylic acid **Alcohol** **Ester**

Note that the acid catalysed esterification is an equilibrium reaction. The equilibrium can be shifted to the right side towards products it we are able to remove water or the ester from the reaction mixture. Also if we use excess of one reagent, then the equilibrium shifts towards the right side to give the ester. Normally, we take excess of alcohol and use it as a solvent to carry out esterification.

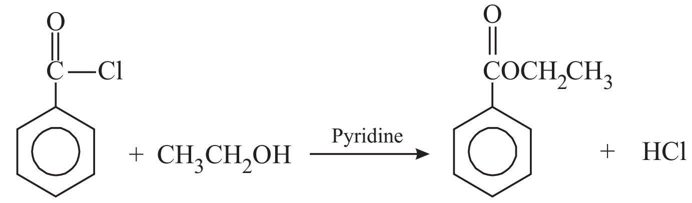


$$CH_3\overset{\overset{\large O}{\|}}{C}-OH + CH_3OH \underset{-H_2O}{\overset{H_2SO_4,\,\Delta}{\rightleftharpoons}} CH_3\overset{\overset{\large O}{\|}}{C}OCH_3$$

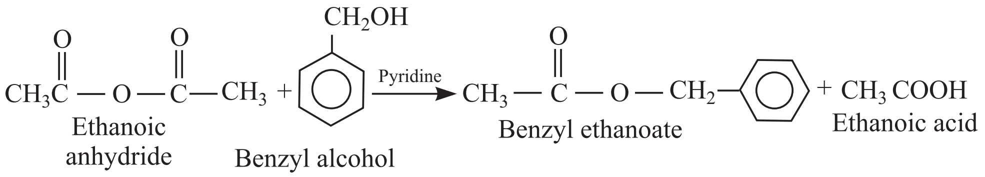
Ethanoic acid **Methanol** **Methyl ethanoate**

Esters are named as **alkyl alkanoates.** The alkyl part comes from the alcohol while the alkanoate portion is derived from the carboxylic acid. Therefore, the above ester is called **methyl ethanoate** because it is obtained from ***methyl* alcohol** and ***ethanoic* acid.**

Esters can also be prepared by the reaction of **acid chlorides** or **acids anhydrides** with alcohols. Thus, we can see that these acid derivatives can be converted to one-another.

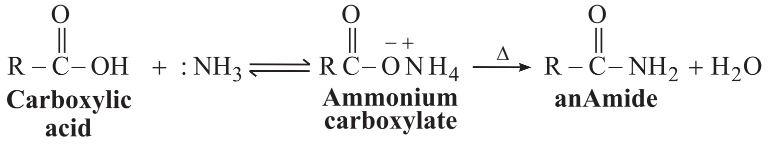


Benzoyl chloride **Ethanol** **Ethyl benzoate**



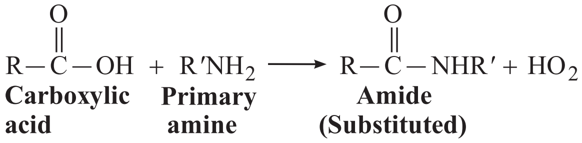
(iv) Formation of Amides

Carboxylic acids react with ammonia or amines to give amides. The reaction involves the formation of an ammonium carboxylate salt as an intermediate which on heating gives amide.



$$R-\overset{O}{\overset{\|}{C}}-OH + :NH_3 \rightleftharpoons R\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

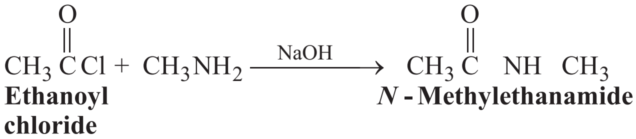
Carboxylic acid **Ammonium carboxylate** **anAmide**



$$R-\overset{O}{\overset{\|}{C}}-OH + R'NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHR' + HO_2$$

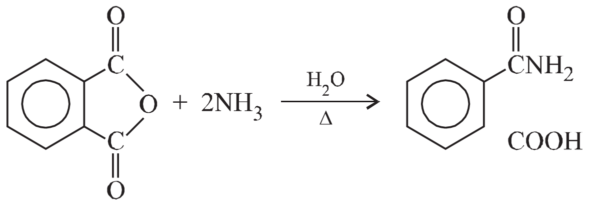
Carboxylic acid **Primary amine** **Amide (Substituted)**

Amides can also be obtained by the reaction of ammonia or amines with **carboxylic acid halides, anhydrides** and **esters.**

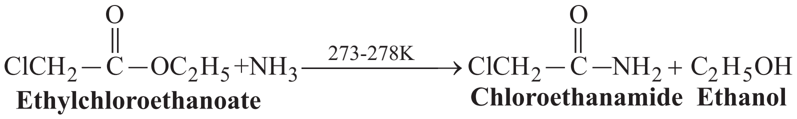


$$CH_3\overset{O}{\overset{\|}{C}}Cl + CH_3NH_2 \xrightarrow{NaOH} CH_3\overset{O}{\overset{\|}{C}}\ NH\ CH_3$$

Ethanoyl chloride ***N*-Methylethanamide**



Phthalic anhydride **Pnhthalamic acid**



$$ClCH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5+NH_3 \xrightarrow{273\text{-}278K} ClCH_2-\overset{O}{\overset{\|}{C}}-NH_2 + C_2H_5OH$$

Ethylchloroethanoate **Chloroethanamide** **Ethanol**

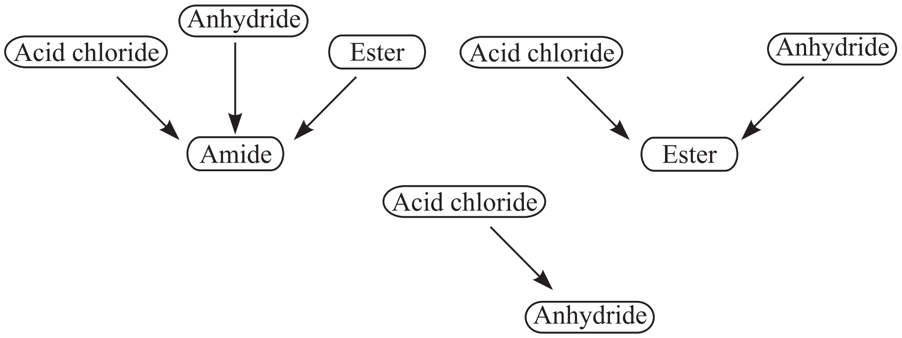
Thus, we can make one carboxylic acid derivative from another. Generally, the **less reactive acid (acyl) derivatives can be prepared from the more reactive ones.**

The order of reactivity of various carboxylic acid derivatives is as follows :

Acid chloride > Acid anhydride > Ester > Amide

Thus, acid chlorides are the most reactive ones whereas the amides are the least reactive.

Since the least reactive derivative can be prepared from the more reactive ones, we can summarise which derivative can be prepared from which other one in the following way:



Of course, *these derivatives can be synthesised from the carboxylic acids as well.*

INTEXT QUESTIONS 27.2

1. Match the following compounds given in column I and their classes given in column II:

	Column I		Column II
(i)	CH_3COOH	(a)	Carboxylic acid halide
(ii)	CH_3CONH_2	(b)	Carboxylic acid
(iii)	CH_3COOCH_3	(c)	Carboxylic acid anhydride
(iv)	CH_3COCl	(d)	Carboxylic acid amide
(v)	$CH_3COOCOCH_2Cl$	(e)	Ester

2. Arrange the following acids in the increasing order of their solubility in water:

   CH_3COOH, $CH_3(CH_2)_3COOH$ p-ClC_6H_4COOH

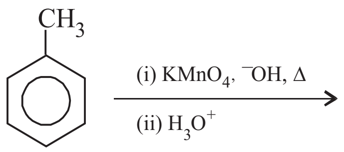
3. Which one of the following will be most acidic and why ?

   Butanoic acid, 2-Chlorobutanoic acid, 3-Chlorobutanoic acid, 4-Chlorobutanoic acid

4. Give the products of the following reactions :

   (i) $BrCH_2CH_3 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) NaCN}}$

(ii)



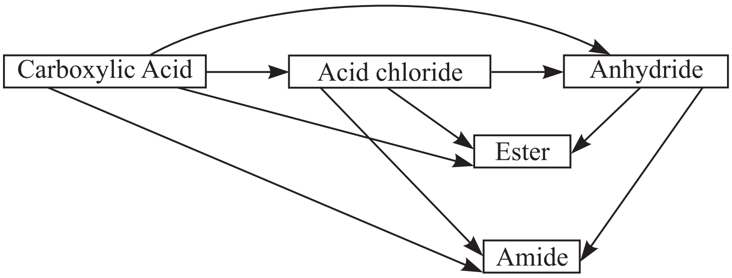
(iii) $CH_3COOH + PCl_3 \longrightarrow$

5. Why are carboxylic acids more acidic than alcohols ?

WHAT YOU HAVE LEANT

In this lesson, you have learnt that

- Aldehydes and ketones constitute the carbonyl compounds. Aldehydes are known as **alkanals** whereas ketones are called **alkanones.**
- Aldehydes and ketones can be prepared by oxidation of alcohols, ozonolysis of alkenes, hydration of alkynes and Friedel–Craft's acylation.
- Carbonyl group is polar in nature and carbonyl-carbon is susceptible to nucleophilic attack. Thus, aldehydes and ketones undergo nucleophilic addition reactions with many reagents. They also exhibit condensation reactions.
- Since the α-hydrogen is acidic in nature, aldehydes and ketones show specefic reactions at α-carbon atom such as halogenation and aldol condensation.
- Carboxylic acids are an important class of compounds.
- The methods of preparation of carboxylic acids being oxidation of alkenes, aldehydes and ketones and alkylbenzene, hydrolysis of nitriles and carbonation of Grignard reagents.
- The molecules of carboxylic acids show hydrogen bonding and can exist as dimers.
- Carboxylic acids are acidic in nature. Their acidity is affected by various factors including the nature of substituents attached to the carbon chain bearing the carboxylic group.
- Carboxylic acids form salts with strong bases such as metal hydroxides. They undergo halogenation at α-carbon atom and can be reduced to primary alcohols using $LiAlH_4$.
- Carboxylic acids gives rise to a number of carboxylic acid derivatives such as carboxylic acid halides, anhydrides, esters and amides by nucleophilic acyl substitution reactions. They can be prepared from one another as shown below :



TERMINAL EXERCISE

1. Write the structural formulae and IUPAC names of the compounds containing a carbonyl functional group and having the molecular formula C_3H_6O.
2. How can you prepare primary, secondary or tertiary alcohols using aldehydes or ketones?
3. Write the mechanism of addition of HCN to propanone.
4. What is Tollen's Test?
5. Explain keto-enol tautomerism.
6. What is haloform reaction?
7. How will you test a carboxylic acid in the laboratory?
8. Which reagent can reduce a carboxylic acid to a primary alcohol?
9. What are carboxylic acid anhydrides ? Give their method of preparation from carboxylic acids.
10. Which carboxylic acid derivative is most reactive?

    (a) Acid amide (b) Ester (c) Acid halide (d) Acid anhydride

ANSWERS TO INTEXT QUESTIONS

27.1

1. (i) aldehyde, Ethanal

   (ii) ketone, Butan-2-one

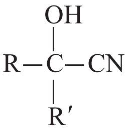
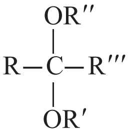
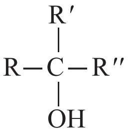
   (iii) ketone, 1-Phenylethanone

   (iv) aldehyde, Propanal

2. Using hydration with Hg^{2+}, H^+.

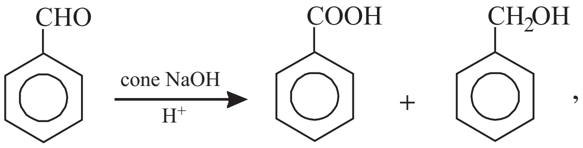
3. Because they have one alkyl group whereas a ketone has two alkyl group. Hence, the carbonyl carbon in aldehydes is more positive.

   Also, the two alkyl groups lead to more crowding in ketones.

4. (i) 
$R-\overset{OH}{\underset{R'}{C}}-CN$
(ii) 
$R-\overset{OR''}{\underset{OR'}{C}}-R'''$
(iii) 
$R-\overset{R'}{\underset{OH}{C}}-R''$

5. By Wolff- Kishner reduction or Clemmensen reduction.

6. The product formed by the condensation of two aldehyde molecules having α-hydrogen atom. Aldol contains both an aldehyde and an alcohol functional group.

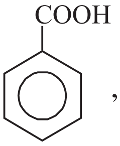
7. 

27.2

1. (i). (b) (ii). (d) (iii). (e) (iv). (a) (v) e

2. $p-ClC_6H_4COOH < CH_3(CH_2)_3COOH < CH_3COOH$

3. 2-Chlorobutanoic acid, because of maximum –I effect of –Cl at 2 – position.

4. (i) $HOOCCH_2CH_3$, (ii) 

,

   (iii) $3CH_3COCl + H_3PO_3$

5. Because of resonance stabilization of carboxylate anion. The alkoxide ion cannot stabilize by resonance.

313en28

28

COMPOUNDS OF CARBON CONTAINING NITROGEN

In the previous lesson, you have studied the chemistry of organic compounds containing oxygen atom as a part of the functional group. Now, you will learn about organic compounds containing nitrogen atom as a part of the functional group. An historical importance can be associated with these compounds as the first ever organic compound synthesised in the laboratory was urea which contains nitrogen. Nitrogen containing compounds have wide applications in our daily life. They form a part of dyes, drugs, fertilizers, alkaloids, proteins, etc. Only two classes of nitrogen containing compounds, *viz.* amines and nitro compounds are discussed in this lesson. First, the IUPAC nomenclature of amines has been explained followed by their preparation and chemical properties. The difference in the basicities of aliphatic and aromatic amines has also been described. Finally, the chemistry of nitro compounds is briefly discussed.

OBJECTIVES

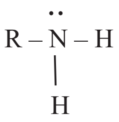
After reading this lesson, you will be able to:

- classify amines as primary, secondary, or tertiary amines;
- write the IUPAC names of amines and nitro compounds;
- describe the general methods of preparation, properties and uses of primary amines;
- explain the relative basicities of primary, secondary and tertiary aliphatic amines and compare them with the basicities of ammonia and aromatic amines;
- differentiate primary, secondary and tetracy amines;
- discuss the important reactions of diazonium salts and explain their utility in synthesis of organic compounds;
- describe the methods of preparation of nitro compounds;

- discuss important reactions of nitro compounds, and
- list important uses of nitro compounds.

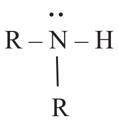
28.1 AMINES

Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified into three different types as primary (1°), secondary (2°) and tertiary (3°) depending on the number of hydrogen atoms replaced by alkyl or aryl groups. In primary amines, only one alkyl or aryl group is attached to the nitrogen atom. In secondary amines, two alkyl or aryl groups are attached to the nitrogen while tertiary amines contain three alkyl or aryl groups attached to the nitrogen atom.
This is illustrated below.



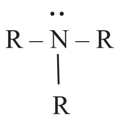
$$R-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-H$$

A primary amine



$$R-\overset{\cdot\cdot}{\underset{\underset{R}{|}}{N}}-H$$

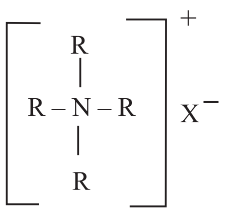
A secondary amine



$$R-\overset{\cdot\cdot}{\underset{\underset{R}{|}}{N}}-R$$

A tertiary amine

If four alkyl groups are attached to the nitrogen atom, then the quaternary ammonium ion or salt is formed.

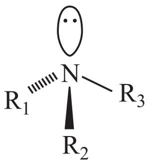


$$\left[R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}-R\right]^{+}X^{-}$$

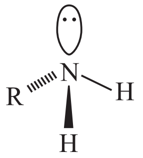
A quaternary ammonium salt

Structure of Amines

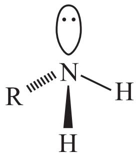
The nitrogen atom of amines is approximately sp^3 hybridised. The three alkyl groups or hydrogen atoms occupy the three corners of the tetrahedron while the unshared pair of electrons is directed towards the other corner of the tetrahedron.



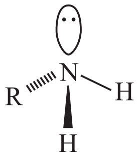
If we consider the three groups attached to the nitrogen as R_1, R_2 and R_3 then the shape of the molecule can be described as *trigonal pyramidal*. These three groups could be either alkyl groups or hydrogen atoms. Accordingly, the amine is called primary, secondary or tertiary,



Primary amine



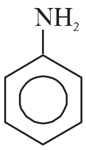
Secondary amine



Tertiary amine

However, if we consider lone pair of electrons also as a group attached to the nitrogen, then the geometry of the molecule is called *tetrahedral.* The bond angles R–N–R are close to the tetrahedral angle of 109.5°.

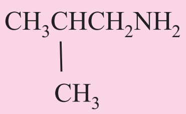
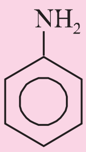
The amino group in aromatic amines is directly bonded to the benzene ring. Aromatic amines are aryl derivatives of ammonia. The parent aromatic amine is known as aniline.



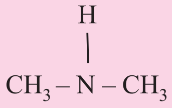
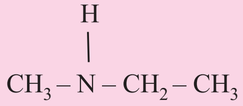
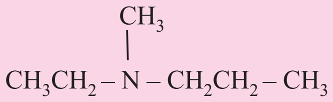
Aniline

28.2.1 IUPAC Nomenclature of Amines

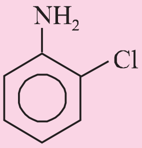
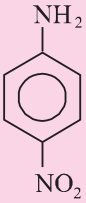
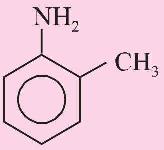
Similar to other classes of compounds which you have studied, amines can also be named according to the IUPAC system. In case of primary aliphatic amines, the longest continuous chain of carbon atoms determines the root name of the compound. The ending *–e* in the name of the corresponding alkane is changed to-*amine*. The other substituents along the carbon chain are given numbers. This is illustrated by the following examples.

Compounds	*IUPAC name*	*Common name*
CH_3NH_2	Methanamine	Methyl amine
$CH_3CH_2NH_2$	Ethanamine	Ethyl amine
$CH_3CH_2CH_2NH_2$	Propan-1-amine	Propyl amine
 $CH_3\underset{\underset{\displaystyle CH_3}{\vert}}{C}HCH_2NH_2$	2-Methyl propan-l-amine	—
	Benzenamine	Aniline

Secondary and tertiary amines are named by using the prefix *N* for each substituent on the nitrogen atom.

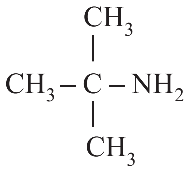
Compound	*IUPAC name*	*Common name*
 $CH_3-\overset{H}{\overset{\vert}{N}}-CH_3$	*N*-Methylmethanamine	Dimethylamine
 $CH_3-\overset{H}{\overset{\vert}{N}}-CH_2-CH_3$	*N*-Methylethanamine	Ethylmethylamine
 $CH_3CH_2-\overset{CH_3}{\overset{\vert}{N}}-CH_2CH_2-CH_3$	*N*-Ethyl-*N*-methylpropan-1-amine	—

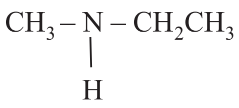
The IUPAC names of other aromatic amines are given as derivatives of aniline shown below :

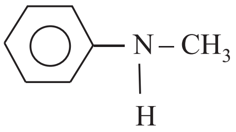
Compound	*IUPAC name*	*Common name*
	2-Chloroaniline	*o*-Chloroaniline
	4-Nitroaniline	*p*-Nitroaniline
	2-Methylaniline	*o*-Toluidine

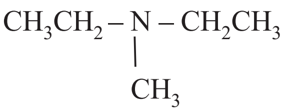
INTEXT QUESTIONS 28.1

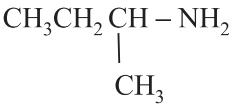
1. Classify the following as primary, secondary, tertiary amines and quaternary ammonium salts :

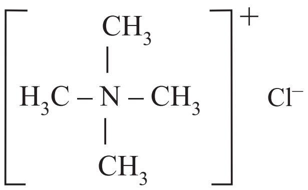
(i)  $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-NH_2$

(ii)  $CH_3-\underset{H}{\underset{\vert}{N}}-CH_2CH_3$

(iii) 

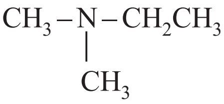
(iv) 
$CH_3CH_2-N(CH_3)-CH_2CH_3$

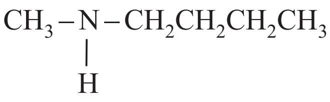
(v) 
$CH_3CH_2CH(CH_3)-NH_2$

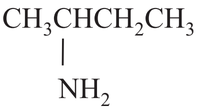
(vi) 
$[H_3C-N(CH_3)_2-CH_3]^+ Cl^-$

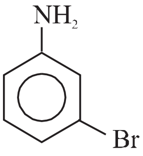
2. Write IUPAC names for the following amines :

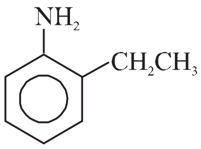
(i) $CH_3CH_2CH_2CH_2NH_2$

(ii) 
$CH_3-N(CH_3)-CH_2CH_3$

(iii) 
$CH_3-NH-CH_2CH_2CH_2CH_3$

(iv) 
$CH_3CH(NH_2)CH_2CH_3$

(v) 

(vi) 

28.2.2 Preparation of Amines

Several methods are available for the preparation of primary aliphatic and aromatic amines. In this section, you will learn some of the methods which are generally used for their perparation.

(i) *From alkyl halides*

Alkyl halides react with ammonia to form primary amines.

$$R-X + 2\,NH_3 \longrightarrow R\,NH_2 + NH_4X$$

The primary amine so formed may further react to give a secondary amine, tertiary amine or a quaternary ammonium salt. So in order to get good yield of the primary amine, the reaction is carried out using excess of ammonia. For example, bromoethane on reaction with excess of ammonia gives ethanamine.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br} + 2\,NH_3 \longrightarrow \underset{\textbf{Ethanamine}}{C_2H_5NH_2} + NH_4Br$$

(ii) *By reduction of nitriles (cyanides), amides and nitro compounds*

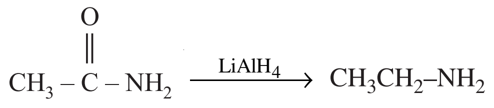
Compounds containing cyano, amido or nitro groups can be reduced into the corresponding primary amines.

Nitriles can be reduced by hydrogen in the presence of platinum catalyst or by sodium in presence of ethanol to corresponding primary amines. For example, propanenitrile (cyano ethane) on reduction gives propan-l-amine.

$$CH_3CH_2C{\equiv}N \xrightarrow[\text{or Na / }C_2H_5OH]{H_2\text{ / Pt}} CH_3CH_2CH_2{-}NH_2$$

Propanenitrile **Propan-l-amine**

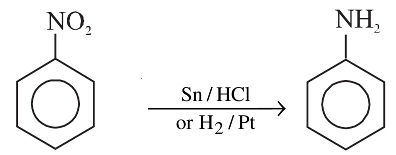
Similarly, amides are reduced by $LiAlH_4$ to primary amines having same number of carbon atoms as in the starting amide. For example, ethanamide gives ethanamine on reduction.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} CH_3CH_2{-}NH_2$$

Ethanamide **Ethanamine**

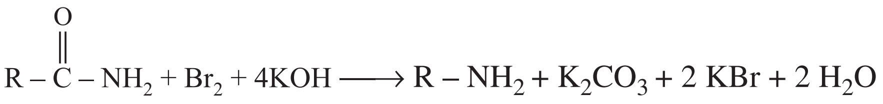
Reduction of nitro compounds can be carried out by using hydrochloric acid and a metal such as Sn or Fe. They can also be reduced with hydrogen in presence of Ni or Pt as catalyst. Such a reduction of nitrobenzene by any of these methods provides aniline.



Nitrobenzene **Aniline**

(iii) *By Hofmann bromamide reaction*

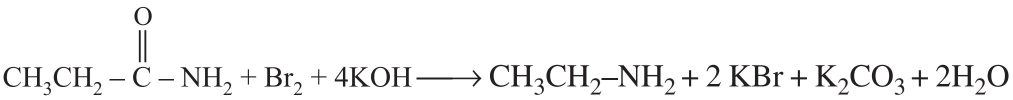
Aliphatic amides on treatment with bromine and a strong base like potassium hydroxide are converted into primary amines having one carbon less than those present in the starting amide.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow R-NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

Amide **Amine**

Thus, ethanamine is obtained by treating propanamide with bromine and KOH.



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow CH_3CH_2{-}NH_2 + 2\,KBr + K_2CO_3 + 2H_2O$$

Propanamide **Ethanamine**

28.2.4 Physical Properties of Amines

Aliphatic amines containing up to three carbon atoms are gases whereas higher amines are liquids. Some higher aromatic amines are even solids. Methyl and ethyl amines have smell like ammonia. Amines have higher boiling points than the corresponding hydrocarbons because they form hydrogen bonds amongst themselves. Lower amines are soluble in water and the solubility decreases with the increase in size of the alkyl group. This solubility is because of the presence of hydrogen bonding between the amino group and water molecules. All amines are soluble in organic solvents like benzene, alcohol, ether etc.

28.2.5 Chemical Properties of Amines

(i) *Basic Character*

Amines are basic in nature due to the presence of a lone pair of electrons on nitrogen. You know that the strength of a base depends upon the availability of electrons. Basicities of amines can be compared with respect to ammonia, by comparing the availability of pair of electrons on nitrogen. Ammonia and amines, both when dissolved in water, attract a proton from water to form an ammonium or alkylammonium ion, respectively, and a hydroxide ion.

$$\ddot{N}H_2 + H-O-H \longrightarrow \underset{\textbf{Ammonium ion}}{NH_4^+} + OH^-$$

$$R-\ddot{N}H_2 + H-O-H \longrightarrow \underset{\textbf{Alkylammonium ion}}{R-NH_3^+} + OH^-$$

You know that aliphatic amines contain one or more alkyl groups in place of hydrogen atoms of ammonia. Since alkyl groups are electron releasing groups, they increase the electron density on nitrogen. This makes the lone pair of electrons on nitrogen atom to be easily available for sharing and hence, this increases the basicity of the amine. So, we expect that the basicities of the amines would increase as we move from primary to secondary to tertiary amines.

But the order of the basicities has been found to be

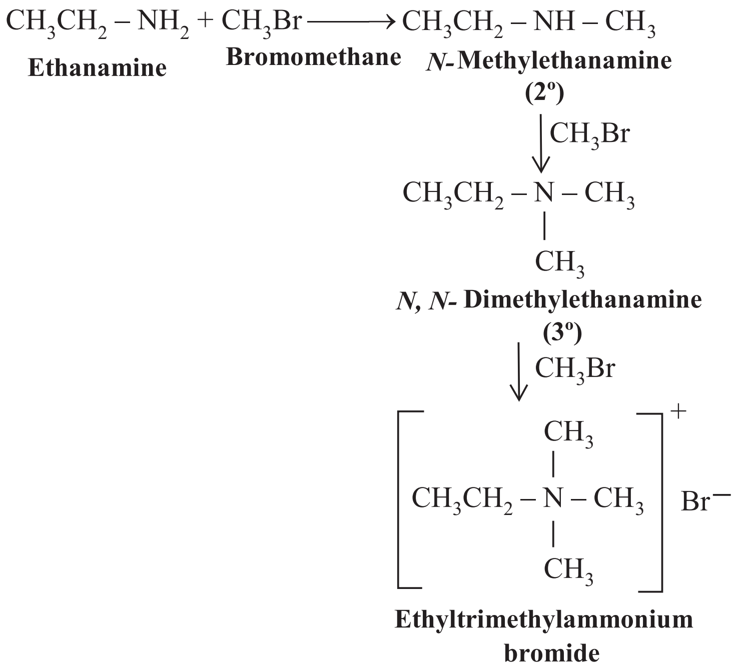
$$\underset{\textbf{Primary }(1^0)}{R-NH_2} < \underset{\textbf{Secondary }(2^0)}{R_2NH} > \underset{\textbf{Tertiary }(3^0)}{R_3N}$$

The tertiary amines are less basic than secondary amines. The reason is that a tertiary amine, though has three alkyl groups which can donate electrons to the nitrogen atom but they also cause crowding (also called *steric hinderance*) around nitrogen. This hinders the protonation at nitrogen atom and hence, reduces the basicity.

The aromatic amines are weaker bases than ammonia because the aromatic ring is electron withdrawing. It reduces the electron density at nitrogen and makes the aromatic amines less basic. So we can express the basic character of aliphatic and aromatic amines as shown below.

Aromatic amines < Ammonia < Aliphatic amines

(ii) ***Alkylation :*** Primary amines react with alkyl halides to give secondary amines. The reaction may continue further to form a tertiary amine and a quaternary ammonium salt. For example, the reaction of ethanamine with bromomethane proceeds as shown below.



$$CH_3CH_2-NH_2 + CH_3Br \longrightarrow CH_3CH_2-NH-CH_3$$

Ethanamine **Bromomethane** ***N*-Methylethanamine (2°)**

$$\downarrow CH_3Br$$

$$CH_3CH_2-\underset{\underset{CH_3}{|}}{N}-CH_3$$

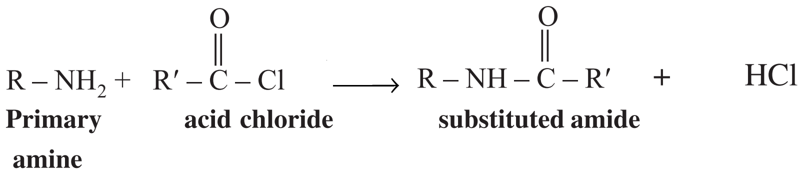
***N, N*- Dimethylethanamine (3°)**

$$\downarrow CH_3Br$$

$$\left[CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^+ Br^-$$

Ethyltrimethylammonium bromide

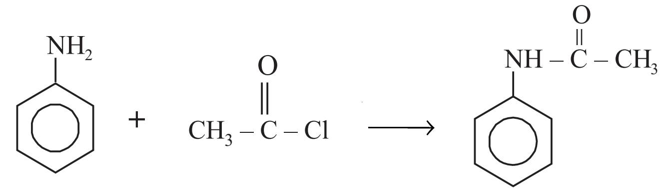
(iii) ***Acylation :*** Primary amines on reaction with acid chlorides or acid anhydrides give *N*-substituted amides.



$$R-NH_2 + R'-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-NH-\overset{\overset{O}{\|}}{C}-R' + HCl$$

Primary amine **acid chloride** **substituted amide**

For example, aniline on reaction with ethanoyl chloride (acetyl chloride) gives acetanilide.



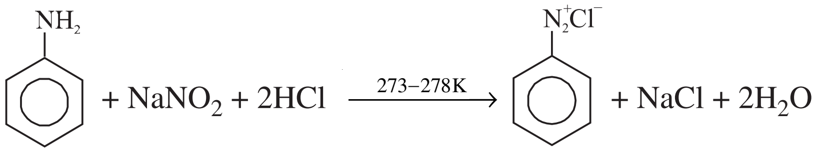
Aniline **Ethanoyl chloride** **Acetanilide**

(iv) ***Carbylamine reaction :*** When a primary amine is heated with chloroform in the presence of alcoholic potassium hydroxide, then the corresponding isocyanide is formed. Isocyanides are also known as **carbylamines**, hence this reaction is called as **carbylamine reaction**. For example, aminoethane on undergoing this reaction, gives ethyl carbylamine.

$$\underset{\textbf{Ethylamine}}{CH_3CH_2\text{–}NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\textbf{Ethyl carbylamine}}{CH_3CH_2\,N \equiv C} + 3KCl + 3H_2O$$

Isocyanides give a very offensive odour, so this reaction is also used as a test for primary amines.

(v) ***Reaction with nitrous acid :*** Primary aromatic amines react with nitrous acid to give diazonium salts and this reaction is known as **diazotisation**. Nitrous acid is an unstable compound and can not be stored, so it is prepared during the reaction by mixing sodium nitrite and hydrochloric acid. The reaction is specifically carried out at low temperature between 273 – 278 K. For example, aniline reacts with nitrous acid to give benzene diazonium chloride.



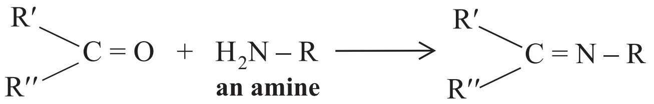
Aniline **Benzene diazonium chloride**
(a diazonium salt)

Primary aliphatic amines also react in a similar way but the diazonium salts formed are unstable and decompose to give alcohols and nitrogen gas. Thus, ethanamine gives ethanol when subjected to this reaction.

$$\underset{\textbf{Ethanamine}}{CH_3CH_2\text{–}NH_2} \xrightarrow{NaNO_2/HCl} \underset{\substack{\textbf{Ethyldiazonium chloride}\\ \textbf{Unstable diazonium salt}}}{[CH_3CH_2\,N_2^+\,Cl^-]} \xrightarrow{H_2O}$$

$$\underset{\textbf{Ethanol}}{CH_3CH_2\text{–}OH} + N_2\uparrow + HC$$

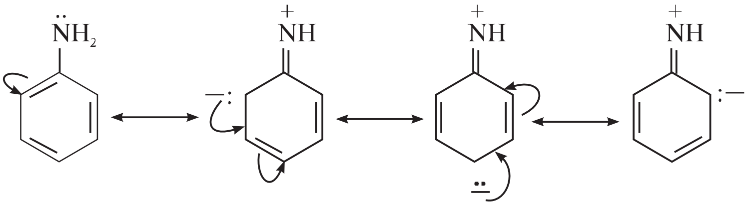
(vi) Primary amines undergo condesnsation with aldehydes or ketones to form **imines**. These products are also called **Schiff's bases**. The reaction can be shown as follows :



$$\begin{matrix}R' \\ R''\end{matrix}\!\!>C=O + \underset{\textbf{an amine}}{H_2N-R} \longrightarrow \begin{matrix}R' \\ R''\end{matrix}\!\!>C=N-R$$

a Schiff's base

(vii) ***Ring substitution in aromatic amines :*** You know that – NH_2 group is a strong activating and *ortho*-, *para*- directing group for electrophilic aromatic substitution reactions. This directive influence can be explained by the following resonating structures of aniline.

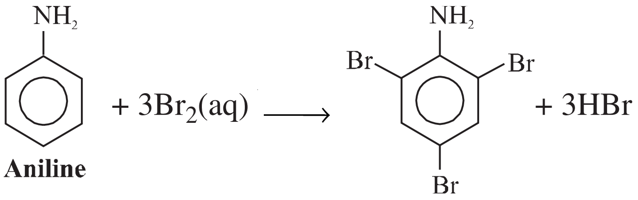


Resonance structures of aniline

As a result of this resonance, the electron density is more at *ortho*- and *para*-positions; hence, the electrophilic substitution occurs at these positions.

Some important ring substitution reactions of aromatic amines are halogenation, nitration and sulphonation.

(a) ***Halogenation :*** Aniline on treatment with an aqueous solution of bromine gives 2,4,6 - tribromoaniline.



2,4,6-Tribromoaniline

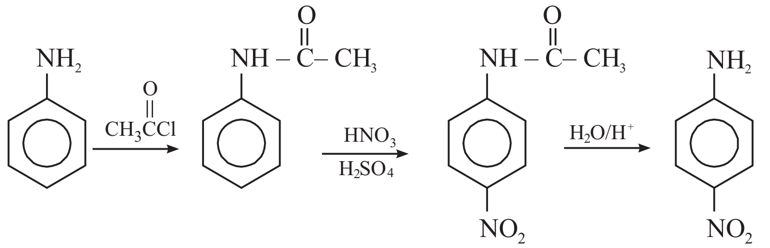
Aniline is very reactive and all the three hydrogen atoms at *ortho*- and *para*-positions are substituded with bromine atoms.

(b) ***Nitration :*** Nitration of aniline is carried out on the acetylated amine (acetanilide) rather than on the free amine itself. There are two reasons for this.

(i) The free amine is very susceptible to oxidation and thus much of it is lost in the form of a black-sticky material which is fomed as result of its oxidation.

(ii) The free amine is very reactive but acetyl the group protects it and reduces its reactivity.

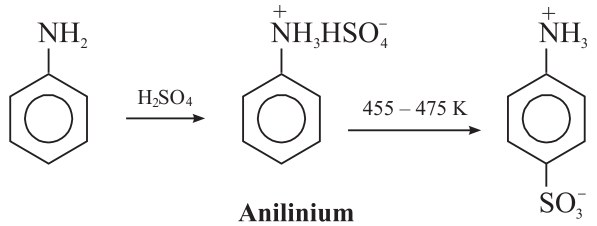
The nitration of aniline with the protection of the amino group is shown below:



Aniline **Acetanilide** ***p*-Nitroacetanilide** ***p*-Nitroaniline**

The first step consists of acetylation of the amino group in aniline. The conversion of $–NH_2$ to $–NH–\overset{\overset{O}{||}}{C}–CH_3$, lowers the activity of $–NH_2$ group because of electron withdrawal by $–\overset{\overset{O}{||}}{C}–CH_3$. This step is followed by nitration (conc. HNO_3 / H_2SO_4) which gives mainly the *p*-nitroacetanilide. This, 'on acid hydrolysis' yields the desired product *p*-nitroaniline.

(c) ***Sulphonation :*** Sulphonation is carried out in the presence of sulphuric acid. The amino group in aniline is a basic group. Therefore, an acid-base reaction takes place to form anilinium hydrogensulphate salt. This salt undergoes rearrangement at a high temperature to give sulphanilic acid.



Aniline **Anilinium hydrogensulphate** **Sulphanilic acid**

28.2.6 Uses of Amines

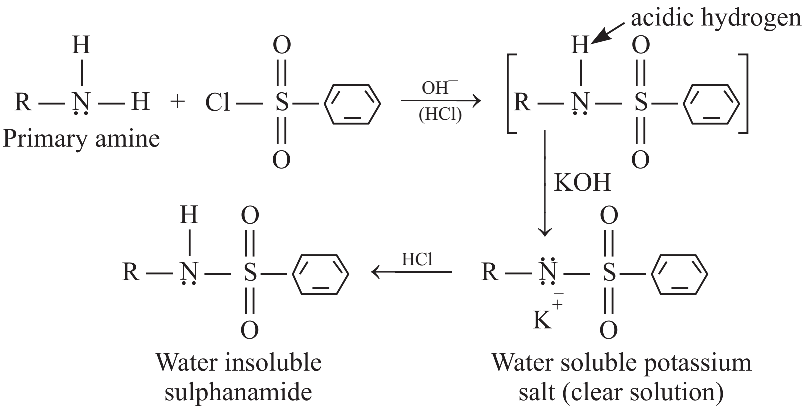
Amines are very useful compounds. They are used for a variety of purposes in the laboratory as well as in the industry. Some aliphatic amines are used as solvents and intermediates in drug synthesis. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents. Aromatic amines e.g. aniline and its derivatives, are used for the production of dyes, drugs and photographic developers. 1,4-Diaminobenzene is the main ingredient of all hair dyes. Many dithiocarbamates which are the compounds derived from primary amines, are used as herbicides. Diazonium salts obtained from primary aromatic amines form the basis of synthesis of many other organic compounds.

28.2.7 Identification of Primary, Secondary and Tertiary amines

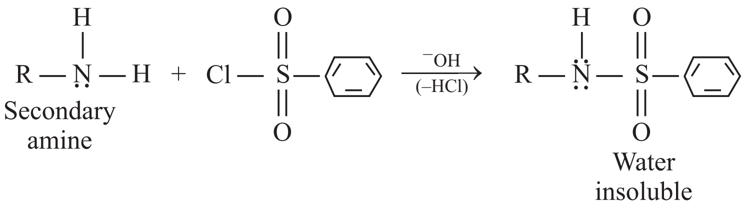
Primary, secondary and tertiary amines can be distinguished from each other using **Hinsberg test**. In this test, a small amount of the amine and benzene sulphonyl chloride is shaken with excess of potassium hydroxide. After allowing the reaction to take place, the mixture is acidified. The following is observed for different types of amines.

The **primary amines** react with benzene sulphonyl chloride to form *N*-substituted benzene sulphonamide which in turn, forms, water soluble potassium salt, with excess of potassium hydroxide.

This clear solution on acidification gives water-insoluble *N*-substituted sulphonamide which precipitates out.



The **secondary amines** react with benzene sulphonyl chloride in aqueous potassium hydroxide to give insoluble *N*, *N*-disubstituted sulphonamides which form a precipitate. These sulphonamides are not soluble in aq. KOH because they do not have an acidic hydrogen. Hence, on further acidification also, there is no change in the reaction mixture.

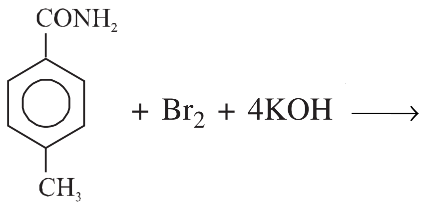


In case of tertiary amines, if the amine is water insoluble then no change will take place on addition of benzene sulphonyl chloride and aq. KOH as no reaction will take place. However, when we acidify this mixture, the tertiary amine will dissolve as a water soluble salt will form.

INTEXT QUESTIONS 28.2

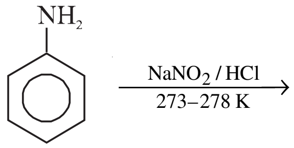
1. Predict the major product of the following reactions :

(a)

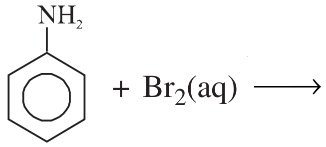


(b) $CH_3CH_2NH_2 \xrightarrow{NaNO_2\,/\,HCl}$

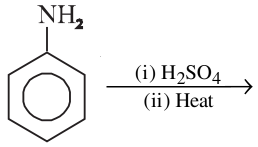
(c)



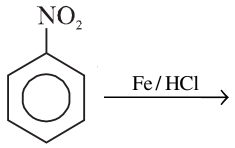
(d)



(e)



(f)



2. Why is aniline very reactive towards bromination?
3. Name the test which uses potassium hydroxide and chloroform for identifying a primary amine.
4. Can aniline be nitrated directly?
5. How will you obtain sulphanilic acid from benzene?

28.3 DIAZONIMUM SALTS: REACTIONS AND IMPORTANCE IN SYNTHETIC CHEMISTRY

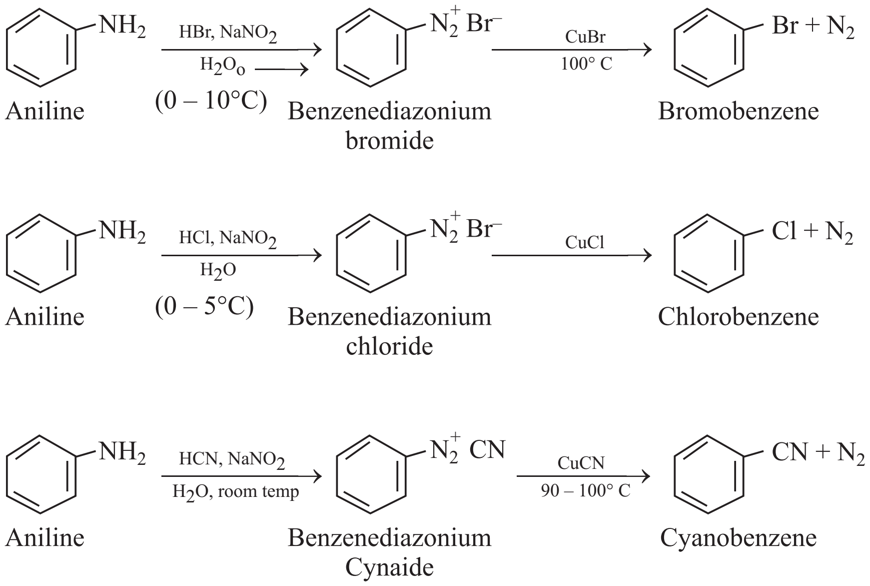
Most of the arenediazonium salts (formed from aromatic amines) are unstable at temperatures above 5–10°C. These salts explode when dry.

Therefore, many of their further reactions are carried out without isolating them.

The reactions of diazonium salts are very important synthetically because the diazonium group can be replaced by a variety of other groups such as –F, –Cl, –Br, –I, –CN, –OH and –H. These reactions are given below.

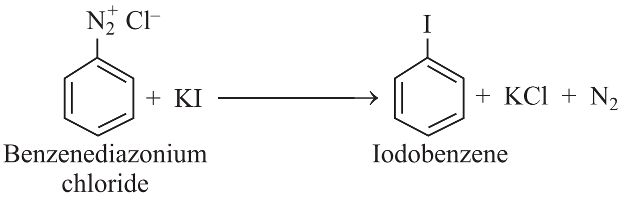
(i) The Sandmeyer reaction

In this reaction, the arene diazonium salts are reacted with cuprous bromide, cuprous chloride and cuprous cyanide in the presence of HBr, HCl and HCN, respectively. Some of the examples of **Sandmeyer reaction** are given below: You can see in these reactions that the diazonium group is replaced by –Br, –Cl and –CN group.



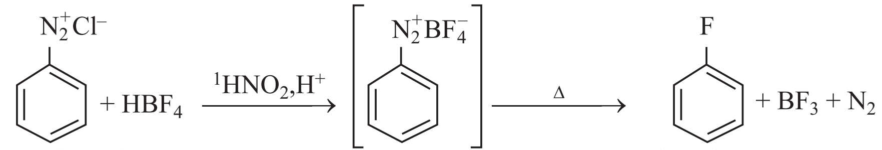
(ii) Replacement of diazonium group by –I group

In this reaction, the dizonium salt is treated with potassium iodide to give the product in which diazonium group has been replaced by –I group.



(iii) Replacement of diazonium group by –F group

Here, the diazonium salt is first treated with fluoroboric acid (HBF_4) and the diazonium fluoroborate precipitated is isolated and dried. It is then heated until it starts decomposing to give the aryl fluoride product.

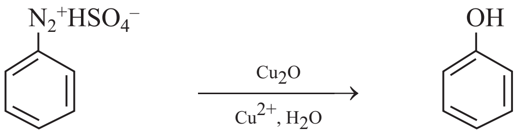


Benzenediazonium chloride

Fluorobenzene

(iv) Replacement of dizonium group by –OH group

If cuprous oxide is added to a dilute solution of the diazonium salt containing a large excess of cupric nitrate, then the diazonium group is replaced by a hydroxyl group.

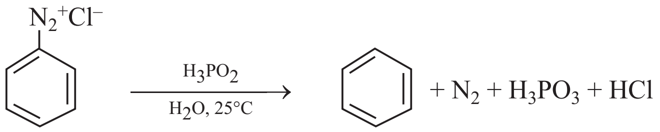


Benzen diazonium hydrogen sulphate

Phenol

(v) Replacement of diazonium group by a hydrogen atom

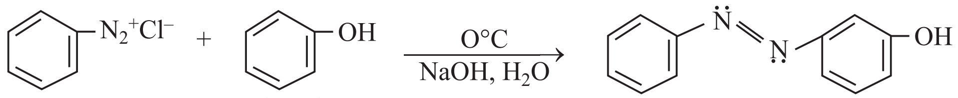
The reaction of diazonium salts with hypophosphorous acid (H_3PO_2) replaces the diazonium group by a hydrogen atom.



Benzene

(vi) Coupling Reactions of Arenediazonium Salts

Arenediazonium salts react with phenols and tertiary aryl amines to give azo compounds which are known *azo dyes*. This reaction is called *diazo coupling reaction*.



Benzane diazoniaum chloride

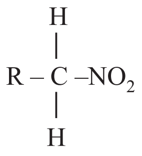
Phenol

P -Hydrozyazobenzene

Hence, by using the above reactions, we can synthesize a variety of compounds.

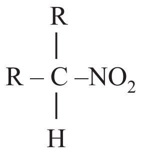
28.4 NITRO COMPOUNDS

Nitro compounds are those derivatives of hydrocarbons in which a hydrogen atom is replaced by a nitro (–NO_2) group. They may be aliphatic or aromatic. Nitroalkanes are divided into primary (1°), secondary (2°) or tertiary (3°) nitro alkanes depending upon the attachment of nitro group to primary, secondary or tertiary carbon atom, respectively.



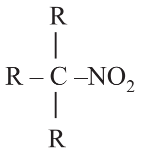
$R-\overset{H}{\underset{H}{C}}-NO_2$

***p*-nitroalkane**



$R-\overset{R}{\underset{H}{C}}-NO_2$

sec-nitroalkane

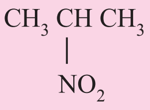
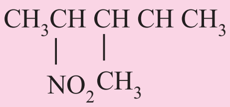
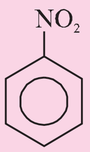
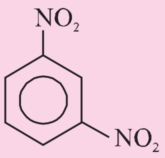


$R-\overset{R}{\underset{R}{C}}-NO_2$

tert-nitroalkane

28.4.1 IUPAC Nomenclature of Nitro Compounds

According to IUPAC system, nitro compounds are named by prefixing the word nitro before the name of the parent hydrocarbon. The number of nitro groups and their positions are suitably indicated as shown in some examples given below.

Compound	IUPAC Name
CH_3-NO_2	Nitromethane
$CH_3CH_2-NO_2$	Nitroethane
 $CH_3\underset{NO_2}{CH}CH_3$	2-Nitropropane
 $CH_3\underset{NO_2}{CH}\underset{CH_3}{CH}CH\,CH_3$	2-Nitro - 3- methylbutane
	Nitrobenzene
	1, 3 - Dinitrobenzene (*m* - Dinitrobenzene)

28.4.2 Preparation of Nitro Compounds

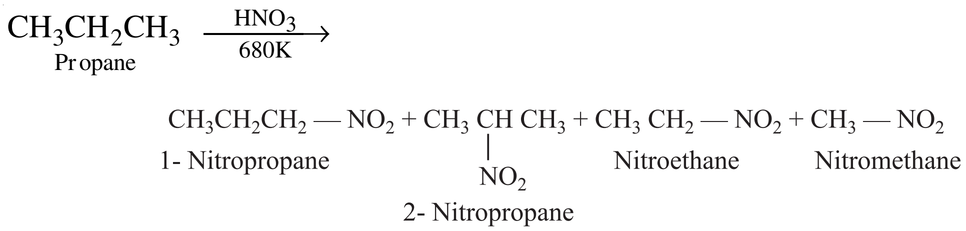
(i) ***From alkyl halides :*** Nitroalkanes are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite. In this reaction, a small amount of isomeric alkyl nitrites (R–O–N = O) is also obtained.

$$R - X + AgNO_2 \longrightarrow R - NO_2 \quad + \quad AgX$$

For example. bromoethane on reaction with silver nitrite gives nitroethane.

$$\underset{\textbf{Bromoethane}}{CH_3CH_2Br} + AgNO_2 \longrightarrow \underset{\textbf{Nitroethane}}{CH_3CH_2NO_2} \; + \; AgBr$$

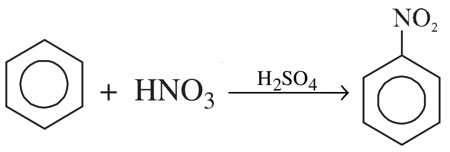
(ii) ***By nitration of alkanes :*** Nitroalkanes can also be prepared by the nitration of alkanes in vapour phase. For this reaction, a mixture of the alkane and nitric acid is passed through a metal tube at about 680 K. This reaction always yields a mixture of compounds due to the cleavage of the starting alkane. For example, propane on nitration gives a mixture of following compounds.



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[680K]{HNO_3}$$

$$\underset{\text{1- Nitropropane}}{CH_3CH_2CH_2 - NO_2} + \underset{\text{2- Nitropropane}}{\underset{\underset{NO_2}{|}}{CH_3\,CH\,CH_3}} + \underset{\text{Nitroethane}}{CH_3\,CH_2 - NO_2} + \underset{\text{Nitromethane}}{CH_3 - NO_2}$$

(iii) ***By nitration of aromatic compounds :*** Aromatic nitro compounds are almost always prepared by direct nitration. For example, nitration of benzene gives nitrobenzene. The reaction is generally carried out with a mixture of concentrated nitric acid and concentrated sulphuric acid.



Benzene **Nitrobenzene**

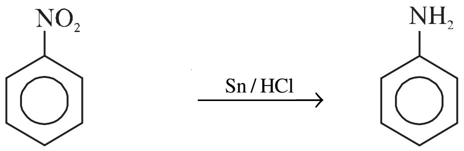
28.4.3 Physical Properties of Nitro Compounds

Nitroalkanes are colourless oily liquids in the pure state. They have pleasant smell. They possess higher boiling points than the corresponding alkanes because of their polar nature. Amongst the aromatic nitro compounds, nitrobenzene is a yellow liquid with the smell of bitter almonds. Most other aromatic nitro compounds are yellow crystalline solids. All the nitro compounds are heavier than water and insoluble in it. They are, however, soluble in organic solvents like alcohol, ether, benzene, chloroform etc.

28.4.4 Chemical Properties of Nitro Compounds

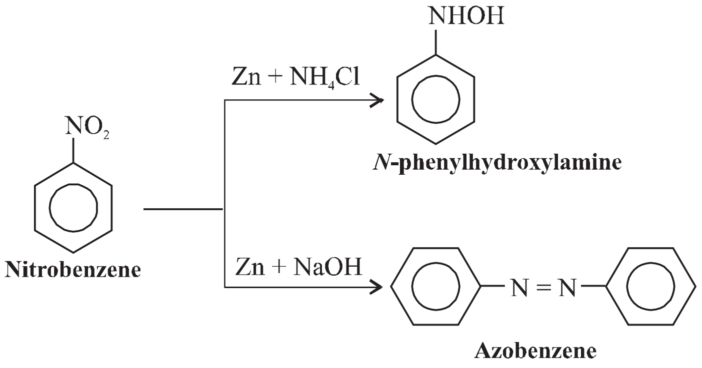
(i) ***Reduction :*** One of the important reactions of nitro compounds is reduction. Nitro compounds can be readily reduced to primary amines by a variety of reducing agents. For example, (a) hydrogen in presence of catalyst like nickel or platinum (b) a metal like tin or iron in presence of hydrochloric acid and (c) lithium aluminium hydride. Reduction of nitroethane and nitrobenzene provides ethanamine and aniline, respectively.

$$\underset{\textbf{Nitroethane}}{CH_3CH_2-NO_2} + 3H_2 \xrightarrow{Ni} \underset{\textbf{Ethanamine}}{CH_3CH_2-NH_2} + 2H_2O$$



Nitrobenzene **Aniline**

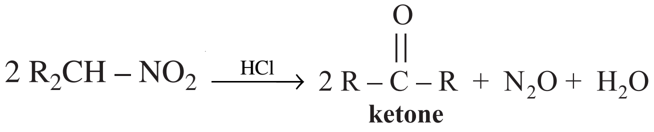
Nitrobenzene on reduction in neutral medium, using zinc dust and ammonium chloride yields *N*-phenylhydroxylamine whereas its reduction in alkaline medium using zinc and sodium hydroxide yields azobenzene.



(ii) ***Hydrolysis :*** Primary nitroalkanes on reaction with dilute hydrochloric acid or sulphuric acid undergo hydrolysis to produce carboxylic acids and hydroxylamine.

$$RCH_2-NO_2 + H_2O \xrightarrow{HCl} \underset{\textbf{A carboxylic acid}}{R-COOH} + \underset{\textbf{Hydroxylamine}}{NH_2OH}$$

Secondary nitroalkanes on hydrolysis form ketones.

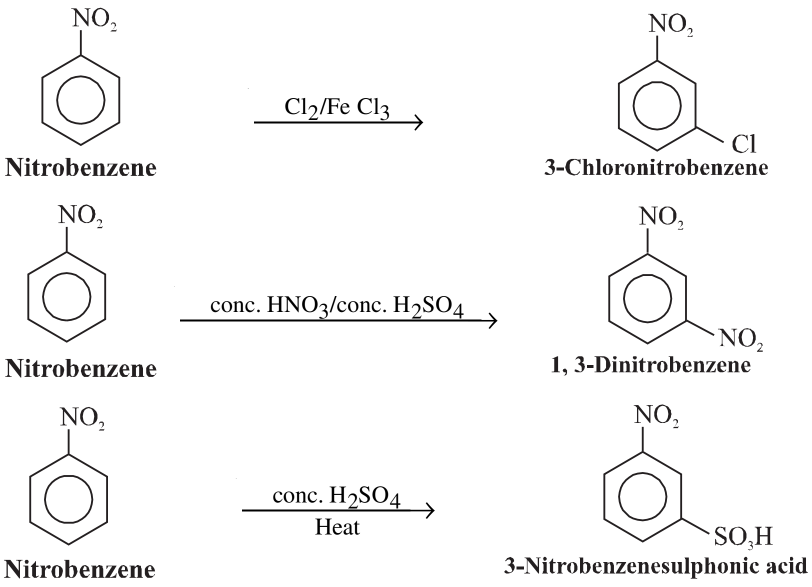


$$2\,R_2CH-NO_2 \xrightarrow{HCl} 2\,\underset{\textbf{ketone}}{R-\overset{\overset{\displaystyle O}{||}}{C}-R}} + N_2O + H_2O$$

(iii) ***Thermal decomposition :*** Nitroalkanes decompose with explosion on heating. Advantage is taken of this reaction in the commercial use of nitroalkanes as explosives. It is due to the formation of large volume of gaseous products on heating which produce high pressure.

$$2\,CH_3NO_2 \xrightarrow{\Delta} N_2 + 2\,CO_2 + 3\,H_2$$

(iv) ***Ring substitution in aromatic nitro compounds*** : You know that $-NO_2$ group is a deactivating and *meta* - directing group for electrophilic substitution reactions. It is due to the electron withdrawing tendency of $-NO_2$ group. Thus, nitrobenzene on halogenation, nitration or sulphonation gives the *meta*-substituted products as shown below.

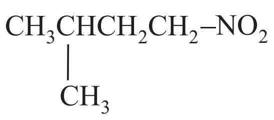


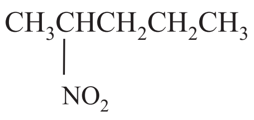
28.4.5 Uses of Nitro Compounds

1. Nitroalkanes are used as solvents for rubber, cellulose acetate etc.
2. They are used as intermediates in the industrial production of explosives, detergents, medicines, amines etc.
3. Nitro compounds are also used as fuel in small engines and rockets.

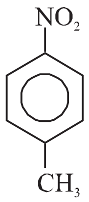
INTEXT QUESTIONS 28.4

1. Write IUPAC names of the following :

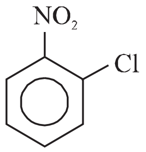
(a)

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2CH_2{-}NO_2$$

(b)

$$CH_3\underset{\displaystyle NO_2}{\underset{|}{C}H}CH_2CH_2CH_3$$

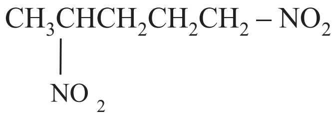
(c)



(d)



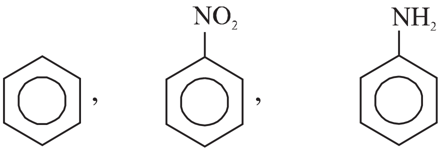
(e)



$$\underset{\displaystyle NO_2}{CH_3\underset{|}{C}HCH_2CH_2CH_2-NO_2}$$

2. Write the product formed when 1,3 - dinitrobenzene is treated with tin and hydrochloric acid.

3. Arrange the following compounds in increasing order of their reactivity towards halogenation.



4. Which reaction of nitroalkanes makes them suitable to be used as rocket fuel?

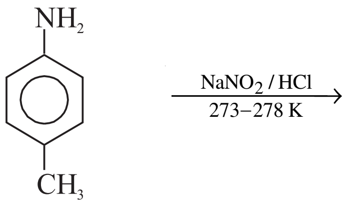
WHAT YOU HAVE LEARNT

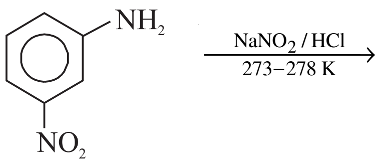
- Amines are considered as derivatives of ammonia. They are classified as primary, secondary or tertiary based on how many alkyl groups have replaced the hydrogen atoms of ammonia.
- Reaction of alkyl halides with ammonia produces a mixture of primary, secondary or tertiary amines alongwith quaternary ammonium salts.
- Reduction of nitriles, amides and nitro compounds gives amines having the same number of carbon atoms.
- In Hofmann bromamide reaction, the amine formed has one carbon less than the starting amide.
- Both aliphatic and aromatic amines are basic in nature. But aromatic amines are less basic and aliphatic amines are more basic than ammonia. An aliphatic secondary amine is more basic than primary and tertiary amines.
- Primary amines can be differentiated from secondary and tertiary amines by carbylamine reaction.
- Aliphatic primary amines undergo diazotisation to form alcohols whereas aromatic primary amines form diazonium salts.

- The amino group (–NH_2) is an activating and *ortho*-, *para*-directing group towards the electrophilic aromatic substitution reactions.
- Nitroalkanes are obtained by the reaction of alkyl halides with alcoholic silver nitrite.
- Nitrobenzene is obtained by the direct nitration of benzene with conc. HNO_3 in the presence of conc. H_2SO_4.
- Primary nitroalkanes are hydrolysed in acidic medium to give carboxylic acids whereas secondary nitroalkanes give ketones.
- All nitro compounds are reduced into amino compounds by (i) hydrogen in presence of catalyst or (ii) tin or iron in presence of hydrochloric acid.
- Nitro group is deactivating and *meta*-directing group towards electrophilic aromatic substitution reactions.

TERMINAL EXERCISE

1. Write the structural formula of the following compounds :
   (i) 2-Methylpropan - 2-amine
   (ii) Butan - 2-amine
   (iii) *N*-Ethyl - *N*-methylbutan - 1-amine
   (iv) 2-Methyl - 2-nitropropane
   (v) 4-Nitrotoluene
2. What do you understand by diazotisation? Write the product of following reactions.

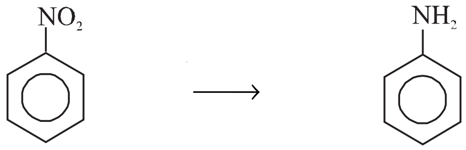
(i) 

(ii) 

(iii) $CH_3–CH_2–CH_2–NH_2 \xrightarrow[273-278\ K]{NaNO_2\ /\ HCl}$

3. How will you prepare butan-1-amine starting from a suitable amide? Name the reaction involved.

4. What different reagents can be used for the following conversion?



5. Arrange the following amines in increasing order of their basicities :

   Ethanamine, *N*-Methylethanamine, Aniline

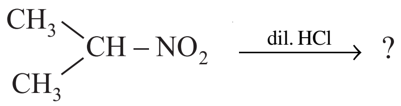
6. How will you prepare sulphanilic acid from nitrobenzene?

7. What happens when ethanamine is treated with excess of chloroethane?

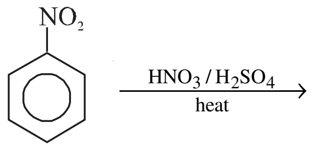
8. Write the reaction sequence to convert nitromethane into ethanamine.

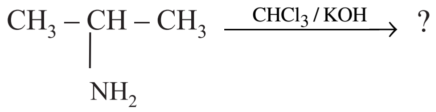
9. How will you prepare *para*-bromoaniline from nitrobenzene? Can this compound be obtained by direct bromination of aniline with aqueous solution of bromine? Explain.

10. Complete the following reactions :

(i)

$(CH_3)_2CH-NO_2 \xrightarrow{\text{dil. HCl}} ?$

(ii) $CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2/KOH} ? \xrightarrow[273-278\text{ K}]{NaNO_2/HCl} ?$

(iii)


(iv)

$CH_3-\underset{NH_2}{CH}-CH_3 \xrightarrow{CHCl_3/KOH} ?$

(v) $CH_3CH_2CH_2-Br + AgNO_2 \xrightarrow{\text{alcohol}} ?$

ANSWERS TO INTEXT QUESTIONS

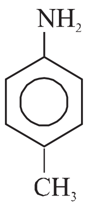
28.1

1. (i) Primary amine (ii) Secondary amine
   (iii) Secondary amine (iv) Tertiary amine
   (v) Primary amine (vi) Quaternary ammonium salt

2. (i) Butan-1-amine
   (ii) *N, N*-Dimethylethanamine
   (iii) *N*-Methylbutan-1- amine
   (iv) Butan-2-amine
   (v) 3-Bromoaniline
   (vi) 2-Ethylaniline

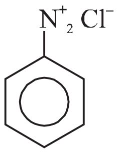
28.2

1. (i)

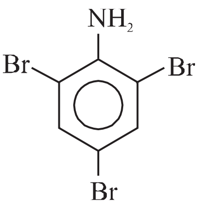


(ii) CH_3CH_2OH

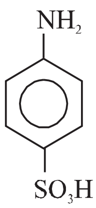
(iii)



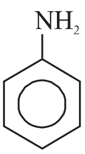
(iv)



(v)



(vi)

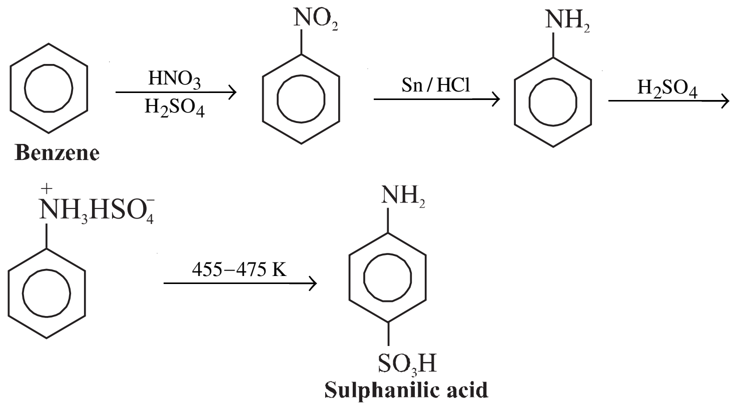


2. Aniline is very reactive towards bromination because the $–NH_2$ group is a highly activating group.

3. Carbylamine test.

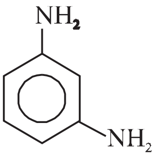
4. No

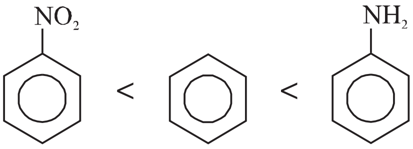
5.



28.3

1. (i) 3-Methyl-1-nitrobutane
   (ii) 2-Nitropentane
   (iii) 4- Nitrotoluene
   (iv) 2-Chloronitrobenzene
   (v) 1,4 –Dinitropentane

2. 

3. 

4. Nitroalkanes decompose on heating and produce large volume of gases. The formation of gaseous products at high pressure produces the thrust which is necessary for the movement of rocket.

313en29

29

BIOMOLECULES

You are aware that our body, plants and other animals are made up of many chemical substances. There are certain complex organic molecules which form the basis of life. These build up living organisms and are also required for their growth and maintenance. Such molecules are called **biomolecules.** The main classes of biomolecules are carbohydrates, proteins, lipids, nucleic acids, enzymes, hormones etc. In this lesson, you will study about the structures and functions of some important biomolecules.

OBJECTIVES

After reading this lesson you will be able to :

- discuss different types of biomolecules;
- describe the important structural features of biomolecules;
- classify carbohydrates, proteins and lipids on the basis of their structure and functions;
- give the composition of proteins and nucleic acids;
- explain the difference between DNA and RNA;
- differentiate between oils and fats;
- explain the action of enzymes and their characteristic features and
- discuss important hormones and their importance
- name some important vitamins and give their deficiency symptoms.
- list the functions of biomolecules in biological systems.

29.1 CARBOHYDRATES

Carbohydrates form a very large group of naturally occurring organic compounds which play a vital role in daily life. They are produced in plants by the process of

photosynthesis. The most common carbohydrates are glucose, fructose, sucrose, starch, cellulose etc. Chemically, the carbohydrates may be defined as **polyhydroxy aldehydes** or **ketones** or **substances which give such molecules on hydrolysis**. Many carbohydrates are sweet in taste and all sweet carbohydrates are called as **sugars**. The chemical name of the most commonly used sugar in our homes is sucrose.

29.1.1 Classification of Carbohydrates

Carbohydrates are classified into three groups depending upon their behaviour on hydrolysis.

(i) **Monosaccharides**: A polyhydroxy aldehyde or ketone which cannot be hydrolysed further to a smaller molecule containing these functional groups, is known as a *monosaccharide*. About 20 monosaccharides occur in nature and glucose is the most common amongst them.

Monosaccharides are further classified on the basis of the 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**. The number of carbon atoms present is also included while classfying the compound as is evident from the examples given in Table 29.1. Name of some naturally occuring monosaccharides are given in brackets.

Table 29.1 Classification of monosaccharides

No. of carbon atoms present	Type of monosaccharide	
	Aldose	Ketose
3	Aldotriose (Glyceraldehyde	Ketotriose
4	Aldopentose ((Xylose)	Ketopentose
5	Aldotetrose (Erythrose)	Ketotetrose
6	Aldohexose (Glucose)	Ketohexose
7	Aldoheptose	Ketoheptose

(ii) **Disacccharides:** Carbohydrates which give two monosaccharide molecules on hydrolysis are called disaccharides e.g. sucrose, maltose, lactose etc.

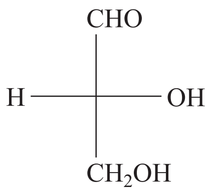
(iii) **Oligosacharides:** Carbohydrates that yield 2–10 molecules of monosascharides are called **oligosaccharides.**

(iv) **Polysaccharides:** Carbohydrates which yield a large number of monosaccharide units on hydrolysis e.g. starch, glycogen, cellulose etc.

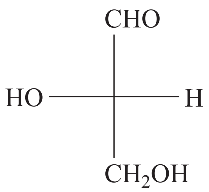
29.1.2 Structure of Monosaccharides

Although a large number of monosaccharides are found in nature.

D-or L-before the name of monosaccharides indicates the configuration of particular stereoisomer. Various stereoisomers are assigned relative configurations as D– or L –. This system of assigning the relative configuration refers to their relation with the glyceraldehyde. Glyceraldehyde contains one asymmetric carbon atom and hence exists in two enantiomeric forms as shown below.

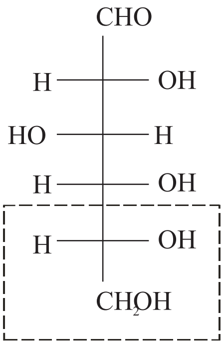


D-(+) –glyceraldehyde

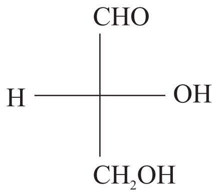


L-(–) –glyceraldehyde

All those compounds which can be correlated to (+) -glyceraldehyde are said to have D-configuration and those can be correlated to (–) -glyceraldehyde are said to have L–configuration. In monosaccharides, it is the lowest asymmetric carbon atom (shown in the box) by which the correlation is made. As in (+) glucose, the lowest asymmetric carbon atom has –OH group on the right side which matches with (+) glyceraldehyde; hence, it is assigned D-configuration.



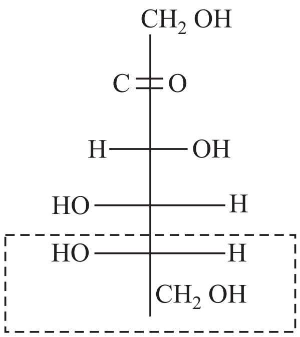
**(+) – glucose or
D-glucose**



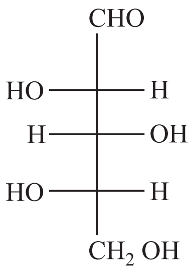
**(+) – glyceraldehyde or
D-glyceraldehyde**

L-Configuration Examples

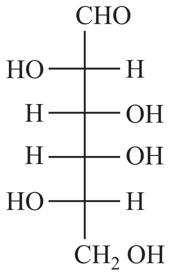
Some example of molecules having L-configuration are shown below:



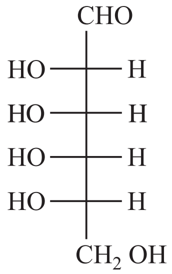
L - fructose



L - Xylose



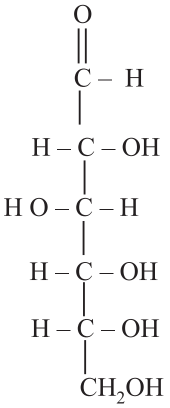
L - Galactose



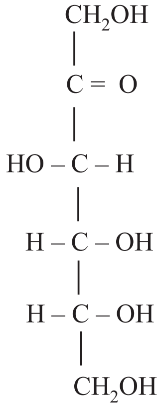
L - Allose

We will confine our discussion here to four of them only viz. D-glucose, D-fructose,D-ribose and 2-deoxy-D-ribose.

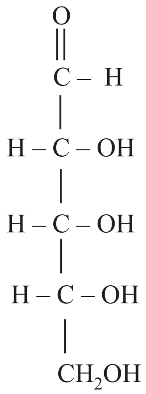
D-Glucose (an aldohexose) is the monomer for many other carbohydrates. Alone or in combination, glucose is probably the most abundant organic compound on the earth. D-Fructose (a ketohexose) is a sugar that is found with glucose in honey and fruit juices. D-Ribose (an aldopentose) is found in ribonucleic acids (RNA) while. 2-Deoxy-D-ribose is an important constituent of the deoxyribonucleic acids(DNA). Here, the prefix 2-Deoxy indicates that it lacks oxygen at carbon no. 2.



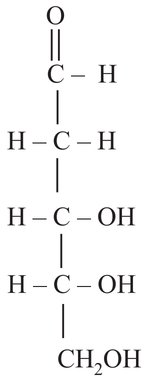
D-Glucose



D-Fructose



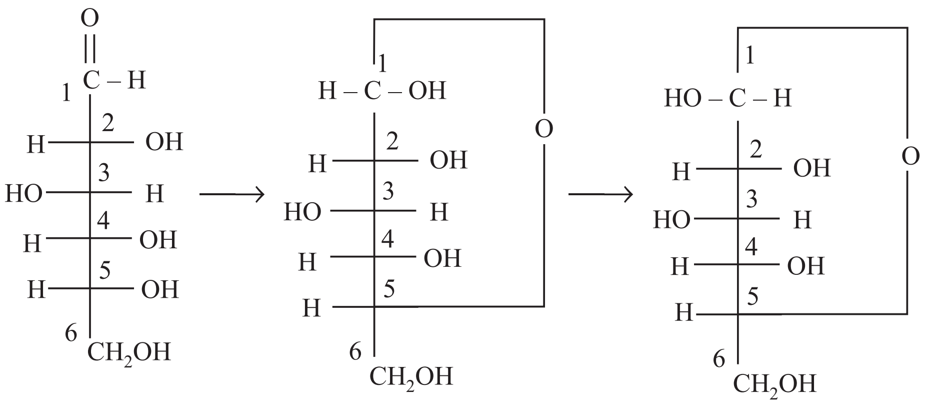
D-Ribose



2-Deoxy-D-ribose

These monosaccharides generally exist as cyclic compounds in nature. A ring is formed by a reaction between the carbonyl group and one of the hydroxyl groups present in the molecule. Glucose preferentially forms the six membered ring which can be in two different isomeric forms called α- and β-forms (shown below as I and II). The two forms differ only in the arrangement of the hydroxyl group at carbon No.1. Such isomers are called **anomers**.

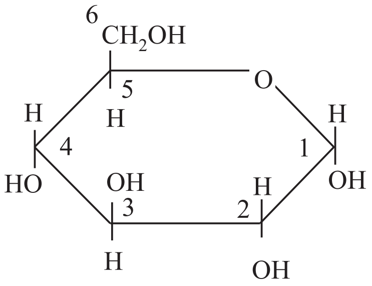
Formation of these cyclic structures (I and II) from the open chain structure can be shown as follows.



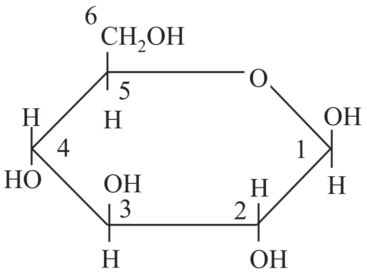
(I) α – D – glucose

(II) β – D –glucose

The cyclic structures I and II are more appropriately represented as Ia and IIa.

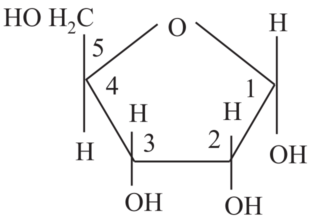


(Ia)

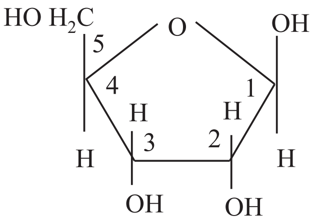


(IIa)

The α- and β-forms of other sugars also exist in the cyclic form. D-Ribose forms a five membered ring structure as shown below :



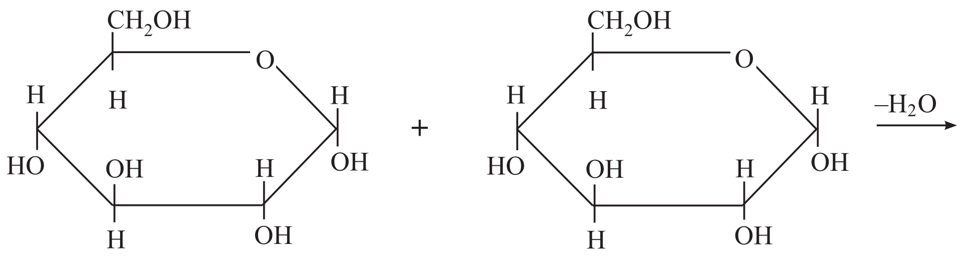
α – D – ribose



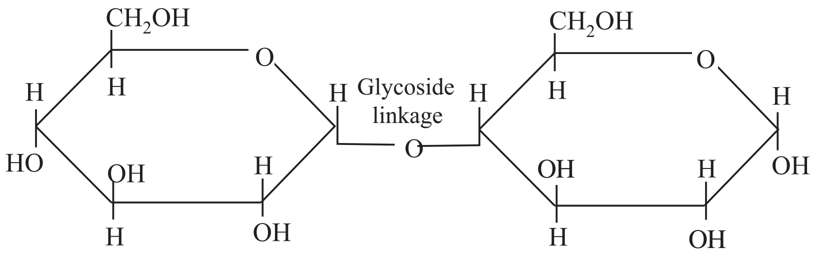
β – D – ribose

29.1.3 Structure of Di-Saccharides, Oligo Saccharides and Polysaccharides

Disaccharides are formed by the condensation of two monosaccharide molecules. These monosaccharides join together by the loss of a water molecule between one hydroxyl group on each monosaccharide. Such a linkage, which joins the monosaccharide units together is called **glycoside linkage**. If two α-glucose molecules are joined together, the disaccharide maltose is formed.

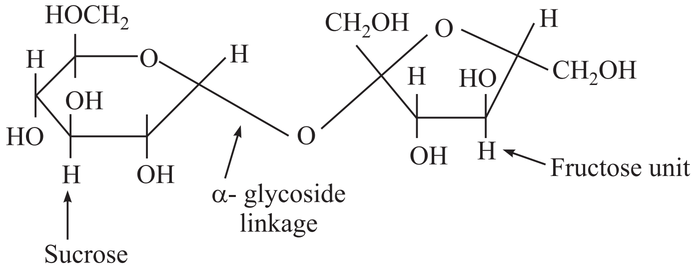


2 molecules of α – glucose

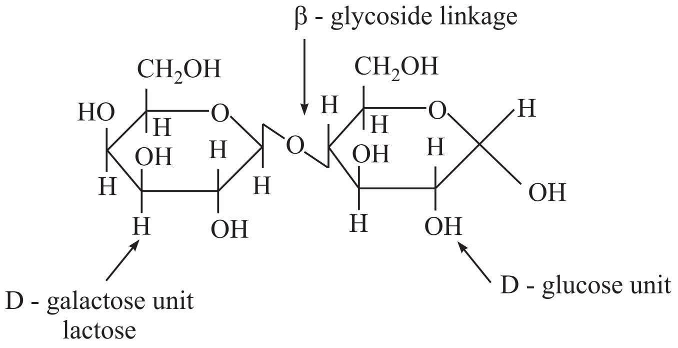


Maltose

Similarly, sucrose (the common sugar) consists of one molecule of glucose and one molecule of fructose joined together.



Lactose(or milk sugar) is found in milk and is formed by joining of one molecule of glucose and one molecule of galactose.



If a large number of monosaccharide units are joined together, we get polysaccharides. These are the most common carbohydrates found in nature. They have mainly one of the following two functions- either as food materials or as structural materials. Starch is the main food storage polysaccharide of plants. It is a polymer of α-glucose and consists of two types of chains- known as **amylose** and **amylopectin**.

Amylose is a water soluble fraction of starch and is a linear polymer of α-D-glucose. On the other hand, amylopectin is a water insoluble fraction and consists of branched chain of α-D-glucose.

Cellulose is another natural polysaccharide which is the main component of wood and other plant materials. It consists of long chain of β-D-glucose molecules.

Glycogen

The carbohydrates are stored in animal body as glycogen and its structure is similar to amylopectin.

It is a polysaccharide containing the α-D-glucose monosaccharide and does the same energy storage function in animals which the starch does in plants. The carbohydrates which are not needed immediately by the body are converted by the body to glycogen for long term storage. Glycogen molecules are larger than those of amylopectin and are having more branched structure.

29.1.4 Biological Importance of Carbohydrates

(i) Carbohydrates act as storage molecules. For example they are stored as starch in plants and as glycogen in animals.

(ii) D-Ribose and 2-deoxy-D-ribose are the constituents of RNA and DNA, respectively.

(iii) Cell walls of bacteria and plants are made up of cellulose. It may be of interest to note that human digestive system does not have the enzymes required for the digestion of cellulose but some animals do have such enzymes.

(iv) Some carbohydrates are also linked to many proteins and lipids. These molecules are known as glycoproteins and glycolipids, respectively. These molecules perform very specific functions in organisms.

INTEXT QUESTIONS 29.1

1. Name three constituents of your diet which provide carbohydrates.
2. How are carbohydrates produced in nature?

Notes

3. What are the hydrolysis products of starch and sucrose?
4. Write the linear and ring forms of D-glucose.

29.2 PROTEINS

Proteins are the most abundant macromolecules in living cells. The name protein is derived from the Greek word **'proteios'** meaning 'of prime importance'. These are high molecular mass complex amino acids. You will study about amino acids in the next section. Proteins are most essential class of biomolecules because they play the most important role in all biological processes. A living system contains thousands of different proteins for its various functions. In our every day food pulses, eggs, meat and milk are rich sources of proteins and are must for a balanced diet.

29.2.1 Classification of Proteins

Proteins are classified on the basis of their chemical composition, shape and solubility into two major categories as discussed below.

(i) Simple proteins: Simple proteins are those which, on hydrolysis, give only amino acids. According to their solubility, the simple proteins are further divided into two major groups **fibrous** and **globular proteins**.

(a) Fibrous Proteins: These are water insoluble animal proteins eg. collagen (major protein of connective tissues), elastins (protein of arteries and elastic tissues), keratins (proteins of hair, wool, and nails) are good examples of fibrous proteins. Molecules of fibrous proteins are generally long and thread like.

(b) Globular Proteins: These proteins are generally soluble in water, acids, bases or alcohol. Some examples of globular proteins are albumin of eggs, globulin (present in serum), and haemoglobin. Molecules of globular proteins are folded into compact units which are spherical in shape.

(ii) Conjugated proteins: Conjugated proteins are complex proteins which on hydrolysis yield not only amino acids but also other organic or inorganic components. The non-amino acid portion of a conjugated protein is called **prosthetic group**.

Unlike simple proteins, conjugated proteins are classified on the basis of the chemical nature of their prosthetic groups. These are

a. Nucleoproteins (protein + nucleic acid)
b. Mucoproteins and glycoproteins (protein+ carbohydrates)
c. Chromoproteins (proteins + a coloured pigment)
d. Lipoproteins (proteins + lipid)

e. Metalloproteins (metal binding proteins combined with iron, copper or zinc)

f. Phosphoproteins (proteins attached with a phosphoric acid group).

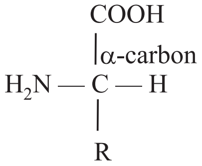
Proteins can also be classified on the basis of functions they perform, as summarized in table 29.2.

Table 29.2 : Classification of proteins according to their biological functions

Class	Functions	Examples
1. Transport Proteins	Transport of oxygen, glucose and other nutrients	Haemoglobin Lipoproteins
2. Nutrient and storage Proteins	Store proteins required for the growth of embryo	Gliadin(wheat) Ovalbumin(egg) Casein (milk)
3. Structural Protiens	Give biological structures, strength or protection	Keratin(Hair, nails,etc.) collagen(cartilage)
4. Defence Proteins	Defend organisms against invasion by other species	Antibodies Snake venoms
5. Enzymes	Act as catalysts in biochemical reactions	Trypsin,Pepsin
6. Regulatory Proteins	Regulate cellular or physiological activity	Insulin

29.2.2 Structure of Proteins

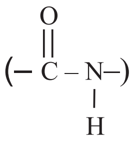
Protein molecules are polymers of different sizes and shapes with different physical and chemical properties. The monomer units for proteins are amino acids. All the amino acids that are found in proteins have an amino group(-NH_2) on the carbon atom adjacent to carbonyl group, hence are called α-amino acids. The general formula of α-amino acids is shown below.



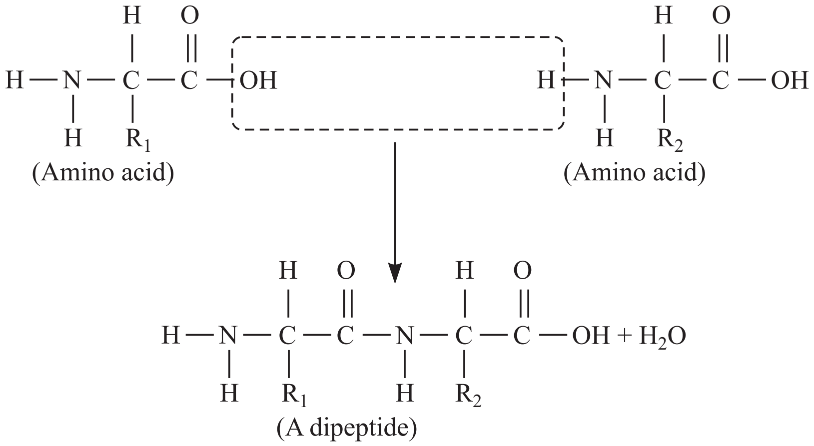
$$H_2N-\overset{\overset{COOH}{|\ \alpha\text{-carbon}}}{\underset{\underset{R}{|}}{C}}-H$$

All proteins found in nature are the polymers of about twenty (20) different α-amino acids and all of these have L-configuration. Out of these ten (10) amino acids cannot be synthesized by our body and hence must form the part of our diet. These are called **essential amino acids**.

All proteins have one common structural feature that their amino acids are connected to one another by *peptide linkages*. By a peptide linkage we mean an



amide $(-\overset{\overset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-)$ bond formed when the carboxyl group of one amino acid molecule reacts with the α-amino group of another. In the process, a molecule of water is given off. The product of the reaction is called a *peptide* or more precisely a dipeptide because it is made by combining two amino acids, as shown below:



$$\mathrm{H-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{R_1}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH} \qquad \mathrm{H-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{R_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH}$$

(Amino acid) (Amino acid)

$$\downarrow$$

$$\mathrm{H-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{R_1}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{R_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH + H_2O}$$

(A dipeptide)

If a third amino acid is joined to a **dipeptide** in the same manner, the product is a **tripeptide**. Thus, a tripeptide contains three amino acids linked by two peptide linkages. Similar combinations of four, five, six amino acids give a **tetrapeptide**, a **pentapeptide**, a **hexapeptide**, respectively. Peptides formed by the combination of more than ten amino acid units are called **polypeptides**. **Proteins are polypeptides** formed by the combination of **large number of amino acid units**. There is no clear line of demarcation between polypeptides and proteins. For example insulin, although it contains only 51 amino acids, is generally considered a small protein.

The amino acid unit with the free amino group is known as the ***N***-terminal residue and the one with the free carboxyl group is called the ***C***-terminal residue. By convention, the structure of peptide or proteins written with the ***N***-terminal residue on the left and the ***C***-terminal on the right.

The actual structure of a protein can be discussed at four different levels.

(i) **Primary structure**: Information regarding the sequence of amino acids in a protein chain is called its primary structure. The primary structure of a protein determines its functions and is critical to its biological activity.

(ii) **Secondary structure**: The secondary structure arises due to the regular folding of the polypeptide chain due to hydrogen bonding between $-\underset{\underset{O}{\|}}{C}-$ and $>N-H$ group. Two types of secondary structures have been reported. These are – α helix (Fig. 29.1) when the chain coils up and β-pleated sheet (Fig. 29.2) when hydrogen bonds are formed between the chains.

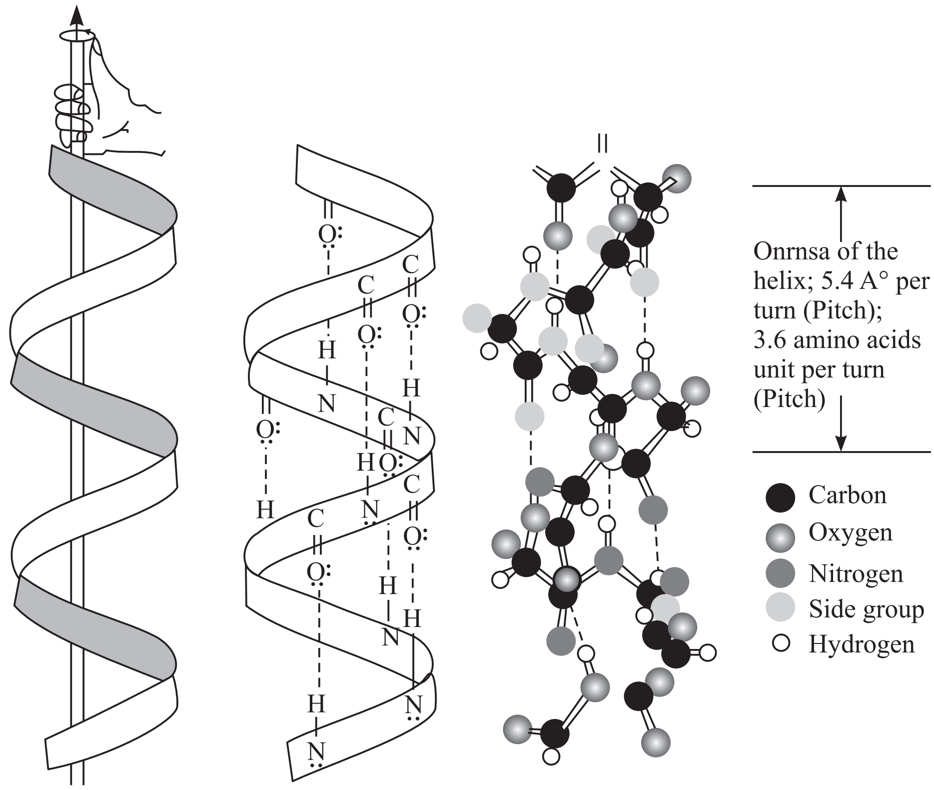
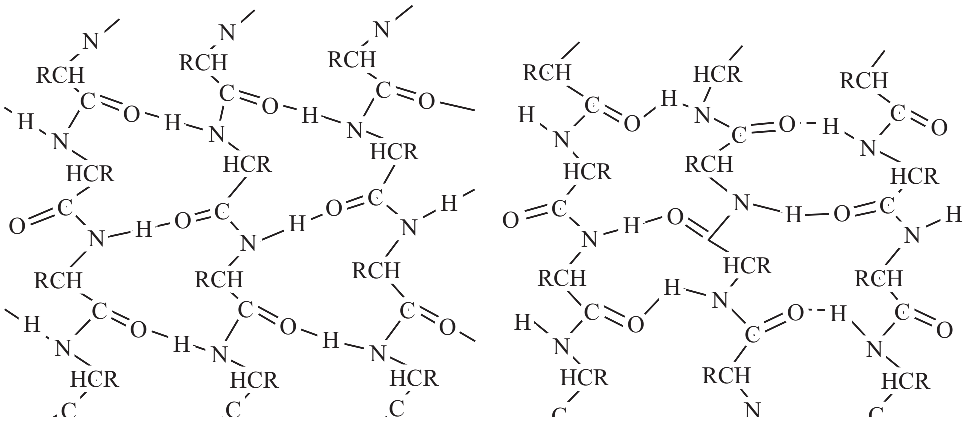


Fig. 29.1 : *The a-helix structure of protein*



Parallel β-Conformation **Antiparallel β-Conformation**

Fig. 29.2 : *The β-pleated-sheet structure of protein*

(iii) Tertiary structure: It is the three-dimensional structure of proteins. It arises due to folding and superimposition of various a-helical chains or b-plated sheets. For example Fig. 29.3 represents the tertiary structure for the protein myoglobin.

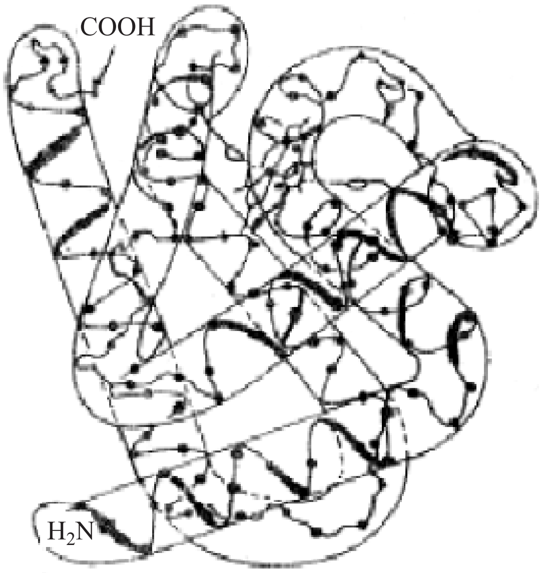


Fig. 29.3 : *Structure of myoglobin*

(iv) **Quaternary structure:** The quaternary structure refers to the way in which simple protein chains associate with each other resulting in the formation of a complex protein.

By different modes of bonding in secondary and tertiary structural levels a protein molecule appears to have a unique three-dimensional structure.

29.2.3 Denaturation

One of the great difficulties in the study of the structure of proteins is that if the normal environment of a living protein molecule is changed even slightly, such as by a change in pH or in temperature, the hydrogen bonds are disturbed and broken. When attractions between and within protein molecules are destroyed, the chains separate from each other, globules unfold and helices uncoil. We say that the protein has been denatured.

Denaturation is seen in our daily life in many forms. The curdling of milk is caused by bacteria in the milk which produce lactic acid. The change in *p*H caused by the lactic acid causes denaturation, coagulation and precipitation of the milk proteins. Similarly, the boiling of an egg causes precipitation of the albumin proteins in the egg white. Some proteins (such as those in skin, fingernails, and the stomach lining) are extremely resistant to denaturation.

29.2.4 Biological Importance of Proteins

(i) Proteins are structural components of cells.

(ii) The biochemical catalysts known as enzymes are proteins.

(iii) The proteins known as immunoglobins serve in defence against infections.

(iv) Many hormones, such as insulin and glucagon are proteins.

(v) Proteins participate in growth and repair mechanism of body tissues.

(vi) A protein called fibrinogen helps to stop bleeding.

(vii) Oxygen is transported to different tissues from blood by haemoglobin which is a protein attached to haeme part.

INTEXT QUESTIONS 29.2

1. What do you understand by primary structure of protein ?
2. What do you mean by a peptide bond?
3. Write the general structural formula of an a-amino acid?
4. What are conjugated proteins ?

29.3 LIPIDS

The lipids include a large number of biomolecules of different types. The term lipid originated from a Greek word '*Lipos*' meaning fat. In general, those constituents of the cell which are insoluble in water and soluble in organic solvents of low polarity (such as chloroform, ether, benzene etc.) are termed as *lipids*. Lipids perform a variety of biological functions.

29.3.1 Classification of Lipids

Lipids are classified into three broad categories on the basis of their molecular structure and the hydrolysis products.

(i) Simple Lipids: Those lipids which are esters and yield fatty acids and alcohols upon hydrolysis are called simple lipids. They include oils, fats and waxes.

(ii) Compound Lipids: Compound lipids are esters of fatty acids and alcohol with additional compounds like phosphoric acid, sugars, proteins etc.

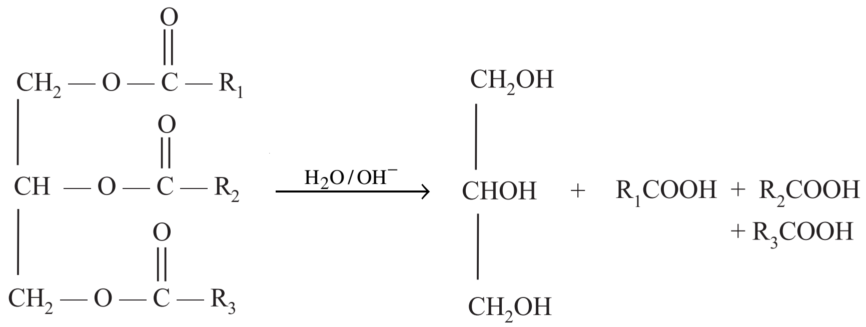
(iii) Derived Lipids: Compounds which are formed from oils, fats etc. during metabolism. They include steroids and some fat soluble vitamins.

29.3.2 Structure of lipids

The structure of all three types of lipids are breifly discussed below.

(i) Simple Lipids

The simple lipids are esters. They are subdivided into two groups, depending on the nature of the alcohol component. Fats and oils are triglycerides, i.e. they are the esters of glycerol with three molecules of long chain fatty acids. Variations in the properties of fats and oils is due to the presence of different acids. These long chain acids may vary in the number of carbon atoms (between C_{12} to C_{26}) and may or may not contain double bonds. On hydrolysis of a triglyceride molecule, one molecule of glycerol and three molecules of higher fatty acids are obtained as shown below:

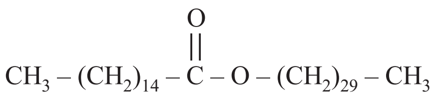


(Oil or fat) **Glycerol** **(Fatty acids)**

By definition, a fat is that triglyceride which is solid or semisolid at room temperature and an oil is the one that is liquid at room temperature. Saturated fatty acids form higher melting triglycerides than unsaturated fatty acids. The saturated triglycerides tend to be solid fats, while the unsaturated triglycerides tend to be oils. The double bonds in an unsaturated triglyceride are easily hydrogenated to give a saturated product, and in this way an oil may be converted into a fat. Hydrogenation is used in the manufacture of *vanaspati ghee* from oils.

Fats and oils are found in both plants and animals. Our body can produce fats from carbohydrates. This is one method that the body has for storing the energy from unused carbohydrates. The vegetable oils are found primarily in the seeds of plants.

The second type of simple lipids are waxes. They are the esters of fatty acids with long chain monohydroxy alcohols 26 to 34 carbons atoms. Waxes are wide-spread in nature and occur usually as mixtures. They form a protective coating on the surfaces of animals and plants. Some insects also secrete waxes. The main constituent of bees wax obtained from the honey comb of bees is myricyl palmitate:



$$CH_3-(CH_2)_{14}-\overset{\overset{\displaystyle O}{||}}{C}-O-(CH_2)_{29}-CH_3$$

myricyl palmitate

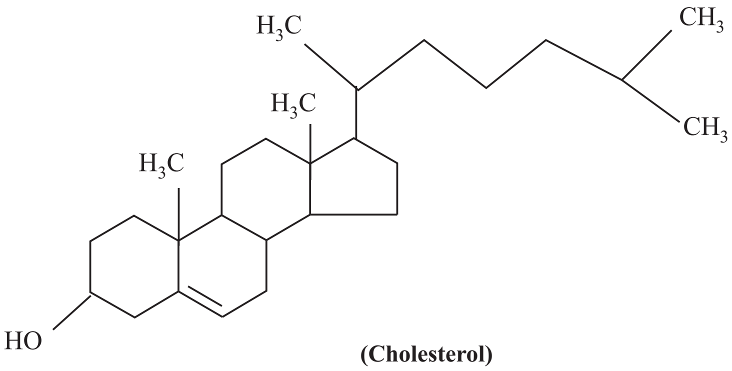
The waxes discussed above should not be confused with household paraffin wax which is a mixture of straight chain hydrocarbons.

(ii) Compound Lipids

Compound lipids on hydrolysis yield some other substances in addition to an alcohol and fatty acids. The first type of such lipids are called phospholipids, because they are the triglycerides in which two molecules of fatty acids and one molecule of phosphoric acid are present. Glycolipids contain a sugar molecule in addition to fatty acid attached to an alcohol.

(iii) Derived Lipids

Steroids are another class of lipids which are formed in our body during metabolism. These are the compounds with a distinctive ring system that provides the structural backbone for many of our hormones. Steroids do not contain ester groups and hence cannot be hydrolysed. Cholesterol is one of the most widely distributed steroids in animal and human tissues.



(Cholesterol)

Another important group of derived lipids is that of fat-soluble vitamins. This includes vitamins A, D, E and K, whose deficiency causes different diseases.

29.3.3 Biological Importance of Lipids

(i) Fats are main food storage compounds and serve as reservoir of energy.

(ii) Presence of oils or fats is essential for the efficient absorption of fat soluble vitamins A, D, E and K.

(iii) Subcutaneous fats serve as biological insulator against excessive heat loss.

(iv) Phospholipids are the essential component of cell membrane.

(v) Steroids control many biological activities in living organisms.

(vi) Some enzymes require lipid molecules for maximum action.

INTEXT QUESTIONS 29.3

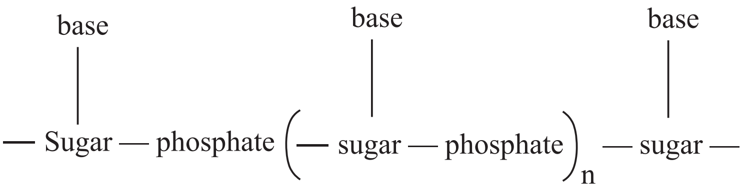
1. What are lipids?
2. What are the products of hydrolysis of an oil?
3. Name two important types of compound lipids.
4. What is the basic difference between fats and oils?

29.4 NUCLEIC ACIDS

Why is a dog a dog and not a cat? Why do some people have blue or brown eyes and not black? From a chemical standpoint, how does the body know what particular type of protein is to be synthesized? How is this information transmitted from one generation to the next? The study of the chemistry of heredity is one of the most fascinating fields of research today. It was recognized in the 19th century that the nucleus of a living cell contains particles responsible for heredity, which were called chromosomes. In more recent years, it has been discovered that chromosomes are composed of nucleic acids. These are named so because they come from the nucleus of the cell and are acidic in nature. Two types of nucleic acids exist which are called DNA (deoxyribonucleic acid) and RNA(ribonucleic acid).They differ in their chemical composition as well as in functions.

29.4.1 Structure of Nucleic Acids

Like all natural molecules, nucleic acids are linear polymeric molecules. They are chain like polymers of thousands of nucleotide units, hence they are also called polynucleotides. A nucleotide consists of three subunits: a nitrogen containing heterocyclic aromatic compound (called base), a pentose sugar and a molecule of phosphoric acid. So a nucleic acid chain is represented as shown below.



$$-\overset{\text{base}}{\overset{|}{\text{Sugar}}}-\text{phosphate}\left(-\overset{\text{base}}{\overset{|}{\text{sugar}}}-\text{phosphate}\right)_n-\overset{\text{base}}{\overset{|}{\text{sugar}}}-$$

In DNA molecules, the sugar moity is 2-deoxyribose, whereas in RNA molecules it is ribose. In DNA, four bases have been found. They are adenine (A), guanine (G), cytosine (C) and thymine (T). The first three of these bases are found in RNA also but the fourth is uracil (U).

The sequence of different nucleotides in DNA is termed as its primary structure. Like proteins, they also have secondary structure. DNA is a double stranded helix. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The hydrogen bonds are specific between pairs of bases that is guanine and cytosine form hydrogen bonds with each other, whereas adenine forms hydrogen bonds with thymine. The two stands are complementary to each other. The overall secondary structure resembles a flexible ladder (Fig. 29.4). This structure for DNA was proposed by James Watson and Francis Crick in 1953. They were honoured with a Nobel Prize in 1962 for this work.

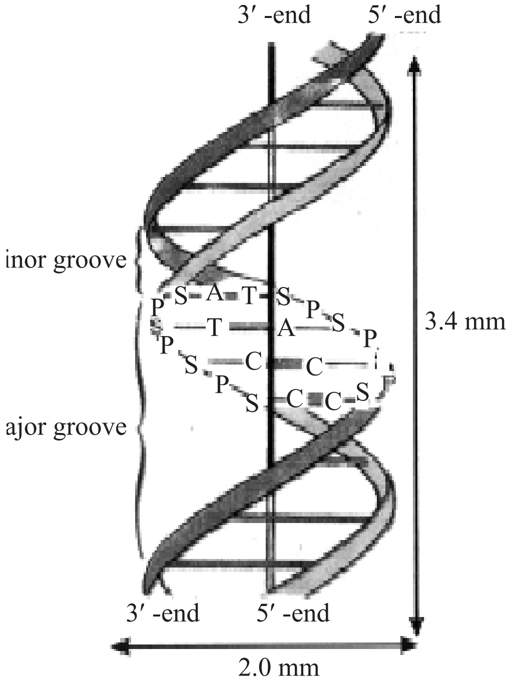


Fig. 31.4 : *Watson and Crick's double helix structure of DNA*

Unlike DNA, RNA is a single stranded molecule, which may fold back on itself to form double helix structure by base pairing in a region where base sequences are complimentary. There are three types of RNA molecules which perform different functions. These are named as messenger RNA(*m*-RNA), ribosomal-RNA(*r*-RNA) and transfer RNA (*t*-RNA)

29.4.2 Biological Functions of Nucleic Acids

A DNA molecule is capable of self duplication during cell divisions. The process starts with the unwinding of the two chains in the parent DNA. As the two strands separate, each can serve as a master copy for the construction of a new partner. This is done by bringing the appropriate nucleotides in place and linking them together. Because the bases must be paired in a specific manner (adenine to thymine and guanine to cytosine), each newly built strand is not identical but complimentary to the old one. Thus when replication is completed, we have two DNA molecules, each identical to the original. Each of the new molecule is a double helix that has one old strand and one new strand to be transmitted to daughter cells (Fig. 3.15).

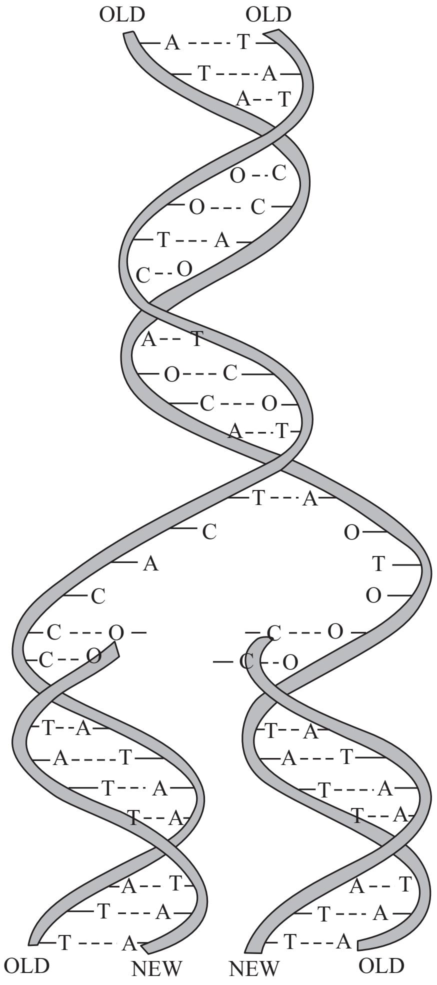


Fig. 29.5 : *Replication of DNA*

Another important function of nucleic acids is the protein synthesis. The specific sequence of bases in DNA represents coded information for the manufacture of specific proteins. In the process, the information from DNA is transmitted to another nucleic acid called messenger RNA, which leaves the nucleus and goes to the cytoplasm of the cell. Messenger RNA acts as template for the incorporation of amino acids in the proper sequence in protein. The amino acids are brought to the messenger RNA in the cell, by transfer RNA. Where they form peptide bonds. In short it can be said that DNA contains the coded message for protein synthesis whereas RNA actually carries out the synthesis of protein.

INTEXT QUESTIONS 29.4

1. What is a nucleotide?
2. Why structure DNA is called a “doublehelix”?
3. Write two main structural differences between DNA and RNA.

29.5 ENZYMES

In a living system, many complex reactions occur at the temperature of about 310K. An example of this is the digestion of food, during which stepwise oxidation to CO_2 and water and energy production. These reactions are carried out under such mild conditions due to presence of certain chemicals which are called enzymes. They act as catalysts for biochemical reactions in living cells. Almost all the enzymes are globular proteins.

Enzymes are very selective and specific for a particular reaction. They are named after the compound or class of compounds upon which they work or after the reaction that they catalyze. The ending of an enzyme name is- **ase**. For example, maltase is an enzyme that specifically catalyzes the hydrolysis of maltose into glucose. Similarly, an esterase is an enzyme which induces hydrolysis of ester linkage.

29.5.1 Mechanism of Enzyme Action

Just like chemical catalysts, enzymes are needed only in small quantities. Similar to the action of chemical catalysts, enzymes lower the energy barrier that reactants must pass over to form the products. For example, hydrolysis of the ester that needs boiling with aqueous NaOH in the laboratory, whereas it occurs at nearly neutral pH and at moderate temperature when catalyzed by an enzyme.

There is a particular enzyme for each substrate and they are said to have lock and key arrangement. It is said that first the substrate molecule binds to the active site of the enzyme which results in the formation of an enzyme-substrate complex. In this complex, the substrate is placed in the right orientation to facilitate a given reaction (Fig.29.6). This complex then breaks to give the molecule of the product and regenerates the enzyme for the next molecule of the substrate.

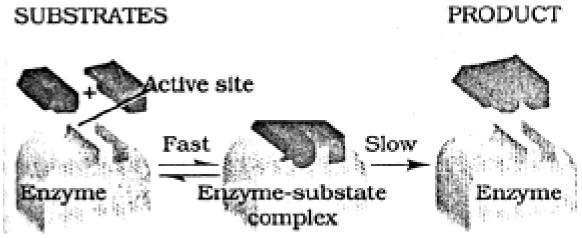


Fig. 29.6 : *Lock and Key arrangement of enzyme action*

29.5.2 Characteristics of Enzymes

(i) Enzymes speed up biochemical reactions up to ten million times compared to the uncatalysed reaction.

(ii) Enzyme catalysed reactions rapidly attain equilibrium.

(iii) Enzymes function in dilute aqueous solutions, at moderate temperatures and at a specific pH.

(iv) They are very specific and selective in their action on substrates.

(v) Enzymes are highly efficient and are needed in small amounts only.

(vi) In addition to the protein structure, most active enzymes are associated with some non-protein component required for their activity, called *coenzymes*. For example nicotinamide adenine dinucleotide (NAD) is a coenzyme which is associated with a number of dehydrogenation enzymes.

29.6 HORMONES

Hormones are chemical messengers which are secreted by endocrine glands. They are carried through the blood stream to the target tissues.

Majority of the hormones in humans are steroids. The two important classes of steroid hormones are **sex hormones** and **adrenocortical hormones**. The sex hormones control maturation, tissue growth and reproduction whereas the adreno-cortical hormones regulate various metabolic processes. Two most important male sex hormones or **androgens are testosterone** and **androterone**. They are responsible for the development of male secondary sex characteristics during puberty and for promoting tissue and muscle growth.

The female sex hormones or **estrogens** include **estrogen** and **estradiol** as examples. These hormones are responsible for the development of female secondary sex characteristics and for regular of menstrual cycle.

Another important female hormone is **progesterone** which prepares the lining of the uterus for the implantation of the fertilized ovum. The continued secretion of progerterone is important for the completion of the pregnancy.

Synthetic estrogens have been developed and they are used in combination with synthetic pregnancy hormones as oral contraceptines.

The adrenocritical hormones are secreted by adrenal glands which are small organs located near the upper end of each kidney. The **aldosterone** controls the tissue swelling by regulating cellular salt balance between Na^+ and K^+. Another hormone called **hydrocortisone** is involved in the regulation of glucose metabolism and in the control of inflammation.

Two important hormones which are polypeptides in nature are **vasopressin** and **oxytocin**. Oxytocin occurs in females only and stimulates uterine contraction during child birth. Vasopression occurs both in males and females and causes contraction of peripheral blood vessels and an increase in blood pressure.

Insulin, another important polypeptide hormone, is secreted from pancreases. It regulates the metabolism of glucose in the body. The deficiency of insulin in human causes diabetes mellitus.

INTEXT QUESTIONS 29.5

1. Name two important classes of steroid hormones.
2. What is oxytocin? Give its role.

29.7 VITAMINS : CLASSIFICATION AND THEIR FUNCTIONS

A variety of organic molecules act as coenzymes. Many of them are vitamins. Vitamins are small organic molecules which are taken in diet and there are required in trace amounts for proper growth.

Vitamins can be fat soluble or water soluble. A list of important vitamins and their deficiency symptoms is given below.

	Vitamin	Deficiency Symptom
A. Water Soluble		
(i)	Ascorbic Acid (Vitamin C)	Bleeding gums, Bruising
(ii)	Thiamin (Vitamin B_1)	Fatigue, Depression
(iii)	Riboflavin (Vitamin B_2)	Cracked lips, Scaly skin
(iv)	Pyridoxine (Vitamin B_6)	Anemia, Irritability
(v)	Niacin	Dermatitis, Dementis
(vi)	Folic acid (Vitamin M)	Megalobastic Anemia
(vii)	Vitamin B_{12}	Megalobastic Anemia, Neuro degeneration
(viii)	Pantothenic acid	Weight loss, Irreitability
(ix)	Biotin (Vitamin H)	Dermatitis, anorexia, depression
B. Fat Soluble		
(x)	Vitamin A	Night blindness, dry skin
(xi)	Vitamin D	Rickets, osteomalacia
(xii)	Vitamin E	Hemolysis of RBCs
(xiii)	Vitamin K	Hemorrahage, delayed blood clotting

INTEXT QUESTIONS 29.6

1. Match the following vitamins mix their deficiency symptoms:

(i) Vitamin C	(a) Anemia
(ii) Vitamin B_2	(b) Bleeding guns
(iii) Vitamin B_6	(c) Scaly skin

2. What is night blindness? Why is it caused?
3. How do enzymes increase the rate of a reaction?
4. What do you understand by lock and key arrangement?

WHAT YOU HAVE LEARNT

- Carbohydrates are polyhydroxy aldehydes or ketones or substances which provide such molecules on hydrolysis.
- They are classified as mono-, di-and polysaccharides.
- Proteins are the polymers of α-amino acids which are linked by peptide bonds.
- All proteins are the polymers of twenty different α-amino acids. Out of these 10 amino acids cannot be synthesized by our body and hence must form the part of our diet. These are called essential amino acids.
- Proteins are very important to us and perform many functions in a cell that are absolutely necessary for our survival.
- Chief sources of proteins are pulses, milk, meat, eggs, etc.
- Biomolecules which are insoluble in water and soluble in organic solvents are called lipids. They are classified as simple, compound and derived lipids.
- Nucleic acids are the compound which are responsible for the transfer of characters from parents to offsprings.
- There are two types of nucleic acids- DNA and RNA. They are polymers composed of repeating units called nucleotides.
- DNA contains a five carbon sugar molecule called 2-deoxyribose whereas RNA contains ribose.
- The four bases present in DNA are adenine, cytosine, guanine and thymine whereas RNA contains uracil in place of thymine.

- DNA is a double strand molecule whereas RNA is a single strand molecule.
- DNA is present in the nucleus and have the coded message for proteins to be synthesized in the cell.
- Proteins are actually synthesized by RNA which are of three types – messenger-RNA (*m*-RNA), ribosomal-RNA (*r*-RNA) and transfer- RNA (*t*-RNA).
- Enzymes are biocatalysts which speed up the reactions in biosystems.
- Chemically all enzymes are proteins. They are very specific and selective in their action on substrates.

TERMINAL EXERCISE

1. How is excess glucose stored in our body?
2. What is a disaccharide? Give an example.
3. What are the products formed by the hydrolysis of lactose?
4. What are essential amino acids?
5. Differentiate between globular and fibrous proteins with suitable examples.
6. What are triglycerides? Mention one of its important uses.
7. What is a nucleotide?
8. Differentiate between the nucleotides of RNA and DNA.
9. What are different types of RNA found in the cell? Mention their functions.
10. What are enzymes?
11. What is insulin? Why is it important for us?
12. List the deficiency symptoms caused by deficiency of vitamin B12 and vitamin D.

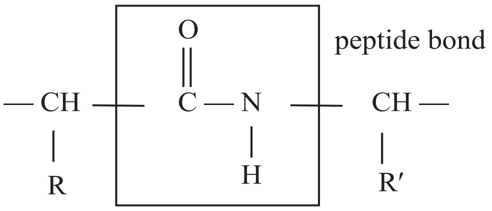
ANSWERS TO INTEXT QUESTIONS

29.1

1. Cereals, fruits and sugar.
2. Plants produce carbohydrates during photosynthesis.
3. Starch on hydrolysis gives glucose whereas sucrose on hydrolysis gives glucose and fructose.
4. Refer to section 29.1.2.

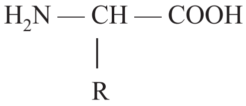
29.2

1. Information regarding the sequence of amino acids in a protein chain is called its primary structure.
2. Proteins are made up of many α-amino acids which join together by the formation of an amide bond between $-NH_2$ group of one amino acid and $-COOH$ group of another. When two amino acids combine in this way, the resulting product is called a dipeptide and the amide bond between them is called a peptide bond.



$$-\underset{\substack{|\\R}}{CH}-\boxed{\overset{\substack{O\\\|}}{C}-\underset{\substack{|\\H}}{N}}-\underset{\substack{|\\R'}}{CH}-$$

3. An α-amino acid may be represented as



$$H_2N-\underset{\substack{|\\R}}{CH}-COOH$$

4. Refer to section 29.2.1.

29.3

1. Biomolecules which are insoluble in water and soluble in organic solvents like benzene, ether or chloroform are called lipids.
2. Oils on hydrolysis give glycerol and long chain fatty acids.
3. Two types of compound lipids are phospholipids and glycolipids.
4. A triglyceride which is solid at room temperature is called a fat and if it is liquid then it is called an oil.

29.4

1. A nucleotide consists of three subunits which are (i) a nitrogen containing heterocyclic aromatic compound, also called a base; (ii) a pentose sugar (ribose or 2-deoxy ribose) and (iii) a molecule of phosphoric acid.
2. In DNA, two chains are wound around each other in the form of helix, hence the structure is called a double helix.
3. Two main structural differences between DNA and RNA are :
   (i) DNA molecules are double stranded whereas RNA are single strand molecules.

(ii) In DNA molecules, the sugar moity is 2-deoxyribose whereas in RNA molecules, it is ribose.

29.5

1. Refer to section 29.5.1
2. Refer to section 29.5.1

29.6

1. Six hormones and adrenocortical hormones.
2. Oxytocin is a female hormone. It stmulates uterine contraction during child birth.
3. (i) – (b)

   (ii) – (c)

   (iii) – (a)
4. Night blindness is a deficiency sympton. It is caused by the deficiency of vitamin A.

313en30

30

DRUGS AND MEDICINES

The association of mankind with pain and disease is probably as old as man himself. Humans have always been looking for remedies to overcome their pain and suffering. The earliest attempts at this, involved use of various plants. The knowledge was based on experience and was handed on from generation to generation. It is being used even today.

In an attempt to conquer pain and disease, a large number of synthetic chemicals have been discovered. The chemicals used as medicines are known as pharmaceuticals. Today pharmaceutical industry has grown to be one of the biggest industries in the world.

In this lesson we will try to introduce you to the area of drugs and medicines. In the process we would attempt to differentiate between drugs and medicines (though commonly used interchangeably). You will also learn about classification of medicines and other important aspects of drugs and medicines.

OBJECTIVES

After reading this lesson you will be able to :

- define drugs and medicines;
- differentiate between drugs and medicines;
- classify medicines on the basis of their action (use);
- cite examples and effects of analgesics, antipyretic, antiseptics, disinfectants, antacids, antimalarials, anaesthetics, antimicrobials (sulpha drugs and antibiotics), anti-fertility drugs, etc.;
- differentiate between analgesics and antipyretics;
- differentiate between antiseptics and disinfectants;

- explain habit forming and non-habit forming drugs;
- differentiate between broad spectrum and narrow spectrum antibiotic;
- differentiate between local and general anaesthetics;
- describe self-medication and
- alternate systems of medicine.

30.1 WHAT ARE DRUGS AND MEDICINES?

When we fall ill we take some tablets, pills, injections or apply some ointments to get well. All these are collectively known as medicines. Some time we may use some parts of plants or some preparations made from herbs, minerals, animals, etc. All these substances used for the treatment or prevention of diseases, can also be called medicines. Medicines contain a single chemical or a number of chemicals in different amounts to have the desired effect.

The mode of action of the chemicals of a medicine is quite varied and complicated. In many a cases mode of action may not be fully known to us, but we continue to use them as they are useful to us.

Early man used several plants or parts of plants to cure diseases, without knowing of the chemical components, responsible for it. For example bark of willow tree was used for relieving pain (as analgesic). Later, it was found that its bark contained 2-hydroxy benzoic acid, which is closely related to acetyl salicylic acid (also known as aspirin). Parts of a plant *Rauwolfia serpentina* (Hindi name, sarpagandha) have been used in Ayurvedic drugs for the treatment of hypertension (high blood pressure). Later on it was discovered that a compound called reserpine was responsible for reducing blood pressure. Thus reserpine became the first modern medicine to control blood pressure.

In most of the cases nature led to the discovery of modern medicine. Thousands of chemists all over the world are constantly searching for better, efficient, cheaper and safer medicines.

As mentioned earlier the term drugs and medicines are used interchangeably, but there is a difference between the two. Let us try to understand the difference between drugs and medicines. The term drug is often used for preparations or formulation whose chemical components and their quantities are not known fully. These may be extracts of certain plants, herbs, animal parts or may be minerals.

The term medicine is used when the chemical composition and the quantities of various chemical components are known. Further, the effects of the chemical compounds present in a medicine and their side effects have been properly and extensively studied. The medicines are approved by the relevant governmental authorities like Drug Controller of India.

The term drug is also used for substances, which are habit forming and are often abused, for example, narcotics like cocaine, morphine, heroine, marijuana, etc.

As you read in newspapers terms like illegal drug trade, drug trafficking, drug mafia, drug peddler are used to refer to illegal dealing with habit forming substances, referred to as drugs.

However the difference between drug and medicine is far from clear.

INTEXT QUESTIONS 30.1

1. Write a definition of medicines.
2. Most of the chemicals used in medicines are poisonous. Is this statement true or false?
3. What are pharmaceuticals?
4. Name the compound which is present in the plant sarpagandha and is responsible for reducing blood pressure.

30.2 CLASSIFICATION OF MEDICINES

You may be familiar with some of the common medicines used for relieving pain, reducing fever or for treating common cold, etc. The number of medicines is very large therefore medicines are classified according to their action or use. Table 30.1 provides a list of some important classes of medicines. The terms like analgesics, antibiotics, antiseptics, etc. are common household words. Let us try to understand the meaning of this classification in a little more detail.

Table 30.1 : Some Important Classes of Medicines and their Action

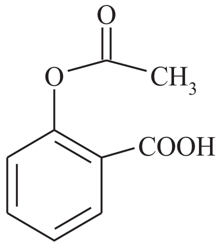
S.No.	Class	Action or Usage
1.	Antipyretics	Reduce body temperature
2.	Anti histamines	Reduce allergy
3.	Analgesics	Reduce pain
4.	Antimalarials	Used for treatment of malaria
5.	Germicides	Kill germs
6.	Antiseptics	Kill germs (can be safely used on living tissue)
7.	Disinfectant	Kill germs (cannot be used on living tissue)
8.	Antacids	Reduce acidity in stomach
9.	Anaesthetics	Loss of sensation
10.	Antimicrobials, Sulpha drugs and Antibiotics	Kill microorganisms
11.	Tranquilizers and hypnotics	Reduce anxiety and bring calmness
12.	Birth Control Medicines (Contraceptives)	Birth control

1. Antipyretics

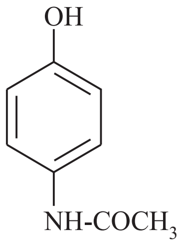
Antipyretics are the substances which are used to reduce body temperature or to control fever.

The word antipyretic is derived from pyro which means fire (means hot) anti means against. Thus antipyretic means it counteracts heat (high body temperature).

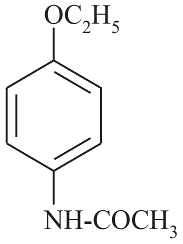
Aspirin, paracetamol and phenacetin are commonly used antipyretics. You get them in the market with different trade names like crocin, anacin, disprin, etc.



Aspirin



Paracetamol



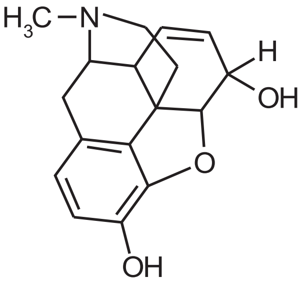
Phenacetin

Aspirin is the most popular antipyretic in use. It gets hydrolyzed in stomach and salicylic acid is released. Overdose and using it over a long time may cause side effects. It may cause bleeding in the stomach wall and even ulcers. Therefore, overdose and prolonged use should be avoided. However, calcium and sodium salts of aspirin are more soluble in water and are less harmful than aspirin.

2. Analgesics

Analgesics are the substances, that reduce pain which may be due to swelling of tissues, injury, inflammation or some other disorders. Analgesics are of two types, namely narcotic & non-narcotic.

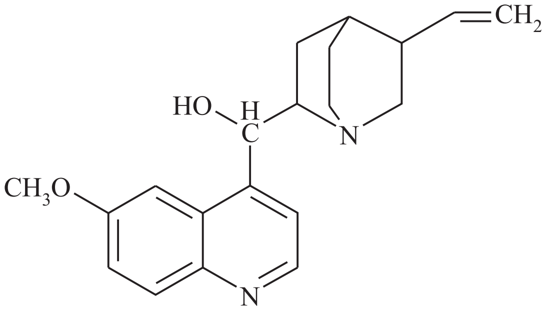
Narcotic analgesics are the ones which induce sleep and thus help to reduce the feeling of pain alkaloids present in opium, viz. morphine, codeine, etc. are common examples of narcotics. In higher doses these may cause unconsciousness. These are habit-forming and cause addiction. Due to addiction a person wants to have it regularly and in larger amounts. Such a person feels upset and uncomfortable if he doesnot get it. Narcotic analygesies do not induce sleep and are not habit forming. A common example of this type of narcotics is morphine.



Morphine

3. Antimalarials

Antimalarial medicines are used to treat malaria. Quinine and chloroquine are widely used antimalarials. Quinine is one of the earliest drugs, which was first obtained from the bark of a plant (cinchona) and later on synthesized in laboratories.



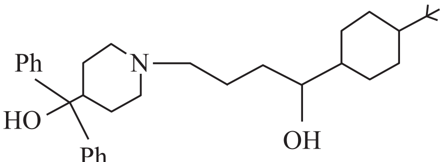
Quinine

4. Antihistamines

Some persons are hypersensitive towards some medicines like penicillin, sulpha drugs and may be sensitive to food and environment due to different sensitizing substances (antigens) derived from them. The hypersensitivity is called allergy. It is due to release of a chemical substance called histamine in the body.

"Anthistamine are the chemical substances (drugs) which control or abolish the effect of histamines released in the body." These drugs are also called anti-allergic drugs.

Histamine is also responsible for the nasal congestion (discharge), mild asthama associated with common cold, cough, allergic response to pollengrains etc. Histamine contract the smooth muscles in bronchi and gut, relaxes other muscles present in the walls of fine blood versels. Antihistamine are widely used for treatment of hay-fever, itching of eyes, nose and throat, conjuctivities. Some antihistamine drugs are diphenhydramine (Benadryl) pheniramine maleate (Avil) chlorspheniramine maleate (zect), citrazine and terfenadine (seldane)



Seldane

5. Germicides, Disinfectant and Antiseptic

Germicides are the chemicals, which prevent growth of germs (microorganisms). Germicides are classified as antiseptic and disinfectant. Both kill microorganisms but the difference lies in the way we use them.

Antiseptics kill microorganisms and are safe to be used on living beings (tissues). Antiseptics are used on wounds, cuts or skin abrasions. These are used to dress wounds, etc. For example, iodoform (CHI_3), tincture of iodine, ethyl alcohol, a 0.2 percent aqueous solution of phenol and boric acid (H_3BO_3) are common antiseptics.

Some dyes have the ability to kill microorganisms. These dyes were the earliest compounds to be used as antiseptics. Examples are acriflavine (a yellow coloured dye), mercurochrome (a red coloured dye), methylene blue (a blue coloured dye). These dyes are still in use as antiseptics.

Iodine is a powerful antiseptic. It is used as tincture of iodine. Tincture of iodine is 2 to 3 percent solution of iodine dissolved in ethyl alcohol. Iodoform is a yellow coloured solid, which is used as an antiseptic.

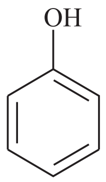
Disinfectants kill germs (microorganisms) but are used on non-living substances like surgical instruments, floors, bathrooms, lavatories, etc. Disinfectants are harsh and are not safe to be used on living beings as disinfectants can damage living tissues.

Chlorine is a powerful oxidizing agent. It is used for disinfecting water. A concentration of 0.2 to 0.4 ppm (parts per million) is enough to kill microorganisms present in water.

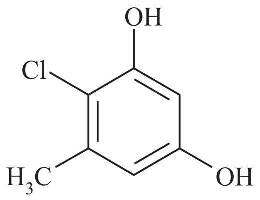
Low concentration of sulphur dioxide is used to kill microorganisms in jams, jellies and squashes. Thus it acts as a food preservative. Sulphur dioxide is used for fumigation in rooms, operation theaters, etc. to sterilize them. Bleaching powder ($CaOCl_2$), chlorine (Cl_2), mercuric chloride ($HgCl_2$), sodium hypochlorite ($NaClO$), sulphur dioxide (SO_2) etc. are other examples of disinfectants.

Is Phenol Antiseptic or Disinfectant?

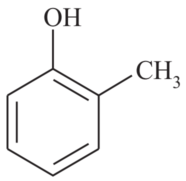
It is interesting to note that 0.2 percent aqueous solution of phenol is used as antiseptic by making. It is safe to be used on living tissues in low concentrations (less than 0.2 percent). If concentration of phenol is high then it can damage tissues. Therefore, at higher concentration (1 percent or more) phenol is used as disinfectant.



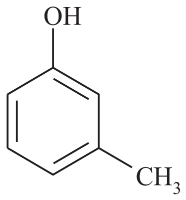
Phenol



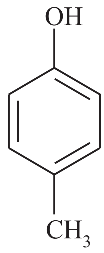
Chloro-xylenol



***o*-Cresol**



***m*-Cresol**

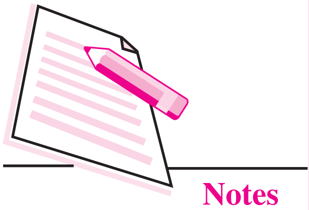


***p*-Cresol**

Most antiseptics and disinfectaints are powerful poisons (Table 30.2). They are able to kill microorganisms as they interfere with their metabolism. While some others are able to kill microorganisms because of their powerful oxidizing or reducing nature (Table 30.2).

Table 30.2 : Nature of Some Important Antiseptics and Disinfectants

Poisons	Oxidising agents	Reducing agents
Dyes		
Acriflavine (a yellow dye)	Bleaching powder	Sulphur dioxide
Gentian violet	Chlorine	
Mercurochrome	Hydrogen peroxide	
Methylene blue	Iodine	
	Tincture of iodine	
Phenols	Iodoform	
	Potassium permanganate	
Phenol	Sodium hypochlorite	
Cresols		
Resorcinol		
Chloroxylenol		
Others		
Formaldehyde		
Boric acid		
Mercuric chloride		
Silver nitrate		



6. Antacids

Antacids are the medicines which neutralize the excess acid present in the stomach.

Stomach juice contains hydrochloric acid (HCl). This acid helps the process of digestion of food. Due to illness or anxiety or some other reasons more acid is produced in the stomach. The stomach juice becomes more acidic than necessary. This causes problems in digestion, bleeding in the lining of stomach or even ulcers. Some medicines are used to neutrialise the excess acid and correct the pH of the stomach fluid.

For example, sodium bicarbonate ($NaHCO_3$) or a suspension of magnesium hydroxide is used to neutralize excess of acid present in the stomach. Milk of magnesia contains magnesium hydroxide, 'ENO fruit salt' contains sodium bicarbonate which helps to neutralise excess acidity in the stomach juice. Medicine like digene, gelusil, used as an antacid contain magnesium hydroxide.

7. Antimicrobials

Many diseases are caused due to infection in the body by certain microorganisms (bacteria, fungus or viruses). Some examples of diseases caused by microbes are dysentry, pneumonia, typhoid, urinary tract infection, etc.

Antimicrobials are the chemicals, which are used to kill microorganisms (which has infected the body) without causing much damage to the body of the patient.

Thus an antimicrobial is a chemical, which is capable of curing diseases caused by various microbes.

An ideal antimicrobial should kill disease-causing microbe and should not have any harmful effect on the patient. In fact there may not be any such antimicrobial which is totally safe and without any side effect.

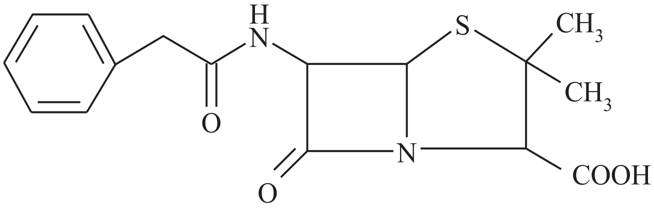
The most common antimicrobials available are the sulhpa drugs and antibiotics.

8. Antibiotics

Antibiotics are the metabolic products produced by some microorganisms (mould or fungi). They inhibit growth and even kill disease causing microorganisms (like bacteria, fungi, etc) by inhibiting their life processes. Therefore they are referred to as antibiotics (anti means against and biotic means life).

Penicillin was the first antibiotic to be discovered. Alexander Fleming isolated penicillin in 1929 from a mould *Pencillium notatum*. Penicillin has been used for the treating diseases caused by several bacteria. It has been effectively used for treatment of pneumonia, bronchitis, sore throat, abscesses, etc.

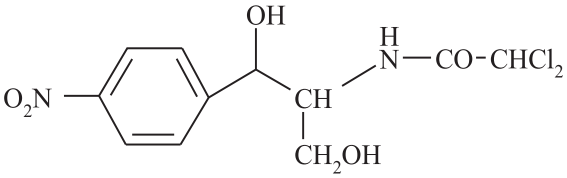
Later on attempts have been made to improve the quality of penicillin. It has led to the discovery of different varieties of penicillin. For example, Penicillin G (also known as benzyl penicillin), penicillin F, penicillin K are the more common varieties of penicillin.



Penicillin G (benzyl peniclin)

Ampicillin and amoxicillin are the semi-synthetic modifications of penicillin. In this case the metabolic product of mould is obtained and then some reactions are carried out to bring the desired changes in the antibiotic molecule to get ampicillin or amoxicillin.

Attempts are being made to discover better and better antibiotics. This search for finding better antibiotics is a never-ending process. Now a large number of antibiotics are available. Some examples are streptomycin and chloromycetin (chloroamphenicol) and tetracycline.



Chloroamphenicol

Streptomycin is used for the treatment of tuberculosis (TB). Chloromycetin is used for the treatment of typhoid. Tetracycline is used for the treatment of several diseases.

Broad-spectrum antibiotics are those antibiotics, which kill a wide range of disease-causing microorganisms.

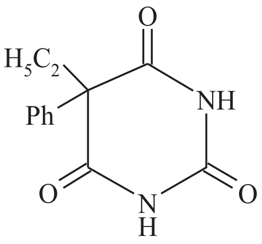
Broad-spectrum antibiotics can be used for the treatment of several diseases. For example, streptomycin, tetracycline and chloroamphenicol are broad-spectrum antibiotics. Narrow spectrum antibiotics are effective in the treatment of a few diseases.

9. Allergic Reactions of Antibiotics

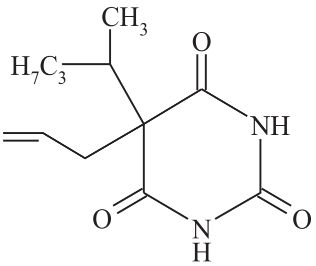
Some people may show allergic reactions to some antibiotics. These reactions may be mild like rashes appearing on the skin or may be very serious and can even be fatal. You might have observed that a doctor gives a small dose of antibiotic by injection and then waits for some time to watch if there is any unwanted reaction. If there is no adverse (bad) reaction, then only the doctor gives the full dose of the antibiotic.

10. Tranquilizers and Hypnotics

Tranquilizers and hypnotics are used to reduce anxiety, and they also make a person calm. Sleeping pills are made up of these compounds. Most of them are habit-forming. Their indiscriminate and over use should be avoided. Otherwise it may lead to addiction and many other complications,

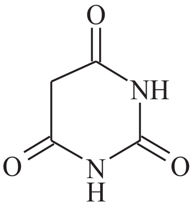


Luminal

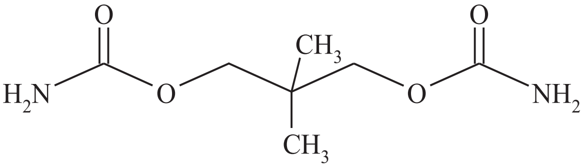


Seconal

Luminal, seconal and equanil are the most commonly used tranquilizers. Barbituric acid and some other compounds related to barbituric acid are used in making sleeping pills.



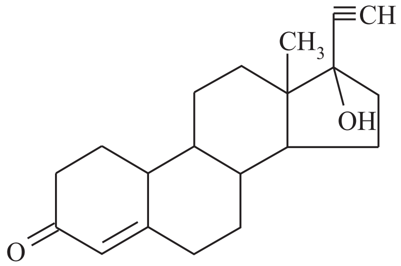
Barbituric acid



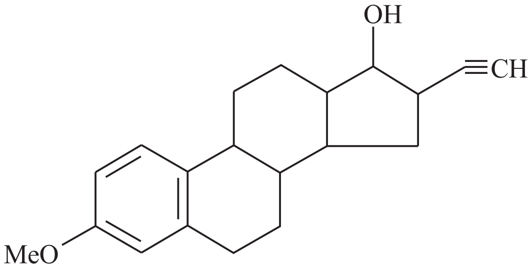
Equanil

11. Fertility Control Medicines

It is a concern of everyone to control human population. Medicines are available which help prevent pregnancy. The medicines, which help prevent pregnancy, are known as contraceptives. These are generally available in the form of tablets and are to be taken regularly by females. Chemicals like norethindrone and mestranol are used as contraceptives (birth control pills). Chemically these are similar to female sex hormones.



Norethindrone



Mestranol

The birth control pills may have some side effects in some cases. Therefore, the birth control pills should be used under the guidance of some expert.

30.3 HAZARDS OF SELF MEDICATION

When medicines are taken by a patient without the advice of a qualified doctor, it is called self-mediation.

Self-medication is very harmful and a dangerous practice. One should never try self-medication. Some of the harmful effects are:

1. A medicine, which has worked well for some one, may not be good for you and can even cause some serious harm.
2. You may take a medicine in quantity more than necessary. It may be harmful for you.
3. You may take quantity less than necessary. The disease-causing microorganisms may gain resistance to the medicine and the medicine may become ineffective.

You should avoid self-medication. Without advice of a doctor avoid use of common medicines over prolong periods. Improper use of even most common medicines, which are readily available without a prescription of a doctor, can have harmful effect.

The medicines, which you can buy without a prescription of a doctor, are called over-the-counter medicines. For example cough syrups, crocin, aspirin, etc are over the counter medicines.

The medicines, which you can buy after showing a prescription of a qualified doctor, are known as scheduled drugs. Improper use of scheduled drugs is likely to cause more serious problems. Therefore, their sale is controlled and regulated by the government.

Most of good chemists do not sell scheduled medicines without a proper prescription. Some irresponsible chemists may sell such medicines without a prescription. It is not a good practice you should not encourage it.

INTEXT QUESTIONS 30.2

1. Give two examples of antipyretics.
2. Give one example of a narcotic type analgesic.
3. What is the difference between an antiseptic and disinfectant?
4. What are antacids? Name two chemicals commonly used as antacids.
5. What is the difference between local anaesthetic and general anaesthetic.
6. Define antibiotics. Give one example of an antibiotic.
7. Which type of medicines are usd in hey-fever, itching of eyes; nose and throuts.
8. What is the use of tranquilizers and hypnotics?
9. Give one example of a tranquilizer.
10. What are contraceptives?
11. What are over the counter medicines?

30.3.1 Chemicals in foods – Preservatives and artificial sweetening agents

Food Preservatives: "Chemical substances which are used to protect food materials against microorganisms (bacteria yeasts and moulds) are called preservatives."

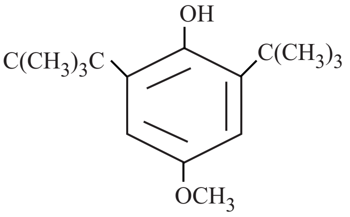
Some commonly used preservatives are

1. **Common Salt, Sugar and oils:** The sufficient amount of salt resist the activity of microorganisms in food it is called salting. It is used to preserve raw mango, bean, fish and meat, etc. Sugar syrup used for preserving like apple, mango, amla and carrot etc. Sugar, oil, vinegar & citric acid are used to preserve pickles, ketchups and jams, etc.
2. **Sodium benzoate (C_6H_5COONa):** It is used for preserving of food material like fruit juices, soft drinks, squashes and jams. It is soluble in water. It is metabolized as hippuric and which is excreted in urine.
3. **Sodium meta bisulphite ($Na_2S_2O_5$):** Its preservative action is due to SO_2 which from sulphurous acid when dissolved in water. It also inhibits the growth of yeasts, moulds and bacteria. It is used to preserve fruitams, juices, squashes, pickles, apples, etc.
4. Sodium and Potassium Salts of propionic acid, sorbic acid are also used as preservatives.

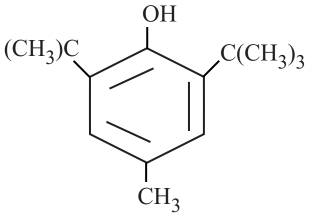
30.3.2 Antioxidants

The unsaturated fat and oils are readily oxidized on storage, the taste and smell are changed and become rancid. To prevent this oxidation, rancidity and spoilage, certain chemical substances are added, are called antioxidant (food additives).

When these are added to food items containing fats and oils retard the oxidation because they are more reactive towards oxidation than fats and oils. So the oxidation of food is prevented. Antioxidants react with free radicals and stop the oxidation of food. The most familiar antioxidants are butylated hydroxyl toluene (BHT) and butylated hydroxyl anisole (BHA)



(BHA)



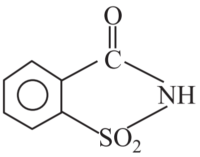
(BHT)

These are added to butter, meats, cereals chewing gum, snack gum, baked food and beer etc. It increases the life of food from months to years. It shows more active synergetic effect when added with Vitamin C (ascorbic acid) and citric acid.

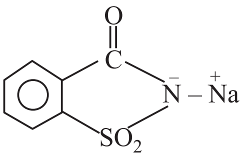
30.2.3 Artificial Sweetening Agents

"The chemical compounds which give sweetening effect to the food are called sweeting agent." Sucrose and Glucose are widely used as natural sweetening agent. The excess intake of natural sugar cause to obesity diabetics and tooth decay. Natural sugar is a good source of energy. While the artificial sweetening agents does not provide energy. It is excreted from the body in urine unchanged. Some commonly used artificial sweetening agents are saccharin, aspartame, alitame, sucrolose, etc.

1. Saccharin (O-Sulpho benzimide) Saccharin is insoluble in water but sodium salt is highly soluble in water. It is 550 times sweeter than sugar. It is not metabolized by our body. So it does not provide energy and has no calorific values.

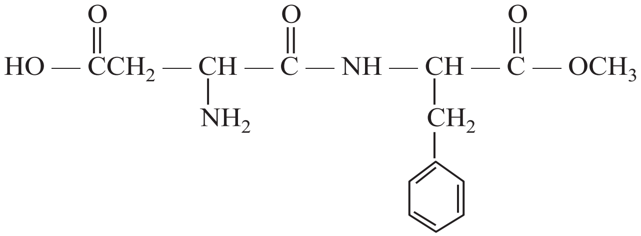


Saccharine
(Insoluble inwater)



Sodium salt of
Saccharine
(Solube in water)

2. **Aspartame** – It is methyl ester of dipetide derivative derived from aspartic acid and phenylalanine. It is 100 times as sweet as sugar. It is unstable at cooking temperatures. It is used in cold drinks and soft drinks. It is an exception because the body breakes it down in to amino acid and menthol.



(Aspartame)

3. **Alitame:** It is very high potency sweetener, It is about 2000 times sweeter than sugar. It is more stable at cooking temperatures. It is very difficult to control the sweetness of food.
4. **Sucrolose:** It is trichloro derivative of sucrose. It's taste is like sugar. It is also stable at cooking temperatures. It is about 600 times sweeter than sugar.

Sucrolose is expected to become a great commercial artificial sweeting agent.

INTEXT QUESTIONS 30.3

1. What type of change take place on storage the fat & oil?
2. Write the name of preservative used with soft drinks.
3. What change will take inner body on taking exercise sugar (N).

WHAT YOU HAVE LEARNT

- Medicines are the chemicals or mixture of chemicals used for the prevention, cure, treatment, management of diseases and disorders or recovery of patients
- Medicines are obtained from plants or parts of plants or synthesized in laboratories.
- Medicines may contain only one chemical compound or it may be a mixture of several compounds.
- Drugs may be the crude mixtures and the identity of all the chemical components and their amount present in them may not be accurately known.
- Antipyretics are used to reduce body temperature for example aspirin and paracetamol.

- Analgesics reduce body pain for example aspirin and morphine.
- Antiseptics kill microorganisms and are safe to be used on a living tissue while disinfectants are used on inanimate objects.
- Aqueous solution (less than 0.2 percent) of phenol is used as an antiseptic. In higher concentrations phenol is used as a disinfectant.
- Antibiotics are the metabolic products produced by certain microorganisms which can kill some microorganisms. For example penicillin, streptomycin, tetracycline, etc.
- Broad spectrum antibiotics can kill several different microorganisms, therefore, can cure several diseases.
- On storage the taste and smell are changed and become rancid.
- Certain chemical substances are added to control oxidation spoilage and rancidity.
- Butylated hydroxyl toluene (BHT) and Butylated hydroxyl anisole (BHA).
- Common Salt, sugar and oils are natural food preservatives.
- Sodium benzrate is familiar food predervative.
- Aspartame is unstable at cooking temp. so used in cold drinks and soft drinks.
- Alitame is more stable at cooking temp.
- Suerolose is mare stable at cooling tamp and easy to control the sweetness of food.

TERMINAL EXERCISE

1. How are medicines classified?
2. Who isolated the first antibiotic?
3. Name a medicine, which is used as analgesic as well as antipyretic.
4. What is a non-narcotic analgesic?
5. Why is 2.0 percent aqueous solution of phenol used as a disinfectant?
6. What do you understand by allergic reactions of antibiotics?
7. What are scheduled drugs?
8. Which medicines can you purchase without the prescription from a doctor?
9. What is self-medication? Describe some of its ill effects.
10. Write the two names of chemicals which increases the life of food from months to years.
11. Which artificial sweatening agents is more suitable at cooking temperatures.
12. Which is responsible for perservation action of sodium meta bisulphite?

ANSWERS TO INTEXT QUESTIONS

30.1

1. Medicines are all those substances or formulations which are used for cure, treatment, prevention of diseases or disorders and recovery of a patient.
2. True
3. Pharmaceuticals are the chemicals which are used as medicines.
4. Reserpine

30.2

1. Aspirin and Paracetamol.
2. Morphine.
3. Disinfectants kill germs but can damage living tissues Anticeptics are safe for living tissues and yet kill germs.
4. Medicines used to neutralise excess acid in the stomach. Magnesium hydroxides and sodium carbonate.
5. Local anesthetics cause loss of sensation of pain over a small area while general anesthetics cause loss of concsiousness.
6. Metabolic products of certain microorganisms and can kill some other microorganisms. Penicilin is an example of antibiotic.
7. Anti histomines are used.
8. Tranquilizers and hypnotics are used to reduce anxiety and these also make a person calm.
9. luminal
10. Contraceptives are the medicines used for prevention of pregnancy.
11. Over-the-counter medicines are those which can be purchased without a prescription from a doctor.

30.3

1. On storage of fat and oil get oxidised, the taste and smell are changed and become rancid.
2. Sodium benzoate (C_6H_5COONa) is used as perservative with soft drinks.
3. The excess intake of natural sugar cause to obesity and tooth decay.

313en31

31

SOAP, DETERGENTS AND POLYMERS

In the previous lesson module VII you have studied about the chemistry of organic compounds. In this module you would learn about the meaning of soaps, detergents and polymers. The synthetic detergents are better than soaps but due to non biodegradibility causes water pollution and soil pollution. You would also learn about type of soaps and detergents. Today polymers have influenced our life style to the extent that it would not be wrong to say that we are in polymer age. Now-a-days polymers find wide range of uses starting from common household utensils, automobiles, clothes, furniture, etc., to space-aircraft and biomedical and surgical components.

Polymeric materials are light weight but can possess excellent mechanical properties and can be easily processed by different methods. In this lesson you would learn more about polymers, their types and some important-synthetic and natural polymers.

OBJECTIVES

After reading this lesson, you will be able to :

- distinguish between soaps and detergents;
- explain types of detergents;
- list advantages and disadvantages of detergents over soaps;
- explain cleansing action of soaps and detergents;
- define the terms like monomers, polymer, homopolymer, copolymer and polymerization;
- classify polymers on the basis of their source, molecular forces and method of preparation;

- list the monomers of the polymers like natural and synthetic rubber;
- list the monomer of the polymer like polythene, polystyrene, Buna- S, PMMA, PVC, teflon, polyester, Nylon 66 and Nylon 6;
- define biodegradable polymers; and
- cite examples of some biopolymers.

31.1 CLEANSING AGENTS (SOAPS AND DETERGENTS)

Soaps and detergents are widely used as cleaning agents. Chemically soaps and detergents are quite different from each other. The common feature of soaps and detergents is that when dissolved in water the molecules of soap and detergent tend to concentrate at the surface of the solution or at interface. Therefore, the surface tension of the solution is reduced, it causes foaming of the solution.

Soaps and detergents lower the surface tension of the solution. Such substances are called surface-active agents or surfactants.

To sum up, soaps and detergents:

1. are used as cleansing agents
2. cause foaming of the solution
3. lower surface tension
4. molecules tend to concentrate near the surface of the solution
5. are the surface active agents
6. are the surfactants
7. can emulsify grease
8. can remove dirt, etc.

Hydrophilic and Lipophilic Parts

Both soap and detergent molecules have two parts. One part of the molecule is polar (ionic) in nature. Polar nature is due to the presence of groups like carboxylate ($–COO^-$) or sulphonate ($–SO_3^-$). The polar group is a hydrophilic group. The hydrophilic group makes soaps and detergents soluble in water. The other part of the soap or detergent molecule is non polar (nonionic) that is lipophilic. The lipophilic part (a long chain alkyl or a long chain substituted aryl group) makes the molecule oil soluble.

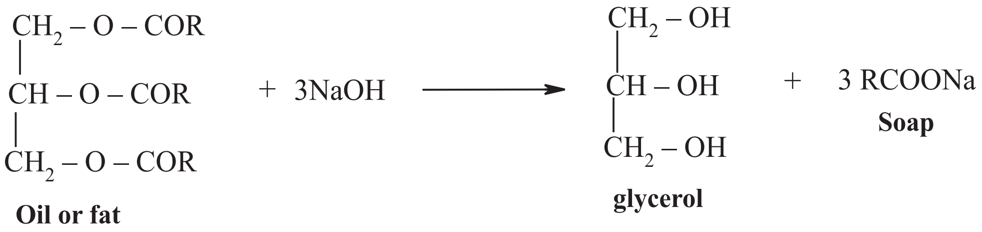
Depending on the nature of the hydrophilic (polar) part in the soap or detergent molecule these are classified as anionic, cationic or non-ionic type. For example, soap has a carboxylate anion therefore soap is anionic type (table 8.5.1). Synthetic detergents have sulphonate anion thus they are also classified as anionic type. Anionic types are the most common. However, cationic and non-ionic detergents are also known.

Soaps

Soaps are the sodium or potassium salts of long chain fatty acids. These fatty acids are present in oils and fats in the form of glycerides. The glycerides present in oils and fats are the esters of glycerol and long chain carboxylic acids for example palmitic acid and stearic acid.

Saponification

Saponification is the process of making soap. Saponification is done by hydrolysis of oils or fats (of vegetable or animal origin) with the help of alkali like sodium hydroxide (NaOH) or potassium hydroxide (KOH)

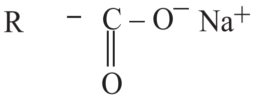


$$\underset{\textbf{Oil or fat}}{\begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-COR \end{array}} + 3NaOH \longrightarrow \underset{\textbf{glycerol}}{\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}} + \underset{\textbf{Soap}}{3\,RCOONa}$$

(where R= long chain alkyl group containing 11 to 17 carbon atoms)

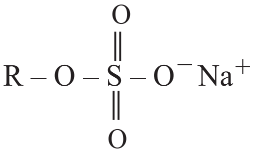
Synthetic Detergents

Synthetic detergents are used as cleaning agents much like soaps. Chemically, detergents are sodium salts of long-chain alkyl hydrogen sulphate or sodium salts of long-chain alkyl benzene sulphonic acids. (Remember that soap is a sodium or potassium salt of long-chain fatty acid.)



$$R-\underset{\underset{O}{\|}}{C}-O^-\,Na^+$$

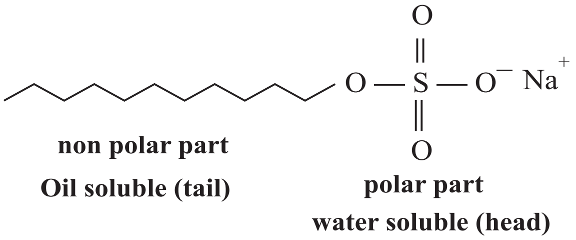
(Soap)



$$R-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^-\,Na^+$$

(Detergent)

Detergent molecules are similar to that of soap molecules, that is they have an oil-soluble (lipophilic) long chain of carbon atoms and a polar (hydrophilic) water-soluble part. For example, sodium lauryl sulphate ($C_{12}H_{25}$–O – SO_3Na) has a 12 carbon atom hydrocarbon like alkyl chain. The long carbon chain is oil-soluble (lipohilic) part and the sulphate is polar (hydrophilic) part that makes the molecule water-soluble. The water-soluble part is referred to as water-soluble head and the long chain of carbon atoms is referred to as oil-soluble tail.

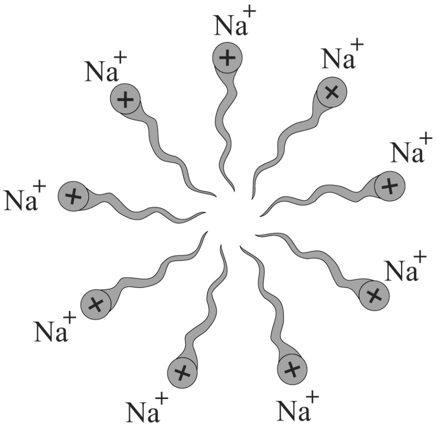


31.1.1 Cleansing action of soap and detergents

The molecules of soaps and detergents are smaller than the colloidal particles. These molecules associate and get the colloidal particle size range. This associate form is known as micelles. Soap and detergents dissociate in ions when dissolve in water being electrolyte in nature.

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} \longrightarrow C_{17}H35COO^{-} + Na^{+}$$

The long chain of hydrocarbon, which is hydrophobic is nature (insoluble in water) directed towards the centre while the head (hydrophylic water soluble part) is on the surface in control of water.



The initial concentration at which micellization begins is called critical micellization concentration (CMC). The formation of micelles starts above a definite temp, that is called kraft temperature (TK).

The cleansing action of soap is due to micelles. The micelles are absorbed by grease/dirt in cloth. Because both are non polar. The polar head is directed towards water the rubbing by hands or mechanical stirring break the grease particles in to smaller droplets and form emulsion with water. As a result, the cloth gets free from dirt and grease. The droplets and washed away with water.

31.1.2 Advantages and Disadvantages of Synthetic Detergents

The synthetic detergents are better than soaps in certain respects. Synthetic detergents can be used for washing of clothes even if the water is hard. Calcium and magnesium ions present in hard water make corresponding salts with detergent molecules. The calcium and magnesium salts of detergent molecules are soluble in water (unlike that formed by soap molecules).

However, detergent containing branched alkyl benzene sulphonate is not completely biodegradable (Table 32.2). Soap is completely biodegradable. Therefore, excessive use of synthetic detergents is a cause of worry. The problem has been partly solved by using linear alkyl benzene sulphonate, which has better bio-degradability then the branched alkyl benzene sulphonate (Table 31.1)

Table 31.1 : Bio-degradability and class of soaps and some synthetic detergents

Detergent	Class	Polar Group	Bio-degradable
Soaps	anionic	Carboxylate	100%
Branched alkyl benzene sulphonate	anionic	Sulphonate	50-60%
Linear alkyl benzene sulphonate	anionic	sulphonate	90%
Lauryl alcohol	anionic	Sulphate	100%

INTEXT QUESTIONS 31.1

1. What is the active component in soaps ?
2. What are the raw materials used for the manufacture of soaps ?
3. What is the polar part in a soap molecule ?
4. What is the polar part (hydrophilic) in a synthetic detergent molecule ?
5. What is the oil-soluble (lipophilic) part in the soap molecule ?
6. Branched alkyl benzene sulphonate is more bio-degradable than linear alkyl benzene sulphonate. Is it true or false ?

31.2 WHAT ARE POLYMERS

A Polymer is a giant molecule formed by inter molecular linkage between same or different types of smaller molecules called **monomers**. If a large number of monomers (A) are linked together then the polymer is represented as $(-A_n-)-(-A-A-A-A-A)_{\overline{n}}$ is a polymer of the monomer of (A). For example, polyethene $-\!\left(CH_2-CH_2\right)_{\overline{n}}$ is a polymer of the monomer ethylene ($CH_2=CH_2$).

Polymer is a high molecular mass molecule formed by linking up of two or more small molecules called monomers.

Monomers are the small molecule which are capable of linking amongst themselves to form big molecules called polymers.

In some polymers more than one type of monomers combine with each other to give the polymer. For example, a polymer may be obtained from two monomers (A) and (B) viz,

$$-A-B-A-B- \quad \text{or} \quad -\!\left(A-B\right)\!-_{n}$$

31.2.1 Types of Polymers

Depending upon the nature of the repeating structural units (monomers), polymers are divided into two broad categories viz., homopolymers and copolymers

(a) **Homopolymer**

A polymer formed from only one kind of monomers is called homopolymer. Polyethene $-\!\!\left(\mathrm{CH_2-CH_2}\right)\!\!-_n$ is an example of homopolymer.

(b) **Copolymer**

A polymer formed from more than one kind of monomer units is called **copolymer or mixed polymer**. For example, Buna-S rubber which is formed from 1, 3-butadiene ($\mathrm{CH_2=CH-CH=CH_2}$) and styrene ($\mathrm{C_6H_5CH=CH_2}$) is an example of copolymer.

31.3 POLYMERIZATION

The process by which the monomers get linked up is called **polymerization**.

Polymerization is represented as :

$$\mathrm{M{+}M} \longrightarrow \underset{\text{Dimer}}{\mathrm{M-M}} \xrightarrow{+\mathrm{M}} \underset{\text{Trimer}}{\mathrm{M-M-M}} \xrightarrow{+\mathrm{M}^*} \underset{\text{Polymer}}{\mathrm{M-(M)_n-M}}$$

where M stands for the monomer

31.3.1 Types of Polymerization

Depending upon the mode of reaction, polymerisation is classified as :

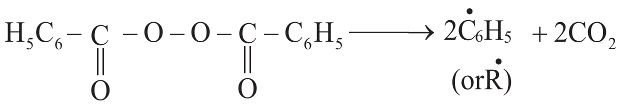
(a) addition polymerization and

(b) condensation polymerization.

(a) Addition Polymerization : This process involves the addition of monomer units to themselves to form a growing chain by a chain reaction mechanism. It is for this reason that the process is also known as **chain growth polymerization**.

Addition polymerization is achieved by adding a catalyst (known as initiator), which provides some reactive species like free radicals.

For example benzoyl peroxide provides free radical 'benzyl' to initiate the chain polymerization reaction.



$$\mathrm{H_5C_6-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5} \longrightarrow \underset{(\text{or}\,\dot{\mathrm{R}})}{2\dot{\mathrm{C}}_6\mathrm{H}_5} + 2\mathrm{CO_2}$$

Initiation $$\dot{R} + \underset{\text{(Monomer)}}{CH_2 = CH_2} \longrightarrow R - CH_2 - \dot{C}H_2$$

These free radicals (R) then attack the unsaturated monomer and form a new free radical which goes on successively adding monomers and thus grows the chain, this is called **Chain propagation** :

$$R - CH_2 - \dot{C}H_2 + CH_2 = CH_2 \longrightarrow R - CH_2 - CH_2 - CH_2 - \dot{C}H_2$$

or $$M - MMMMMMMM^{\bullet}$$

The final **termination** of the two growing chains leads to a polymer. This is called **chain termination** :

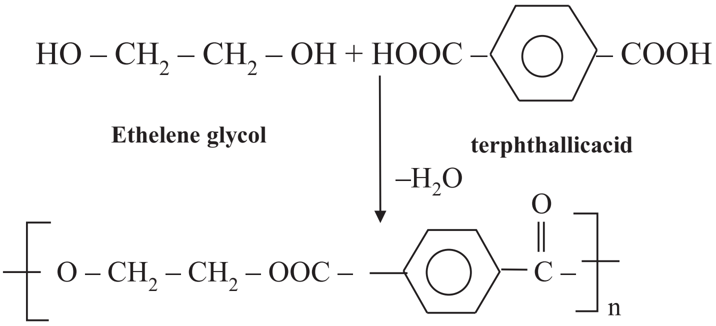
$$\begin{array}{c} MMMMMMMM^{\bullet} + {}^{\bullet}MMMMMMMMM \\ \downarrow \\ M\ MMMMMMMMMMMMMMMMMM \end{array}$$

Polymer

Condensation Polymerization : In this, the monomers combine with the elimination of a small molecule like H_2O, ROH or NH_3, etc. The reaction is called (step growth) condensation polymerization and the product formed is called condensation polymer.

The process involves the elimination of by product molecules, therefore, the molecular mass of the polymer is not the integral multiple of the monomer units.

For example polyester or Terylene is a condensation polymer of ethylene glycol and terphthallic acid.



Poly (ethylene terphthalate) or (Terylene)

These two processes of making polymers have several characteristics which distinguish them from each other. These are shown in (Table 31.2).

Table 31.2 : Some differences between addition polymerization and condensation polymerization

Addition Polymerization	Condensation polymerization (Polycondensation)
1. Involves unsaturated monomer like ethylene, vinyl chloride, styrene etc.	1. Involves substances with at least 2 functional groups like ethylene glycol (2-OH groups), adipic acid (2-COOH groups).
2. Fast addition of monomers	2. Step-wise slow addition
3. At any instant, only monomer and polymers are present.	3. No monomer. Mixtures of dimers, trimers and tetramers etc. are present
4. Initiator is necessary to catalyse the polymerization.	4. Catalyst is not necessary.
5. No small molecules are eliminated.	5. Small molecules like H_2O, HCl, CO_2, CH_3OH are often eliminated.
6. Polymers are made for example, polyethene, polypropylene, polybutadiene, polyvinylchloride.	6. Polymer are made for example, terylene, nylon, Formaldehyde-resins, silicones.

INTEXT QUESTIONS 31.2

1. Define the terms :

   (i) Polymer (ii) Monomer

2. Write one example of each of :

   (i) Addition polymerization (ii) Condensation polymerization.

3. Differentiate between homopolymers and copolymers.

4. Write monomers of Terylene and Nylon-66.

31.4 CLASSIFICATION OF POLYMERS

The polymers can be classified in a number of ways. Some of these are discussed below for a systematic investigation of their properties and uses.

(a) Classification of Polymers on the Basis of Origin.

On the basis of origin, polymers are classified as :

1. Natural polymers
2. Synthetic polymers

1. **Natural Polymers :** The polymers obtained from nature (plants and animals) are called natural polymers. Starch, cellulose, natural rubber, proteins, etc. are some examples.

2. **Synthetic Polymers :** The polymers which are prepared in the laboratories are called **synthetic polymers.** These are also called **man-made polymers.** Polyethene, PVC, nylon, feflon, bakelite, terylene, synthetic rubber, etc. are common examples.

(b) Classification of Polymers on the Basis of structure

On the basis of structure of polymers, these can be classified as :

1. Linear polymers
2. Branched chain polymers
3. Cross-linked polymers.

1. **Linear polymers :** These are polymers in which **monomeric units** are linked together to form linear chains. These linear polymers are well packed (Fig. 31.1) and therefore, have high densities, high tensile (pulling) strength and high melting points. For example, polyethelene, nylons and polyesters are examples of linear polymers.

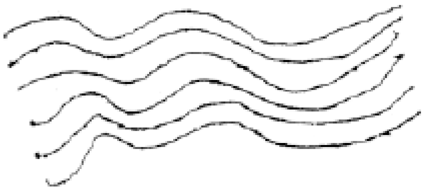


Fig. 31.1 : *Linear Polymers*

Fig. 31.2 : *Branched chain polymers*

2. **Branched chain polymers :** These are polymers in which the monomers are joined to form long chain with side chains or branches of different lengths (Fig. 31.2). These branched chains polymers are irregularly packed and therefore, they have lower tensile strength and melting points than linear polymers. For example, low density polyethene, glycogen, starch, etc.

3. **Cross-linked polymers :** These are polymers in which long polymer chains are cross-linked together to from a three dimensional network. These polymers are hard, rigid and brittle because of the network structure. (Fig. 31.3 bakelite, melamine and formaldehyde resin are some examples of this type.

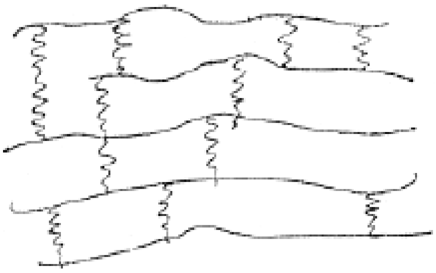


Fig. 31.3 : *Cross linked polymers*

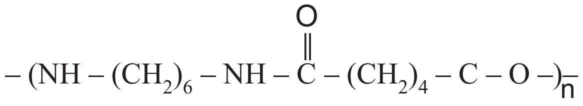
(c) Classification of Polymers on the Basis of Method of Polymerisation

On the basis of method of polymerisation the polymers are classified as :

1. **Addition polymer :** A polymer formed by direct addition of repeated monomers without the elimination of any small molecule is called **addition polymer.** In this type, the monomers are unsaturated compounds and are generally derivatives of ethene. The addition polymers have the same empirical formula as their monomers. Examples are polyethene, polypropylene and polyvinyl chloride, etc.

2. **Condensation polymer :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc. is called **condensation polymer.** In this type, each monomer generally contains two functional groups. For example, nylon – 66 is obtained by the condensation of two monomers; hexa methylenediamine and adipic acid with the loss of water molecules.

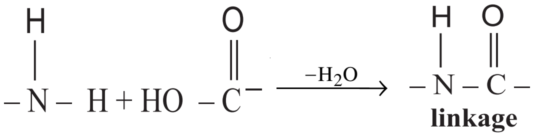
$$n\,H_2N-(CH_2)_6-NH_2+nHOOC-(CH_2)_4-COOH-\xrightarrow{-n\,H_2O}$$



$$-(NH-(CH_2)_6-NH-\overset{\overset{\textstyle O}{\|}}{C}-(CH_2)_4-C-O-)_{\overline{n}}$$

nylon - 66

In this polymerization reaction – NH_2 group of hexamethylenediamine reacts with – COOH group of adipic acid forming – NH –CO – linkage with the elimination of H_2O.



$$-\overset{\overset{\textstyle H}{|}}{N}-H+HO-\overset{\overset{\textstyle O}{\|}}{C}-\xrightarrow{-H_2O}-\overset{\overset{\textstyle H}{|}}{N}-\overset{\overset{\textstyle O}{\|}}{C}-$$

linkage

Examples of condensation polymers are Nylon 66, terylene, bakelite, alkylresins, etc.

(d) Classification of Polymers on the Basis of Molecular Forces

Depending upon the intermolecular forces between monomer molecules, the polymers have been classified into four types.

1. Elastomers 2. Fibers 3. Thermoplastics 4. Thermosetting

1. **Elastomers :** In case of elastomers the polymer chains are held together by weak **van der waals forces.** Due to weak forces, the polymers can be easily stretched on applying small stress and they regain their original shape when the stress is removed. This is due to the presence of few- 'cross links' between the chains, which help the polymer to retract to its original position after the force is removed, as in vulcanized rubber.

   The most important example of elastomer is **natural rubber.**

2. **Fibres :** These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. Because of the strong forces, the chains are closely packed, giving them high tensile strength and less elasticity. These polymers can be drawn into long, thin and thread like fibres and therefore can be woven into fabrics. The common examples are nylon-66, dacron, silk, etc.

3. **Thermoplastics :** These are linear polymers with very few cross linkages or no cross linkages at all. The polymeric chains are held by weak VANDER WAAL forces and slide over one another. Due to lack of cross linkages these polymers soften on heating and harden or become rigid on cooling. Thus they can be moulded to any shape. Polythene, PVC, polystyrene are addition type thermoplastics and Terylene, nylon are condensation type thermoplastics.

   Plasticizers : Certain plastics do not soften much on heating. These can be easily softened by the addition of some organic compounds which are called **plasticizers.** For example, polyvinyl chloride (PVC) is very stiff and hard but is made soft by adding di-n-butylphthalate (a plasticizer). Some other common plasticizers are dialkyl phthalates and cresyl phthalate.

4. **Thermosetting polymers :** Usually thermosetting polymer can be heated only once when it permanently sets into a solid which can not be remelted and remoulded. Thermosetting polymers are produced from relatively low molecular mass semi fluid polymers (called polymers) which on heating develop extensive cross-linkage by themselves or by adding some cross-linking agents and become infusible and insoluble hard mass. The cross links hold the molecules in place so that heating does not allow them to move freely. Therefore, a thermosetting plastic is cross linked and is permanently rigid. The common example are bakelite, melamine, formaldehyde resin, etc.

   Some important differences in the properties of thermosetting and thermoplastic polymers are summerized in Table 31.3.

Table 31.3 : Distinction between Thermoplastic and Thermosetting polymers

Themoplastic	Thermosetting polymers
1. Linear Polymers.	1. Cross-linked polymers.
2. Weak van der Waals intermolecular forces and thus soften/melt on heating.	2. Chemical cross-linking make them infusible materials. Do not melt on heating.
3. Molten polymer can be moulded in desired shape. It can be remoulded by heating again.	3. Cross-linking is usually developed at the time of moulding where they harden irreversibly.
4. Examples are polystyrene, PVC, SBR, Teflon, PMMA terylene.	4. Examples are Glyptals, epoxy polymers, formaldehyde resins.

INTEXT QUESTIONS 31.3

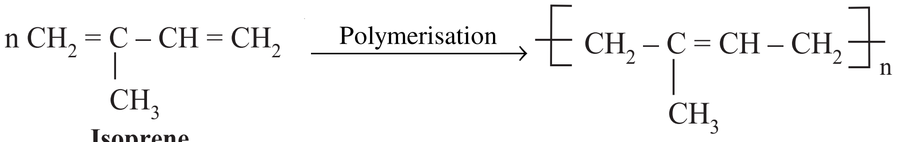
1. Define natural and synthetic polymers with examples?
2. What are cross linked polymers? Give one example of this type.
3. How do thermoplastic differ from thermosetting polymers?
4. Arrange the following polymers in the increasing order of their intermolecular forces. Also classify them as addition and condensation polymers.
   Nylon – 66, Buna-S, Polyethene.

31.5 SOME COMMERCIALLY IMPORTANT POLYMERS

31.5.1 Polydiens

These polymers are obtained when an unsaturated hydrocarbon with two double bonds or when a diene (2 double bond compound) is polymerized with a substituted alkene. The polymers belonging to this class are rubbers or elastomer. They can be natural or artificial. Consequently we have natural rubber and synthetic rubber.

(1) Natural Rubber : It is a polymer of unsaturated hydocarbon, 2-methyl-1, 3-butadiene also called isoprene. It is obtained from the latex of rubber trees found in tropical and semi-tropical countries such as India (southern part), Indonesia, Malayasia, Ceylon, South America, etc. The latex contains about 25-40% of rubber hydrocarbons dispersed in water alongwith stabilizer proteins and some fattyacids. It is a natural polymer and possess remarkable elasticity.



$$n\,CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2 \right]_n$$

Isoprene
2-methyl–1, 3–butadiene

Polyisoprene
(natural rubber)

In natural rubber 10,000 to 20,000 isoprene units are linked together.

Drawbacks of raw rubber

Raw natural rubber has a number of drawbacks. For example :

1. Rubber is brittle at low temperature and becomes very soft at high temperatures. Thus it can be used only in the limited temperature range of 10-60°C
2. It is too soft to be used for heavy duty operation.
3. On stretching, it undergoes permanent deformation.
4. Not resistant to mineral oils, organic solvents and even action of water. It has large water absorption capacity.

Vulcanization of Rubber

The wide applications of rubber are due to its property called elasticity and that is why rubber is said to be an **elastoplastic** or **elastomer.** Accidentally, in 1893, Charles Goodyears discovered that addition of sulphur to hot rubber cause changes that improve its physical properties in a spectacular manner. This process is called **vulcanization.** It is carried out by heating crude rubber in presence of sulphur or dipping it in a solution of S_2Cl_2 in CS_2. **Vulcanisation depends upon :**

(i) The amount of sulphur used : by increasing the amount of sulphur rubber can be hardened

(ii) Temperature

(iii) Duration of heating.

Crude rubber is intimately mixed with about 3% ground sulphur, an accelerator and activator and then heated to about 150^0C (for tyres it is 153^0C). Vulcanisation is a progressive reaction and is allowed to a definite stage. The detailed mode of vulcanization process may be difficult to visualize, but probable structure of vulcanized rubber is depicted below (Fig. 33.4).

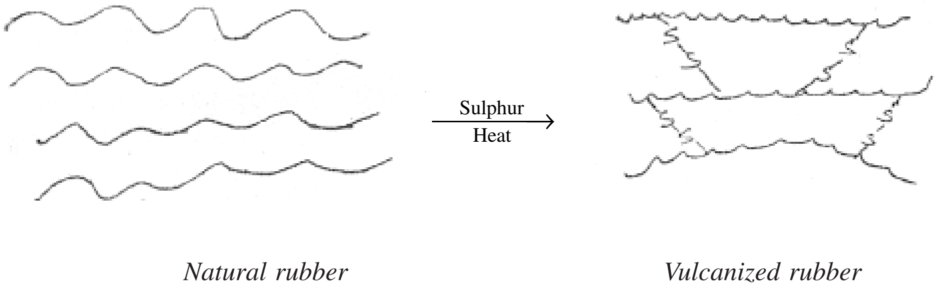


Fig. 31.4 : *Process of vulcanization of rubber*

Table 31.4 Comparison of some properties of natural rubber and vulcanized rubber :

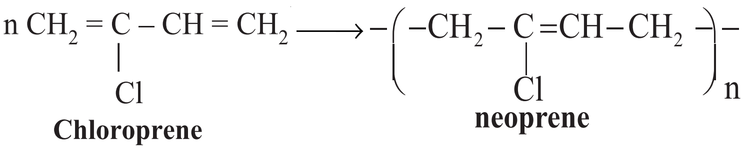
Natural Rubber	Vulcanised rubber
1. Natural rubber is soft and sticky.	1. Vulcanized rubber is hard and non-sticky.
2. It has low tensile strength.	2. It has high tensile strength.
3. It has low elasticity.	3. It has high elasticity.
4. It can be used over a narrow range of temperature (from 10^0 to 60^0C).	4. It can be used over a wide range of temperature (- 40^0 to 100^0C).
5. It has low wear and tear resistance.	5. It has high wear and tear resistance.
6. It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	6. It is insoluble in most of the common solvents.

(2) Synthetic Rubbers

Synthetic high polymers possessing similar physical properties as that of natural rubber are called **synthetic rubber.** Usually synthetic rubber is an improvement over natural rubber, specially with respect to its resistance to oils, gas, solvents.

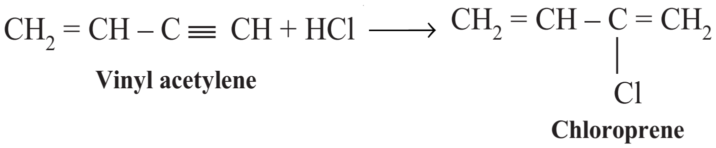
Some synthetic rubbers are made by polymerization of only one monomer, for example Neoprene is made by polymerization of chloroprene, while synthetic rubbers like Buna-S, Buna N and Butyl rubber etc. are copolymers as these have more then one monomer.

Neoprene : This synthetic rubber resembles natural rubber in its properties. It is obtained by polymerization of chloroprene.



$$\mathrm{n\,CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2 \longrightarrow -\!\left(-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-\right)\!\!-_n}$$

Chloroprene is obtained by the reaction of HCl with vinylacetylene



$$\mathrm{CH_2=CH-C\equiv CH+HCl \longrightarrow CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2}$$

Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to oils, gasoline and other solvents

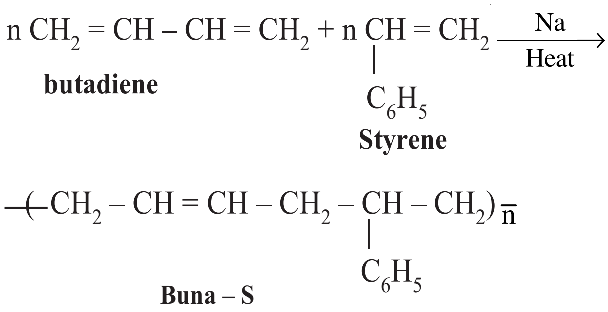
Neoprene is used for

(i) making belts, hoses, shoe heals, stoppers, etc. and

(ii) manufacture of containers for storing petrol, oil and other solvents.

Buna – S:

It is obtained by polymerization of butadiene and styrene in presence of sodium metal.



$$n\,CH_2=CH-CH=CH_2 + n\,\underset{\displaystyle C_6H_5}{\underset{|}{CH}}=CH_2 \xrightarrow[\text{Heat}]{\text{Na}} -\!\!\left(CH_2-CH=CH-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2\right)_{\overline{n}}$$

In Buna – S, Bu stands for butadiene, Na for sodium and S stands for styrene. It is also called S.B.R. (Styrene Butadiene Rubber). It has slightly less tensile strength than natural rubber.

Buna-S is used for

(i) making automobile tyres.

(ii) rubber soles, belts and hoses etc.

Buna – N : It is obtained by copolymerization of two parts of butadiene and one part of acrylonitrile in presence of sodium metal.

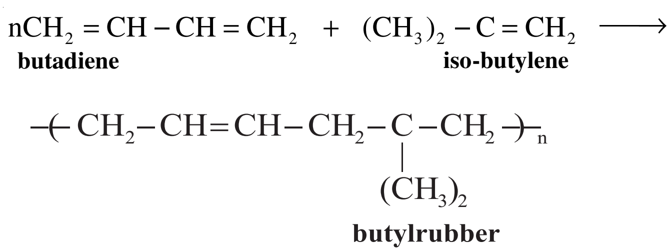
Buna – N is hard and extremely resistant to the swelling action by oils (petrol), solvents and is resistant to heat, etc.

Uses :

(i) It is used for the manufacture of storage tanks for solvents and

(ii) For making oil seals.

Butyl Rubber : This is obtained as a result of co-polymerization of butadiene and isobutylene. It is generally carried out in the presence of small quantity of isoprene. The function of isoprene is not exactly known.



$$nCH_2=CH-CH=CH_2 + (CH_3)_2-C=CH_2 \longrightarrow -\!\!\left(CH_2-CH=CH-CH_2-\underset{\displaystyle (CH_3)_2}{\underset{|}{C}}-CH_2\right)_n$$

Butyl rubbers are inert towards acids and alkalies, but have poor resistance towards petroleum products.

Uses :

(i) It is used for making inner tubes of tyres and

(ii) For making conveyor belts, tank linings and insulation of high voltage wires and cables etc.

INTEXT QUESTION 31.4

1. Write the IUPAC names and structures of monomers of the following polymers:

   (i) Natural rubber (ii) Neoprene

2. What is the function of sulphur in the vulcanization of rubber?

3. What is Buna – S? How is it synthesized?

4. Compare the properties (at least three) of natural rubber and vulcanized rubber?

After the detailed discussion of rubbers, we shall now discuss some other commercially important polymers.

31.5.2 Polyolefins

Polyolefins is a major class of synthetic polymers made by the polymerization of an olefin (alkene) or its suitable derivative. Most of these are obtained from petro chemical industry. Polyethylene, polypropylene, PVC, Teflon, etc. belong to the class of polyolefins. Some important members of this class are discussed here with.

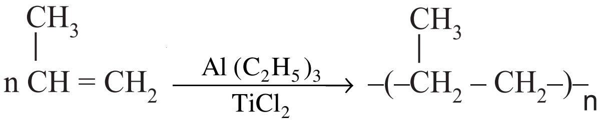
(1) Polyethylene or polyethene is formed by polymerization of ethylene ($CH_2 = CH_2$). It is manufactured in large quantities and is the most common polymer which you find almost every where.

Polyethene is of two types Low Density Polyethene (LDPE) and High Density Polyethene (HDPE) depending upon the nature of has branching in polymer chain and is not compact in polymer molecules. Low density polyethene has branching in polymer chains and is not compact in packing. While high density polyethere has linear chain of molecules which are packed in a more compact fashion (Fig. 33.1 and Fig. 33.2).

$$\underset{\textbf{ethylene}}{n\,CH_2 = CH_2} \longrightarrow \underset{\textbf{Polyethylene}}{-(CH_2 - CH_2)_{\overline{n}}}$$

Polyethylene is used for making pipes, insulators, packing films, carry-bags, etc.

(2) Polypropylene : The monomer units are propylene molecules. It is generally manufactured by passing propylene through n-hexane (inert solvent) containing Ziegler-Natta catalyst (a mixture of triethyl aluminium and titanium chloride)



$$n\,\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}H} = CH_2 \xrightarrow[TiCl_2]{Al(C_2H_5)_3} -\!(\!-\overset{\overset{\displaystyle CH_3}{|}}{C}H_2 - CH_2-\!)\!-_n$$

Propylene **Polypropylene**

Polypropylene is harder, stronger and lighter than polyethene Polypropylene is used for packing of textile material and food, lining of bags, gramophone records, ropes, carpet fibres, etc.

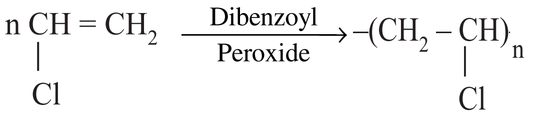
(3) Teflon or Polytetrafluoro ethylene (PTFE) : The monomer unit is terafluoroethylene molecule. Teflon is prepared by heating tetra fluoroethylene under pressure in the presence of ammonium peroxosulphate. $[(NH_4)_2S_2O_8]$.

$$n\,CF_2 = CF_2 \xrightarrow[\text{Heat, pressure}]{(NH_4)_2S_2O_8} -\!(\!-CF_2 - CF_2-\!)\!-_n$$

Tetrafluoroethylene **Teflon**

Teflon is a very tough material and is resistant towards heat, action of acids or bases. It is bad conductor of electricity. Teflon is used for coating utensils to make them non-sticking, making seals and gaskets which can with stand high pressures, insulation for high frequency electrical installations.

(4) Polyvinylchloride (PVC) : The monomer units are vinyl chloride molecules. PVC is prepared by heating vinyl chloride in an inert solvent in the presence of dibenzoyl peroxide.

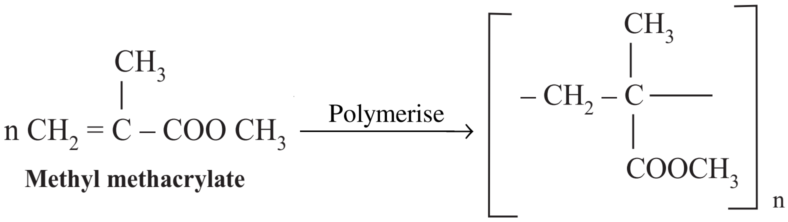


$$n\,\underset{\underset{\displaystyle Cl}{|}}{C}H = CH_2 \xrightarrow[\text{Peroxide}]{\text{Dibenzoyl}} -\!(CH_2 - \underset{\underset{\displaystyle Cl}{|}}{C}H)_n$$

Vinyl chloride PVC

PVC is a hard horny material. However, it can be made to acquire any degree of pliability by the addition of a plasticizer. It is resistant to chemicals as well as heat. It is used for making rain coats, hand bags, toys, hosepipes, gramophone records, electrical insulation and floor covering.

(5) Polymethyl Methacrylate (PMMA) : Its monomer unit is methyl methacrylate.



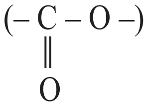
$$n\,CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - COO\,CH_3 \xrightarrow{\text{Polymerise}} \left[\; - CH_2 - \underset{\underset{\displaystyle COOCH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - \;\right]_n$$

Methyl methacrylate

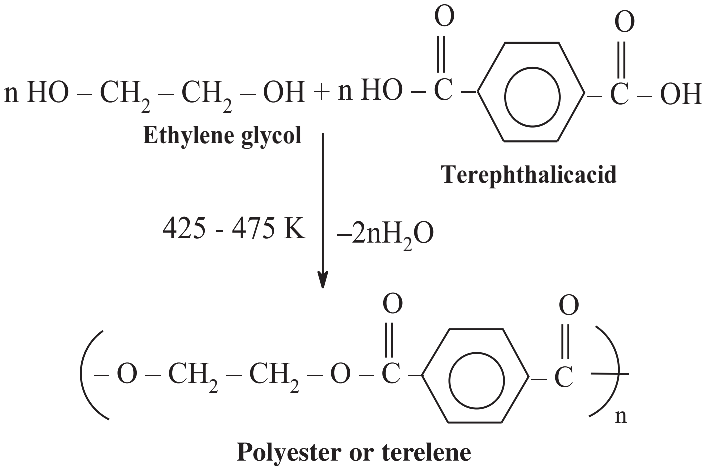
Polymethyl metha acrylate (PMMA)

PMMA is a hard and transparent polymer and quite resistant to the effect of heat, light and ageing. It has high optical clarity. It is used in the manufacture of lenses, transparent domes and skylights, dentures, aircraft windows and protective coatings. Its commercial names are Lucite, Plexiglass, Acrylite and Perspex.

31.5.3 Polyester

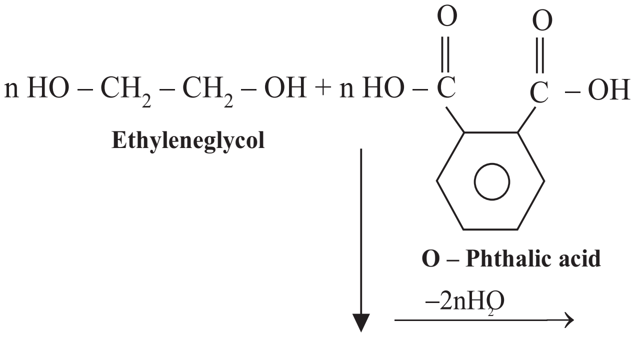
Some synthetic polymers have ester group  $(-\underset{\underset{O}{\|}}{C}-O-)$ in them. These are condensation polymers. The important members of this class are polyester and glyptal resins.

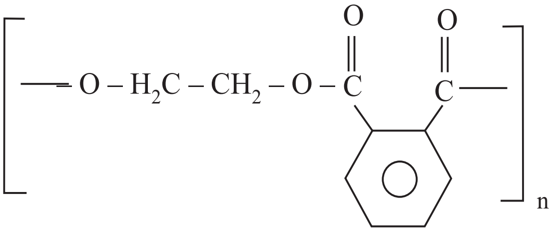
Terelene : It is a polymer obtained by the condensation reaction between ethylene glycol and terephthalic acid.



Terelene is resistant to the action of most of the common chemicals and biological substances and also to abrasion. It has a low moisture absorbing power. As such it is widely used in making wash and wear fabrics. The polyester textile fibres made from the polymer are marketed under the trade name terelene or dacron. It is also blended with cotton and wool in clothing.

Glyptal or Alkyl resin : Glyptal is a general name of all polymers obtained by condensation of di-basic acids, and polyhydroxy alcohols. The simplest glyptal is (poly ethelene glycol phthalate) which is obtained by a condensation reaction between ethylene glycol and ortho-phthalic acid.





(Poly ethylene glycol phthalate)

Glyptal resins are three dimensional cross-linked polymers. Poly (ethylene glycol phthalate) dissolves in suitable solvents and the solution on evaporation leaves a tough and non-flexible film. Thus, it is used in adherent paints and lacquers.

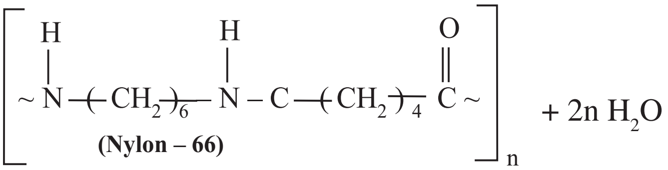
31.5.4 Polyamide

Polyamides are the polymers having amide group $(-\underset{\underset{O}{\|}}{C}-NH-)$ in them. The important polyamide is Nylon-66 which is a synthetic polymer. In nature also the polymer have amide linkages in their molecules.

Nylon – 66 : It is a polymer of adipic acid (tetra methelene dicarboxylic acid) and hexamethelene diamine

$$n\,H_2N-(CH_2)_6\,NH_2 + n\,HOOC\,(CH_2)_4-COOH \xrightarrow[\approx 525K]{\Delta}$$

Hexamethelene diamine **Tetramethelene dicarboxylic acid**



(Nylon – 66)

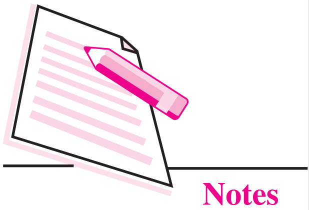
$$\left[\sim\underset{}{\overset{\overset{H}{|}}{N}}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}\sim\right]_n + 2n\,H_2O$$

Nylon – 66 (read as nylon – six-six) can be cast into a sheet or fibres by spinning devices. Nylon fibres have high tensile strength. They are tough and resistant to abrasion. They are also somewhat elastic in nature.

Nylon finds use in making bristles and brushes, carpets and fabrics in textile industry, elastic hosiery in the form of crinkled nylon.

INTEXT QUESTIONS 31.5

1. What does PMMA represent?
2. Write the names of monomers of terylene?



Notes

3. How is nylon - 66 synthesised?
4. Write equations for the synthesis of the following polymers :

   (i) glyptal (ii) Teflon

In this section we shall discuss about Biopolymers. (Natural Polymers)

31.5.5 Biopolymers

Many polymers which are present in plants and animals such as polysaccharides (starch, cellulose), proteins and nucleic acids etc. which control various life processes in plants and animals are called **biopolymers.**

(i) **Starch :** It is polymer of glucose. It is a chief food reserve of plants.

(ii) **Cellulose :** It is also a polymer of glucose. It is a chief structural material of the plants. Both starch and cellulose are made by plants from glucose produced during photosynthesis.

(iii) **Proteins :** These are polymers of **amino acids.** They have generally 20 to 1000 amino acids joined together in a highly organized arrangement. These are building blocks of animals and constitute an essential part of our food.

(iv) **Nucleic acids :** These are polymers of various nucleotides. For example, RNA and DNA are common nucleotides. These biopolymers are very essential for our life.

31.6 ENVIRONMENTAL PROBLEMS AND BIODEGRADABLE POLYMERS

In this section we shall discuss those polymers which will not cause any environmental pollution.

With the increasing use of polymers, the problem of disposal of waste of these products is posing alarming curse. Since most of the synthetic polymers are in the form of plastics, it is frequently used in abundance in the form of packing material and throw away bags. Since ordinary polymers do not degrade naturally by light, oxygen, water or micro-organisms, there is a serious problem of their disposal. The environmental problems caused by careless use of non-biodegradable polymers can be reduced by proper disposal of these materials and reusing them and remoulding them for other uses. Another way is to collect them and depolymerise them back to monomers. Though it has a limited application.

Another option is to produce biodegradable polymers which can be broken into small segments by enzyme-catalysed reactions. The required enzymes are produced by micro-organisms. It is a known fact that the carbon-carbon bonds of chain growth polymers are inert to enzyme catalysed reactions, and hence they are non-biodegradable. To make such polymers biodegradable we have to insert certain bonds in the chains so that these can be easily broken by the enzymes. When such polymers are buried as waste, micro organisms present in the soil can degrade the polymer, so that they do not cause any serious affects on the environment.

One of the best method of making a polymer biodegradable is by inserting hydrolysable ester group into the polymer.

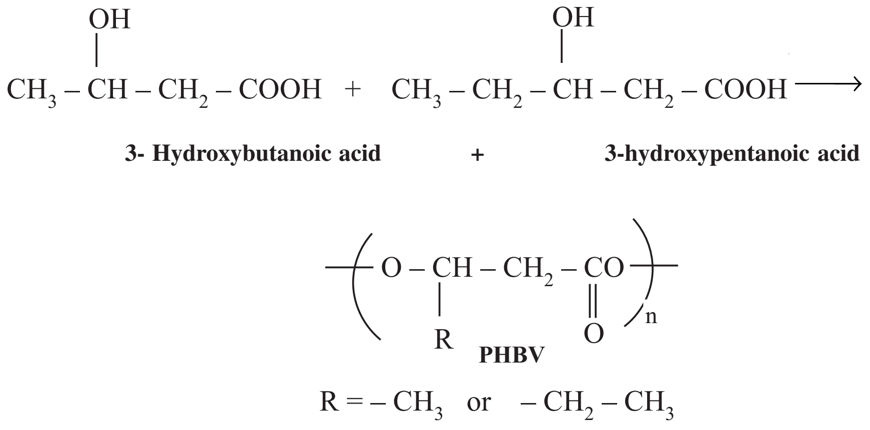
31.6.1 Some Biodegradable Polymers

A large number of bio degradable polymers are now available and more are being added to the list. However, these are expensive, therefore, these find use in special situations where cost factor can be ignored. In future, as their cost reduces these will find greater use in daily life and will replace non-bio-degradable polymers.

Some important biodegradable polymers are PHBV, PGA, PLA and PCL.

(PHBV) Poly-Hydroxybutyrate – co – β - Hydroxyvalerte

PHBV is a copolymer of 3 – hydroxy butanoic acid, and (3 – hydroxypentanoic acid), in which, the monomer units are connected by ester linkages.



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-COOH + CH_3-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-COOH \longrightarrow$$

3- Hydroxybutanoic acid **+** **3-hydroxypentanoic acid**

$$\left(O-\underset{\underset{R}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{CO}\right)_n$$

PHBV

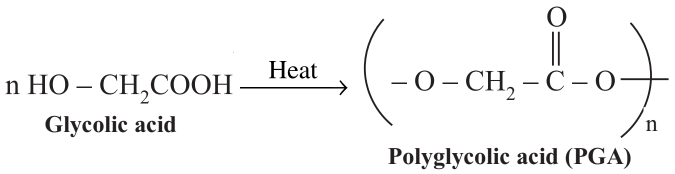
$R = -CH_3$ or $-CH_2-CH_3$

The properties of PHBV vary according to the ratio of both the acids. 3 – Hydroxybutanoic acid provides stiffness and 3 – hydroxypentanoic acid imparts flexibility to the copolymer.

(i) PHBV is used in orthopaedic devices and

(ii) In controlled drug release. The drug put in PHBV capsule is released after this polymer is degraded by enzymatic action. It can also be degraded by bacterial action.

PGA Polyglycolic acid is obtained by the chain polymerization of dimer of glycolic acid, $HO-CH_2COOH$.

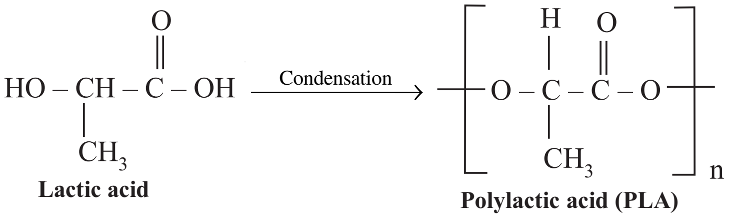


$$n\,HO-CH_2COOH \xrightarrow{\text{Heat}} \left(-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right)_n$$

Glycolic acid

Polyglycolic acid (PGA)

PLA Polyactic acid is obtained by polymerization of the dimer of lactic acid ($HO–CH(CH_3)$ COOH) or by micro biological synthesis of lactic acid followed by the polycondensation and removal of water by evaporation.

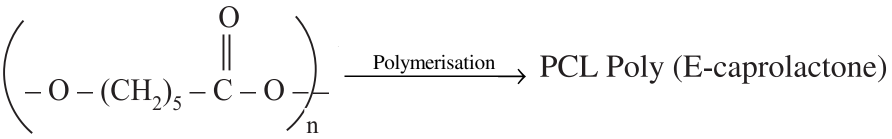


$$\underset{\underset{\displaystyle CH_3}{|}}{HO-CH}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{\text{Condensation}} \left[-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right]_n$$

Lactic acid

Polylactic acid (PLA)

PCL Poly (E–caprolactone) is obtained by chain polymerization of the lactone of 6 – hydroxy hexanoic acid.



$$\left(-O-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right)_n \xrightarrow{\text{Polymerisation}} \text{PCL Poly (E-caprolactone)}$$

Most of the biodegradable polymers find use in stiching wounds and cuts.

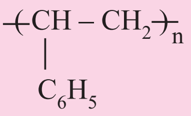
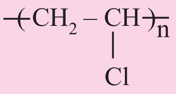
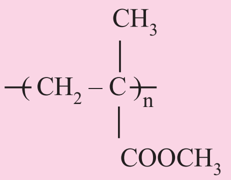
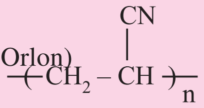
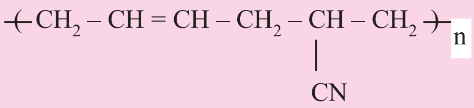
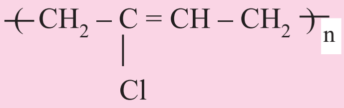
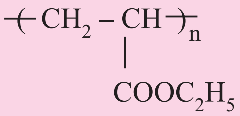
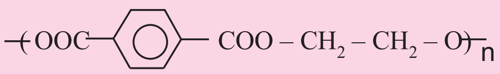
1. In medical goods such as surgical sutures.
2. In agriculture materials such as films, seed coatings.
3. In food wrappers, personal hygiene products, etc.

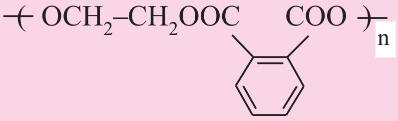
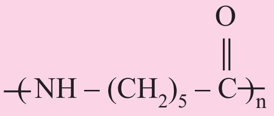
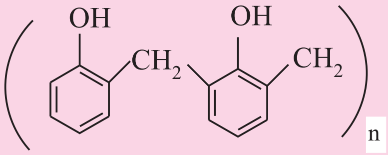
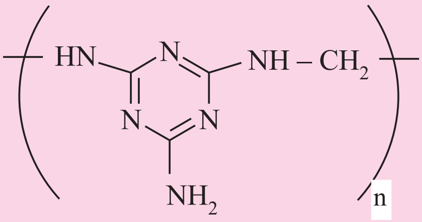
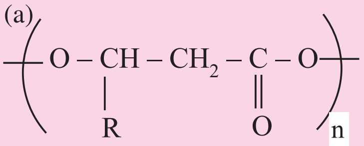
INTEXT QUESTIONS 31.6

1. What is PHBV?
2. Give two examples of biopolymers?
3. Define biodegradable polymers? Give three examples?
4. Which polymer is used for post-operative stitches?

In the following Table 33.4 we shall now give a brief account of the various commercially important polymers alongwith their structures and uses.

Table 31.5

S. No.	Name of Polymer	Structure	Uses
1.	Polythene	$-\!\left(CH_2 - CH_2\right)_n\!-$	As Insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	 $\left(\underset{C_6H_5}{CH} - CH_2\right)_n$	As Insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	 $\left(CH_2 - \underset{Cl}{CH}\right)_n$	In manufacture or raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Teflon	$-\!\left(CF_2 - CF_2\right)_n\!-$	As lubricant, insulator and making cooking wares.
5.	Polymethyl metha acrylate (PMMA) or Flexi glass	 $\left(CH_2 - \underset{COOCH_3}{\overset{CH_3}{C}}\right)_n$	As substitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)	 $\left(CH_2 - \overset{CN}{CH}\right)_n$	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or BuNa-S)	 $\left(CH_2 - CH = CH - CH_2 - \underset{C_6H_5}{CH} - CH_2\right)_n$	In making automobile tyres and footwear.
8.	Nitrile rubber (Buna-N)	 $\left(CH_2 - CH = CH - CH_2 - \underset{CN}{CH} - CH_2\right)_n$	In making oil seals manufacture of hoses and tank linings.
9.	Neoprene	 $\left(CH_2 - \underset{Cl}{C} = CH - CH_2\right)_n$	As insulator, making conveyor belts and printing rollers.
10.	Poly ethyl acrylate	 $\left(CH_2 - \underset{COOC_2H_5}{CH}\right)_n$	In making films, hose pipes and furnishing fabrics.
11.	Terylene (Dacron)		For making fibres, safety belts, tyre cords, tents, etc.

12.	Glyptal		As binding material in preparation of mixed plastics and paints.
13.	Nylon 6	 $+\!\!\left(NH-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right)\!\!_n$	In making fibres, plastics, tyre cords and ropes.
14.	Nylon 66	$-\!\!\left(NH-(CH_2)_6-NHCO\,(CH_2)_4\,CO\right)\!\!-_n$	In making brushes synthetic fibres, parachutes, ropes and carpets.
15.	Bakelite		For making gears, protective coating and electrical fittings.
16.	Urea formaldehyde resin	$-\!\!\left(NH-CO-NH-CH_2\right)\!\!-_n$	For making unbreakable cups and laminated sheets.
17.	Melamine formaldehyde resin		Formaking plastic crockery, un breakable cups and plates.
18.	Poly-β-hydroxy butyrate-co-βhydroxy valerate (PHBV)	(a)  $-\!\!\left(O-\underset{R}{\underset{\|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O\right)\!\!-_n$ R = CH_3, – C_2H_5	As packging, orthopaedle devices and in controlled drug release.

WHAT YOU HAVE LEARNT

- Difference between soaps and detergents
- Lipophilic and hydrophilic parts of soap and detergent molecules
- Advantages and disadvantages of detergents over soaps
- Cleansing action of soaps and detergents
- Soap does not make leather with hardwater due to formation of salt with calcium and magnesium.

- Linear Alkyl benzene sulphonate is better biodegrable than branched alkyl benzene sulphonates detergents.
- Polymers, the high molecular mass macrosized molecules consisting of repeating units of monomers of synthetic or natural origin.
- Synthetic polymers are classified with respect to their composition, mode of poly merization and nature of molecular forces.
- Polymerization is classified into two categories (i) addition polymerization (ii) condensation polymerization.
- Addition polymers are formed by addition of large number of monomers without the elimination of any smaller molecules.
- Condensation polymers are formed by elimination of smaller molecules such as H_2O, NH_3 etc.
- Natural rubber is a linear polymer of isoprene, and is vulcanized by heating with sulphur, which forms cross link between different chains.
- Vulcanized rubber has much improved physical properties.
- Synthetic rubbers are usually obtained by copolymerization of an alkene and 1,3-butadiene derivatives.
- Synthetic polymers due to their inertness to degradation have created environmental problems.
- Since biopolymers degrade enzymatically, synthetic biodegradable polymers having functional groups such as ester, amide etc. have potential use as sutures, implants, drug release materials, are developed as alternatives. For example, PHBV, PLA, etc. constitute such materials.

TERMINAL EXERCISE

1. What is the difference in between soaps and detergents?
2. Write the cleansing action of soap sand detergents.
3. Write the names of two anti oxidants.
4. Which type of soap and detergents are biodegradable?
5. What is spanification?
6. Explain the difference between chain growth and step growth polymerization.
7. Define the terms thermosetting and thermo-plastics. Give one example of each.
8. What is a copolymer. Give one example.

9. Differentiate between addition polymer and condensation polymer with the help of one example each.
10. What are elastomers? Give the chemical equation for the preparation of Buna-S.
11. Write the information asked for the following polymers :
    - (i) Neoprene : Materials required for preparation.
    - (ii) PVC : monomer unit.
    - (iii) Synthetic rubber : monomer units
12. What is vulcanization of rubber? What are the advantages of vulcanized rubber?
13. Give examples of two plasticizers.
14. How are polymers classified into different categories on the basis of intemolecular forces? Give one example of a polymer of each of these categories.
15. What are biodegradable polymers? Give three examples.
16. Write the names and structures of monomers of the following polymers :
    - (a) Polystyrene (b) Teflon
    - (c) PMMA (d) PVC
    - (e) PHBV (f) Polypropylene.
17. How will you prepare the following? Give chemical reaction only :
    - (a) PVC (b) Nylon-66 (c) PMMA

ANSWERS TO INTEXT QUESTIONS

31.1

1. Sodium or potassium salt of higher fatty acid.
2. Sodium or potassium hydroxide and oils and fats.
3. Carboxylate anion
4. Sulphonate anion.
5. Long normal alkyl chain.
6. False

31.2

1. (i) Polymer is a giant chain like molecule obtained by inter-molecular combinations of similar or different types of smaller molecules.

   (ii) Monomers are the low molecular mass simple molecules capable of forming inter-molecular linkage to give gaint molecules called polymers.

2. (i) Polyethene (ii) Terelene
3. (i) Hompolymers are polymers made of single monomer units, for example, polythene, polystyrene, or polybuta diene.
   (ii) A copolymer is one which is formed by the co–polymerisation of two monomers. For example, Buna (or SBR, styrene - butadiene rubber)
4. (i) Ethelene glycol and terephthallic acid
   (ii) Hexamethelene diamine and adipic acid.

31.3

1. (i) Natural polymers are found in nature, (in animals and plants) e.g. proteins and nucleic acids.
   (ii) Synthetic polymers are man-made. e.g. Nylon, polyesters and rubbers.
2. The polymers in which the linear polymer chains are cross linked to form a three-dimensional network structure are called cross-linked polymers. The common example of this type of polymer is bakelite.
3. Thermoplastics differ from thermosetting plastics in terms of mode of linkage and intermolecular forces. Thermoplastic polymer can be moulded in desired shape but thermosetting polymers set to shape on heating and can not be moulded.
4. Polyethene < Buna-S< Nylon-66

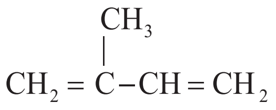
   Nylon 66 : Condensation polymer

   Buna-S : Addition polymer

   Polyethene : Addition polymer

31.4

1. (i) Monomer of natural rubber is

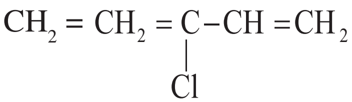


$$\mathrm{CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2}$$

Isoprene

2-methyl buta-1,3-diene

   (ii) Monomer of Neoprene is



$$\mathrm{CH_2=CH_2=\underset{\underset{\displaystyle Cl}{|}}{C}-CH=CH_2}$$

Chloroprene

2-Chlorobuta – 1,3-diene

2. Sulphur makes the rubber more elastic, more ductile, less plastic and non-sticky.
3. Buna-S is obtained by co-polymerization of butadiene and styrene in presence of sodium metal. Bu stands for butadiene, na for sodium and S stands for styrene, It is also called S.B.R.
4.
   1. Natural rubber is soft and sticky, but vulcanised rubber is hard and non-sticky.
   2. Natural rubber has less tensile strength while vulcanised rubber has high tensile strength.
   3. Natural rubber is soluble in solvents like ether, carbon tebrachloride, petrol etc. whereas vulcanised rubber is insoluble in all common solvents.

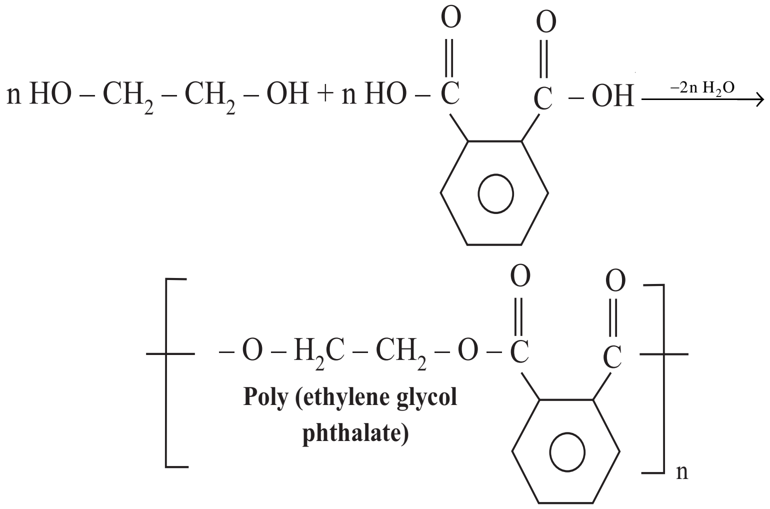
31.5

1. Polymethyl methacrylate (PMMA)
2. Ethelene glycol and terphthalic acid.
3. Nylon – 6, 6 is synthesised by the polymerisation of two monomer units adipic acid and hexamethelene diamine.

$$n\,H_2N\text{-}(CH_2)_6\text{-}NH_2 + n\,HOOC\text{-}(CH_2)_4\text{-}COOH \xrightarrow[525K]{\Delta}$$

$$\underbrace{\left[-N\text{-}(CH_2)_6\text{-}NH-CO\text{-}(CH_2)_4\text{-}CO-\right]_n}_{\textbf{Nylon – 66}} + 2n\,H_2O$$

4. (i) Glyptal



(ii) Teflon $n\;CF_2 = CF_2 \xrightarrow[\Delta,\ \text{pressure}]{(NH_4)_2S_2O_8} \left(-CF_2-CF_2-\right)_n$

31.6

1. PHBV is a copolymer of 3 – Hydroxy butanoic acid and 3-hydroxypentanoic acid. It is used in making capsules. It is biodegradable in nature.
2. Nucleic Acids, proteins.
3. Polymers, which are degraded by microorganisions are called biodegradable polymers. For examples, PHBV, Polyglycolic acid, Polylactic acid, etc.
4. Polyglycolic acid (PGA) and poly Lactic Acid (PLA).

313en32

32

ENVIRONMENTAL CHEMISTRY

The earth has just the right kind of conditions of temperature range, air, water, soil for supporting life and is protected from harmful rays from the outer space by the ozone layer. With progressive increase in human population and human activities, the quality of air, water, soil and other natural sources get degraded and become unfit for use by organisms. Increasing population, urbanisation and industrialisation has led to the decreased availability of water. The quality of water used is also being deteriorated as it is getting more and more polluted. You may be aware of at least some health hazards and harmful effects of water pollution. The main components of soil are 90–95%. Inorganic matter and 5–10% organic matter besides soil contains water and air, the composition of the soil varies considerably place to place.

Soil has become dumping ground of most of the waste products There will be a great loss of earth crust. The dumping of nuclear waste is a world side problem, cause of soil pollution. In this lesson a detailed account of various types, sources and effects of water pollutants is given. Some methods of water pollution control and legislatures involved have also been discussed.

It causes unwanted effects. In this lesson you shall learn about the sources of pollutants and their effects on environment. Thus the pollution in many ways threaten the existence of many organisms including human being on the earth. Therefore, any threat of degradation or damage to the environment should be a matter of concern the green chemistry is environment friendly living on design of chemical products with their impacts on human health and on environment. it reduces the use of hazardous substances.

OBJECTIVES

After reading this lesson you will be able to :

- define environment and biosphere;

- differentiate the varions environmental segments;
- explain nature of threats to environment;
- define pollutants and its types;
- list sources of pollutants and
- explain the effects of pollutants on environment, organisms and humans in particular.
- list earth's water resources;
- define water pollution and its different parameters;
- list the major types of water pollutants, their sources and effects;
- distinguish between natural and man -made pollutants;
- use the concept of biological oxygen demand (BOD) and account for the changes in a water body;
- state methods for the prevention of water pollution;
- compare primary, secondary and tertiary treatment of sewage;
- identify the sources of soil pollution;
- how to control of soil pollution,
- explain the principles of green chemistry;
- the achievements of green chemistry; and
- explain strategies to control environmental pollution.

32.1 COMPONENTS OF ENVIRONMENT

Different organisms live in different types of surroundings such as air, water and soil. Different kinds of living organisms share these surroundings. The surroundings are the "environment" of an organism.

Environment has two components

(i) physical or abiotic (non-living) components and

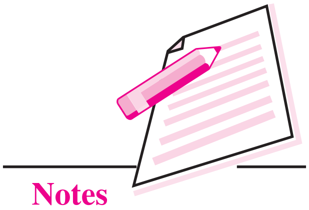
(ii) living or biotic components.

Abiotic components of environment are air, water, soil, energy radiation, etc. **Biotic components** of environment are microbes (such as bacteria, algae and fungi), plants, animals, etc.

Environment is the sum total of living and non living components surrounding an organism.

Environment consists of four segments such as

(i) Biosphere (ii) Atmosphere (iii) Hydrosphere, and (iv) Lithosphere



Biosphere : All the parts of the earth are not suitable for survival of organisms. Some parts are too hot or very cold to support life.

The part of earth on which organisms can survive and reproduce is called biosphere.

Survival of organisms depend upon a delicate balance between themselves and with the various components of the environment. Any disturbance, damage or adverse change in the quality of environment poses a threat to the survival and well being of organisms. Therefore, any threat of degradation or damage to environment should be a cause of concern to all of us.

Atmosphere : Atmosphere is the only place where free oxygen and water vapour exist.

Atmosphere is a thin layer of air (mixture of gases) around the earth which is a great source to all living organisms.

Hydrosphere : Water plays an important role in the biosphere, without it life is impossible.

Hydrosphere is the part of earth on which all types of water resources exists, viz., oceans, seas, rivers, lakes, glaciers, ice caps, ground water, etc.

Lithosphere : Soil is a part of lithosphere which supports life.

Lithosphere is the part of the earth where all types of minerals, metals, organic matters, rocks, soils, etc. exist

Global Environmental Damages

Some example of global damages are discuss below.

(i) Chloroflouro carbons (CFCs), used as refrigerants, and various kinds of sprays or sols (eg. perfumes, air freshner, etc.). CFCs cause ozone holes in the ozone layer. Ozone hole refer to depletion of ozone molecules in the ozone layer due to the reacton of CFCs.The holes in the ozone layer appear elsewhere and not where these chemicals are used.

(ii) More ultraviolet radiations reach the earth through the ozone holes and the reflected radiations from the earth are absorbed by CO_2 water vapour, etc. The traped radiations release more and more heat resulting in the phenomenon of **Global Warming.** This effect is also known as **Green House Effect.**

Global environment damage affects quality of environment over a much larger area and is not localised to the area where the damage is initiated. Global warming will cause ill effects and are not confined to the area causing the damage. It causes wide range of effects like melting of glaciers, polar caps, rise in water level of sea and flooding of costal plains, etc.

INTEXT QUESTIONS 32.1

1. Define environment.
2. What are the two components of environment?
3. List three biotic components?
4. How do CFCs affect the ozone layer?
5. What are the different segments of environment?

32.2 POLLUTION

In ancient times human settlements began and flourished along river banks as rivers provided them basic facilities. Growth of population forced people to move to other places. They started utilising natural resources such as trees and soil (mud) to build shelters. More waste material started collecting at places they inhabited. Humans themselves created conditions for disposal of waste (sanitation). Humans then started industries to manufacture goods for their own comforts. Pesticides and chemical fertilisers were manufactured to grow more food for the growing demand by population. Industries also generated wastes, which ultimately finds its way to water sources. Pesticides and chemicals were washed into natural water bodies such as sea, river, lakes and ponds and affected the aquatic organisms. Supply of potable (safe for drinking) water diminished. All this badly affects life of organism including humans. All such waste generated through human activities and spoiling the natural environment is termed as **pollutants**. Damaging the natural environment by pollutants is termed as **pollution.**

Pollution refers to deterioration or unclean objectionable conditions in the quality of natural resources such as air, water and soil because of the action or presence of unwanted substances beyond a certain limit.

32.3 POLLUTANTS

Pollutants are the substances or effect introduced into the environment in significant amounts in solid, semi solid, liquid gas or sub molecular particle form which has a detrimental (bad) effect on the environment.

The pollutants may be classified in the following ways (Fig.32.1).

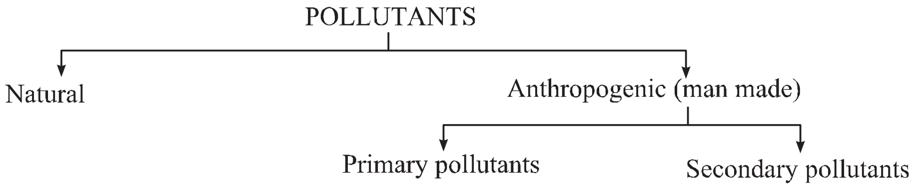


Fig. 32.1 : *Classification of pollutants*

Notes

32.3.1 Natural Pollutants

There can be several natural sources which are the cause of pollution. Some of them are listed below :

(i) Fires in forests may be caused when lightening strikes the trees. Burning of tree produces a lot of CO_2 which is released to the atmosphere.

(ii) Soil erosion increases suspended particulate matter and dust in air. These may even enter water bodies as they are washed down by rain or natural water falls.

(iii) Volcanic eruptions also add pollutants like SO_2 and solid particles to the environment.

(iv) Volatile organic compounds from leaves, trees and dead animals naturally enter the atmosphere.

(v) Natural radioactivity and the other natural pollutants have been entering the environment since ages. (But the low level of pollution has rarely endangered lives of organisms).

32.3.2 Anthropogenic Pollutants

Increased human activities releases a large amount of pollutants to the environment and poses a threat to the human life. Pollutants added to the environment through human activities are termed *anthropogenic pollutants*. These are of two kinds**.**

(i) Primary pollutants: Primary pollutants are added directly in a harmful form to the atmosphere. eg CO_2 and CO from burning of fossil fuel; SO_2 and oxides of nitrogen from vehicular combustion, thermal power stations, etc.

(ii) Secondary Pollutants: Secondary pollutants are the products of reaction between the primary pollutants and normal environmental constituents.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

Thus, SO_2 a primary pollutant which reacts with oxygen of air to give SO_3. Further, SO_3 reacts with water vapour present in the atmosphere and forms H_2SO_4. Thus SO_3 and H_2SO_4 are secondary pollutants.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$2NO + O_2 \longrightarrow 2NO_2$$

Nitric oxide (NO), a primary pollutant reacts with oxygen to give NO_2 which is a secondary pollutant.

Depending on the sources. anthropogenic pollutants may be classified further into

(i) Industrial Pollutants

(ii) Domestic Pollutants

(i) **Industrial Pollutants:** Paper, textile industries, tanneries and distilleries dispose various effluents like oil, grease, plastic and metallic wastes into the environment.

(ii) **Domestic Pollutants:** Detergents, fluoride toothpastes, edible colours, food flavouring agents, polythene bags and wrappers find their way into the environment as pollutants. Methane is produced in cattle stomach and in stagnant paddy fields is also a domestic pollutant.

INTEXT QUESTIONS 32.2

1. Define a pollutant.
2. Name two sources of natural pollution.
3. Define a secondary pollutant.
4. What do you mean by environmental pollution?

32.4 SOURCES OF POLLUTANTS

Many of the pollutants in our environment have natural as well as human related origins. For example, the natural origin of pollutants includes the release of sulphur dioxide (SO_2) from volcanic eruptions, erosion of soil by wind and water, dissolved minerals carried on to rivers and ocean by surface run off, etc.

The sources of pollutants are also classified :

(i) Stationary and

(ii) Mobile sources

Stationary Sources : The pollutants relased from a fixed location or a well defined area is known as stationary source. e.g. smokestacks of power plants, smelters, surface mines, etc.

Mobile Sources : The pollutants released from diffused sources or the sources that move from place to place is termed as a mobile source. e.g. automobiles, buses, aircrafts, ships, trains, etc.

The various pollutants of water, their sources and effects are given in Table 32.1

Table No. 32.1 : Major Air Pollutants their Sources and Effects

Major Pollutants of Air	Some of the Sources	Some of the Effects
SO_2	Vehicular combustion, fossil fuel burning	Irritation to the eyes, acid rain premature falling of leaves
CO and CO_2	Vehicular combustion and burning of fuels and hydrocarbons	Global warming, green house effect CO has great affinity for haemoglobin and forms the carboxy haemoglobin
Smoke, fly ash and soot	Thermal power stations	Respiratory diseases.
Lead and mercury	Auto exhaust from gasoline, paints, storage batteries. fossil fuel burning	Affects the nervous system and circulatory system causing nerve and brain damage.
CFCs	Refrigerants and aerosol	Kidney damage and ozone depletion.

The various pollutants of water, their sources and effects are summerised in Table No. 32.2

Table 32.2 : Major Water Pollutants their Sources and Effects

Major Pollutants of Water	Some of the Sources	Some of the Effect
Pesticides and insecticides like DDT, BHC	Improper use in agriculture, mosquitos repellants	Toxic to fishes, predatory birds and mammals.
Plastics	Homes and industries	Kills fishes and animals like cows.
Chlorine compounds	Water disinfection with chlorine, paper and bleaching powder	Fatal for plankton (organisms floating on the surface of industries water) foul taste and odour, can cause cancer in humans.
Lead	Leaded gasoline, paints, etc.	Toxic to organisms
Mercury	Natural evaporation and dissolved industrial wastes, fungicides	Highly toxic to humans
Acids	Mine drainage, industrial wastes	Kills organisms
Sediments	Natural errosion, run off from fertilizer and other factories, mining and construction activities.	Reduces ability of water to assimilate oxygen.

The general effects of pollutants are produced due to interactions of pollutants among themselves.

Contamination

Contaminations refer to the mere presence of undesirable materials to a medium like air, water, soil, etc. making it unfit for a particular use. For example, contamination of air by hazardous exhaust from automobiles. It becomes a pollutant if its concentration exceeds the level which can cause harmful effect.

32.5 AIR POLLUTION

You have just learnt how nature has its own means of using up and getting back its components such as CO_2, O_2 and N_2. If the balance of CO_2, O_2 or N_2 is disturbed by human activity then it will have adverse affect on life on the earth. Now you know why environmentalists are deeply concerned about environmental pollution, tree plantations and afforestation.

Undesirable changes have occurred in the physical and chemical constituents of air due to human activities. Undesirable change in the atmosphere is air pollution. Pollutant gases such as SO_2 oxides of nitrogen, CO and excessive amount of CO_2 have been added to the atmosphere. Air pollutant may be classified as particulate matter, liquid droplets and gaseous pollutants (Fig 32.2) :

Air Pollutants

Particulate pollutants	Liquid droplets	Gaseous pollutants
Soot	Hydrocarbons	SO_2
Fly ash		H_2S
Flourides		$NO_{(x)}$
Lead		NH_3
Dust from cement		CO_2 and CO
and other industries	Photo-chemical	
Sodium chloride		oxidants (O_3, PAN)
Agricultural chemicals		Tobacco smoke

Fig. 32.2 : *Classification and Example of Air pollutants*

32.5.1 Particulate Pollutants

Particulate pollutants such as soot and fly ash are released by various industries as by products of industrial processes. They are blown away by wind when they come out of the chimneys and other outlets of industries and mix with air.

Suspended particulate matter is also emitted by exhaust of polluting diesel vehicles and ill managed coal fired power plants. In nature, forest fires, wind erosion and volcanic eruptions add suspended particulate matter into air. Examples of particulate pollutants are soot, flyash from thermal power plants, cement dust, petrocoke from petroleum refineries. Some of the particulate pollutants are discussed in detail below:

Fluoride: Aluminium, steel and electrochemical plants, blast furnaces, brick kilns, coal combustion, tile and glass etching factories add fluoride particles which settle

on vegetation. They burn tips of leaves and when cattle eat the vegetation they suffer from fluorosis resulting in loss of teeth, weight and lameness. Humans also suffer from fluorosis. Volcanoes also release fluorides which form gaseous as well as particulate pollutant.

Lead: Lead particles come into air from automobile exhausts. Lead is used as an antiknock agent in automobile gasoline which contains tetraethyl lead. Paint, ceramic and pesticide industries also add lead particles to the atmosphere. Manufacture of lead storage battries and recycling of discarded battries add to lead pollution. Lead interferes with development of red blood corpuscles and causes anaemia (lack of haemoglobin - the oxygen carrying pigment of blood). Lead is a cumulative poison and prolonged exposure even in low concentration may damage kidneys and liver.

Dust: Particulate matter less than 10 microns in size is dust. It reaches lungs, deposits along the respiratory tract and causes asthma or even lung cancer. Dust from stone crushers is another example of particular pollutant.

Sodium chloride: Sodium chloride is used to remove snow in winter and remains in the enviromnent. Some sodium chloride is also added to the environment when waves of the sea spray it. Excess sodium chloride has been found to cause defoliation (leaf falling), suppression of flowering and breaking of terminal shoots of apple.

Agricultural chemicals: Chemical insecticides, herbicides and other pesticides are known to have damaging effects on plants. They are toxic to animals and humans also. Residues of pesticides get suspended as particulate matter in air.

32.5.2 Hydrocarbons

Hydrocarbons which may be in the form of liquid droplets or gas pollute air. As liquid droplets they spill or are added through seepage of oil fields and natural gas leakage. Methane is emitted in the swamps and paddy fields by methanogenic bacteria. Methane (CH_4) is also generated in stomachs of ruminant animals. Incomplete combustion of fuels release 3, 4 benzopyrene which causes lung cancer. Pesticides, paints and solvents also release hydrocarbons. Hydrocarbons are a source of photochemical smog.

32.5.3 Gaseous Pollutants

SO_2, CO_2, nitrogen oxides are commonly added to the air by human activities. Excess of these have very serious damaging effects on the physical environment as well as on humans.

SO_2 and H_2S : These are released into atmosphere through smelting of ores containing sulphur, manufacture of H_2SO_4 petroleum refining, combustion of fossil

fuels, paper making, burning of sulphur containing refuse and in nature through volcanic eruptions. Plants exposed to SO_2 and H_2S show defoliation (leaves falling off) and reduced growth.

In humans, SO_2 pollution causes headache, vomiting, irritation of eye and respiratory passages. SO_2 reacts with water to form H_2SO_4 which is washed down as acid rain about which you shall study later in the chapter.

Nitrogen Oxides: Anaerobic breakdown of nitrogenous compounds by bacteria is the natural source of nitrogen oxides. Burning fossil fuel also releases them. Power generators, automobile exhausts, explosives and nitrogenous fertilizer industries and the other anthropogenic sources produce nitrogen oxides.

NO_2: causes early dropping off of leaves and fruits in plants. Nitrogen oxides are one source of photochemical smog, acid deposition and greenhouse effect. .

CO_2 and CO : Combustion of oil, gas, coal and wood releases CO_2 in the atmosphere. CO is released chiefly from gasoline engines and burning of coal in defective furnaces. Motor vehicles with internal combustion engines emit high levels of CO and hydrocarbons. Excess of CO_2 can cause global warming, CO causes photochemical smog and has a fatal effect when inhaled by humans.

CO poisoning: CO has a high affinity for haemoglobin. It combines with the blood pigment haemoglobin to form carboxyhaemoglobin. The normal function of haemoglobin is to carry O_2. But CO combines with haemoglobin about two hundred times faster than O_2. Tissues do not get oxygen and die due to lack of oxygen. Carboxy haemoglobin is dark red in colour, the victims of CO poisoning have dark red lips. Mild CO poisoning causes lung disorders like bronchitis and emphysema. CO from cigarette smoke makes haemoglobin non functional in smokers.

Photochemical oxidants: Primary pollutants such as nitrogen oxides and hydrocarbons mix in the atmoshpere and form secondary pollutants like peroxyacetyl nitrate (PAN) and ozone, under the influence of UV radiation from the sun. Both PAN and O_3 form photochemical smog. PAN and O_3 are toxic to plants. In humans they cause irritation of eyes coughing, headache, dry throat, respiratory problems and haemorrhage.

Tobacco smoke: Smoke from burning cigarettes or bidis contains nicotine, aromatic hydrocarbons and tar. These cause problems of blood pressure and heart, windpipe and lungs in the smoker as well as those around the smoker. Cigarette smoke is also carcinogenic. The various human and natural activities which introduce air pollutants into the atmosphere are summarised in Table 32.2

Table 32.3 : Common air pollutants, their sources and contribution of Natural and Anthropogenic pollution

Air Pollutants	Some Sources	Emission (% of total)	
		Natural	Anthropogenic
Sulphur oxide (SO_x)	Fossil fuel burning, industry biomass biomass burning, volcanoes, oceans.	50	50
Carbon monoxide (CO)	Incomplete combustion, methane oxidation, transportation, biomass burning, plant metabolism.	91	9
Nitrogen oxide (NO_x)	Fossil fuel burning, lightening, biomass burning, soil microbes.	40	60
Hydrocarbons (HC)	Fossil fuels, industrial processes, evaporation of organic solvents, agricultural burning, plant isoprenes and other biogenics.	84	16
Suspended Particulate Materials (SPM)	Biomass burning, dust, sea salt, biogenic aerosols, gas to particle conversion.	89	11

INTEXT QUESTIONS 32.3

1. What is atmospheric pollution?
2. Name two particulate pollutants.
3. Name two gaseous pollutants?
4. Name one source which causes pollution due to methane.
5. Name two air pollutants which form photochemical smog.

32.6 EFFECTS OF EXCESSIVE ATMOSPHERIC POLLUTANTS ON NATURE (OUTDOOR POLLUTION)

You are now familiar with the various atmospheric pollutants. Most of these are products of fuel combustion. These pollutants have been released into atmosphere ever since human first started burning wood and coal. Later on, pollutants are being released into air due to increased industrial activity. The nature has not been able to remove all these pollutants because much more pollutants are added than the nature can handle to maintain the balance. Therefore, pollutants have now accumulated in the atmosphere to a proportion whereby atmospheric composition of air has been significantly altered. It is the causes of physical phenomena such as photochemical smog, acid rain, ozone depletion, greenhouse effect and global warming. These are damaging to plants, animals and humans.

The figure Fig. 32.3 shows the four major effects of atmospheric pollutants. In the diagram, arrows from the pollutant depicts its involvement in the physical phenomenon. The sources of the pollutants are depicted below the names of the pollutants. The four major phenomena are subsequently discussed one by one. They are temperature inversion, photochemical smog, acid rain, greenhouse effect and ozone layer (shield) depletion.

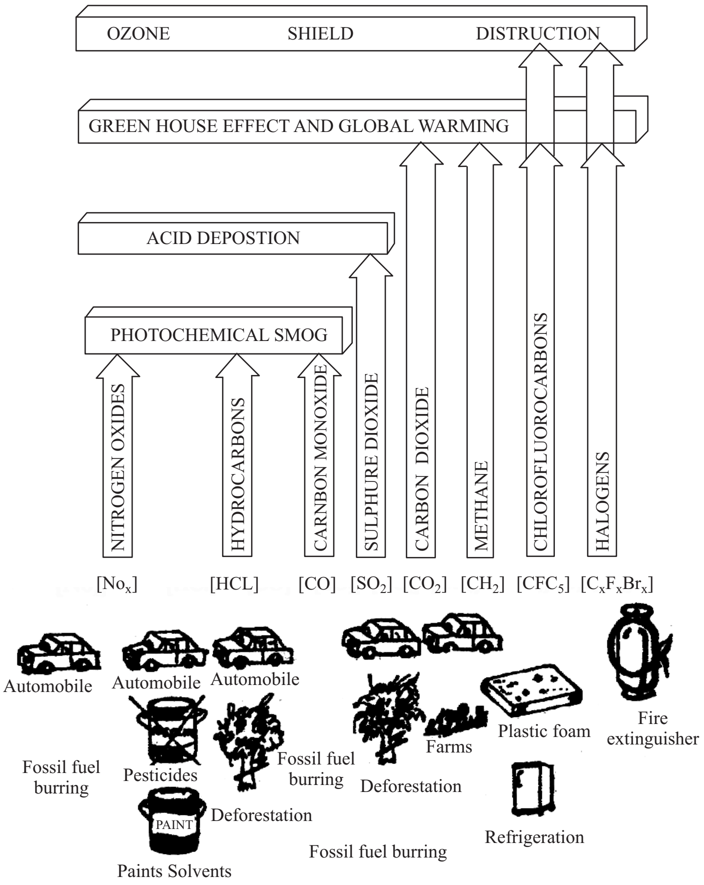


Fig. 32.3 : *Four Major Effects of Atmospheric Pollutants*

32.7 TEMPERATURE INVERSION AND PHOTO-CHEMICAL SMOG

Pollutants like sulphur dioxide which is released while burning sulphur containing fuels (fossil fuels) and particulate matter like soot present in stagnant air masses, get modified in sunlight and form a sheet called photochemical smog.

Smog is a combination of fog, smoke and fumes released by mills and factories, homes and automobiles.

When sunlight falls on stagnant air under low humid conditions in the presence of pollutants such as SO_2 soot, nitrogen oxides and hydrocarbons, photochemical smog is formed (photochemical: chemical reactions in the presence of light). Smog stays close to the ground and reduces visibility and causes irritation.

Photochemical smog is also called *PAN* ***smog*** due to the formation of peroxyacetyl nitrate or PAN and ozone which are formed from hydrocarbons and nitrogen oxides in the presence of solar radiation. PAN and ozone are called photochemical oxidants. Both of these are toxic irritants to human lungs.

Smog formation is accompanied by ***Temperature inversion or Thermal inversion,*** Temperature inversion causes smog to settle and remain near the ground till wind sweeps it away. Normally, warm air rises up into atmosphere. When a layer of cool air at the ground level is held there by an overlying layer of warm stagnant air. It is called **temperature** or **thermal inversion** (Fig.32.4).

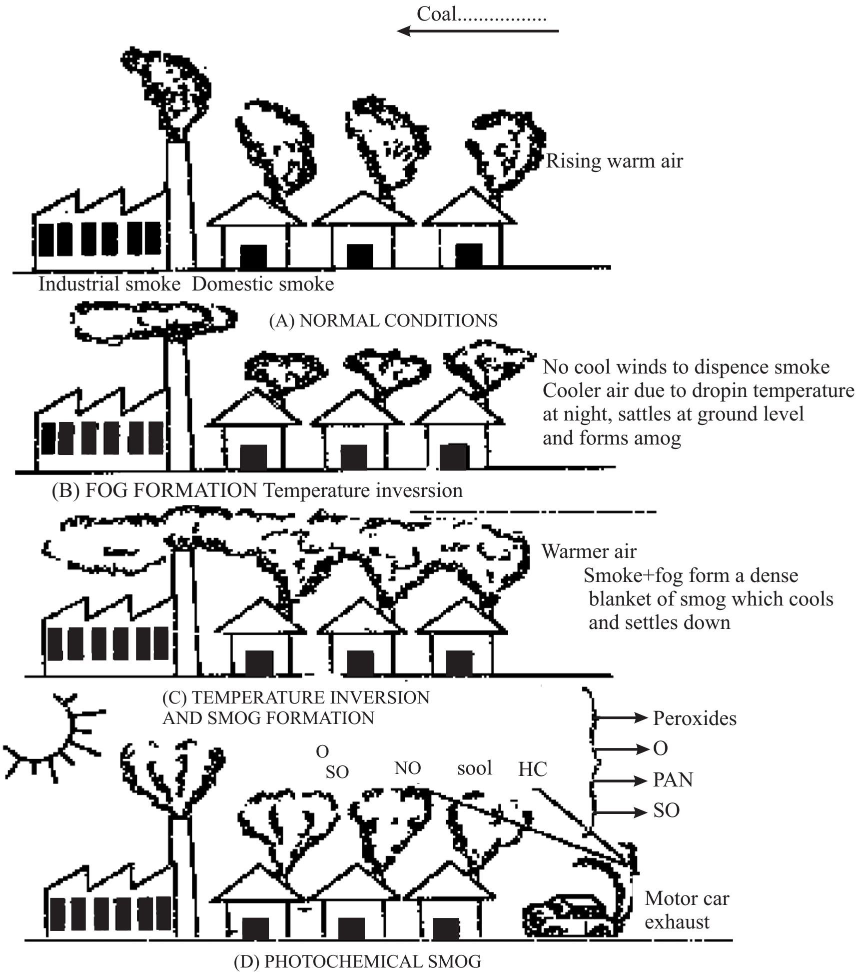
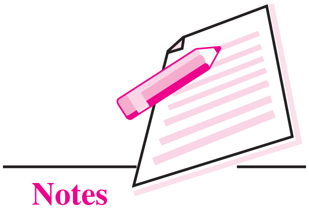


Fig. 32.4 : *Formation of Photochemical Smog and Temperature Inversion*

Exposure to smog causes respiratory problems, bronchitis, sore throat, cold, headache and irritation to eyes (red shot eyes). Smog also damages crops and reduces crop yield.



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32.8 ACID RAIN

Coal and oil burned by power plants and other industries release SO_2 into air because coal and oil contain small amount of sulphur. Automobile exhausts add SO_2 and nitrogen oxides to the air. Both SO_2 and nitrogen oxides are converted into acids HNO_3 and H_2SO_4 when they combine with oxygen and water vapour in the atmosphere as per the following photo chemical reactions.

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

This reaction is promoted by O_3 in smog. The acids, so formed are washed down from air to earth during rain or snow fall. It is called acid rain or acid snow. The acids react with minerals present in soil to form sulphates and nitrates due to acid rain.

Rain water even in its purest form is slighlty acidic with pH 5.6 due to dissolved CO_2. But areas near coal and oil burning industries and where motor vehicles ply in large numbers, pH goes down to 2 and rain becomes strongly acidic. Mountain foot hills are the worst affected. There is moisture laden air rises to higher altitudes it condenses to fall as rain or snow, dropping its load of pollutants. In spring. snow melts and adds pollutants to lakes and other water bodies.

When the dissolved pollutants drop as rain or snow (wet deposition) it is termed acid precipitation. Deposition of dry gases and salts is dry deposition. Acid rain spreads over areas of several hundreds to several thousand kilometers.

32.8.1 Effects of Acid Rain

Some of the effects of acid rain are listed below:

(1) Excessive acid concentrations are phytotoxic (toxic to plants). There have been widespread death of trees in forests due to acid rain.

(2) Sea waters are rich in minerals and have great buffering capacity. But buffering capacity of fresh water bodies is low and acid deposits have a toxic effect on the fresh water ecosystems.

(3) Mature (capable of reproduction) fish survives in acid rain fed water bodies but fails to reproduce. So there are no young fish in such waters.

(4) Exposed surfaces of buildings, statues get corroded. Limestone or marble ($CaCO_3$) structures are specially damaged (Fig. 32.5).

The chemical reaction is like
$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$.

The sulphates are leached out by rain water.

(5) Acidic sulphate when present in the atmosphere causes laziness. Acidic mist falling on the ground reduces visibility.

Fig. 32.5 : *A Stone statue showing corrosive effects of Acid Rain*

32.9 GREEN HOUSE EFFECT AND GLOBAL WARMING

The literal meaning and function of green house is to trap the heat. You must have seen delicate plants being grown in a glass chamber which is comparatively warmer inside than outside. Glass permits solar radiations to come in but restricts the outward movement of heat. The radiations get trapped inside the glass chamber and raises the temperature.

Gases such as CO_2, NO_2, CFCs (chloro fluorocarbons) allow sun rays to pass through them but then absorb and reradiate the heat back towards the earth. These are therefore termed as **green house gases**.

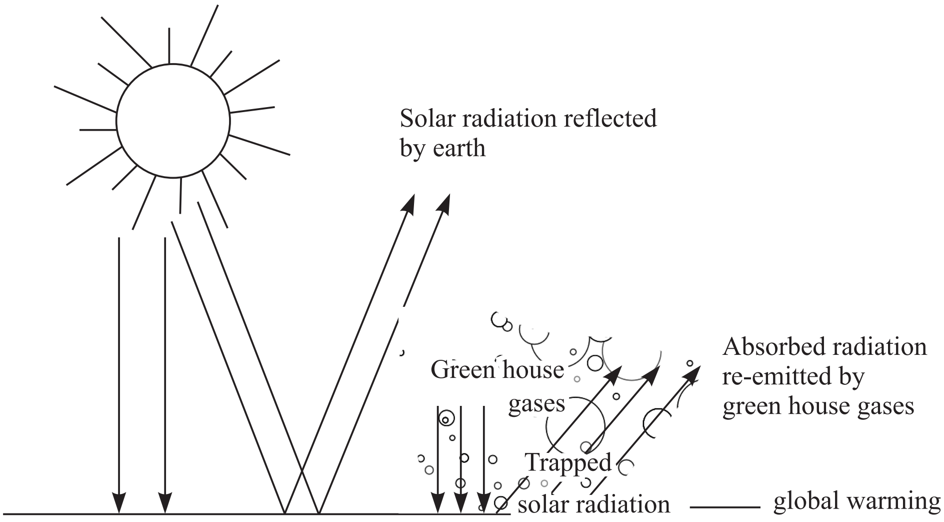


Fig. 32.6 : *Green House Effect*

32.9.1 Greenhouse Gases

The common green house gases and their sources of pollution are listed below:

(1)	CO_2	-	from fossil fuel burning.
(2)	NO_2	-	from fertilizer plants, automobile exhaust use and animal waste.
(3)	CH_4	-	from bacterial decomposition, biogas, flooded rice fields.
(4)	CFCs	-	from freon, (a refrigerant), areosol sprays.
(5)	HALONS (halocarbons)	-	from fire extinguishers.

32.9.2 How Does Earth's Atmosphere Trap Heat?

Radiations (ultra violet) from the sun penetrate the earth's atmosphere and reach earth. The surface of earth partially absorbs the radiations. The rest is re-radiated as infrared radiation from the earth's surface. In polluted air, molecules of CO_2, CH_4, CFCs, N_2O, O_3 and water vapours are present. These gases can absorb infrared radiations but cannot absorb the ultra violet radiations. Energy of these trapped radiations raise the temperature of earth and its atmosphere. Thus if proportion of green house gases increases in the atmosphere heat trapped by them will raise the temperature of the earth and will cause global warming.

Greenhouse effect leading to global warming shall have severe effects on rainfall, sea level, plant and animal growth..

Global warming is defined as the increase in the average global temperature of the atmosphere near earth's surface.

(1) **Rise in sea level:** It is estimated that by the turn of the century a rise of 5°C in global temperature will be due to effect of greenhouse gases if not checked now. Polar ice caps would melt because of rise in temperature and add more water to sea. Moreover water expands when it heats up. This will lead to rise of sea level. It will flood the low lying coastal area and many cities will get submerged in water.

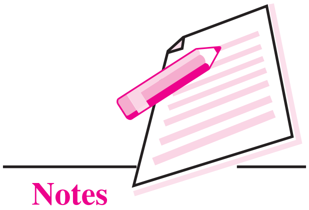
(2) **Drought:** A 3° C warming will result in 10% decrease in precipitation (rain fall) and this will decrease rain fall causing drought conditions.

(3) **Effect on plant growth:** Drought will reduce photosynthesis in plants and lead to reduced growth of plants.

(4) **Effect on animals:** Warmer conditions will encourage growth of pests.

(5) **Water shortage:** Increase in temperature will lead to increased evaporation leading to shortage of water for agricultural, municipal and industrial use.

(6) **Climatic changes :** It has great effect on climate changes. For example, spring now occurs about a week earlier than normal time.



(7) **Increase in CO_2:** Warmer conditions accelerate microbial degradation of organic matter and add more CO_2

(8) **Day and Night temperature :** Night temperatures have increased more than day temperature as green house gases prevent heat from escaping at night.

(9) **Formation of ozone hole :**

The atmosphere has two layers, the stratosphere and troposphere. Stratosphere lies 15 km to 50 km above the surface of earth. The energy of the sun splits some molecular O_2 in this layer to give individual (O) atoms which combine with intact molecular oxygen to give O_3. The layer of O_3 forms a shield as it absorbs UV rays and prevent them from striking the earth. If UV rays penetrate our atmosphere the life would not be possible as organisms cannot tolerate heavy doses of UV radiation. Troposphere is the atmospheric layer closest to the earth's surface whose compostion you have already studied. Chloro fluorocarbons and halons released into the atmosphere have destroyed the ozone shield and an **ozone hole** has been detected at the South Pole of Antartic and North Pole of Arctic.

32.10 DEPLETION OF OZONE LAYER

Ozone shield depletion is primarily caused due to the following reasons:

(a) Chlorofluorocarbons (CFCs) are the heat transfer agents used in refrigerators and air conditioners, and foaming agents in foam cups and cartons.

(b) Halons or halocarbons are anti fire agents used in fire extinguishers.

The ozone in the stratosphere is being depleted by the presence of mainly chlorofluorocarbons (CFCs) and halogen gas, particularly chlorine. The highly energetic ultra violet radiation splits up the CFCs, releasing chlorine. The released chlorine is responsible for convertion of the ozone into oxygen molecule consequently depletion of ozone layer occurs as per the following equations.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

It is believed that one molecule of CFC is capable of destroying 1,00,000 ozone molecules in the stratosphere. The area where the ozone is completely destroyed is known as **ozone hole.** The first ozone hole was observed over Antaractic Ocean.

The important function of ozone layer in the stratosphere in to protect us from dangerous ultra violet (UV) radiations from the sun by absorbing it.

32.10.1 Effects of Ozone Depletion

Ozone layer depletion will allow more UV rays to enter the troposphere and will cause a series of harmful effects such as :

(1) Plants and animals living on the surface will start dying.

(2) UV radiation will fasten the formation of smog

(3) Temperature of the earth will increase leading to rise in sea level and flooding of low lying areas.

(4) More UV rays will directly fall on the skin of humans causing skin cancer.

(5) Leaves of plants will show chlorosis (loss of chlorophyll and yellowing),

32.11 EFFECTS OF AIR POLLUTION ON HUMANS

Air is mobile and impact of air pollution on ecosystems is reduced as wind blows away pollutants. But when winds are calm, air pollution becomes not only damaging but life threatening.

The damaging effects of atmospheric pollution have been described along with the account on pollutants. Long term exposure to moderate pollution causes more disease and death. Some adverse effects of air pollution on humans are summarised in table 32.4.

Table 32.4 : Effects of air pollutants on humans

Disease / Discomfort	Caused by
Emphysema. Bronchitis	CO, SO_2, PAN, O_3
Eye irritation, headache	SO_2, PAN, O_3
Silicosis. Asbestosis	Suspended particulate matter like silica, asbestos.
Coronary artery disease	Tobacco smoke
Anemia, kidney, liver damage	Pb
Fluorosis, Skin Cancer	Fluorides
Poisoning death	CO

32.12 CONTROL OF AIR POLLUTION

The alarming rate at which the atmosphere is being polluted, soon there will be more ailing human beings than healthy. The need of the hour is to put a quick check to atmospheric pollution.

Since most of air pollutants are emitted during combustion of fossil fuels, there are two practical approaches for air pollution control which are discussed below:

(i) One approach is control undesirable changes in the air we breathe by observing the following precaution :

(a) Limiting pollutants into air by using sulphur-free oil and coal, using catalytic convertors in automobiles and avoiding burning of waste material.

(b) Taking stringent measures against release of emissions from industries.

(ii) The other approach is to use sources of energy other than fossil fuels such as wind, water, solar power, etc. Use bicycles and battery powered cars rather than vehicles with internal combustion engines. Service vehicles should use lead free petrol.

Above all, it is necessary to educate the general public. Air pollution should become every human being's concern. Only then will the air become more congenial to healthy living.

INTEXT QUESTIONS 32.4

1. What is smog?
2. Name two photochemical oxidants.
3. Name two gases which form acid rain.
4. Mention any four greenhouse gases.
5. What are the sources of freons and halons in air?
6. What effect does acid rain have on marble statues ?
7. Mention one measure to control air pollution.

32.13 WATER POLLUTION – PARAMETERS

A large amount of water is discharged back after domestic and industrial usage. This is contaminated with domestic waste and industrial effluents. When this contamination reaches beyond certain allowed concentrations, it is called **pollution** and the contaminants are called the **pollutants**. **Water pollution** may be defined as the contamination of streams, lakes, seas, underground water or oceans by substances, which are harmful for living beings. If the concentration of substances naturally present in water increases then also the water is said to be polluted.

Water pollution may be defined as the contamination of streams, lakes, seas, underground water or oceans by substances, which are harmful for living beings. Industrialisation and population explosion are two important factors for water pollution.

Water may be called polluted when the following parameters stated below reach beyond a specified concentration in water.

(i) **Physical parameters**. Colour, odour, turbidity, taste, temperature and electrical conductivity constitute the physical parameters and are good indicators of contamination.

For instance, colour and turbidity are visible evidences of polluted water while an offensive odour or a bitter and difference than normal taste also makes water unfit for drinking.

(ii) **Chemical parameters**: These include the amount of carbonates, sulphates, chlorides, fluorides, nitrates, and metal ions. These chemicals form the total dissolved solids, present in water.

(iii) **Biological parameters**: The biological parameters include matter like algae, fungi, viruses, protozoa and bacteria. The life forms present in water are affected to a good extent by the presence of pollutants. The pollutants in water may cause a reduction in the population of both lower and higher plant and animal lives. Thus, the biological parameters give an indirect indication of the amount of pollution in water.

32.14 WATER POLLUTION – SOURCES

Water pollutants refer to the substances which are capable of making any physical, chemical or biological change in the water body. These have undesirable effect on living organisms. As mentioned earlier, the water used for domestic, agricultural and industrial purposes is discharged with some undesirable impurities in it. This contamination leads to the pollution of water, which is generally called the **fresh water pollution**. Fresh water pollution may be classified into two types: **surface water pollution** and **ground water pollution**.

32.14.1 Surface Water Pollution

When pollutants enter a stream, river or lake these gives rise to surface water pollution. The surface water pollution has a number of sources. These can categorised as:

- Point and Non-point Sources
- Natural and Anthropogenic Sources

(i) Point and Non-point Sources

The well-defined sources that emits pollutants or effluents directly into different water bodies of fresh water are called **point sources**. Domestic and industrial waste are examples of this type. The point sources of pollution can be effectively checked. On the other hand, the **non-point sources** of water pollution are scattered or spread over large areas. This type of sources deliver pollutants indirectly through environmental changes and account for majority of the contaminants in streams and lakes. For example, the contaminated water that runs off from agriculture farms, construction sites, abandoned mines, enters streams and lakes. It is quite difficult to control non-point sources.

(ii) Natural and Anthropogenic Sources

As mentioned earlier, an increase in the concentration of naturally occurring substances is also termed pollution. The sources of such an increase are called **natural sources**. **Siltation** (which includes soil, sand and mineral particles) is one such natural source. It is a common natural phenomenon, which occurs in most water bodies. Indiscriminate deforestation makes soil loose and flood waters bring silt from mountains into streams, rivers and lakes.

On the other hand, the human activities that result into the pollution of water are called **anthropogenic** or man made sources of water pollution**.** For example, domestic (sewage and waste water), industrial and agricultural wastes that goes into the rivers, lakes, streams and seas are anthropogenic sources. Certain materials that are leached from the land by run-off water and enter the various water bodies also belong to this category. The anthropogenic sources of water pollution are shown in Fig. 32.7.

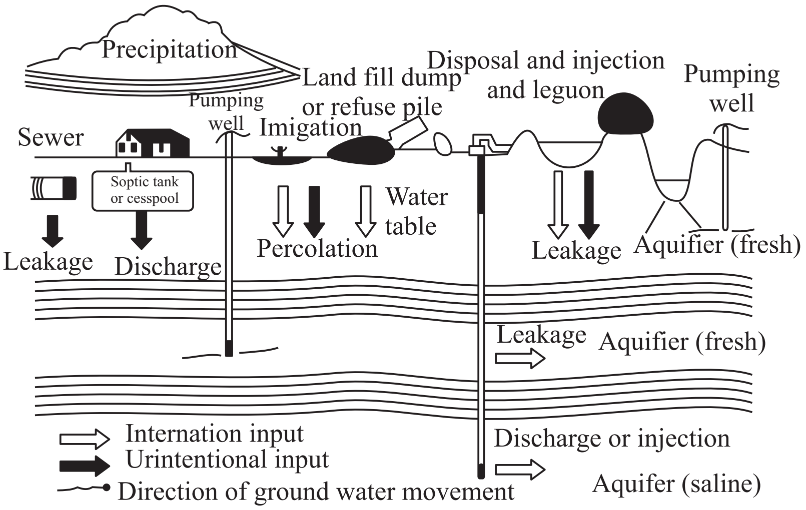


Fig. 32.7 : *Anthropogenic Sources of water pollution*

32.14.2 Ground Water Pollution

When the polluted water seeps into the ground and enters an aquifer it results into **ground water pollution**. The most of our villages and many townships, ground water is the only source of drinking water. Therefore, pollution of groundwater is a matter of serious concern. Groundwater gets polluted in a number of ways. The dumping of raw sewage on soil, seepage pits and septic tanks cause pollution of groundwater. Fig. 32.3. The porous layers of soil hold back solid particles while the liquid is allowed to pass through. The soluble pollutants are able to mix with the groundwater. In addition to these, the excessive use of nitrogenous fertilizers and unchecked release of toxic wastes and even carcionogenic substances by industrial units many ressult in slow trickling down

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through the earth's surface and mixing with the groundwater. This problem is very serious especially in areas where water table is high (i.e., where water is available near surface of earth).

The ground water can move over large distances by virtue of the large empty space available below the earth's surface. This way if some impurities seep into the ground water at one point, they may be observed at a different point far removed from the point of source. In such a case it is difficult to estimate the source of water pollution. However, suspended impurities and bacterial contaminants are removed in the process of seepage by the soil acting as an absorbent and filter, and water acting as a solvent.

Since the movement of groundwater through the porous rock is very slow, pollutants which get mixed with the groundwater are not readily diluted. Furthermore, groundwater does not have access to air (in contrast to surface water) therefore, oxidation of pollutants into harmless products in groundwater does not occur.

32.15 WATER POLLUTANTS

You have read the various sources from where pollutants enter the water bodies. Let us now learn about the various types of pollutants arising out of these sources. These can be broadly put under the following types.

(i) Sewage Pollutants (Domestic and Municipal Waste)

(ii) Industrial Pollutants

(iii) Agricultural Pollutants

(iv) Radioactive and Thermal Pollutants

(i) Domestic and Municipal Pollutants : The sewage contains garbage, soaps, detergents, waste food and human excreta and is the single largest sources of water pollution. Pathogenic (disease causing) microogranisms (baccteria, fungi, protozoa, algae) enter the water system through sewage making it infected. Typhoid, chloera, gastroenteritis and dysentery are commonly caused by drinking infected water. Water polluted by sewage may carry certain other bacteria and viruses cannot grow by themselves, but reproduce in the cells of host organisms. They cause a number of diseases, such as, polio, viral hepatitis and may be cancer which are resistant to like the organic matter are oxygen demanding substances. They are responsible for deoxygenation of water-bodies which is harmful for aquatic life.

Other ingedients which enter the various water bodies are the plant nutrients, i.e., nitrates and phosphates. They support growth of algae, commonly called **algal bloom** (blue-green species). This process is called **eutrophication** and is discussed in details in the next section.

(ii) **Industrial Pollutants :** Many industries are located near rivers or fresh water streams. These are responsible for discharging their untreated effluents into rivers like highly toxic heavy metals such as chromium, arsenic, lead, mercury, etc. along with hazardous organic and inorganic wastes (e.g., acids, alkalies, cyanides, chlorides, etc.). River Ganges recives wastes from textile, sugar, paper and pulp mills, tanneries, rubber and pesticide industries. Most of these pollutants are resistant to breakdown by microorganisms (called nonbiodegradable), therefore damage the growth of crops and the polluted water is unsafe for drinking purposes.

Factories manufacturing plastic, caustic soda and some fungicides and pesticides release mercury (a heavy metal) along with other effluents in nearby water body. Mercury enters the food chain through bacteria, algae, fish and finally into the human body. The toxicity of mercury became evident by the Minamata Bay tragedy in Japan during the period 1953-60. Fish died due to mercury consumption and those who ate fish were affected by mercury poisoning and quite a few died. The milder symptoms of mercury poisoning are depression and irritability but acute toxic effects can cause paralysis, blindness, insanity, birth defects and even death. The high concentration of mercury in water and in fish tissues results from formation of soluble monomethylmercury ion, (CH_3, Hg^+) and volatile dimethylmercury [$(CH_3)_2Hg$] by anaerobic bacteria in sediments.

(iii) **Agricultural Waste:** Manure, fertilizers, pesticides, wastes form farms, slaughterhouse, poultry farms, salts and silt are drained as run-off from agricultural lands. The water body receiving large quantities of fertilizers (phosphates and nitrates or manures becomes rich in nutrients which leads to eutrophication and consequent depletion of dissolved oxygen. Consumption of water rich in nitrates is bad for human health especially for small children.

Pesticides (DDT, dieldrin, aldrin, malathion, carbaryl etc.) are used to kill insect and rodent pests. Toxic pesticide residues enter the human body through drinking water or through food chain (biomagnification). These compounds have low solubility in water but are highly soluble in fats. For example, the concentration of DDT in river water may be very low but some fish over a period of time accumulate so much of DDT that they become unfit for human consumption. The use of pesticides in our country is increasing very rapidly.

Some of these chemicals which are highly toxic become metabolised by animals that graze on fields. Therefore, these poisonous chemicals have been often observed in the humanfood chain. The presence of these chemicals in humans even in minute amounts can cause hormonal imbalance and may lead to cancer.

(iv) Physical Pollutants: Physical pollutants can be of different types. Some of them are discussed below :

(a) Radioactive Wastes : Radionucleides found in water are radium and potassium-40. These isotopes originate from natural sources due to leaching from minerals. Water bodies are also polluted by accidental leakage of waste material from uranium and thorium mines, nuclear power plants and industries, research laboratories and hospitals which use radioisotopes. Radioactive materials enter human body through water and food, and may be accumulated in blood and certain vital organs. They cause tumours and cancer.

(b) **Thermal Sources**: Various industries, nuclear power plants and thermal plants require water for cooling and the resultant hot water is often discharged into rivers or lakes. This results in thermal pollution and leads to the imbalance in the ecology of the water body. Higher temperature lowers the dissolved oxygen level (which is very essential for marine life) by decreasing the solubility of oxygen in water. Fish and other aquatic organism can get affected by a sudden change in water temperatures.

(c) **Sediments** : Soil particles carried to streams, lakes or oceans form the sediments. The sediment become polluting due to their large amount. Soil erosion defined as the soil carried by flood water from crop land, is responsible for sedimentation. The sediments may damage the water body by introducing a large amount of nutrient matter.

(v) Petroleum Products: Petroleum products are widely used for fuel, lubrication, plastics manufacturing, etc. and happen to be poisonous in nature. Crude oil and other related products generally get into water by accidental spillage from ships, tankers, pipelines etc. Besides these accidental spills, oil refineries, oil exploration sites and automobile service centres pollute different water bodies. Oil slick which floats on the water surface causes death of marine life and severely affects the ecosystem of the ocean.

A list of various types of water pollutants, their sources and effects have been summarised in Table 32.1.

Table 32.1: Types of water pollutants, their sources and effects

	Pollutant	Sources of Pollutants	Effects and Significance
1	Pathogens	Sewage, human and animal wastes, natural and urban runoff from land, industrial waste	Depletion of dissolved oxygen in water (foul odour) health effects (outbreaks of water borne diseases)

2	Organic pollutants ● Oil and grease ● Pesticides and weedicides ● Plastics ● Detergents	Automobile and machine waste, tanker spills, offshore oil leakage Chemicals used for better yield from agriculture Industrial and household waste Industrial and household waste	Disruption of marine life, aesthetic damage Toxic effects (harmful for aquatic life), possible genetic defects and cancer; kills fish Eutrophication, aesthetics
3	Inorganic pollutants Fertilizers (phosphates and nitrates)	Agricultural runoff	Algal bloom and eutrophication, nitrates cause methemoglobenemia
	Acids and alkalies	Mine drainage, industrial wastes, natural and urban runoff	Kill fresh water organisms, unfit for drinking, irrigation and industrial use.
4	Radioactive materials	Natural sources, uranium mining and processing, hospitals and research laboratories using radioisotopes	Cancer and genetic defects
5	Heat	Cooling water for industrial, nuclear and thermal plants	Decreases solubility of oxygen in water, disrupts aquatic ecosystems
6	Sediments	Natural erosion, runoff from agricultural land and construction sites	Affects water quality, reduces fish population

INTEXT QUESTIONS 32.5

1. Define water pollution.
2. List any three anthropogenic sources of water pollution.
3. List the parameters indicating water pollution.

32.16 WATER POLLUTION AND SOME BIOLOGICAL EFFECTS

The natural source of water in the form of precipitation or rain is the purest form available in nature. However after reaching the surface and then underground it gets contaminated by a number of pollutants. There are some biological factors also mentioned earlier responsible for spoiling the quality of water. These include the lower plants like algae and bacteria which are the causes of nutrient accumulation in aquatic systems. This nutrient accumulation gives rise to a condition called eutrophication explained below.

32.16.1 Eutrophication

Eutrophication is a process by which a water body slowly becomes rich in plant nutrients such as nitrates and phosphates due to soil erosion and run off from the

Notes

surrounding land. Let us try to understand this phenomenon. A water system like a lake or any reservoir may get a large inflow of organic matter from domestic wastes and run off from the surrounding land. Increasing human population, intensive agriculture and rapid industrial growth have led to an increasing release of domestic waste, agricultural residues, industrial wastes and land run-off into various water bodies. Nutrients are released from organic waste by aerobic (oxygen requiring) bacteria which start decomposing it. Dissolved oxygen is consumed in this process. As more and more organic matter enters a water body, more is the deoxygenation of the water body and larger is the production of nutrients. These nutrients fertilize an abnormal growth of algae and other large water plants such as duckweed. As more plants grow, some of them die also due to larger oxygen demand and therefore oxygen deficiency in the water body (i.e., deoxygenation of the water body). Such a water body is said to be **eutrophied** and the process is called **eutrophication**. The word eutrophication is derived from the Greek word which means well nourished as (eu:true, trophos:feeding)

Eutrophication of a water body results due to the release of large amount of nutrients by the action of aerobic bacteria on organic wastes entering a water body naturally or by human activity.

The above discussion leads us to a concept called biological oxygen demand (BOD). Let us try to understand by the description given below.

32.16.2 Biological Oxygen Demand (BOD)

The quality of oxygen used up by microorganisms at 27°C and in darkness during 3 days in breaking down organic wastes in a water body is called its **biological oxygen demand (BOD).**

It can be explained in the following manner.

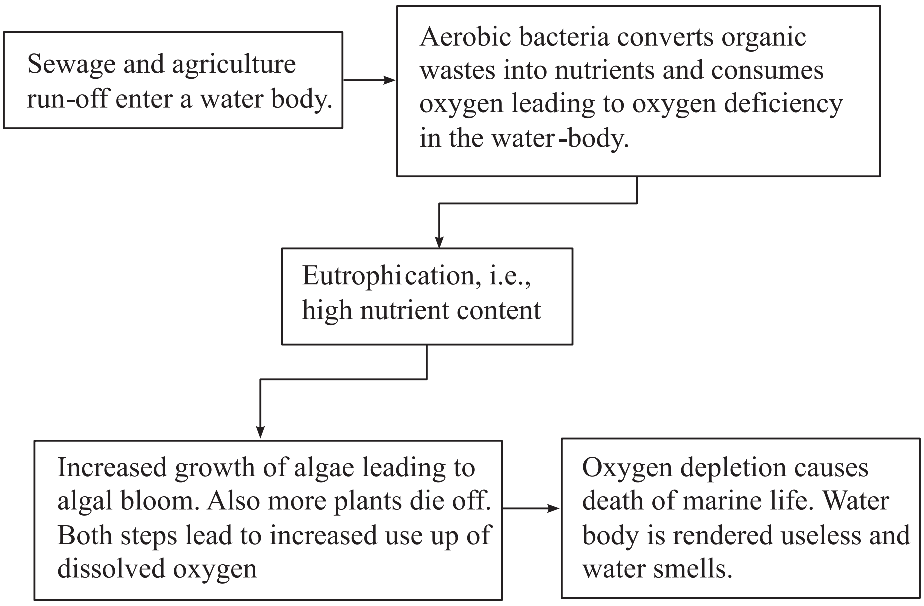
You know that there are many organic compounds or waste present in a water body. The microorganisms present in the system act upon this waste for their own consumption and growth. In the process the metabolic activity requires oxygen which is met by the dissolved oxygen present in water. It is this amount of oxygen which is defined as **biological oxygen demand (BOD).** The BOD value of an aquatic system depends upon:

- the type and amount of organic waste
- the organisms acting on it
- temperature and pH

The greater the amount of organic waste in the water body, the greater is the amount of oxygen required to break it down biologically and therefore higher is the BOD value of water. This value is a good measure in evaluating the degree of pollution in a water body. The less polluted water shows comparatively low value of BOD. Its value is used as a criterion for managing water pollution of a water body. An evaluation is made by determining oxygen concentration in water before and after incubation at 20°**C** in dark for 5 days.

32.16.3 Biomagnification

A variety of toxic chemicals move through food chains. Toxic pesticides may be sprayed for controlling insect pests, fungi, herbs, but they concentrate in the food chain and harm to other (non target) organisms. For example, DDT was sprayed in the U.S. to control mosquitoes at a concentration expected to be harmless to non target organisms like fish and birds. DDT accumulated in the marshes and planktons. Planktons were eaten by fish and the fish had a higher concentration of DDT in its body. Further, when birds ate the fish, they accumulated still higher concentration. This increase in concentration of accumulated toxic chemicals as one goes higher in the food chain is termed **biomagnification.** Biomagnification has at times threatened the reproduction and survival of carnivores (secondary consumers) who occupy the highest level of the food chain.



32.17 WATER POLLUTION – SOME CONTROL MEASURES

Waste water generated by household activity, industries or garbage landfills is called **sewage** which is classified as the municipal water pollution. Sewage contains solid matters in the form of suspended colloidal and dissolved organic matter, detergent, mineral matter, nutrients and gases. Sewage is one of the major causes of water borne diseases and therefore the treatment of sewage is one of the important tasks. For a long time treatment of municipal waste in the form of sewage involved mainly of the removal of suspended solids, oxygen demanding materials and harmful bacteria. Now the disposal of the solid residue from sewage has been improved by applying municipal treatment processes.

The treatment of this waste water is carried out in the following three stages:

(i) Primary treatment

(ii) Secondary treatment, and

(iii) Tertiary treatment

Primary Treatment: When the waste water is to be dumped off into a river or flowing steam, the treatment is carried out by sedimentation, coagulation and filtration. This is known as primary treatment. If the water is required for drinking purposes, it has to undergo further treatment called secondary and tertiary treatments. The following steps are performed to do primary treatment of water:

(i) Sedimentation: This step is carried out in large tanks specially built for this purpose in sewage treatment plant. The polluted water is allowed to settle so that silt, clay and other matter settle to be bottom and water is slowly allowed to move out. Fine particles do not settle and are thus required to be removed in the next step.

(ii) Coagulation: Fine particles and colloidal suspension are combined into large particles by a process called coagulation. This step is carried out by the addition of special chemicals called coagulants (flocculants) such as potash alum. The large particles either settle to the bottom or are moved in the next step.

(iii) Filtration: Suspended particles, flocculants, bacteria and other organisms are filtered by passing the water through a bed of sand or finely divided coal or through some fibrous materials. The total impurities collected in these steps are called **sludge**. It is used as a valuable fertilizer. On composting (i.e. the action of anaerobic bacteria), it releases sludge gas. It consists mainly of methane gas which is used for cooking purposes.

Secondary or Biological Treatment: The water after primary treatment is not fit for drinking purposes and has to undergo further treatment. This is done through secondary or biological treatment. A commonly used method is to allow polluted water to spread over a large bed of stones and gravel so that the growth of different microorganisms needing nutrients and oxygen is encouraged. Over a period of time a fast moving food chain is set up. For example, bacteria consume organic matter from the polluted water; protozoa live on bacteria. Every form of life including algae and fungi help in the cleaning up process. This is called secondary treatment of water. It involves the following processes

(i) Softening : By this treatment undesirable cations of calcium and magnesium are removed from hard waters. Either water is treated with lime and soda ash to precipitate Ca^{2+} ions as carbonates or it is passed through cation exchangers. This makes water soft.

(ii) Aeration: In this process, soft water is exposed to air by forcing air through it to add oxygen to water. This encourages bacterial decomposition of organic matter into harmless products such as carbon dioxide and water. The addition of oxygen reduces carbon dioxide. sulphide etc.. The water is as yet not fit for drinking purposes. The pathogenic and other microorganisms need to be killed. This is done in the next treatment.

Tertiary Treatment : The tertiary treatment is actually disinfecting water. Chlorine is the most commonly used disinfectant used for killing bacteria. However, chlorine also reacts with traces of organic matter present in water and forms undesirable chlorinated hydrocarbons (toxic and potentially carcinogenic). It is therefore desirable to reduce the organic matter in water before passing chlorine gas. Other methods of disinfection such as ultraviolet radiation, ozone gas treatment or reverse osmosis are preferred over chlorine treatment. But these methods are more expensive. Fig. 32.8 gives a clear picture of the process of sewage treatment in total.

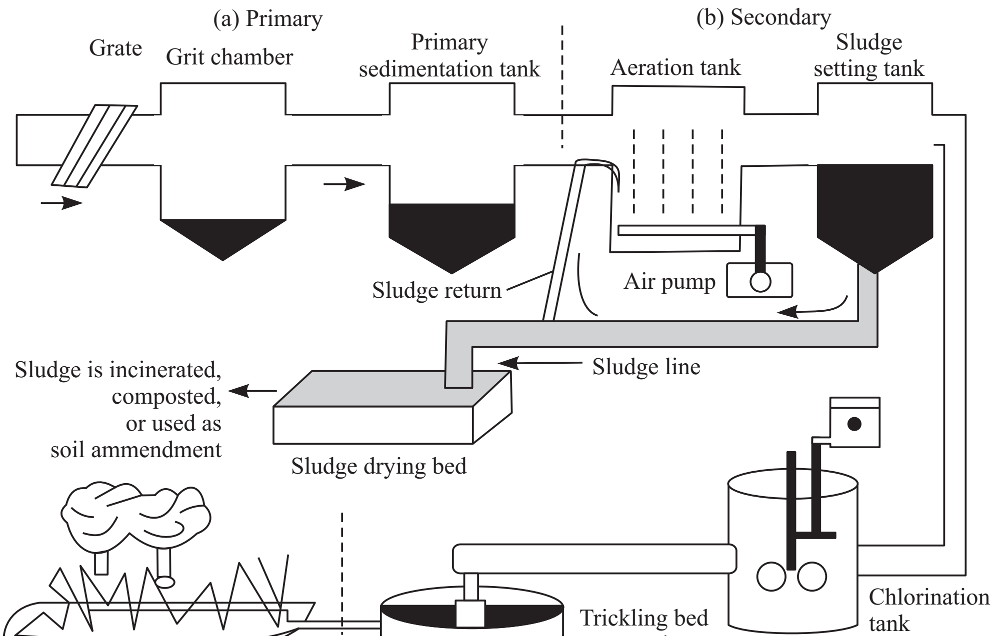


Fig. 32.8 : *Treatment process of sewage*

In a treatment plant, the waste is passed through a series of screens, chambers and chemical processes to reduce its bulk and toxicity. During primary treatment a large percentage of suspended solids and inorganic material is removed from sewage. The secondary stage reduces organic material by accelerating natural biological processes. Tertiary treatment is done when water is to be reused. Here 99% of solids are removed and various chemical processes are used to ensure that water is free from infecting materials.

Notes

INTEXT QUESTIONS 32.6

1. Define eutrophication.
2. Why does aquatic life get killed in an eutrophied pond?
3. What is the significance of BOD?
4. What is biomagnification?

32.18 SOIL POLLUTION

The adulteration of soil (land) by the addition of unwanted substances is known as soil pollution.

Sources of pollution

1. **Industrial waste:** The industrial wastes are the major cause of soil pollution because the wastes are toxic due to presence of cyanides, chromates, acids, alkalies, metal like nickel, cadmium, mercury and lead. Some industries like paper industries Sugar mills, textile mills and distilleries, chemical industries & cement industries are also responsible for soil pollution. The wastes of these industries are not bio-degradable.
2. **Urban and domestic waste:** The urban and domestic wastes referred as soil refuse, containing garbage, and rubbish, paper pieces, glass, plastics polythene bags, cans detergents and cakes. These substances emit gases, toxic hydrocarbons and pathogenic microbes cause to disease.
3. **Agricultural chemicals:** The fertilizers, pesticides, herbicides insecticides and fungicides are commonly used to save and increase the yield of crops but they have polluted the soil. Some time the entry of these chemicals in food chain has cause to adverse effects on health of consumers.
4. **Fertilizers:** The fertilizers increase the yield crop it has no doubt but the excessive use has adverse effects. It disturb the pH of soil, ionic balance and the presence of certain elements. So they have a number of health hazards. The nitrites cause to cancer in human body.
5. **Pesticides:** The chemicals are used to kill or to stop the growth of unwanted organisms and entry of these chemicals into food and water cause cause effect on the health of animals and human beings.
6. **Insecticides:** Some chemicals like DDT, BHC, aldrin, dieldrin are used to kill the insects, the use of DDT is banned by the Government because It is not biode gradable. It also effects the next crop in the field due to observed by the soil. Some bio degradable organ phosphates, carbonates may be used in place of insecticides.

7. **Herbicides:** The compounds used to control the growth of weeds, some inorganic compounds like sodium chlorate and sodium arsenite (Na_3AsO_3) were commonly used as herbicids. These one toxic in nature. So Now-a-days organic herbicide Triazines are preferred.

8. **Fungicides:** Fungicides are used to chock the growth of fungi. Fungi is one those plants in which chlorophyll is not present i.e. they can not make their food by the process photosynthesis. They live an dead organic matters as saprophytes. Organic compounds of mercury have been used as fungicides. Many people in Iraq resulted to death due to eating breads made from grains that been treated with methyl mercury fungicide. It's use have many disastrous consequences because these compounds breakdown in soil.

Control of soil Pollutions: The following steps have been suggested to control the soil pollutioins:

(i) The use of chemical fertilizers can be reduced by applying bio-fertilizers and manures.

(ii) Re cycling and recovery of materials appears to be a reasonable solution for reducing soil pollutions. Materials like papers, gas and some kinds of plastics can be recycled.

(iii) Control of land loss can be attempted through restoring forests and grass cover to check soil erosion and flood.

(iv) Proper methods should be adopted for the disposal of solid wastes.

INTEXT QUESTIONS 32.7

1. What is refuse?
2. Write the name of one insectide?
3. What is soil erosion?

32.19 GREEN CHEMISTRY AS AN ALTERNATIVE TOOL FOR REDUCING POLLUTION

We have discussed about hazards of environmental pollution in these units. The main reasons of this pollution is due to rapid industrialization, productions and use of toxic chemicals. An important initiative to protect the environment from chemical effluents and wastes is known as Green chemistry.

"Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances."

Green chemistry is environment friendly, linking the design of chemical products and processes with their impacts on human health and the environment.

Principles of Green Chemistry

(i) The use of starting materials, reagents and solvents which are less hazardous to man and his environment.

(ii) More efficient use of raw materials.

(iii) Utilisation of chemical reactions which completely incorporate the starting materials in to final products and last amount of by product.

(iv) Search new alternatives which are environmental friendly.

(v) It is better to prevent the waste than to treat or cleanup the waste after it has been created.

Achievements of Green chemistry

(i) Development of dense phase CO_2. Dense phase CO_2 has been recently developed chemical product with amazing characteristics. It has ability to clean everything. It can be used as recyclable solvent and finds number of applications in food industries.

(ii) Development of fuel cells of cellular phones which can last for the full life time of the phone.

(iii) Development of process involving use of CO_2 as a blowing agent for manufacture of poly styrene foam. This technology discard the use of chloro fluoro carbon.

(iv) H_2O_2 hydrogen peroxide gives better results and not harmful for bleaching of clothes in the laundary instead of tetrachloro ethene ($Cl_2C{=}CCl_2$). This compound is suspected to be carcinogenic and continimated the ground water.

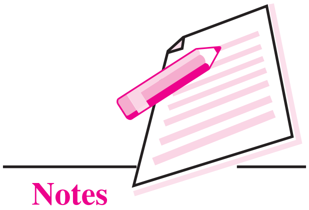
(v) Hydrogen peroxide (H_2O_2) is used with catalyst for bleaching papers, instead of toxic chlorine gas.

(vi) Ethanal (CH_3CHO) is now a days being prepared an a commercial scale by one step oxidation of ethane in presence of ionic catalyst in aqueous solution

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{in water}]{Pd(II)Cu(II)} CH_3CHO\ (90\%)$$

32.20 STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTIONS

Environmental pollutions affects the plants, animals and human beings as well as materials. The production and improper disposal of waste are causes for the great deal of environmental pollution. In addition to the have hold waste



thesewage and municipal garbage, many toxic industrial wastes from manufacturing processes require treatment and safe disposal. The biodegradable and non-biodegradable waste like polythene bags plastics, metal scrap should be put in separate boxes. The biodegradable waste is deposited in the land fills.

Industrial wastes are also sorted as biodegradable and non-biodegradable, should be put in separate boxes. Fly ash, furnace stag mud and failings and gypsun like non-biodegradable wastes have produce great problem. Some chemical industries producing inflammable wastes and hazardous chemicals as by products.

Some methods are usually employed one given below

1. Recycling: When materials one recycled, there are several benefits, apart from savings on the cost of raw materials, waste disposal costs are reduced.
   - (i) the collections and recycling of glass.
   - (ii) Iron scrap can be used in manufacturing steel.
   - (iii) Polythene bags and plastics can also recycled.
   - (iv) The newspapers, used copies, and magazines can be used for making papers.

Sewage treatment

Sewage is the liquid waste which includes house hold wastes, Industrial wastes ground wastes, etc. which contains 99.9 water with inorganic, organic matters in dissolved, suspension and colloidal states. It involves the following stages.

(i) The removal of large solid particles. It can be done by screening and sedimentation. The solid wastes are deposited in land fillsites.

(ii) It is allowed to stand is tanks. Many solids settle down by the use of the chemicals like alums and ferrousulphate while oil, grease, float on the surace which can be shimmed off.

(iii) Next stage involve the biological oxidation of organic content of waste materials by microorganisms followed by filtration.

(iv) Finally some physical and chemical processes are applied to remove some chemicals like phosphates and adding chlorine to improve the quality of waste water.

(i) **Incineration:** It convert the organic and biogical wastes to carbon dioxide and water at higher temp 1273 k and excessive supply of oxygen. Exhaust gases must be filtered. The incomplete oxidation of Poly chlorinated biphynyls (PCBs) may convert to toxic polychlorobidenzodioxins (PCDDs). Main problem of this process is air pollution due to incomplete oxidations.

(ii) **Digestion:** In digestion, sluge is kept in a closed tank in the absence of air for a prolonged period whereby it goes anaerobic respirations, yields gases like carbon dioxide methane and ammonium sulphide. The methane gas can be used as fuel.

$$2(CH_2O) \longrightarrow CO_2 + CH_4$$

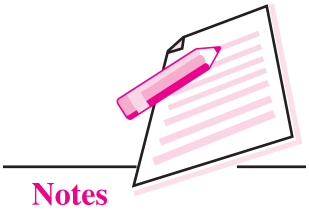
(iii) **Dumping:** Dumping of the sewage stage into sea has been very common. However dumping of the sluge into land is increasing now-a-days. Because it has nitrogen and phosphorous which act as fertilizers for the soil.

INTEXT QUESTIONS 328

1. Write the names of those wastes which can be recycled
2. Name the chemicals which are used in sedimentation of solid waste.
3. How the incrination cause to air pollutions?

WHAT YOU HAVE LEARNT

- Surroundings in which we live is our environment.
- There are two components of environment : physical or abiotic and living organisms or biotic
- Pollutants may be defined as substances added to natural surroundings.
- There are two major sources of pollutants - stationary and mobile.
- Pollutants have adverse effects on environment and living organisms.
- SO_2, CO_2, CO, smoke, Pb, Hg, CFC, etc. pollute air. Their sources and effects are varied.
- Pollution in simple words is the unhealthy and harmful condition for living organisms and non-living things.
- Pesticides, plastic, detergents, chlorine, mercury, etc. pollute water and endanger life of aquatic organisms.
- Unwanted sounds are termed as noise. Sounds is measured in decibels. Beyond 70 decibels noise has harmful effects on humans.
- The Government of India has set up various environmental laws and judiciary system to punish the polluters.
- Nature's balance has beeen upset by human activities releated to urbanisation, industrialisation and intensive agriculture.



Notes

- Atmosphere is made up of gases of which nitrogen - 78%, oxygen - 21%, carbondioxide - 0.1 to 0.3%, inert gases 1 %
- Increase of temperature with altitude is known as positive lapse rate where as decrease in temperature with increase of altitude is negative lapse rate of temperature.
- Air pollution is due to

  (i) particulate matter (soot, dust)

  (ii) aerosols composed of hydrocarbons

  (iii) gases like SO_2, NO_2 are mostly released by burning fossil fuels.
- NO_2 and hydrocarbons are modified by sunlight to form photochemical smog. Smog is a combination of smoke and fog. Automobile exhausts give out NO_2 and hydrocarbons. They form PAN (peroxyacetyl nitrate) which along with ozone and SO_2 forms photochemical smog.
- Smog cools and settles down near the earth and forms a blanket, while warmer air covers it. Thus there is a 'temperature inversion' with warm air above and cool air below unlike in the normal conditions.
- SO_2 and NO_2 form acids which drop as H_2SO_4 and HNO_3 on statues and spoil them. This is called acid precipitation. Acid rain kills trees, prevents reproduction in fish and causes poor visibility.
- Greenhouse gases are CO_2, NO_2, CH_4, chlorofluorocarbons and halons. They trap solar radiation and cause global warming.
- Global warming due to greenhouse effect leads to drought, rise in sea level, lack of rain and water shortage.
- There is a layer of ozone in stratosphere, which protects us from UV radiation by absorbing it.
- Chlorofluorocarbons which are used in refrigerators and foam cups as aerosols and halons used in fire extinguishers, when released into the air cause depletion of ozone shield which protects us from harmful effects of solar radiations. It is feared that ozone depletion will have damaging effects on humans such as causing skin cancer.
- Complete destruction of ozone layer over an area is termed as ozone hole.
- Air pollution causes respiratory diseases such as emphysema and bronchitis, eye irritation, fluoroisis, cancer and may even be fatal.
- Control measures include use of sulphur free oil and coal, use of alternative sources of energy such as wind and solar power, use bicycle and battery powered vehicles, stop burining waste indiscriminately, have stringent measures for release of emissions from industries and above all educate general public and caution them against releasing air pollutants.

- Water pollution refers to any physical, chemical or biological change that has an undesirable affect on living organisms.
- Sewage, industrial, agricultural pollution and physical pollutants are the various sources of water pollution. These sources may be limited to a point sources or spread over large areas (non-point sources).
- Sewage, fertilizers, detergents, toxic wasters released by industries are some of the sources of groundwater pollution.
- Phosphatic, and nitrogenous fertilizers cause algal bloom and severe oxygen depletion in water body. The water body is said to be eutrophied.
- The quantity of oxygen needed by micro-organisms in degrading organic wastes in a water body is defined in terms of its biological oxygen demand (BOD).
- Biological magnification of toxic materials released into water bodies poses a serious threat to aquatic life and eventually to human life.
- Polluted water may be made useful for human consumption by subjecting it to various treatments.
- Legislative measures have been enacted in our country to restrict the pollution of various water bodies.

TERMINAL EXERCISE

1. What is environment?
2. Explain the term anthropogenic pollutants.
3. Write four major pollutants of water, their sources and effects.
4. Differentiate between the Primary and Secondary Pollutants.
5. What are the damaging effects of SO_2 and NO_2 on plants and animals?
6. Write a note on carbon monoxide poisoning.
7. What is thermal inversion and how is it caused?
8. Enumerate the various effects of acid rain.
9. What is ozone hole? What are the effects of ozone depletion?
10. Why does sea level rise due to global warming?
11. How do greenhouse gases cause global warming.
12. Mention five disease/discomforts in humans caused by different air pollutants.
13. Enumerate the various measures of control of air pollution.
14. How the industrial wastes and domestic wastes are helpful in soil pollution?

15. What one fungicides.
16. How to control soil pollution?
17. Explain main effects of water pollutions.
18. What are the various types of water pollutants? State their consequences.
19. What are the effects of detergents on fresh water bodies?
20. What are the various sources of groundwater pollution?
21. How is the disease 'methaemoglobinaemia' caused?
22. How can domestic waste be used as manure?
23. What will be the problem arise due to abundance of phyto plankton?
24. Write in brief about sewage treatment.

ANSWERS TO INTEXT QUESTIONS

32.1

1. The air, water, earth and living beings in a joint form is called environment.
2. There are two components of environment namely biotic and abiotic.
3. Living organisms such as plants, animals, microbles, etc.
4. Causes holes in the ozone layer.
5. Atmosphere, biosphere, hydrosphere and lithosphere.

32.2

1. Any substance which is present in its excess concentration such as CO_2, CO, SO_2.
2. Volcenicerruptions and run-off from surface mines.
3. Secondary pollutants are the products of reaction between the primary pollutant and the normal environmental constituents.
4. Environmental pollution is the deterioration or unclean objectionable conditions in the quality of natural resources such as air water and soil because of the action or presence of unwanted substances in undesirable concentration.

32.3

1. undesirable level of undesirable and harmful substances in the atmosphere
2. soot, fluoride, Pb dust, NaCl (any two)
3. SO_2, CO_2, CO, NH_3, H_2S (any two)

4. methanogenic bacteria, ruminant stomach, fermentation in water logged paddy fields (any one).
5. PAN and O_3

32.4

1. fog and smoke
2. O_3 and PAN
3. SO_2 and NO
4. CO_2, NO_2, CH_4, CFC, Halons
5. refrigerants, fire extinguishers
6. corrode them
7. reducing use of fuel which releases air pollutants and use clean renewable fuels. Educate everyone about dangers of pollution.

32.5

1. Refer to section 32.2
2. Refer to section 32.3.1. (ii)
3. Refer to section 32.1

32.6

1. Refer to section 32.5.1
2. Refer to section 32.5.1
3. Refer to section 32.5.2
4. Refer to section 32.5.3

32.7

1. The urbon and domestic wastes referred as soil refuse containing.
2. DDT or BHC,
3. The loss of fertile layer (dipper layer) of soil is called soil erosion.

32.8

1. Glass, polythene, ion, paper etc.
2. Potash Alumns and ferrous sulphate.
3. The conversion of biological wastes to CO_2 and water at 1273 K. The incomplete oxidation PCBS are also causes to air pollutions.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