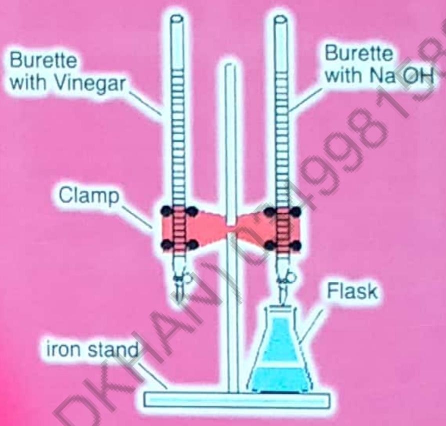
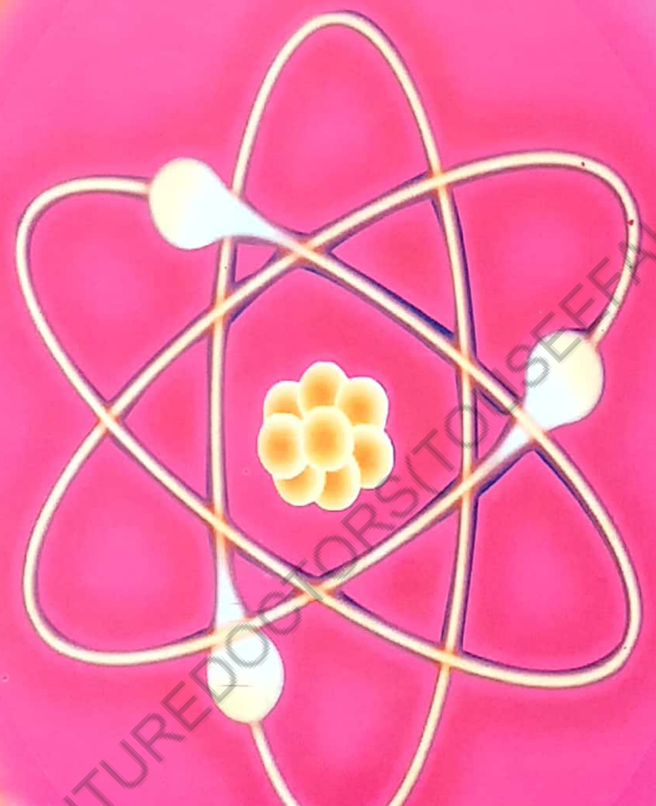
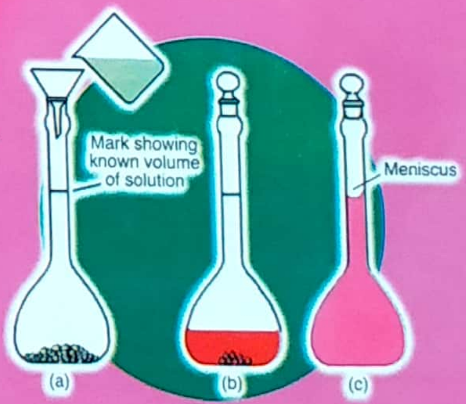
CHEMISTRY

For Classes IX - X







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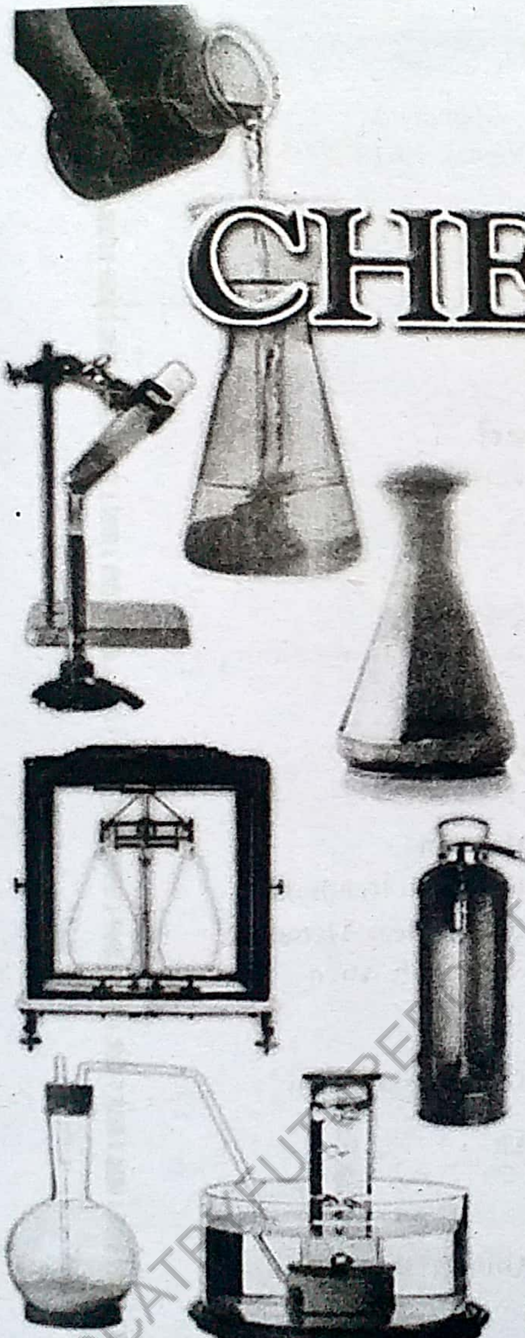

TEXTBOOK OF

CHEMISTRY

For
Classes IX -X

SINDH TEXTBOOK BOARD,
JAMSHORO.

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Contents

PREFACE

The present day age is the age of science and technology. No nation can flourish without literacy particularly without scientific knowledge. Realising the developments in the science of chemistry which have taken tremendous strides, have involved, changes in the contents of the syllabus. Ministry of Education (Curriculum Wing), Islamabad, prepared a new syllabus of chemistry and got it approved by the government.

This book for classes IX - X has been prepared by the Sindh Textbook Board, Jamshoro in accordance with the new latest syllabus of chemistry. The Board has been able to secure the services of the competent teachers, who performed their duties with the best of their abilities and experiences in the field of chemistry.

In preparing this textbook, the authors have had in their mind a student of secondary level. At secondary level, the chemistry is begun before the student has acquired enough needed background in elementary mathematics for true understanding. However, mathematics is a part of the language of chemistry and a lack of familiarity with mathematics can become a barrier to success in understanding chemistry.

In order to increase the interest and the curiosity of the student at the secondary level; the subject matter has been made more effective by adding figures and diagrams and some points. Each chapter is divided into fairly short sections, using figures, tables, flow-diagrams to reinforce the text. S.I. units are used throughout the book.

Some of the salient features of this textbook are as follows:

(i) Basic concepts, relating to fundamentals of chemistry have been prepared in a logical, coherent and academic way. Historical backgrounds of chemistry are also introduced.

(ii) The topics are dealt, keeping in mind the secondary class students, to develop an interest in students in the study of chemistry as a discipline.

(iii) Every chapter begins with the introduction of the contents of the chapter, which are then dealt in the chapter with the wider context. Numerous worked out examples are introduced.

(iv) Each chapter concludes with a summary of the important facts and ideas to enable students to revise the contents of each chapter with ease.

(v) Review questions at the end in the exercise of each chapter provide interesting materials for tests, class discussions, revisions and homework.

Multiple-choice questions and fill in the blanks are also provided in the exercise of each chapter.

The latest curriculum, states the following learning objectives.

(a) To strengthen the concepts developed at secondary level and develop new concepts to provide a solid background for higher studies in chemistry.

(b) To acquaint and also to expose the students to different aspects of chemistry used in our daily life.

The book is written in simple language, and has clear concise and systematic presentation, with total commitment for a national cause.

Since there is always a room for improvement, so we apologize for any errors or omissions and welcome your constructive criticisms and positive suggestions which might improve the matter of book.

Editors

CHAPTER-11

HYDROGEN AND WATER

You will learn in this chapter about:

- * Hydrogen and its industrial preparation, physical and chemical properties of hydrogen.
- * Uses of hydrogen and Nacent hydrogen.
- * Isotopes of hydrogen,Protium,Deuterium and Tritium.
- * Water and its anomalous behaviour.
- * Chemical properties of water and water as universal solvent.
- * Hydrates and water of crystallization.
- * Soft,hard and heavy water, removal of hardness from water.
- * Hygroscopic substances.
- * Drinking water, quality of drinking water and classification of water pollutants.

11.1 HYDROGEN

Introduction:

Hydrogen was discovered by Cavendish in 1766 by the action of zinc metal over dilute hydrochloric acid.

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

The name hydrogen to the gas was given by Lavoisier as it produces water on combustion in air. **Hydro** means water and **genan** means producer, in Greek language, so hydrogen means water producer.

Hydrogen is the lightest element known and it is the first element in the periodic table. It has the simplest structure, containing only one **Proton** in the nucleus with one electron in the first orbit i.e. in K – Shell. Its atomic number is 1 and mass number is also 1. It exists as diatomic molecular gas (H_2). Its molecular mass is 2.016 a.m.u.

Occurrence:

Hydrogen is one of the most abundant element in the universe. We know the sun and the other stars are largely composed of hydrogen. It is the nuclear fuel consumed by the sun and the other stars which produces energy. Although about 70 percent of the universe is composed of hydrogen, it constitutes only 0.89 percent of earth's mass.

In the earth crust, hydrogen is the 9th most abundant element. In the free state in nature, it is found in negligible quantities. However, in the combined state, it occurs as water (H_2O) which is constituting the earth's most abundant compound. In water 11.11 percent by mass is hydrogen, while 88.89 percent by mass is oxygen. Petroleum and other organic materials also contain hydrogen compounds. Petroleum and natural gas are mostly hydrocarbons.

Industrial Preparations of Hydrogen :

1. By Passing Steam Over Coke (Coke – Steam Process):

When steam is passed over red hot coke at about 1000°C, a mixture of carbon monoxide and hydrogen (called water gas) is produced.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1000^0C} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{water gas}}$$

Water gas is a very good fuel and is also used in the preparation of methanol (Methyl alcohol).

From water gas H_2 gas is separated by two methods :

(a) By liquefacation and (b) By oxidation (Bosch Process)

(a) By Liquefacation:

When water gas is cooled upto - 200°C, carbon monoxide liquefies and leaving behind H_2 gas. The traces of CO gas if left in the mixture, then the remaining mixture is treated with caustic soda (NaOH solution). The remaining traces of CO react with NaOH solution to form sodium formate, leaving behind pure H_2 gas.

$$CO_{(g)} + NaOH_{(aq)} \longrightarrow \underset{\text{sodium formate}}{HCOONa_{(aq)}}$$

(b) By Oxidation (Bosch Process):

This is the most suitable method for the separation of H_2 gas from water gas, in this process more steam is passed through water gas at 500°C in the presence of ironoxide (FeO) or chromium oxide (Cr_2O_3) catalyst. Carbon monoxide gas in water gas oxidizes to CO_2 gas. Which is soluble in water under pressure, liberating pure H_2 gas.

$$\underbrace{CO_{(g)} + H_{2(g)}}_{\text{water gas}} + H_2O_{(g)} \xrightarrow[500^0C]{FeO} \underset{\substack{\downarrow \\ \text{Soluble in water}}}{CO_{2(g)}} + 2H_{2(g)}$$

2. From Natural Gas (Hydrocarbon – Steam Process):

Hydrogen is also obtained by passing steam over hydrocarbons, such as methane, which is the major constituent of natural gas in the presence of nickel catalyst at temperature about 900°C to produce water gas.

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow{Ni/900^0C} \underbrace{CO_{(g)} + 3H_{2(g)}}_{\text{water gas}}$$

H_2 gas can be separated from water gas by either of the above mentioned method.

3. By The Thermal Decomposition of Methane:

H_2 gas is commercially prepared also by the thermal decomposition of methane, when methane is heated above 700°C in the absence of air, CH_4 decomposes thermally to produce carbon black and H_2 gas.

$$CH_{4(g)} \xrightarrow[\text{absence of air}]{\text{above } 700^0C} \underset{\text{carbon black}}{C_{(s)}} + 2H_{2(g)}$$

Carbon black is used in rubber industry as a filler for manufacturing motor tyres. It is also used in the preparation of inks, paints, polishes, carbon papers and plastics.

4. By The Electrolysis of Water:

H_2 gas can be produced by the electrolysis of water. When electric current is passed through water in the presence of a few drops of acid or base, H_2 gas is liberated at cathode and O_2 gas a by – product collects at anode. The presence of acid or base helps in the ionization of water. This method due to large consumption of electric power is very expensive but is used in the countries where electricity is very cheap.

$$2H_2O_{(l)} \xrightarrow[\text{(acid or base)}]{\text{electricity}} 2H_{2(g)} + O_{2(g)}$$

Physical Properties:

1. Hydrogen is a colourless, odourless and tasteless gas.
2. It is insoluble in water.
3. It is highly inflammable gas and burns with blue flame.
4. It adsorbs on the surface of certain metals to make the surface sponge like, in which hydrogen gas adsorbs on metals surface to form a fine silvery powder.
5. Its electronegativity is 2.1 while its ionization energy is 13.54 e.v.
6. Its bond dissociation energy (H – H) is 104 K.Cals /mol.
7. It liquefies at – 252°C and freezes at – 259°C.

Chemical Properties:

1. Decomposition of Molecular Hydrogen (H_2):

Molecular hydrogen, H_2, contains stable covalent bonding and is relatively inert at ordinary conditions. Its bond dissociation energy is 104 K.Cals / mol.

$$H-H \xrightarrow[(1000K)]{} \underset{\text{Atomic hydrogen}}{H + \dot{H}} \quad ; \quad \Delta H = 104 \text{ K.Cals/mol. i.e } (+435 \text{ KJ/mol.})$$

2. As a Reducing Agent:

Hydrogen shows greater affinity for oxygen and reduces many metal oxides into free metals.

$$CuO_{(s)} + H_{2(g)} \xrightarrow{heat} \underset{\text{Copper}}{Cu_{(s)}} + H_2O_{(g)}$$

$$\underset{\text{Tungston oxide}}{WO_{3(s)}} + 3H_{2(g)} \xrightarrow{heat} \underset{\text{Tungston metal}}{W_{(s)}} + 3H_2O_{(g)}$$

3. Hydrogenation Reactions:

The addition of hydrogen into other molecular compounds is called hydrogenation reaction. When molecular compounds and hydrogen are heated in the presence of Pt or Pd or Ni and other catalysts to give addition products.

(i) $$CO_{(g)} + 2H_{2(g)} \xrightarrow[400^0C \text{ / high pressure}]{ZnO/Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3-OH_{(l)}}$$

(ii) $CH_2 = CH_{2(g)} + H_{2(g)} \xrightarrow{Ni/300\,^0C} CH_3 - CH_3$

Ethene Ethane

(iii) $\underset{\text{(liquid)}}{\underset{\text{Un saturated}}{\text{Edible oils}}} \xrightarrow[H_{2(s)}]{\text{Ni/high temp.}} \underset{\text{(Solid)}}{\underset{\text{Saturated}}{\text{Vegetable ghee}}}$

4. Reactions With Metals:

Alkali metals like Na, K etc and alkaline earth metals like Ca, Ba react with hydrogen on heating to form ionic hydrides.

(i) $2Na_{(s)} + H_{2(g)} \xrightarrow{200^0C} 2\overset{+}{Na}\overset{-}{H}_{(s)}$

Sodium hydride

(ii) $Ca_{(s)} + H_{2(g)} \xrightarrow{200^0C} Ca^{+2}H^{1-}_{2\ (s)}$

Calcium hydride

5. Reactions With Non – Metals:

Hydrogen reacts with many non – metals under different conditions to form addition products.

(i) $2H_{2(g)} + O_{2(g)} \xrightarrow{\text{ignition}} 2H_2O_{(l)}$

(ii) $N_{2(g)} + 3H_{2(g)} \xrightarrow[Fe_2O_3/K_2O]{500^0C/200\ dtm} 2NH_{3(g)}$

(iii) $H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{sunlight}} 2HCl_{(g)}$

(iv) $H_{2(g)} + S_{(s)} \xrightarrow{450^0C} H_2S_{(g)}$

Uses:

1. Hydrogen is used in the manufacture of fertilizers.
2. It is used in the manufacture of vegetable ghee from edible oils.
3. It is used in the manufacture of tungston bulb filaments.
4. It is used for the purification of metals.
5. It is used as a fuel in the form of water gas.
6. It is used in weather balloons.
7. Hydrogen is used in the formation of **Hydrogen torch** which is used in cutting and welding where temperature reaches upto 4000°C.
8. It is used in the preparations of chemicals like NH_3, CH_3OH, etc.

Nascent Hydrogen (Newly born):

Hydrogen at the time of its generation is chemically more reactive than molecular hydrogen because during the time of generation, it is available in atomic form and atomic hydrogen is chemically reactive. This hydrogen is called nascent hydrogen.

Consider the acidic ferric chloride solution which is of brownish colour, when H_2 gas is passed through ferric chloride, ($FeCl_3$), no appreciable change is observed. But when a piece of Zn metal is added in the acidic $FeCl_3$ solution, nascent hydrogen is generated which reduces $FeCl_3$ into ferrous chloride ($FeCl_2$) which is greenish in colour.

$$FeCl_{3(aq)} + H_{2(g)} \longrightarrow \text{No reaction}$$

$$FeCl_{3(aq)} + \underset{\substack{\text{Nascent}\\\text{hydrogen}}}{[H]} \xrightarrow{Zn/HCl} FeCl_{2(aq)} + HCl_{(aq)}$$

Similarly acidic $KMnO_4$ (pink) solution can be reduced by nascent hydrogen to colourless solution.

$$2KMnO_{4(aq)} + 3H_2SO_4 + \underset{\text{Nascent hydrogen}}{10[H]} \xrightarrow{Zn/H_2SO_4} K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 8H_2O_{(l)}$$

Thus hydrogen at the time of its birth is chemically more reactive than molecular hydrogen and is known as nascent hydrogen.

Isotopes of Hydrogen:

The word isotope is defined as the atoms of the same element, having same atomic number but different mass numbers. In other words isotopes are the atoms with same number of protons but different number of neutrons in their respective nuclei.

Nearly all the elements found in nature are mixtures of several isotopes. There are three isotopes of hydrogen namely;

(i) Protium (ii) Deuterium and (iii) Tritium

(i) Protium or Ordinary Hydrogen Atom ($_1^1H$):

This isotope of hydrogen contains one proton in the nucleus and there is one electron present in the first orbit i.e. in the first shell. Its atomic number is 1 and mass number is also 1. About 99.98% of free hydrogen contains protium. It is stable isotope of hydrogen.

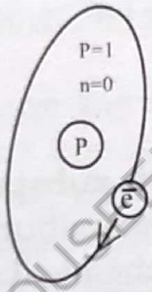


Fig. 11.1 Protium ($_1^1H$)

(ii) Deuterium (D or $_1^2H$):

It is known as heavy hydrogen which is a misnomer. Deuterium was discovered in 1931 by Urey. This isotope of hydrogen contains one proton and one neutron in the nucleus and one electron is present in the first orbit i.e. in the first shell. Its atomic number is 1 and its mass number is 2. It is present in the naturally occurring hydrogen to the extent about 0.0156% that is in the ratio 1:15000. It is also stable isotope of hydrogen.

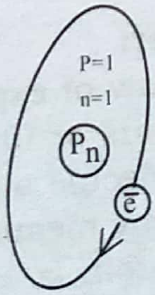


Fig. 11.2 Deuterium (D or $_1^2H$)

(iii) **Tritium** (T or $^{3}_{1}H$) :

This isotope of hydrogen contains one proton and two neutrons in the nucleus and one electron is present in the first orbit i.e. in the first shell. Its atomic number is 1 and its mass number is 3. It occurs in negligible quantities in the naturally occurring hydrogen to the extent about 4 x10^{-15} percent. It is radio active isotope of hydrogen with half life of about 12.5 year. It is used as tracer in the nuclear reactions.

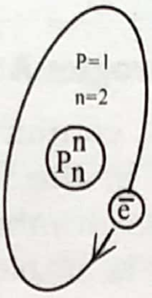


Fig. 11.3 Tritium (T or $^{3}_{1}H$)

11.2 Water

Introduction:

Water is the most common substance known and is a remarkable substance. Water is one of the most abundant compounds on earth. Water is an excellent solvent for many chemical substances and thus never occurs in its pure state in nature. Water which is found in the natural state is known as **natural water**. On the other hand water which has received some form of treatment is known as **treated water**. Treated water is usually prepared for special purposes. Distilled water is the purest form of water.

Water is a colourless, tasteless and odourless liquid. At $4^{0}C$ its density is maximum and it is about $1.00 g/cm^{3}$. Its freezing point is $0^{0}C$ while its normal boiling point is $100^{0}C$. Water possesses many unusual properties, for example it melts and boils at much higher temperature than other liquids. It is one of the few substances that expands upon freezing. All these properties of water are essential to suport life on Earth.

Anomalous Behaviour of Water:

Water does not obey the law of expansion and contraction between zero to $4^{0}C$ and shows anomalous or unusual behaviour. The reason for this is that water is a polar molecule and due to greater polarity, all the water molecules are associated by means of hydrogen bondings, in which the slightly positive hydrogen atom is attracted by the slightly negative oxygen atom of other water molecules. An electrostatic attraction between the neighbouring water molecules is set up when the positive pole of one molecule of water attracts the negative pole of the other neighbouring water molecule. This type of attractive forces which involve hydrogen, are refferred to as **hydrogen bonds**. It is denoted by dotted lines as given in the figure 11.4. Hydrogen bond is a secondary bond.

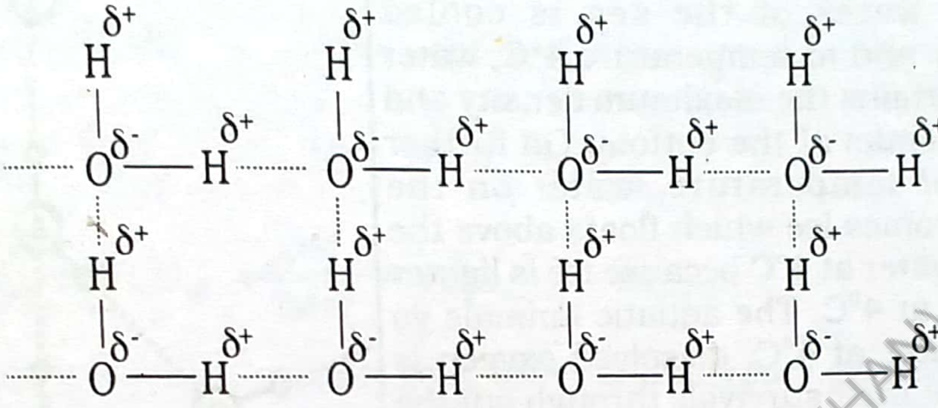


Fig. 11.4 Hydrogen bondings

Although hydrogen bondings are the strongest secondary bonds, it is still weaker than normal covalent bonds. The hydrogen bonds greatly affect the physical properties such as melting point, boiling point, heat of fusion etc. The most interesting impact of hydrogen bonding is observed in the crystal structure of ice which causes water to behave abnormally from 0°C to 4°C. Crystal structure of ice shows a tetra hedral arrangements of H_2O molecules. Each oxygen atom, suppose. "A" is surrounded tetrahedrally by four others such as 1, 2, 3 and 4 as shown in the figure 11.5 . The hydrogen bondings are shown by dotted lines. The arrangement of water molecules in ice is an open structure i.e. honey – combed structure, occupying a larger volume and due to larger volume ice is less dense than liquid water hence floats on water. When ice melts, some of the fixed hydrogen bonds are broken and the molecules pack themselves more closely together, there by decreasing the volume of liquid water, so density of liquid water increases. This breaking down process is not complete until a temperature 4°C is reached at which water has maximum density of about $1.0g / cm^3$.

The density of ice at 0°C is about $0.918\ g/cm^3$, while the density of liquid water at 0°C is $0.998g/cm^3$. On these basis, the anomalous behaviour of water can be explained i.e. water when heated from 0°C to 4°C shows contraction instead of expansion. Similarly when cooled from 4°C to 0°C water expands rather than contraction. This is just contrary to the behaviour of other liquids.

Due to this anomalous behaviour of water, the aquatic animals survive in the winter season in the region where temperature reaches much below 0°C. When winter approaches the temperature falls and water of the sea is cooled accordingly and at temperature 4°C, water of the sea attains the maximum density and that water sinks at the bottom. On further lowering of temperature, water on the surface becomes ice which floats above the surface of water at 4°C because ice is lighter than water at 4^0C. The aquatic animals go down in water at 4°C, dissolved oxygen is sufficient for their survivals through out the winter season. An ice covering above the water also protects them from the direct contact with the cold current and serves as a blanket. Therefore, in winter season in cold countries the aquatic animals spend their lives under the blanket of ice.

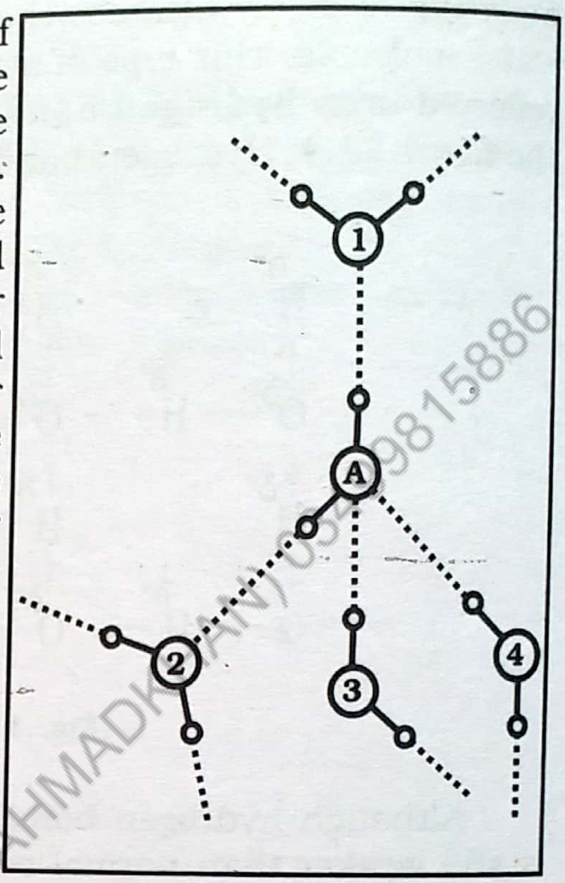


Fig. 11.5 Structure of ice

Chemical Properties of Water:

(1) Reactions of Water With Metals:

Water reacts with metals in number of ways. The degree of reactivity depends upon the nature of the metals and their positions in the electro chemical series.

(a) With More Electropositive Metals (Alkali and Alkaline Earth Metals):

Sodium, potassium, calcium, etc. react with cold water to form their hydroxides with the liberation of H_2 gas. Sodium and potassium reacts vigorously while calcium reacts slowly.

$$2Na_{(s)} + 2H_2O_{(l)} \xrightarrow{cold} 2NaOH_{(aq)} + H_{2(g)}$$

$$2K_{(s)} + 2H_2O_{(l)} \xrightarrow{cold} 2KOH_{(aq)} + H_{2(g)}$$

$$Ca_{(s)} + 2H_2O_{(l)} \xrightarrow{cold} Ca(OH)_{2(aq)} + H_{2(g)} \qquad \text{(Slow)}$$

(b) With Less Electropositive Metals:

Less electropositive metals like magnesium, zinc and iron react with hot water to liberate H_2 gas with the formation of their oxides, iron reacts with excess of steam at red heat.

$$Mg_{(s)} + H_2O_{(l)} \xrightarrow{hot} MgO_{(s)} + H_2$$

$$Zn_{(s)} + H_2O_{(l)} \xrightarrow{hot} ZnO_{(s)} + H_{2(g)}$$

$$3Fe_{(s)} + 4H_2O_{(g)} \underset{heat}{\overset{red}{\rightleftharpoons}} Fe_3O_{4(s)} + 4H_{2(g)}$$

Noble metals like, copper, gold, silver and mercury do not react with water in any form.

(2) Reactions of Water With Non-metals:

(a) With Chlorine:

Chlorine reacts with water to produce HCl and hypochlorous acid (HClO). Hypochlorous acid is unstable and readily liberates atomic oxygen which can bleach dyes and kill bacteria by oxidation. Chlorine, therefore, in water is both bleaching as well as oxidizing agents.

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + HClO_{(aq)}$$

$$HClO_{(aq)} \longrightarrow HCl_{(aq)} + [O]$$

acts as oxidizing and bleaching agent

$$O + O \longrightarrow O_{2(g)}$$

(b) With Carbon:

When steam is passed over heated coke at 1000°C, a mixture of hydrogen and carbon monoxide, known as **water gas** is produced.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1000^0C} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{water gas}}$$

(c) With Silicon:

Silicon reacts with steam at very high temperature to form an oxide of silicon i.e. silicon dioxide with the liberation of H_2 gas.

$$Si_{(s)} + 2H_2O_{(g)} \xrightarrow{\text{high temp.}} SiO_{2(s)} + 2H_{2(g)}$$

3. Action with Calcium Oxide (Quicklime):

Calcium oxide partially dissolves in water to form calcium hydroxide (i.e. slaked lime).

$$\underset{\text{quick lime}}{CaO_{(s)}} + H_2O_{(l)} \longrightarrow \underset{\text{slaked lime}}{Ca(OH)_{2(s)}}$$

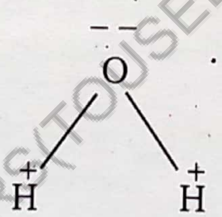
4. Action with N_2O (Nitrous Oxide):

Nitrous oxide dissolves in water to form a neutral solution.

$$N_2O_{(g)} + H_2O_{(l)} \longrightarrow \text{dissolves to form a neutral solution}$$

11.3 WATER AS A UNIVERSAL SOLVENT

Water is an excellent solvent. It dissolves majority of ionic compounds and many covalent compounds. It can dissolve more substances than any other solvent. The great dissolving power of water is because of its large dielectric constant and its polar nature. In water oxygen being more electronegative than hydrogen atom, acquires a partial negative charge or pole and hydrogen atoms get partial positive charges or poles i.e. one side of water molecule is slightly positive while the other side is slightly negative.



As a result of this polar structure, water is an excellent solvent for electrovalent (ionic) solutes such as mineral salts, mineral acids and bases. All covalent compounds which contain hydroxyl group (– OH) also dissolve very easily in water for example glucose, sugar, alcohols, etc. are soluble in water. Some gases can dissolve in water to some extent. Gases which react with water are found to be very soluble. For example, ammonia, hydrogen chloride, nitrogen pentaoxide (N_2O_5) etc. Other gases like SO_2, CO_2, chlorine which ionize only slightly are found to be fairly soluble in water. In general the solubilities of gases decrease with the increase in temperature.

Water of Crystallization:

Most of the ionic salts can crystallize out of the solution by cooling the saturated solutions of the salts or by evaporation in the form of crystals with definite shapes. The crystals thus produced contain few molecules of water as a part of the crystal lattice. The molecules of water are loosly bounded to the crystals of the salts. These water molecules are known as **Water of crystallization** or hydration. The salts containing water molecules as water of crystallization are generally known as **hydrates**. Examples : $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $Na_2CO_3 \cdot 10H_2O$, $AlCl_3 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, etc. Different hydrates contain different number of molecules of water as water of crystallization. It is interesting to note that although hydrated salt like $AlCl_3 \cdot 6H_2O$ or $CuSO_4.5H_2O$ has water molecules attached to its crystals, yet it appears dry.

$$CuSO_{4(s)} + 5H_2O_{(l)} \xrightarrow{\text{evaporation}} CuSO_4 \cdot 5H_2O_{(s)}$$

The minimum amount of heat liberated in the formation of hydrate is called heat of hydration. The molecules of water of crystallization are easily dissociated from their salt crystals by heating. The residue left behind is then said to be anhydrous (shapeless) or anhydrate.

$$\underset{\text{Blue crystals}}{CuSO_4 \cdot 5H_2O_{(s)}} \xrightarrow{\text{heat}} \underset{\text{Anhydrous (white powder)}}{CuSO_{4(s)}} + 5H_2O_{(g)}$$

There are also many salts which crystallize out from the solutions without any water of hydration such as KNO_3, $NaCl$, $AgNO_3$, K_2SO_4, $PbCl_2$ etc. The reason for this is that water molecules are generally attached with smaller cations, having greater cationic charge density.

11.4 SOFT, HARD WATER AND HEAVY WATER

Water containing dissolved impurities of hydrogencarbonates, chlorides and sulphates of calcium and magnesium is called hard water. It does not give lather with soap, hence called hard water.

Water containing dissolved impurities but in small quantities and easily produces lather with soap is known as soft water. Hard water produces curds with soap and affects the cleaning action of soap. Soap contains sodium salts of long chain carboxylic acids such as sodium hexadecanoate (sodium palmitate) and sodium octadecanoate (sodium stearate) etc, where as hard water contains calcium and magnesium ions. When hard water is mixed with soap then Ca^{2+} and Mg^{2+} ions react with anions of soap. (i.e. with palmitate and stearate ions) to form insoluble compounds of Ca and Mg ions which we see as curds in water.

Causes of Hardness:

The rain water on its way to ground, dissolves carbon dioxide gas from the atmosphere. This water while flowing through beds of soil or rocks, containing carbonates of Ca and Mg react with dissolved CO_2 in water to change the carbonates of Ca and Mg into their respective hydrogencarbonates which are soluble in water and causes temporary hardness.

$$CaCO_{3(s)} + CO_2 + H_2O_{(l)} \longrightarrow Ca(HCO_3)_{2(aq)}$$

$$MgCO_{3(s)} + CO_2 + H_2O_{(l)} \longrightarrow Mg(HCO_3)_{2(aq)}$$

Underground water also dissolves chlorides and sulphate of Ca and Mg. This underground water now contains Ca^{2+} and Mg^{2+} ions which make water as hard.

Types of Hardness:

There are two types of hardness in water:

(i) Temporary hardness (ii) Permanent hardness.

(i) Temporary Hardness:

Temporary hardness is due to the presence of dissolved hydrogencarbonates of calcium and magnesium. These salts are water soluble and ionize into water as:

$$Ca(HCO_3)_{2(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)}$$

$$Mg(HCO_3)_{2(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + 2HCO^-_{3(aq)}$$

(ii) Permanent Hardness:

Permanent hardness is due to dissolved chlorides and sulphates of Ca and Mg, for example, $MgCl_2$, $MgSO_4$ and $CaCl_2$. They are also soluble in water and ionize in water as:

$$CaCl_{2(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$$MgCl_{2(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + 2Cl^{1-}_{(aq)}$$

$$MgSO_{4(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$$

Methods To Remove Hardness:

(i) By Heating:

Temporary hardness can be easily removed by boiling. This hardness is caused by the presence of dissolved calcium hydrogencarbonate and magnesium hydrogencarbonate, which decompose on heating to $CaCO_3$ and $MgCO_3$ which are insoluble in water and are removed by filteration.

e.g. $$Ca(HCO_3)_{2(aq)} \xrightarrow{boil} \underset{\text{insoluble}}{CaCO_{3(s)}\downarrow} + CO_{2(g)} + H_2O_{(l)}$$

Once Ca^{2+} ions or Mg^{2+} ions are out of water, any soap when added to water becomes soft, the water and lather formation occurs.

(ii) Clark's Method:

Temporary hardness can also be removed by using slaked lime; $Ca(OH)_2$. This method of removing hardness on a large scale is known as Clark's method. This is a chemical method. In this method temporary hard water containing hydrogencarbonates of Ca and Mg is treated with slaked lime in the tanks. The hydrogencarbonates of Ca and Mg are converted into their insoluble carbonates. These insoluble carbonates settle down at the bottom of tanks, while soft water is drained off for the use.

e.g. $$Ca(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \longrightarrow \underset{\text{insoluble}}{2CaCO_{3(s)}} + 2H_2O_{(l)}$$

$$Mg(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \longrightarrow \underset{\text{insoluble}}{MgCO_{3(s)}} + \underset{\text{insoluble}}{CaCO_3} + 2H_2O_{(l)}$$

(iii) Permanent hardness can be removed by using chemicals. The word permanent is misleading because this hardness can ultimately be removed. It is caused by the dissolved impurities of the chlorides and sulphate of Ca and Mg.

Permanent hardness can be removed by number of methods such as Ion – exchange method in which calcium and magnesium ion from water are removed as insoluble precipitates. The chemicals employed are mostly soluble sodium compounds. These form insoluble precipitates of Ca and Mg ions. Washing soda, caustic soda and zeolite are some of the common chemicals used in removing the permanent hardness.

(a) By Using Washing Soda ($Na_2CO_3 . 10\,H_2O$):

When washing soda is added to permanent hard water, insoluble $CaCO_3$ and $MgCO_3$ are precipitated from the soluble salts of Ca and Mg.

$$CaSO_{4(aq)} + Na_2CO_{3(aq)} \longrightarrow \underset{\text{insoluble}}{CaCO_{3(s)}} + 2Na_2SO_{4(aq)}$$

$$MgCl_{2(aq)} + Na_2CO_{3(aq)} \longrightarrow \underset{\text{insoluble}}{MgCO_{3(s)}} + 2Na\,Cl_{(aq)}$$

(b) By Using Caustic Soda (NaOH):

When caustic soda is added to permanent hard water, insoluble hydroxide of Mg^{2+} ion is precipitated from the salt of Mg while $Ca\,(OH)_2$ is partially soluble in water.

$$MgSO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{insoluble}}{Mg(OH)_{2(s)}} + Na_2SO_{4(aq)}$$

(c) By Using Zeolite or Permutit:

Permutit is an ion – exchange resin used industrially and in the home for softening water. It is a naturally occurring sodium aluminium silicate, commonly called sodium zeolite which can also be prepared artificially. As hard water is passed through the resin, the sodium ions will go into the solution while the unwanted Ca and Mg ions take their place in the complex insoluble Ca and Mg zeolites and their hardness is removed. Soft water is then drawn out at the bottom.

$$CaSO_{4(aq)} + \text{Sod zeolite}_{(aq)} \longrightarrow \underset{\text{insoluble}}{\text{Ca – zeolite}_{(s)}} + Na_2\,SO_{4(aq)}$$

Sodium zeolite can be regenerated by passing a strong NaCl solution through Ca – zeolite.

$$\text{Ca zeolite}_{(s)} + 2NaCl_{(aq)} \longrightarrow \text{Sod zeolite}_{(aq)} + CaCl_{2(aq)}$$

Heavy Water:

Heavy water is a compound of oxygen with heavy hydrogen i.e. deuterium (D or, ${}^{2}_{1}H$). Its molecular formula is D_2O. It is also called deuteriumoxide. Heavy water is present in natural water to the extent of 1part in 7000 parts. It is 1.1 time heavier than H_2O. Some of the important properties of heavy water is given as:

1. Its density is slightly greater than ordinary water and is 1.104 g / cm^3.
2. It has low vapour pressure than ordinary water.
3. Its melting pount is 3.81°C and boiling point is 101.42°C.
4. The refractive index of heavy water (D_2O) is much smaller than ordinary water. This property is used to identify heavy water from ordinary water that is for isotopic analysis.
5. The molecular mass of heavy water is 20 a.m.u, while that of ordinary water is 18 a.m.u.

Uses:

Heavy water is used as **moderator** in nuclear fission power reactions by slowing down the reactions. It is also used as a **tracer** in biological and chemical researches.

11.5 HYGROSCOPIC SUBSTANCES

Hygroscopic substances absorb moisture on exposure to atmosphere. However if the substances are solids, they will not form, solutions but merely become sticky or moist just unlike deliquescent substances, which absorb large amount of water, to from eventually solutions when exposed to atmosphere. On the other hand a liquid like concentrated H_2SO_4 will absorb water from the atmosphere usually diluting itself upto about three times of its original volume. Other examples of hygroscopic substances are; sodium nitrate; $NaNO_3$; copper oxide; CuO; quick lime, CaO etc.

Hydroscopic substances are commonly employed as drying agents in the laboratory. They have strong affinity for moistures or water.

11.6 DRINKING WATER

Introduction:

Water is essential for the survival of any form of life. On an average, a human being consumes about two liters of water every day. Water accounts for about 70 percent of the weight of a human body. Water available is used for drinking, domestic, agriculture, industrial consumption. Owing to increasing industrialization on one hand and exploding population on the other, the demands of water supply have been increasing tremendously.

In our home, water is used for drinking, cooking and washing purposes. Although there is an enormous quantity of water in the world, the reservoirs of fresh and quality water are very limited. Human activities is destroying the quality of water. The quality as well as quantity of clean water supply is of vital significance for the welfare of mankind.

We know water is an excellent solvent, dissolves a wide variety of compounds. Natural water, when it flows over or seeps through the surface of the earth, dissolves various minerals including salts and other substances. Despite these mineral impurities water from most of the lakes, rivers, springs and wells is considered fit for drinking and other domestic uses. Water is considered polluted, when it is contaminated with substances which are harmful and injurious for human beings and other living things. Polluted water is unfit for drinking purposes.

Considerable part of the available water is polluted by sewage, industrial wastes and wide array of synthetic chemicals.

Classification of Water Pollutants:

There are various types of water pollutants which can broadly be classified into different catagories.

1. Oxygen – Demanding Wastes:

These include domestic and animal sewage, bio – degradable organic compounds and industrial wastes from food – processing plants, meat packing plants, slaughter houses, paper and pulp mills, tanneries etc. All these wastes undergo degradation and decomposition due to which there is a rapid depletion of demand oxygen. (D.O) from water which is harmful to aquatic animals. Many aquatic animals can not survive at lower D.O levels in water.

2. Synthetic Organic Compounds:

These are the man-made materials such as synthetic pesticides, synthetic detergents, food additives, pharmaceutals, insecticides, paints, fibres, solvents, plastics etc. These materials are potentially toxic to plants, animals and humans. They cause affensive colours, odours and tastes in water.

3. Disease-Causing Wastes (Micro Organisms)

Disease causing wastes include pathogenic micro-organisms which may enter water along with sewage and other wastes and may cause tremendous demage to public health. These microbes, comprising mainly of viruses and bacteria can cause dangerous **Water-borne diseases** such as typhoid, cholera, polio, dysentary, infections hepatitis in humans. Hence disinfection is the primany step in water pollution control.

4. Agricultural Water Pollutants:

In modern agriculture, pesticides, fertilizers and organic wastes (manure) are essential for producing high yields of crops required for the world's growing population. There are over one thousand chemical compounds that are currently being used. Some common pesticides used in Pakistan are alderin, DDT, dielderin etc. When too much of these are accumulated, they become a cause of pollution.

Some inorganic pollutants, comprising of mineral acids, inorganic salts, finely divided metals, trace elements, cyanides etc. also contaminate water.

Quality of Drinking Water:

Municipal water is mainly used for drinking and for cleaning, washing and other domestic purposes. The water that is fit for drinking purpose is called **potable water**, it should be free from all sorts of pollutants.

Some characteristics of potable water is given as under:

1. It should be colourless, odourless and tasteless.
2. It should be free from germs, bacteria and other pathogenic organisms.
3. It should not contain any toxic dissolved impurity such as heavy metals and pesticides.
4. It should have a pH in the range of 7 – 8.5.
5. It should be moderately soft. Its hardness should not be above 150 p.p.m (parts per million).
6. It should not stain clothes.
7. It should be free from corrosive substances.

The municipal water supplied for drinking and other domestic uses, has to be treated before the supply for the domestic purpose. The raw or impure water obtained from sources such as rivers, lakes, wells and tube wells, etc. should undergo treatment by various steps to make it fit such as:

1. Aeration.
2. Settling.
3. Coagulation.
4. Filteration.
5. Chlorination (for sterilization to destroy bacteria and pathogenic organisms).

SUMMARY

1. Hydrogen is the lightest element and has the simplest atomic structure. It exists as a diatomic molecular gas (H_2). The most abundant compound of hydrogen on the earth surface is water.
2. Hydrogen is commercially prepared by passing steam over red-hot coke by the thermal decomposition of methane and by the electrolysis of water. It is a colourless, odourless and tasteless gas, insoluble in water. It burns in oxygen with bluish flame to produce water.
3. Hydrogen at ordinary condition is chemically inert. It is used in the field of fertilizers and in the manufacture of vegetable ghee from edible oils by the hydrogenation reaction.
4. Hydrogen at the time of its generation is chemically more reactive

than molecular H_2 and is called Nascent hydrogen. Natural hydrogen is a mixture of three isotopes named protium (^1_1H), deuterium (^2_1H, or D) and tritium (^3_1H, or T). Protium is the commonest isotope of hydrogen which is present upto 99.98% in ordinary hydrogen.

5. Water is the most common substance known. It is one of the most abundant compound on earth. It is colourless, odourless and tasteless liquid and is an excellent solvent. Distilled water is the purest form of water. Water is essential to support life on the earth.

6. Water shows anomalous behaviour. Water is a polar solvent. Due to polarity, all the water molecules are associated by means of hydrogen bondings. Hydrogen bondings greatly affect the physical properties such as melting point, boiling point, heat fusion etc of water. Water does not obey the law of expansion and contraction between O to 4^0C. It expands when cooled from 4 to 0^0C and contracts from O to 4^0C. Due to this reason ice (solid water) floats over water.

7. Water reacts with more electropositive metals like Na, K, Ca etc to evolve hydrogen gas along with the formation of their hydroxides. With less electropositive metals like Mg, Zn, Fe etc. hot water reacts to evolve hydrogen gas with the formation of their oxides. Water also reacts with many non-metals. like C, Si, Cl_2, Br_2 etc. and also with some metal and non-metal oxides.

8. Water is an excellent solvent and dissolves majority of ionic compounds and many covalent compounds, and is never found in pure state in nature. The great dissolving power of water is due to its large dielectric constant and its polar nature. Most of the ionic salts can be crystallized out from their aquous solutions by cooling their super saturated solutions, in the form of crystals with definite shapes. These crystals contain some water molecules as a part of the crystal lattice, known as water of crystallization and such salts are called as hydrates. For examples $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $AlCl_3.6H_2O$, $BaCl_2.2H_2O$ etc.

9. Water containing some dissolved compounds of hydrogencarbonates, chlorides and sulphates of calcium and magnesium. It does not give lather with soap and is called hard water. Soft water also contains dissolved impurities but in very small quantity and produces lather with soap. Hard water produces Curds with soap. There are two types of hardness in water; temporary and permanent hardness. Temporary hardness is due to dissolved hydrogencarbonates of calium and magnesium which can be removed easily by heating. On heating hydrogencarbonates decompose into insoluble carbonates of Ca and Mg and can be removed by filtration. Temporary hardness can also be removed by using slaked lime $Ca(OH)_2$.

Permanent hardness is due to dissolved chlorides and sulphates of calcium and magnesium. Permanent hardness can be removed by Ion exchange techniques or by using certain chemicals, such as by using wasing soda, $Na_2CO_3.10H_2O$ caustic soda, NaOH, etc. In ion exchange technique, zeolite is used.

10. Heavy water is a compound of oxygen with heavy hydrogen i.e deuterium. Its molecular formula is D_2O. It is used as moderator in nuclear fission reactions to slow down the neutrons.
11. Some chemical substances absorb moisture from the atmosphere and are called as hygroscopic substances.
12. Water is essential for life. Water which is fit for drinking purposes is called **potable water.** It should be free from all sorts of impurities.

EXERCISE

1. (a) Fill in the blanks:

(i) Natural hydrogen contains __________ percent deuterium.

(ii) Nascent hydrogen is __________ reactive than molecular hydrogen.

(iii) Tritium is an _________ of hydrogen, its mass number is _______.

(iv) Natural hydrogen is a mixture of three isotopes namely _______, __________ and __________.

(v) The bond energy of H_2 is ____________.

(vi) The latent heat of fusion of ice is approximately ______ per _______.

(vii) Ice ______ over water because ice is ______ than water.

(viii) The sterilization or disinfection of water is done by ______ to destroy ____________ and ____________.

(ix) Water molecules are associated together by means of ______

(x) Water is called as ______ solvent.

(b) Point out True and False in the following statements :

(i) Ordinary hydrogen is called protium.

(ii) Hydrogen is a good oxidizing agent.

(iii) Deuterium contains one proton and two neutrons in the nucleus.

(iv) Hydrogenation is the process of addition of hydrogen.

(v) Electrolysis of water in the presence of acid liberates H_2 gas at cathode and O_2 gas at anode.

(c) Multiple choice questions:

(i) Select all those things which result when sodium metal is placed in a beaker of water;
(a) H_2 and NaOH (b) Sodium disappears after sometime
(c) Water becomes acidic (d) No action.

(ii) Hydrogen is a diatomic molecule with bond energy :
(a) 200 KJ/mol (b) 100 KJ/mol
(c) 104 K.Cal/mol (d) 150 K.Cal/mol

(iii) Deuterium is present in natural hydrogen in the ratio :
(a) 1:1200 (b) 1:15000 (c) 100:50000 (d) 1:18000

(iv) The electronegativity of hydrogen is :
(a) 2.1 (b) 3.0 (c) 2.5 (d) 1.0

(v) A human being consumes water about __________ everyday.
(a) 5 litres (b) 2 litres (c) 1 litre (d) 10 litres.

(vi) Polluted water is _________ for drinking purposes.
(a) unfit (b) fit (c) useful (d) used.

(vii) Mol.mass of heavy water is :
(a) 18 (b) 22 (c) 20 (d) 16

(viii) The maximum density of water at 4°C is :
(a) $1.0 g/cm^3$ (b) $0.998 g/cm^3$
(c) $0.918 g/cm^3$ (d) $1.2 g/dm^3$

(ix) The freezing point of heavy water is :
(a) 0°C (b) 3.81°C (c) 4°C (d) 1°C

2. (a) Describe some of the main physical properties of water. What do you understand by the anomalous behaviour of water ? what is the significance of this unusual behaviour of water ?

(b) Complete the following reactions.

(i) $Na + H_2O \longrightarrow$
(ii) $Fe + H_2O \longrightarrow$
(iii) $C + H_2O \longrightarrow$
(iv) $Cl_2 + H_2O \longrightarrow$
(v) $CaO + H_2O \longrightarrow$

3. (a) Define isotope. Discuss various isotopes of hydrogen.
(b) How is hydrogen prepared commercially from coke ?
(c) Give Bosch method to seprate hydrogen gas from water gas.

4. (a) Give reaction of H_2 with,
(i) Ethene (ii) Ca metal (iii) S (iv) Cl_2
(b) Describe the uses of hydrogen.
(c) Show hydrogen is a good reducing agent.

5. (a) What is nascent hydrogen? Describe its reactivity.

(b) What happens when ?

(i) Mg metal is reacted with hot water.

(ii) Methane is heated above 700°C in the absence of air.

(iii) Water gas is heated under pressure in the presence of $ZnO - Cr_2O_3$ catalyst.

(iv) A piece of Zn metal is added to the acidic solution of $FeCl_3$.

6. (a) What do you mean by hard water? Describe the types of hardness. How is the hardness of water removed? Describe the disadvantages of hard water.

(b) What is water of crystallization? Write the formula of some of the hydrates. What happens when hydrates are heated? Define heat of hydration.

(c) What is "potable water"? Write four main characteristics of potable water.

(d) Name only some common treatments to make municipal water fit for drinking purposes.

7. (a) Write notes on:

(i) Heavy water and (ii) Hygroscopic substances.

(b) Describe some chemical characteristics of water.

(c) Name water – borne diseases that are caused by micro – organisms present in water. Name various types of water pollutants and their different catagories.

8. Point out True or False in the following statements :

(i) Water is non – polar.

(ii) Temporary hardness in water is due to dissolved hydrogencarbonates of Ca and Mg.

(iii) Permutit is sodium aluminium silicate, commonly called sod. zeolite.

(iv) The molecular formula of heavy water is H_2O.

(v) Conc. H_2SO_4 absorbs moisture from atmosphere four time of its original volume.

CHAPTER-12

CARBON, SILICON AND THEIR COMPOUNDS

You will learn in this chapter about:

* Carbon and its allotopic modification, bucky ball.
* Diamond and graphite and their structures.
* Physical and chemical properties of carbon and catenation.
* Silicon,its occurrence and preparations.
* Properties and uses of silicon.
* Silica, water glass, chemical garden and silica gel.

12.1 INTRODUCTION:

Carbon and silicon belong to IV – A group of the periodic table because both the elements contain four electrons in their valence shells. The electronic configurations of carbon and silicon are given as:

	K	L	M	N	(Shells)
C^6 =	2	4			
Si^{14} =	2	8	4		

Carbon is a pure non–metal. Silicon is a metalloid and plays an important role in electronic technologies.

Occurrence of Carbon:

Carbon is the sixteenth most abundant element in the earth crust. Carbon occurs in the free state as well as in the combined state in the earth's crust. In the pure elemental form carbon exists in three crystalline forms, ie graphite, diamond and buckminster fullerene i.e. bucky balls.

However the major source of carbon is coal. Coal is a complicated mixture of chemical substances containing elemental carbon, compounds of carbon with hydrogen, oxygen, nitrogen, sulphur and many other elements. The amount of carbon depends upon the stage of conversion of the plant materials into coal. The first stage in the formation of coal is **Peat**. It is soft brown spongy material, made by partially decomposed plant materials. Continued decomposition of peat converts it into **brown coal** or **lignite** then into soft coal or **bitumen** and finally into hard coal known as **anthracite** in which conversion of carbon is almost complete. Anthracite is the hardest form of coal.

The Carbon Contents and Energy Values

S.No.	Fuels	Carbon Content (% mass)	Energy Value (KJ / Kg)
1.	Wood	50.0%	19800 KJ/Kg
2.	Peat	59.9%	18700 KJ/Kg
3.	Lignite	61.8%	20900-25700 KJ/Kg
4.	Bitumen	78.7%	32100 KJ/Kg
5.	Anthracite	91.0%	32600 KJ/Kg

Carbon also exists as carbon black, which is produced by heating methane to high temperature in a limited supply of oxygen.

$$CH_4 + O_2 \xrightarrow{800^0C} \underset{\text{Carbon black}}{C_{(s)}} + 2H_2O_{(g)}$$

Charcoal is formed when wood is heated strongly in the absence of air. It is used to remove offensive odour from air and colours or bad tasting impurities from water.

Coke is a pure form of carbon, formed when coal is heated strongly in the absence of air. It is widely used as reducing agent in metallurgical operations.

In combined state carbon occurs as natural gas and petroleum. Both natural gas and petroleum are mixtures of hydrocarbons i.e. compounds of carbon and hydrogen elements. Carbon also occurs in the form of two principal oxides, carbon monoxide and carbon dioxide in the atmosphere and also as metal carbonates in the earth's rocks. The most common carbonate rock is calcium carbonate ($CaCO_3$) which occurs as marble, chalk and lime stone.

In the free state carbon occurs in the following forms.

1. **Crystalline Forms:**
   (a) Diamond (b) Graphite and (c) Bucky balls.

2. **Amorphous Forms:**
   (a) Lamp black (b) Wood charcoal (c) Coal
   (d) Animal charcoal (e) Gas carbon.

12.2 ALLOTROPY AND ALLOTROPIC FORMS OF CARBON

The existence of two or more different forms of the same element in the same state is called allotropy and different forms are known as **allotropic modifications** or **allotropes**. The allotropes are different forms of the same element in the same state. Allotropes possess same chemical properties but have different physical properties due to different structures or arrangements of the atoms.

There are three solid allotropic forms of carbon.

(a) Diamond (b) Graphite (c) Bucky Balls

(a) Diamond

Diamond is one of the crystalline forms of carbon. It is found chiefly in South Africa, Brazil, Australia and India. In pure state, diamond is transparent and bright. It is the hardest natural substance known. Its density is about 3.51g/cm^3. It has very high refractive index, i.e. 2.45μ, due to which it acquires great brilliance. It is a bad conductor of electricity. It has very high melting point about 3500°C. Colours in diamond are due to the presence of some metal oxides as impurities. Diamond may be of blue, green, yellow, red or black colour. The black coloured diamonds are called **Bort** or **Carbando** which are of inferior qualities and are used for cutting glasses and for drillings and borings of rocks. Other diamonds are used as gems and precious stones. Diamond is carbon as it burns on ignition above 900°C to produce CO_2 gas.

$$\text{Diamond (C)} + O_2 \xrightarrow[900^0C]{\text{Ignition}} CO_{2(g)}$$

(b) Graphite

Graphite occurs naturally as **Plumbago**, an opaque black solid. It is found in Siberia, Canada and Srilanka.

Graphite is of dark grey colour crystalline solid with dull metallic lusture. It is soft and greasy to feel. It is less dense than diamond and has density about 2.2g/cm^3. It is good conductor of electricity and is used in the preparation of electrodes. It leaves black mark on paper, so it is used in the manufacture of lead pencils (graphite + clay). Graphite is also used as a black pigment in paints and also as neutron – moderator in nuclear reactions. It has high melting point about 3000°C. Some times graphite is mixed with oil to form a high temperature lubricant. Graphite on ignition at 700°C burns to produce CO_2 gas.

$$C_{\text{graphite}} + O_2 \xrightarrow[700^0C]{\text{Ignition}} CO_{2(g)}$$

(c) Bucky Balls

Until 1980 pure solid carbon was thought to exist as diamond and graphite. In 1985 a startling discovery was made by two English researchers by the vapourized graphite. The mass spectrum peaks corresponded to clusters of carbon atoms as molecules of 60 carbon atoms (C_{60}) and discovered that it is a different form of carbon, namely C_{60} molecules that were nearly spherical in shape. They proposed that carbon atoms of C_{60} form a ball, exactly like a soccer ball and has a highly symmetric structure. C_{60} was named buckminster fullerene or bucky balls in short. Unlike diamond and graphite the new molecular form of carbon can be dissolved in organic solvents.

Structure of Diamond:

Diamond crystal is usually octahedral in shape. In diamond each carbon atom is covalently bonded with four other carbon atoms to give a basic tetrahedral unit. The crystal lattice of diamond is built up from these basic tetrahedral units. These basic tetrahedral units unite with one another indefinitely forming a giant three – dimensional molecule Fig. 12.1 refers the basic tetrahedral unit and Fig. 12.2 refers the giant three – dimensional molecule of diamond.

As a result of the strength and uniformity of the bonds, the stable and the rigid crystal lattice, diamond is the hardest substance known to man. Because there is no free electron in the crystal of diamond, so diamond is bad conductor of electricity. The C – C bond length is diamond is 1.54A° and bond energy for each C – C bond is 347 KJ/ mol.

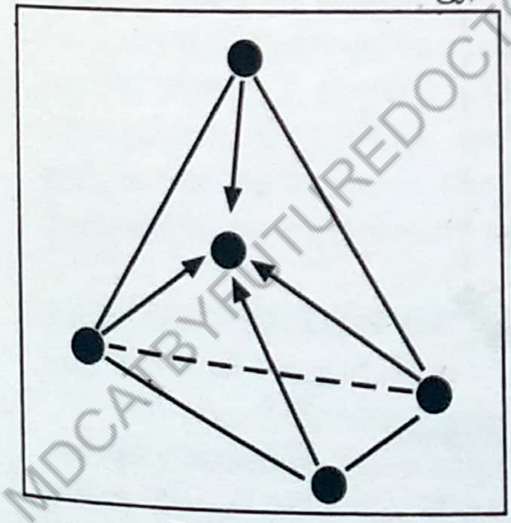


Fig 12.1
Basic tetrahedral unit of diamond
• = Carbon atom
– = Carbon to carbon
Covalent bond

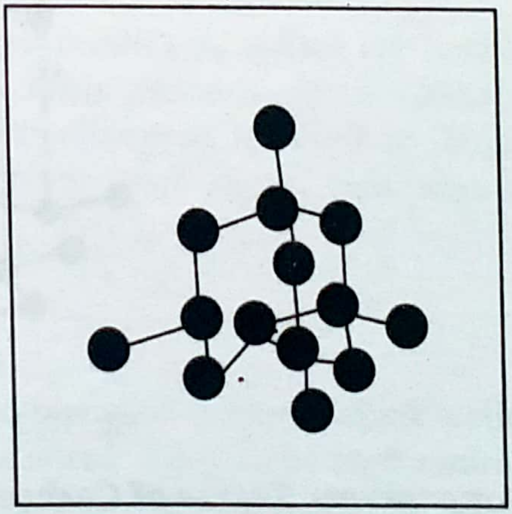


Fig. 12.2
Three dimensional arrangements of carbon atom in diamond.

Structure of Graphite:

In graphite the carbon atoms form flat layers. Each carbon atom in graphite is linked covalently to three other carbon atoms in the same layer to give basic hexagonal ring. Each layer of carbon atoms can be viewed as a two – dimensional sheet polymer or layer lattice. The carbon – carbon bond length within a layer is 1.42A° which is the bond length intermediate to a single and a double carbon – carbon bond. The strong covalent bonds within the layers account for the high melting point of graphite. However the layers are arranged in parallel, forms one above the other and they are far apart from one another and the two successive layers are situated at a distance 3.35A°, which are held together by weak vander waal's forces of attraction. The inter layer binding energy is very low, therefore the layers slide over one another. Thus, graphite is very soft and slippery. Graphite has more open structure, so graphite is less dense than diamond.

Unlike diamond, only three of the four valence electrons are held in definite bond formation. The fourth electron is delocalized over the whole layer i.e. spread uniformly over all carbon atoms. Due to delocalized electrons, graphite conducts electricity parallel to the plane of its layers and not perpendicular to the layers.

The arrangement of different layers in graphite is shown in fig. 12.3.

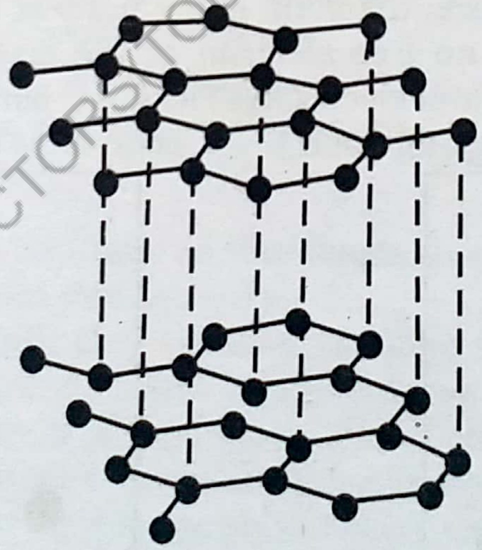


Fig. 12.3 Layer structure of graphite

Amorphous Forms of Carbon:

The amorphous forms of carbon are not considered as allotropes of carbon, because X – rays analysis have revealed that they have structures like graphite with the exception of coal, which is mined directly from natural deposits, the other amorphous forms can be prepared in various ways.

(i) Coal:

Coal originates from the vegetations of the carboniferous era. It is said that the decomposition of plants and trees occurred gradually under the earth in the absence of air and under pressure. CO_2 ,water and methane were liberated, leaving behind a material, containing high percentage of carbon. During the process under the earth, the vegetable material was converted in stages into peat, lignite (brown coal), bituminous coal (soft) and finally to anthracite (hard coal). Various impurities including, nitrogen, sulphur and phosphorous may also be present. Coal can be mined at various depths from the earth surface. Coal is mainly used as fuel.

(ii) Coke:

Coke is produced by heating bituminous coal to very high temperature about (1300°C) in the absence of air to remove all the volatile constituents present in coal. This process is called **destructive distillation** of coal. The other non – volatile products obtained by destructive distillation of coal would be **Coaltar** and Coke. Coke is used as fuel and also as reducing agent in the extraction of metals especially iron. Coke burns in air with no smoke and leaves very little residue.

(iii) Charcoal:

Charcoal can be produced by heating wood, nut shells, bones, sugar etc. Wood charcoal is the most common. It is prepared by burning wood in the limited supply of air. It may contain impurities such as sulphur. It is mainly used as domestic fuel.

Animal charcoal is produced when animal bones and refuse are heated in the limited supply of air. It contains high percentage of calcium phosphate; $Ca_3(PO_4)_2$ as impurity. Animal charcoal is used in sugar industries to remove the brown colours from cane sugar and also in decolourizing petroleum jelly.

12.3 PROPERTIES OF CARBON

(1) Physical Properties:

All the different carbon allotropes are black or greyish black solids except diamond. They are odourless and tasteless. They have high melting point, above 3000°C. They are insoluble in all common solvents like water, alcohols, acids, petrol, etc. That is why carbon deposits formed during incomplete combustion of fuels (Petrols) inside motor engines have to be removed mechanically, this process is called **de-carbonization** of motor engines.

2. Chemical Properties:

Chemically carbon is not very reactive element. All the allotropes of carbon have similar chemical properties because they are all chemically identical and combine to form covalent compounds.

(1) Combustion:

All forms of carbon burn in excess of air (O_2) to produce carbon dioxide (CO_2) gas.

$$C_{(s)} + O_{2(g)} \xrightarrow{\text{Ignition}} CO_{2(g)} \; ; \quad \Delta H = -394 \text{ KJ/mol}$$

The combustion reaction is highly exothermic. Due to this characteristics, carbon in the form of coal, coke or charcoal is usually used as fuel, giving large amounts of heat.

However in the limited supply of air, incomplete combustion may take place to produce carbon monoxide (CO) gas instead of CO_2 gas.

$$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$

2. Combination Reactions:

Carbon combines directly with other elements such as hydrogen, sulphur, calcium, aluminium at very high temperature to form addition products.

(i) $C_{(s)} + 2H_{2(g)} \xrightarrow{\text{high temp.}} CH_{4(g)}$

methane

(ii) $C_{(s)} + 2S_{(s)} \xrightarrow{\text{high temp.}} CS_{2(l)}$ (Carbon disulphide)

(iii) $2C_{(s)} + Ca_{(s)} \xrightarrow{\text{high temp.}} CaC_{2(s)}$

Calcium carbide

(iv) $3C_{(s)} + 4Al_{(s)} \xrightarrow{\text{high temp.}} Al_4C_{3(s)}$

Aluminium carbide

3. As Reducing Agent:

Carbon is a powerful reducing agent because it has greater affinity for oxygen. It reduces many metal oxides and other oxides into free metals and other elements. The reduction occurs at very high temperature to form CO_2 or CO gas.

(i) $Fe_2O_{3(s)} + 3C_{(s)} \xrightarrow{\text{high temp.}} 2Fe_{(s)} + 3CO_{(g)}$

Ferric oxide

(ii) $2ZnO_{(s)} + C_{(s)} \xrightarrow{\text{high temp.}} 2Zn_{(s)} + CO_{2(g)}$

Zinc oxide

(iii) $2PbO_{(s)} + C_{(s)} \xrightarrow{\text{high temp.}} 2Pb_{(s)} + CO_{2(g)}$

Lead oxide

(iv) $2CuO_{(s)} + C_{(s)} \xrightarrow{\text{high temp.}} 2Cu_{(s)} + CO_{2(g)}$

Copper oxide

(v) $Cu_2O_{(s)} + C_{(s)} \xrightarrow{\text{high temp.}} 2Cu_{(s)} + CO_{(g)}$

Cupperous oxide
or Copper (I) oxide

(vi) $H_2O_{(g)} + C_{(s)} \xrightarrow[1000^oC]{\text{high temp.}} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$

(vii) $CO_{2(g)} + C_{(s)} \xrightarrow{\text{high temp.}} 2CO_{(g)}$

4. Reactions With Strong Oxidizing Agents:

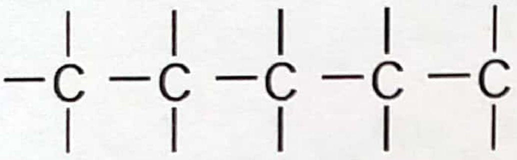
Carbon reacts with strong oxidizing agents like hot concentrated nitric acid (HNO_3) and conc. sulphuric acid (H_2SO_4) and gets oxidized on heating to liberate CO_2 gas.

(i) $C_{(s)} + 4HNO_{3(conc)} \xrightarrow{\text{hot}} CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$

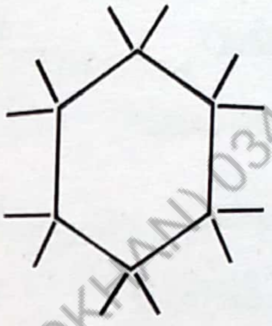
(ii) $C_{(s)} + 2H_2SO_{4(conc)} \xrightarrow{\text{hot}} CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$

Catenation:

Carbon is one of the basic building block of all living things. It is present in our food stuffs, fuels, fabrics, dyes, drugs as well as in house hold items. Catenation is one of the most unique properties of carbon which other elements do not possess. Catenation is the ability of the atoms of carbon to bond itself forming long chains and rings and also to form compounds containing chains and rings together. This property of carbon results in enormous range of compounds of carbon.



(Chain)



(Ring)

Uses of Carbon (Industrial Applications):

Diamonds are used as gems and precious stones because of their sparkling brilliance, especially when they are properly cut and polished. Black diamonds which are of inferior qualities are used in drillings, in the making of instruments for cutting glasses and metals. Its tiny fragments are used as abrasive for polishing tools.

Graphite is used as lubricant to reduce friction in machines, bicycle chains and bearings of some motors, because of high melting point, so graphite lined crucibles are used for making high grade steel and other alloys. It is good conductor of electricity and is used for making inert electrodes in dry cells and in industrial electrolytic processes such as in the extraction of Aluminium metal. Mixed with clay it is used in lead pencils. It is also used as black pigment in paints and as **neutron moderator** in nuclear reactions.

Coal and coke are important fuels and source of energy for homes and industries. In electric power generating stations. Coke is also powerful reducing agent and is used in the extraction of metals from their oxides, especially in the manufacture of iron and steel.

Charcoal is mainly used as a domestic fuel and also as an absorbant due to large number of pores in its open structure. The absorbing power of charcoal can be increased by heating it in super – heated steam. Charcoal when treated in this manner is known as **activated charcoal** which is used in gas masks for absorbing poisonous gases. Animal charcoal is used in decolourizing brown – colour sugar in sugar mills. It is also used for decolourization of petroleum jelly.

Carbon black (soot) consists of finely divided carbon. Carbon is used in manufacturing of rubber tyres as a filler to increase the strength and hardness of rubber. It is also used in black shoe polishes, printer's ink, type – writing papers, etc.

Carbon fibres are produced by carefully heating fibres of materials such as poly propenenitrite until they char to form carbon. Carbon fibres are incorporated into plastics to produce a very light but stiff and strong material.

12.4 SILICON

Introduction:

Silicon is standing midway between metals and non – metals and is a metalloid. It belongs to IV A group in the periodic table. It is the second member of the family just after carbon. Natural silicates and silica i.e. sand (SiO_2) have been known to be present on the earth since ancient times. However in 1823 Berzilius isolated silicon as an amorphous solid, named it silicon derived from the Latin name **Silex**, means silica i.e. sand. Silicon is the second most abundant element found in the earth's crust after oxygen. Clay and most of the rocky portion of the earth crust is composed of silica (SiO_2) and silicates. Over the last four decades, silicon has become exceedingly important in science and technology for making semi – conductors.

Occurrence:

Silicon does not occur in the free state, although silicon is widely distributed in nature. In the combined state it occurs mainly as silicon (iv) oxide; SiO_2 (Silica) which is present in various forms. Such as sand, quartz, flint, kieselguhr, agate, etc. The pure crystalline form is quartz and flint (a very hard stone), such as opal, amethyst and onyx (gem – stones) and in less pure forms as sand, kieselguhr, agate, etc.

In combination with metallic oxides, like Al_2O_3, CaO, MgO, K_2O etc., silicon occurs as complex silicates. The most widely distributed silicates are those of aluminium.

Some common natural silicates are given below with uses in the table.

S. No.	Name of Silicate	Formula	Uses
1.	Feldspar	$K_2O.Al_2O_3.6SiO_2$ or $KAlSi_3O_8$	Ceramics, glass, Pottery and abrasive
2.	Kaolin (China clay)	$Al_2O_3.SiO_2.2H_2O$ Hydrated	Crockery
3.	Mica	$K_2O.3Al_2O_3.6SiO_2.2H_2O$ or $KAl_3Si_3O_{10}$ Hydrated	Electrical insulator resistance to high temp.
4.	Talc (Soapstone)	$3MgO.4SiO_2.H_2O$ Hydrated	Ceramics
5.	Asbestos	$CaO.3MgO.4SiO_2$ or $Ca\ MgSi_4O_{12}$	Heat insulation, fire-proofing

There are more than 1000 silicates present in the earth's crust. Kaolin and china clay consist of hydrated aluminium silicates.

(1) Silicon is also prepared by heating a mixture of pure dry sand (SiO_2) and magnesium metal in a fire – clay crucible in the absence of air. The reaction is very violent and should be performed carefully.

$$\underset{\text{Sand}}{SiO_{2(s)}} + 2Mg_{(s)} \xrightarrow{\text{heat}} Si_{(s)} + 2MgO_{(s)}$$

Dilute hydrochloric acid is then added in the reaction mixture to dissolve unreacted Mg metal and MgO formed. The residue left behind contains amorphous silicon.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$

$$MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$

If unreacted SiO_2 is left, it can also be removed by dissolving it in hydro-fluoric acid (HF).

$$SiO_{2(s)} + 4HF \longrightarrow \underset{\text{silicon tetra fluoride}}{SiF_{4(aq)}} + 2H_2O$$

(2) When the vapours of $SiCl_4$ are passed over heated sodium or potassium metal in an inert atmosphere, silicon is produced by the reduction process.

(i) $SiCl_{4(g)} + 4Na_{(s)} \xrightarrow{\text{heat}} Si_{(s)} + 4NaCl_{(s)}$

(ii) $SiCl_{4(g)} + 4K_{(s)} \xrightarrow{\text{heat}} Si_{(s)} + 4KCl_{(s)}$

(3) Silicon is also prepared by heating SiO_2 with coke in an electric furnace. This is an industrial method.

$$SiO_{2(s)} + 2C_{(s)} \xrightarrow[\text{electric furnace}]{\text{heat}} \underset{\text{crystals}}{Si_{(s)}} + 2CO_{(g)}$$

Properties:

(1) Amorphous silicon is brown coloured hygroscopic powder, having specific gravity 2.35.

(2) Crystalline silicon is grey in colour, opaque lustrous and octahedral crystalline solid, with specific gravity 2.49.

(3) Silicon like carbon is a non – volatile solid with very high melting point and boiling point. Its melting point is about 1410°C and boiling point is 2600°C.

(4) It is hard enough to scratch glass. It is brittle in nature.

(5) It is insoluble in most of the common solvents like water but it dissolves in hydrofluoric acid (HF).

(6) It is poor conductor of electricity at room temperature but its conductivity increases with the increase in temperature. Due to this characteristics it acts as semi – conductor.

(7) Silicon dissolves in hot alkali solutions like NaOH to form its silicate with the evolution of H_2 gas.

$$Si + 2NaOH + H_2O \xrightarrow{\text{hot}} \underset{\text{sodium silicate}}{Na_2SiO_3} + 2H_{2(g)}$$

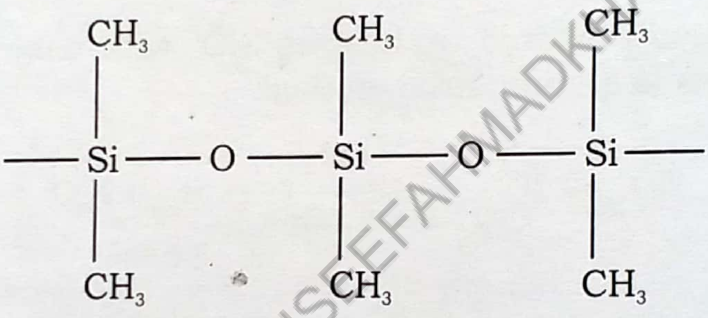
(8) When silicon is heated strongly in air, it forms silicon (iv) oxide i.e. silica (SiO_2).

$$Si_{(s)} + O_{2(g)} \xrightarrow{\text{strong heating}} SiO_{2(s)}$$

Uses:

Silicon is used in bronze and steel alloys to increase their tensile strength.

Very pure silicon is used in making semi – conductors which are of great importance in computers, transistors, solar cells and electronic industries. It is also used for making silicones which are rubber like liquids or solids that are insoluble in water and chemically unreactive. They are used as lubricants, water – repellent, electric insulators and are also used in paints, varnishes and polishes. The important silicone is methyl silicone which is a polymer.



(A unit of methyl silicon)

Silicone is also used in the preparation of refractory materials such as crucible, fire-bricks etc.

12.5 SILICA (SILICON (IV) OXIDE); SiO_2:

Silica occurs naturally in three main crystalline forms namely quartz, tridymite and crysto balite. The commonest of three is quartz.

Preparation:

(i) Silica is prepared by heating silicon in air or oxygen.

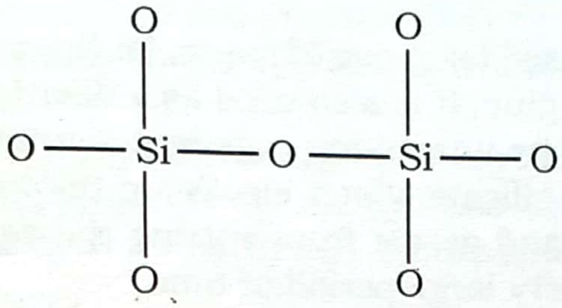
$$Si_{(s)} + O_{2(g)} \xrightarrow{\text{strongheating}} SiO_{2(s)}$$

It can also be prepared in hydrated form as a gelatinous precipitate by warming sodium silicate (Na_2SiO_3) with conc. HCl solution.

$$Na_2SiO_{3(aq)} + 2HCl_{(conc)} \xrightarrow{\text{warm}} \underset{\text{hydrated silica}}{SiO_2.H_2O} + 2NaCl_{(aq)}$$

Properties:

Silica (SiO_2) exists in a colourless crystaline form when pure. It is a macromolecular compound with silicon and oxygen atoms linked together covalently in tetrahedral basic units.



(SiO_2 with tetrahedral units)

Because of its structure, SiO_2 is non – volatile and hard. Its melting point is about 1500°C. When cooled, it forms glass – like solid, known as fused silica (also called quartz glass), which has very low coefficient of expansion and hence is heat – resistant and is frequently used in making laboratory apparatuses.

Uses:

1. Sand (SiO_2) is widely used in making mortar, cement, concrete, glass and refractory silica bricks.
2. Fused silica (quartz glass) is used in making optical lenses and prisms, heat – resisting articles, very fine threads of fused silica are used to suspend component parts in electrical instruments.
3. Large quartz crystals are used for lenses of optical instruments.
4. Powdered quartz is used in the making of silicon carbide (SiC), silicon tetra fluoride (SiF_4), sodium silicate (Na_2SiO_3) and silica bricks for lining furnaces.
5. Kieselguhr (SiO_2) absorbs liquids readily and is used as absorbent of nitroglycerine (explosive) in the making of dynamite. It is also used in medicines for making dry antiseptic dressings.

Sodium Silicate (Na_2SiO_3), Water Glass:

Preparation:

Sodium silicate is prepared by heating strongly two parts by mass of silica i.e. sand (SiO_2) with one part by mass of sodium carbonate (Na_2CO_3) until the mixture melts.

$$Na_2CO_{3(s)} + SiO_{2(s)} \xrightarrow{\text{strong heating}} Na_2SiO_{3(s)} + CO_{2(g)}\uparrow$$

It is obtained as colourless glass-like solid with melting point 1090°C.

Water Glass:

Sodium silicate dissolves in hot water under pressure to form a viscous liquid which is known as **water glass** because it looks like ordinary glass.

Uses:

Sodium silicate is used for sizing of paper, for fire-proofing of wood and textiles and for making glue. It is also used as a filler in saop industries.

Eggs are preserved by immersing eggs in a solution of water glass to form insoluble calcium silicate which blocks up the tiny pores in the egg shell and prevents air and germs from entring the eggs thus preserving eggs from spoiling for very large period of time.

A dilute solution of sodium silicate can be used for making chemical garden in the science fair by students.

Chemical Garden:

Make a dilute solution of water glass (Na_2SiO_3) in a glass trough. Add some crystals of coloured salts such as cobalt chloride, nickel sulphate, copper sulphate, ferric chloride etc. Leave them for few days without touching the trough. You will find your chemical garden grows with colourful plants of chemicals. This is because of the formation of insoluble metal silicates e.g.

$$Cu^{2+}SO^{2-}_{4(aq)} + Na^{+1}_{2}Si^{2-}O_{3(aq)} \longrightarrow \underset{\text{blue ppt}}{CuSiO_{3(s)}} + Na^{1+}_{2}SO^{2-}_{4\ (aq)}$$

Silica Jel:

When an acid is added in a solution of water glass. It turns into a jelly like substance known as jel. The formula for this jel is $SiO_2 \cdot nH_2O$. On complete dehydration of this gel by heating, a hard porous material is obtained known as **silica jel**.

Due to its large surface area, silica jel is used as good absorbent. It is used to absorb gases and vapours. Small bags of silica jel are kept in medicine packings to prevent the medicines being spoiled by water vapours in the atmosphere.

It is also used to recover valuable vapours from industrial effluents and in the refining of petrolium.

SUMMARY

1. Carbon and silicon are the first two members of IVA group elements in the periodic table. Both contain four electrons in their valence shells and normally form four covalent bonds when combine with other elements.
2. Carbon exists in three different physical crystalline forms i.e. allotropic forms, diamond, graphite and bucky balls.
   Carbon also occurs in nature in amorphous forms as coal, coke, lampblack etc.
3. Diamond and graphite differ in their structures i.e. in the arrangements of carbon atoms. Diamond is very hard and is bad conductor of electricity, while graphite is soft and greasy and is good conductor of electricity.
4. Diamonds are used as gem stones and for cutting glasses, metals and for drillings and grindings hard materials. Graphite is used as lubricants and for making electrodes. Coal, coke, charcoal etc are used as fuels for burning. In diamond each carbon atom is covalently linked with four other carbon atoms to give a basic tetrahedral unit which combine three dimensionally to give a cubic rigid structure of diamond.
   In graphite each carbon atom is covalently bonded with three other carbon atoms to form basic hexagonal ring layers. The layers are far apart from one another and are held by weak vander waal's forces of attractions. These layers slide over one another, so graphite is soft.
5. Silicon occurs abundantly in the earth's crust after oxygen. It is found as silica (SiO_2) and silicates. Most rocks, clays and soils are largely composed of these materials.
6. Silicon is obtained by reducing silica with carbon in electric furnace and also with magnesium metal. It is widely used for making semi conductors in transistors, computers, micro chips and similar electronic devices.
7. Water glass is sodium silicate (Na_2SiO_3) which is a useful compound and is used to get silica jel and in soap industries as filler.

EXERCISE

1. Fill in the blanks:
   - (i) Carbon contains ________ electrons in its valence shell and normally forms four ________ bonds with other elements.
   - (ii) Silicon is the second most ________ element in the earth's crust after ________.
   - (iii) The molecular formula of sand is ________.
   - (iv) The hardest natural substance known is ________.
   - (v) ________ is good conductor of electricity.
   - (vi) The formula of water glass is ________.

2. Point out the following statements true or flalse.
   - (i) Amorphous form of silicon is of grey colour.
   - (ii) Silicon is used in computers as semi- conductor.
   - (iii) The allotropes of carbon differ in their chemical properties.
   - (iv) Silica gel is used as absorbent.
   - (v) The driest and hardest type of coal which contains the highest energy value is anthracite.
   - (vi) Diamond is a good conductor of electricity.
   - (vii) Graphite is used in making lead pencils.

3. Choose the correct answer:
   - (i) Graphite bars are used in atomic reactors because graphite is:
     - (a) Soft solid. (b) Good conductor of electricity.
     - (c) More reactive than diamond
     - (d) Slows down the neutrons.
   - (ii) Diamond is used as abrasive because it is:
     - (a) Hard (b) Soft
     - (c) Cubic (d) Bad conductor of electricity.
   - (iii) Silicon is most abundently found in nature as,
     - (a) Silica (SiO_2) (b) Silicon carbide (SiC)
     - (c) sodium silicate (d) Calcium silicate
   - (iv) China clay is used in making of:
     - (a) Glass (b) Electrical insulator
     - (c) Ceramics (d) Crockeries
   - (v) Fused Silica which is also known as quartz glass is used for making;
     - (a) Concrete or cement (b) Silicon carbide
     - (c) Optical lenses and prisms (d) Absorbent

(vi) Melting point of sodium silicate is:

(a) $1100^{0}C$ (b) $1090^{0}C$

(c) $1410^{0}C$ (d) $990^{0}C$

4. (a) What is catenation? Give chief uses of carbon.

(b) Define allotropy. Discuss chief allotropic forms of carbon.

(c) What happens when the following are heated with coke. Give reactions.

(i) Sulphur (ii) Aluminium (Al) (iii) Zinc oxide (ZnO)

(iv) Water as steam (H_2O) (v) Conc. Nitric acid (HNO_3)

5. (a) Explain with reasons why graphite is a good conductor of electricity while diamond is not, although both are the true allotropes of carbon.

(b) Discuss the structures of diamond and graphite.

(c) Compare the general properties of graphite and diamond and mention two uses of each graphite and diamond.

6. (b) Write short notes on the preparations and uses of the following:

(i) Charcoal (ii) Silicon

(iii) Water glass (iv) Silica jel.

7. (a) How does silicon occurs in nature?

(b) What are silicates? Describe some common silicates and their chemical formulas and uses.

(c) Give any four physical properties of silicon.

CHAPTER-13

NITROGEN AND OXYGEN

You will learn in this chapter about:

- Nitrogen, its occurrence and preparation.
- Oxygen,its occurrence and preparation.
- Physical and chemical properties of nitrogen and oxygen.
- Oxides and their classification,normal oxides,peroxides,superoxides and suboxides.
- Hydrogen peroxides, its preparation,properties and uses.
- Oxidation,reduction reactions,oxidizing and reducing agents.
- Ozone,its preparations,properties and uses.
- Ammonia its industrial preparation by Haber's process, properties, uses and ammonia fountain.
- Nitric acid and its industrial preparation from NH_3 by Ostwald's method, properties and uses.
- Aqua regia and its importance as solvent.

INTRODUCTION

1. Nitrogen:

Nitrogen was discovered in 1772 by a Scotish Botanist, Daniel Rutherford. However Chaptal later named the gas **nitrogen** because it was found in nitre (Potassium nitrate KNO_3). It does not sustain combustion or life.

Nitrogen is the most common gas present in the atmosphere and the tenth most abundant element in the earth's crust. Like carbon, nitrogen is one of the major building blocks of living things.

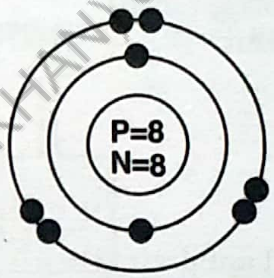
Nitrogen belongs to VA group in the periodic table and is the first member of the family, containing five electrons in its valence shell with electronic configuration given as.

$$N=7=K^2, L^5$$

Occurrence:- Nitrogen occurs in the free state as N_2 gas in air up to 78% by volume and 75% by mass of the earth's atmosphere. Free nitrogen in air is important because it dilutes the oxygen to the point where combustion, respiration and oxidation processes are reasonably slow. In the combined state nitrogen occurs abundantly in the earth's crust as nitrates of sodium, calcium and potassium as well as ammonium salts such as ammonium sulphate, $(NH_4)_2SO_4$.In combined state nitrogen is also found in organic matter such as proteins, urea and vitamin B compounds. Thus the appropriate nitrogen compounds must be present in animal diets and plants fertilizers for the growth, repair and maintenance. Proteins occupy an essential place in the structure of all living things.

2- Oxygen:

Oxygen was discovered independently by Scheel in1772 and Priestley in 1774. However Lavoiser was the first to describe the major properties of the newly discovered gas. He arrived at the conclusion that burning is a chemical reaction between the combustible substance and oxygen gas. He gave the Greek name **Oxygen** to the gas which means acid producer because all acids contained oxygen as major constituent. It is the most essential substance for all living things.Oxygen belongs to VIA group of the periodic table. It is the first member of this family. It contains 6 electrons in its valence shell with electronic configuration given below:



$$O = 8 = K^2, L^6$$

Occurrence:

Oxygen is the most abundant element on earth. It occurs in nature both in the free state as well as in combined state. In the free state oxygen is present as diatomic gas (O_2) in the earth's atmospheric air upto 21% by volume and about 33% by mass as dissolved air in water. In the combined state, oxygen accounts for nearly 50% by mass of the earth's crust, the oceans and the air. It constitutes about 88.8% by mass of water (H_2O) present on the earth's surface, which is the most abundant compound on earth. It is present in silica (SiO_2), silicates, carbonates and oxides of both metals and non-metals, which make up rocks, clays and sand. Even the human body is made up of about two thirds by mass of oxygen in the combined states.

13.1 PREPARATION OF NITROGEN

13.1(a) From Air:

The only important commercial method of producing nitrogen gas is the fractional distillation of liquid air. In this process air is first liquefied to form liquid air, which is then fractionally distilled. Air liquified by successive compression and expansion.

Fractional Distillation of Liquid Air:

Clean air is compressed and then cooled by refrigeration, upon expanding the air, the air further cools and liquefies. The liquid air is filtered to remove carbon dioxide solid and then distilled fig 13.1. Nitrogen is the most volatile component, with boiling point-196^{0}C, distill over. Argon which boils at-185.7^{0}C, is removed from the middle of the column and liquid oxygen, the least volatile component with boiling point-183^{0}C collects at the bottom of the column.

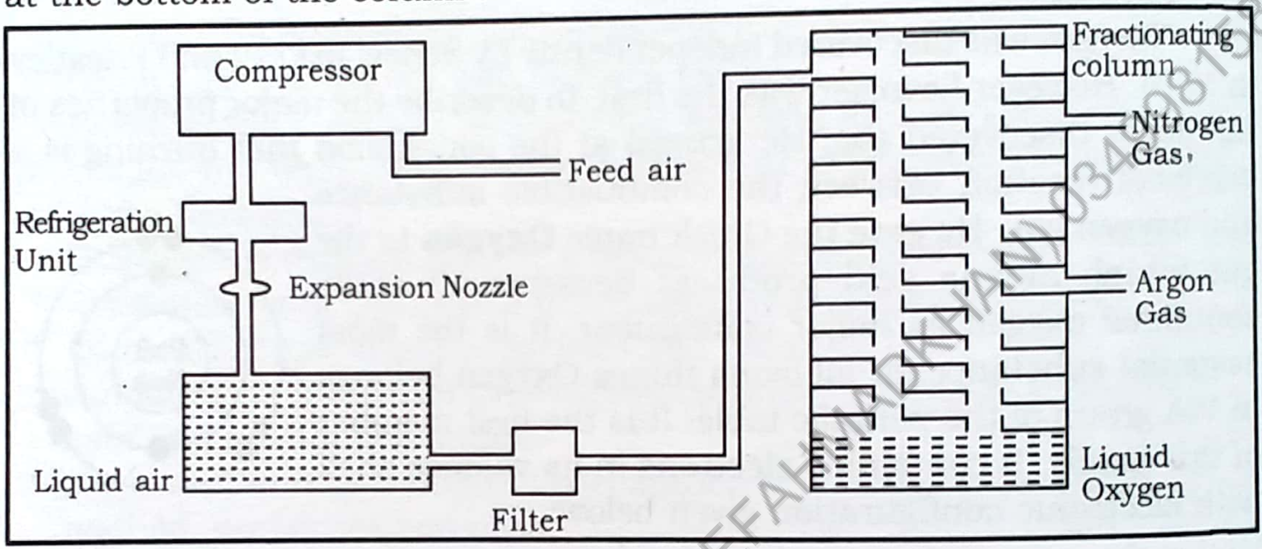


Fig. 13.1 Liquefication of air and fractional distillation of liquid air

13.1(b) In Laboratory:

Pure nitrogen in the laboratory is prepared by heating ammonium nitrite which thermally decomposes to give nitrogen gas. Ammonium nitrite is first obtained by reacting ammonium chloride with sodium nitrite.

(a) Formation of ammonium nitrite

$$NH_4Cl_{(s)} + NaNO_{2(s)} \longrightarrow NH_4NO_{2(s)} + NaCl_{(s)}$$

(b) Preparation of N_2

$$\underset{\text{Ammonium nitrite}}{NH_4NO_{2(s)}} \xrightarrow{\text{heat}} N_{2(g)} + 2H_2O_{(l)}$$

Physical Properties:

1- Nitrogen is a colourless, odourless and tasteless gas.
2- Pure nitrogen is slightly soluble in water. Two volumes of the gas dissolves in 100 volumes of water at room temperature.
3- It is slightly lighter than air.
4- Its boiling point is -196^{0}C, while melting point is -210^{0}C.

Molecular nitrogen (N_2) is unreactive because of strong triple bond between two nitrogen atoms ($N{\equiv}N$). The bond enthalpy i.e. the bond dissociation energy of N_2 is about 941 KJ/mol which is very high. When substances normally burn in air, they combine with oxygen only, although air contains 78% nitrogen by volume. However at very high temperatures and pressures, nitrogen combines directly with hydrogen, oxygen and metals like magnesium to form compounds.

(a) With hydrogen:

$$N_{2(g)} + 3H_{2(g)} \underset{\text{Catalyst}}{\overset{450°C/200\text{-}250\text{ atm}}{\rightleftharpoons}} 2NH_{3(g)}$$

(b) With oxygen: Nitrogen combines with oxygen at about 2000°C to from nitric oxide (NO).

$$N_{2(g)} + O_{2(g)} \xrightarrow{2000^0C} 2NO_{(g)}$$

(c) With magnesium: Nitrogen combines with magnesium directly on heating to red hot to form magnesium nitride.

$$3Mg_{(s)} + N_{2(g)} \xrightarrow{\text{redhot}} Mg_3N_{2(s)}$$

Isolation of Oxygen:

Oxygen is isolated by the fractional distillation of liquid air just like nitrogen, as we know oxygen forms 21% by volume of air.

(1) From Air:

The isolation of oxygen from air involves two steps, namely (i) Liquefication of air and (ii) Fractional distillation of liquid air.

(i) Liquefication of Air:

Air in the gaseous form is first passed through caustic soda to remove CO_2 present in air. It is then compressed, under very high pressure about 200 atmosphere in the compressor, then cooled and allowed to expand rapidly through a nozzle. The sudden expansion of air into a region of lower pressure causes the air to cool even further. The process of compression and expansion are repeated over and over again due to which temperature falls upto-200°C at which air liquefies.

(ii) Fractional Distillation of Liquid Air:

The liquid air is then led to a fractionating column through a filter in order to remove the traces of CO_2 solid if left behind. On distillation nitrogen with lower boiling point of -196°C, evolves first leaving behind a liquid very rich in oxygen. Further heating turns liquid argon into gas which boils out at -185.7°C and passes off from the middle of the column and liquid oxygen, the least volatile component in the air turns into oxygen gas at -183°C. Oxygen gas is dried, compressed and stored in steel cylinders under a pressure about 100 atmosphere.

(2) In Laboratory:

Oxygen can be prepared in the laboratory by heating potassium chlorate mixed with little mangnese dioxide, MnO_2 which acts as a catalyst, the decomposition reaction takes place at lower temperature and at much faster rate.

$$2KClO_{3(s)} \xrightarrow{\text{heat/MnO}_2} 2KCl_{(s)} + 3O_{2(g)}$$

Physical Properties:

1- Oxygen (O_2) is a colourless, odourless and tasteless gas.
2- It is neutral to moist litmus paper.
3- It is slightly soluble in water only about 2% by volume at room temperature. However this solubility is of vital importance for the existence of aquatic life.
4- Gaseous oxygen is about 1.1 times denser than air.
5- It liquefies at -183°C and solidifies at -225°C.

Oxygen reacts with metals, non-metals and other compounds directly.

(i) $2Ca_{(s)} + O_{2(g)} \xrightarrow{\text{heat}} 2CaO_{(s)}$

(ii) $4Li_{(s)} + O_{2(g)} \xrightarrow{\text{heat}} 2Li_2O_{(s)}$

(Lithium oxide)

(iii) $S_{(s)} + O_{2(g)} \xrightarrow{\text{ignition}} SO_{2(g)}$

(iv) $C_{(s)} + O_{2(g)} \xrightarrow{\text{ignition}} CO_{2(g)}$

(v) $CH_{4(g)} + 2O_{2(g)} \xrightarrow{\text{combustion}} CO_{2(g)} + 2H_2O_{(g)}$

(vi) $2H_2S_{(g)} + 3O_{2(g)} \xrightarrow{\text{combustion}} 2SO_{2(g)} + 2H_2O_{(g)}$

(vii) $4FeS_{(s)} + 7O_{2(g)} \xrightarrow{\text{heat}} 2Fe_2O_{3(s)} + 4SO_{2(g)}$

13.2 OXIDES

Oxygen is chemically very reactive it combines readily with all other elements except noble gases and halogens to form its binary compounds. The binary compounds of oxygen with metals and non metals are called as oxides.
Example CaO, Fe_2O_3, CO_2, H_2O, etc.

Classification of Oxides:

On the basis of valence number or oxidation state of oxygen, oxides are classified into several groups, namely normal oxides, peroxides, super oxides and sub oxides.

(1) Normal Oxides:

Normal oxides are those oxides in which oxygen shows normal oxidation state or valence number -2.

Normal oxides are further classified into four types on the basis of their chemical characteristics.

(a) Basic oxides. (b) Acidic oxides.
(c) Amphoteric oxides and. (d) Neutral oxides.

(a) Basic Oxides:

The normal oxides of metals are the examples of basic oxides
For example:

$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$
$$2Pb_{(s)} + O_{2(g)} \longrightarrow PbO_{(s)}$$
$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)} \quad \text{etc}$$

Most of these oxides are soluble in water and produce their hydroxides and turn red litmus blue.

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$
$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$$

They also react with acids to form salts and water.

$$MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$
$$CaO_{(s)} + 2HNO_{3(aq)} \longrightarrow Ca\,(NO_3)_{2(aq)} + H_2O_{(l)}$$

(b) Acidic Oxides:

The normal oxides of non-metals are generally acidic.

For example:

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$
$$N_{2(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)} \text{ etc.}$$

These oxides react with water to form acids which turn blue litmus red.

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow \underset{\text{sulphurous acid}}{H_2SO_{3(aq)}}$$
$$CO_{2(g)} + H_2O_{(l)} \longrightarrow \underset{\text{carbonic acid}}{H_2CO_{3(aq)}}$$
$$N_2O_5 + H_2O_{(l)} \longrightarrow \underset{\text{nitric acid}}{2HNO_{3(aq)}}$$

Acidic oxides of non-metals react with alkalies to form salts and water.

$$CO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$
$$SO_{3(g)} + 2KOH_{(aq)}. \longrightarrow K_2SO_{4(aq)} + H_2O_{(l)}$$

(c) Amphoteric Oxides:

Oxygen with less electro positive metals just like aluminium, zinc, tin etc. form oxides that possess dual characteristics i.e acidic as well as basic. These oxides are known as amphoteric oxides.

For example:

$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$$
$$2Zn_{(s)} + O_{2(g)} \longrightarrow 2ZnO_{(s)}$$

Amphoteric oxides can react with acids and alkalies to form salts and water.

(i) With Acids: Amphoteric oxides react with acids, behaving just like bases to form salts and water.

$$Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$
$$ZnO_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + H_2O_{(l)}$$

(ii) With Bases: Amphoteric oxides react with alkalies behaving just like acids to form salts and water.

$$Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{Sod aluminate}}{2NaAlO_{2(aq)}} + H_2O_{(l)}$$

$$ZnO_{(s)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{sod zincate}}{Na_2ZnO_{2(aq)}} + H_2O_{(l)}$$

(d) Neutral Oxides:

Neutral oxides are neither acidic nor basic. They are neutral to litmus in aqueous solutions, for example, oxide of hydrogen i.e. water (H_2O), nitric oxide (NO), carbon monoxide (CO) and nitrous oxide (N_2O).

(2) Peroxides:

Peroxides are oxides containing higher proportion of oxygen as compared to normal oxides. In these oxides, oxygen has an oxidation state or valence number-1. They contain peroxide ion $(O\text{-}O)^{2-}$ and examples are sodium peroxide (Na_2O_2), barium peroxide (BaO_2) and also hydrogen peroxide (H_2O_2). They produce hydrogen peroxide with acids.

$$Na_2O_{2(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{2(aq)}$$

(3) Super oxides:

The elements of IA group potassium, rubidium and caesium form super oxides. These contain more oxygen than peroxides. In these oxides, oxygen has an oxidation state or valence number -0.5 or $-\frac{1}{2}$. They do not produce hydrogen peroxide with acids, rather they show the tendency to release oxygen (O_2) on heating and are powerful oxidizing agents.

For example: Potassium super oxide (KO_2) rubidium superoxide (RbO_2) and caesium superoxide (CsO_2).

(4) Suboxides: suboxides have less quantity of oxygen than the normal oxides. They are unstable. Very few suboxides are known.

For example: Carbon suboxide (C_3O_2)

HYDROGEN PEROXIDE (H_2O_2)

Introduction:

Oxygen can combine with hydrogen to form two major hydrides, H_2O (Water) and H_2O_2 (hydrogen peroxide). The most common one is water. Thenard was the first to prepare hydrogen peroxide by the action of dilute sulphuric acid on barium peroxide (BaO_2). He discovered that hydrogen peroxide contained one more oxygen atom in its molecule than water (H_2O) and thus called it as **Oxygenated water**.

PREPARATION

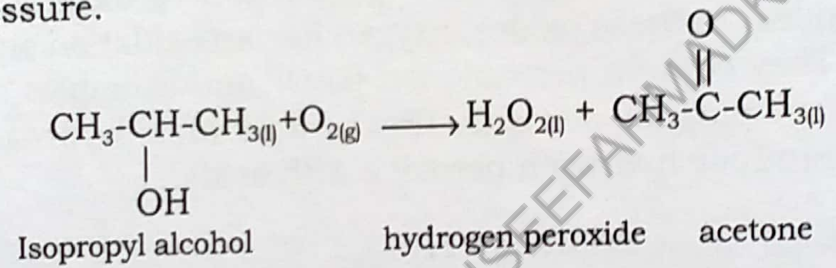
(1) Laboratory Method:

Hydrogen peroxide is usually prepared in the laboratory by the action of dilute sulphuric acid on the peroxides of certain metals, especially on barium peroxide (BaO_2). Barium sulphate is insoluble and can be easily removed by filtration and pure H_2O_2 is obtained.

$$H_2SO_{4(aq)} + BaO_{2(s)} \longrightarrow BaSO_{4(s)} + H_2O_{2(aq)}$$

(2) Industrial Preparation:

Hydrogen peroxide on large scale is usually manufactured by the oxidation of isopropyl alcohol. (i.e. Propan-2-ol) with oxygen under reduced pressure.



$$\underset{\text{Isopropyl alcohol}}{CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_{3(l)}} + O_{2(g)} \longrightarrow \underset{\text{hydrogen peroxide}}{H_2O_{2(l)}} + \underset{\text{acetone}}{CH_3\text{-}\overset{\displaystyle O}{\overset{||}{C}}\text{-}CH_{3(l)}}$$

The solution of hydrogen peroxide obtained can be concentrated by redistillation under reduced pressure. Hydrogen peroxide is easily decomposed by light so it should be stored either in smooth dark glass bottles or in smooth aluminium containers.

Physical Properties:

1. Pure hydrogen peroxide is a pale blue syrupy liquid.
2. It mixes with water to give solution which is slightly acidic.
3. Its boiling point is 150°C but it boils with decomposition. It freezes at about -0.9°C.

Chemical Properties:

(1) When hydrogen peroxide is exposed to air, it decomposes to form water and oxygen. The decomposition is exothermic.

$$2H_2O_{2(l)} \xrightarrow{\text{exposure}} 2H_2O_{(l)} + O_{2(g)} + \text{heat}$$

In the presence of manganese dioxide (MnO_2) as catalyst, this decomposition increases. However in the presence of glycerine the rate of decomposition is retarded i.e. slowed down.

(2) (a) As Oxidizing Agent:

Hydrogen peroxide is a common oxidizing agent, usually in the form of aqueous solution with 3% H_2O_2. The advantage of H_2O_2 over other oxidizing agents is that in most of its reactions, it is converted into water (H_2O).

Hydrogen peroxide is a strong oxidizing agent because it can readily donate oxygen or accept electrons.

(i) $H_2O_{2(l)} \longrightarrow H_2O_{(l)} + \underset{\text{atomic oxygen}}{O}$ (donation of oxygen)

(ii) $H_2O_{2(l)} + 2H^+ + 2e^- \longrightarrow 2H_2O_{(l)}$ (acceptor of electron)

Some of the examples of H_2O_2 as oxidizing agent are given below:

(i) $2KI_{(aq)} + H_2O_2 + H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} + 2H_2O + I_{2(aq)}$.

(ii) If H_2S gas is bubbled through H_2O_2 solution, yellow precipitate of sulphur are obtained by the oxidation of H_2S.

$$H_2S_{(g)} + H_2O_{2(aq)} \longrightarrow \underset{\text{yellow ppt}}{S_{(s)}} + 2H_2O_{(l)}$$

(b) As Reducing Agent:

Hydrogen peroxide in the form of aqueous solution with 3% H_2O_2 can also behave as a reducing agent. When it reacts with more, powerful oxidizing agents, it is converted into gaseous oxygen. In these reactions H_2O_2 gains electrons or donates oxygen.

e.g. Hydrogen peroxide reduces acidic potassium permanganate solution, decolourizing the colour of $KMnO_4$.

$$2KMnO_{4(aq)} + 3H_2SO_{4(aq)} + 5H_2O_{2(aq)} \longrightarrow K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$$

Similarly it reduces chlorine to hydrochloric acid and O_2 gas is given off.

$$\underset{\text{Oxidizing agent}}{Cl_2} + \underset{\text{Reducing agent}}{H_2O_{2(aq)}} \longrightarrow 2HCl_{(aq)} + O_{2(g)}$$

Uses:

(1) **As antiseptic:** Hydrogen peroxide is used as a mild antiseptic in mouth wash as well as for cleaning wounds.

(2) **As bleaching agent:** Hydrogen peroxide is used as bleaching agent in bleaching delicate materials like silk, wool, feathers and human hairs which are usually damaged by other bleaching agents like chlorine, sulphur dioxide etc. It removes unwanted colour from fabrics, hair or other materials.

(3) **Restoring Paintings:** Liquid H_2O_2 is used for restoring paintings. Lead paints containing lead carbonate ($PbCO_3$) when exposed to atmosphere blacken due to exposure to atmospheric H_2S, $PbCO_3$ is converted into lead sulphide, (PbS). The treatment with H_2O_2 oxidizes lead sulphide into $PbSO_4$, thus the white colour is restored.

(4) **As fuel component:** Liquid H_2O_2 is used for providing oxygen for burning fuel in space rockets. It is also used for burning diesel oil in engines of submerged submarines which can not use air.

(5) **Other uses:** It is used in the preparation of compounds like sodium chlorate (III): $NaClO_2$ and some organic peroxides which are used for initiating polymerization reactions.

13.3 OXIDATION AND REDUCTION

Introduction:

Have you ever noticed corrosion at the terminal of an automobile battery or rusting of an iron piece? We call corrosion or rusting of a metal into a metal compound by a reaction between metal and some substance in its environment. The most common corrosion reactions involve oxygen, water, acids or salts as reactants and the processes involved are oxidation reduction reactions.

Oxidation reduction reactions involve two opposing but complementary processes. These processes can never occur singly, that is every oxidation must necessarily be accompanied by its opposing process reduction and vice versa. Due to this reason oxidation reduction reactions which now usually abbreviated as **Redox reactions**. Before coming to redox reactions, the terms involved oxidation, reduction, oxidizing agent and reducing agent must be clearly defined.

(1) **Oxidation:** Oxidation can be defined in a number of ways as:

(a) **Oxidation as addition of oxygen:**

Oxidation is defined as a reaction in which oxygen combines with other elements or substances to produce oxides. The rusting of iron, burning of magnesium, carbon etc. in air. Thus addition of oxygen is oxidation.

Examples:

(i) $$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$
Ferric oxide

(ii) $$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$
Magnesium oxide

(iii) $$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$
Carbon dioxide

(iv) $$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$
Nitirogen peroxide or nitrogen dioxide

(b) Oxidation as removal of hydrogen:

Oxidation is also the process in which the removal of hydrogen occurs from a compound.

Example:

(i) $H_2S_{(g)} + Cl_{2(g)} \longrightarrow S_{(s)} + 2HCl$

(ii) $MnO_{2(s)} + 4HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$

Oxidation as removal or loss of electrons:

Oxidation is also defined as the process or a reaction which occurs by the loss or removal electrons. This definition gives a broader view of oxidation.

Example:

(i) $Sn_{(s)} \longrightarrow Sn^{2+} + 2e^-$

(ii) $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

(iii) $Al_{(s)} \longrightarrow Al^{3+} + 3e^-$

(2) Reduction:

Reduction is the process or a reaction, just opposite to oxidation. Reduction is defined as a chemical process which involves:

(a) Removal of oxygen from a substance.
(b) Addition of hydrogen.
(c) Gain of electrons by a substance.

(a) Removal of oxygen from a substance:

Reduction means the removal of oxygen from substances

For example:

$$CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(l)}$$

In this case the donor of oxygen i.e CuO is oxidizing agent while the acceptor of oxygen (H_2) is reducing agent. CuO is reduced to Cu while H_2 is oxidized to H_2O.

(b) Addition of H_2 (hydrogen):

Reduction also means addition of hydrogen in a substance.

For example:

$$H_2S_{(g)} + Cl_{2(g)} \longrightarrow S_{(s)} + 2HCl$$

reduction

In this reaction Cl_2 adds hydrogen to form HCl, is the reduction process. Cl_2 is oxidizing agent because it removes hydrogen from H_2S while H_2S is reducing agent because it supplies hydrogen. H_2S is oxidized in the process and Cl_2 is reduced.

(c) Gain of electrons:

The process or a reaction in which a substance gains electrons is called reduction. The substance that gains electrons is reduced, but it acts as oxidizing agent.

For example:

(i) $Al^{3+} + 3e^- \longrightarrow Al_{(s)}$

(ii) $2H^+ + 2e^- \longrightarrow H_{2(g)}$

When Zn metal reacts with aqueous solution of H_2SO_4 to form Zn^{2+} ions and H_2 gas.

$$H_2SO_{4(aq)} \rightleftharpoons 2H^+ + SO_4^{2-}$$

$Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$ (oxidation): reducing agent

$2H^+_{(ag)} + 2e^- \longrightarrow H_{2(g)}$ (reduction): oxidizing agent

$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$ (reduction-oxidation reaction) or Net reaction

The most concise definitions of reduction, oxidation reactions is in terms of the electron transfers.

Definition:

Oxidation is defined as the reaction or process that takes place by the loss of electrons and reduction is defined as the reaction or process that takes place by the gain of electrons.

Oxidizing and Reducing Agents:

In oxidation-reduction reactions, the substance which is oxidized because it causes other substance to be reduced and is called as reducing agent. Similarly the substance which itself is reduced and causes the other substance to oxidize is called as oxidizing agent.

Definition (Oxidizing And Reducing Agents):

A substance which accepts or gain electrons is defined as an oxidizing agent and itself gets reduced. Whereas a substance that loses or donates electrons is defined as reducing agent and itself gets oxidized.

For example:

Let us see the following reactions.

(1) $4NH_{3(g)} + 6NO_{(g)} \longrightarrow 5N_{2(g)} + 6H_2O_{(l)}$

In this reaction NH_3 oxidizes to N_2 (oxidation, loss of hydrogen) so it is a reducing agent (NH_3).

NO reduces to N_2 (Reduction, loss of oxygen)

So NO is oxidizing agent.

(2) $H_2S_{(g)} + Cl_{2(g)} \longrightarrow S_{(s)} + 2HCl$

In this reaction H_2S oxidizes to S (Oxidation, loss of hydrogen)

So H_2S is reducing agent.

Cl_2 reduces to 2HCl (reduction, gain of hydrogen)

So Cl_2 is oxidizing agent.

In terms of loss and gain of electrons, it can be described as,

$H_2S \rightleftharpoons 2H^+ + S^{2-}$ and $HCl \rightleftharpoons H^+ + Cl^-$

$S^{2-} \longrightarrow S_{(s)} + 2e^-$ (reducing agent)

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ (oxidizing agent)

13.4 OZONE

Introduction:

Ozone is a pale-blue poisonous gas with a sharp, irritating odour. It is an allotropic form of oxygen with molecular formula O_3. Ozone was first discovered by Schonbein in 1839. However in 1886 J. Soret demonstrated that Ozone (O_3) was actually an allotrope of oxygen (O_2).

Occurrence:

In nature ozone is formed from atmospheric oxygen by lightening flashes, however ozone is very unstable dissociates readily forming reactive oxygen atom.

$$O_{3(g)} \longrightarrow O_{2(g)} + \underset{\text{atomic oxygen}}{O_{(g)}} \quad , \quad \Delta H = -107\,KJ/mol.$$

Ozone exists in a layer at a height of about 20 kilometers above the earth where it is believed to protect the earth's surface from too much ultra violet radiation of the sun. Very small amount of ozone is produced around electrical machinaries when they are in operations.

Preparation:

Ozone can be prepared from oxygen by passing electric discharge through oxygen gas. It is necessary to use silent discharge because sparking would generate heat energy which decomposes ozone produced.

The apparatus used for converting oxygen into ozone is known as **Ozonizer.**

$$\underset{\text{Oxygen}}{3O_{2(g)}} \xrightarrow{\text{electric discharge}} \underset{\text{Ozone}}{2O_{3(g)}}$$

Physical Properties:

1- Ozone is a pale-blue gas at ordinary condition.
2- Ozone has characteristic smell which is sharp irritating like Cl_2 gas.
3- Ozone is very poisonous gas at concentration 100 parts per million (ppm). Exposure to 0.1 to 1 ppm in air produces headache, burning of eyes and irritation to the respiratory passages.
4- Pure ozone can be obtained as blue liquid by cooling ozonized oxygen to -112°C.
5- It is only slightly soluble in water but dissolves in turpentine oil readily.

Chemical properties

Ozone is chemically more reactive than ordinary diatomic oxygen (O_2). It acts as powerful oxidizing agent because O_3 dissociates readily forming reactive oxygen atoms.

$$O_{3(g)} \longrightarrow O_{2(g)} + \underset{\text{atomic oxygen}}{O_{(g)}} \quad ; \quad \Delta H = -107\ \text{KJ/mol.}$$

Ozone oxidizes lead sulphide (PbS), hydrogen sulphide, sulphur dioxide and potassium Iodide in acidic medium liberating oxygen (O_2) gas.

(i) With PbS

$$PbS_{(s)} + 4O_{3(g)} \longrightarrow \underset{\text{lead sulphate}}{PbSO_{4(s)}} + 4O_{2(g)}$$

(ii) With H_2S

$$H_2S_{(g)} + 2O_{3(g)} \longrightarrow \underset{\text{sulphuric acid}}{H_2SO_{4(aq)}} + O_{2(g)}$$

(iii) With SO_2

$$SO_{2(g)} + O_{3(g)} \longrightarrow \underset{\text{sulphur trioxide}}{SO_{3(g)}} + O_{2(g)}$$

(iv) With KI

$$2KI_{(aq)} + O_{3(g)} + H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} + I_{2(aq)} + H_2O_{(l)} + O_{2(g)}$$

ionic form

Uses:

Presently the uses of ozone as an industrial chemical is relatively limited.

(1) Ozone is sometimes used in treatment of domestic water in place of chlorine. Like chlorine it kills bacteria and oxidizes organic compound present in water.

(2) It is used as bleaching agent because all oxidizing agents are also good bleaching agents.

(3) It is largely used in the preparation of pharmaceuticals, synthetic lubricants and other commercially useful organic compounds.

Ozone is an important component of the upper atmosphere, where it serves to screen out the ultra-violet radiations of the sun. In this way ozone protects the earth from the harmful effects of high energy rays. For this reason, depletion of ozone layer is a major scientific concern, now-a-days. But in the lower atmosphere ozone is considered as air pollutant because of its oxidizing power, it causes damage to living systems.

13.5 COMPOUNDS OF NITROGEN (AMMONIA AND NITRIC ACID)

(1) Ammonia (NH_3):

Ammonia is a very important chemical in industry. In nature ammonia is produced during the decay of nitrogenous matter in the absence of air. As a result small traces of ammonia may be present in the air. Due to great solubility in water, it rapidly dissolves in rain water and finds way into the soil where it is converted into the different compounds.

Preparations:

(1) In the laboratory ammonia is prepared by heating ammonium salts usually ammonium chloride (NH_4Cl) with slaked lime i.e. calcium hydroxide.

Reaction:

$$2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \xrightarrow{\text{heat}} CaCl_{2(s)} + 2H_2O_{(l)} + \underset{\text{ammonia}}{2NH_{3(g)}}$$

Slacked lime is chosen because it is cheep and is not deliquescent like NaOH. Note that both the reactants are solids, so they should be thoroughly grinded in order to provide the maximum surface area for the reaction.

(2) Industrial Preparation:

Haber-Bosch process:

On large scale, ammonia was manufactured by the direct combination of nitrogen and hydrogen from Haber-Bosch process. Firtz Haber in 1908 worked out the reaction conditions for the combination of N_2 and H_2 to make ammonia and Carl Bosch did the necessary engineering work required in the process and transferred Haber's laboratory studies into commercial manufacturing process of ammonia. For this work Haber won the noble prize in chemistry in 1918.

In this process a mixture of pure nitrogen and hydrogen in the ratio 1:3 by volumes is allowed to react. The basic problem in ammonia synthesis is that it is a reversible reaction and can be described as:

$$N_{2(g)} + 3H_{2(g)} \underset{Fe_2O_3.Al_2O_3.K_2O}{\overset{400\text{-}450^0C/200\text{-}250\ atm}{\rightleftharpoons}} 2NH_{3(g)}\ ;\ \Delta H= -92\ KJ/mol.$$

To get maximum yield of ammonia, the optimum condition of temperature should be 400-450°C, that of pressure should be 200-250 atmosphere and the appropriate catalyst Fe_2O_3 (Ferric oxide) with small amount of Al_2O_3, CaO, K_2O are required. Ammonia thus obtained is liquefied by cooling, the unused gases are recirculated over catalyst for further formation of ammonia. Millions of tons of ammonia are prepared annually by this method fig 13.2 describes, the industrial preparation of ammonia by Haber's process.

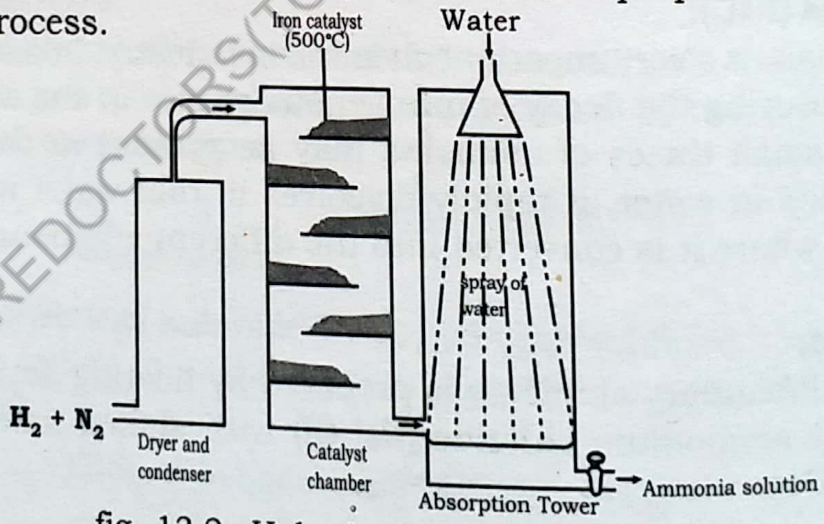


fig. 13.2 Haber's process for ammonia

Activity: (Ammonia Fountain)

For the formation of ammonia fountain, fill the flask with gaseous ammonia and then invert the flask to make its long tube dipped into the beaker of water containing few drops of phenolphethalein. Add water into the flask from the rubber bang. Ammonia is highly soluble in water creates vacuum in the flask causing water in the beaker to go up by the suction.

A fountain of pink colour is created because phenolphethalein turns pink in basic ammonia solution. You can place this fountain in science fare.

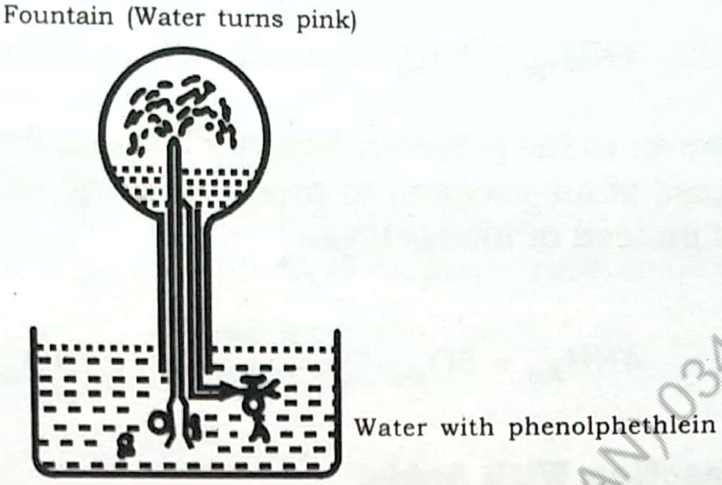


Fig. 13.3 Fountain experiment

Physical Properties:

1- Ammonia is a colourless gas with a characteristic pungent smell.
2- In large quantity, ammonia is poisonous because of its effect on respiratory system.
3- It is highly soluble in water about 1300ml dissolves in 1ml of water at 0^{0}c. Its solution is alkaline as it turns red litmus blue.
4- Ammonia is easily liquefied into a colourless liquid at ordinary temperature by compression.
5- A concentrated solution of ammonia, commonly known as 880 ammonia and has a density about 0.880g/cm^3 and contains 35% by mass of ammonia.

Chemical Properties:

(1) Reaction with water: Ammonia is very soluble in water and reacts with water to form, ammonium hydroxide.

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_4\,OH_{(aq)}$$

Due to the ionization of NH_4OH, hydroxide (OH^-) ions are produced in water, therefore it gives alkaline solution.

On warming aqueous ammonia solution, ammonia (NH_3) gas is liberated. Thus ammonia gas can easily be collected by warming ammonia solution in water (NH_4OH).

(2) Reaction With Oxygen:

Ammonia does not burn in air but it burns readily in oxygen with greenish yellow flame to form nitrogen gas and water vapours.

$$4NH_{3(g)} + 3O_{2(g)} \xrightarrow{\text{ignition}} 2N_{2(g)} + 6H_2O_{(g)}$$

However in the presence heated Platinum (Pt) catalyst ammonia reacts with excess of air (oxygen) to produce nitric oxide i.e. Nitrogen (II) oxide (NO) gas instead of nitrogen gas.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow[600^0C]{\text{Pt Catalyst}} 4NO_{(g)} + 6H_2O_{(g)}$$

(3) Reaction With Acids:

Since ammonia is a base, so it reacts, with acids to form ammonium salts.

$$2NH_{3(g)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{ammonium sulphate}}{(NH_4)_2SO_{4(aq)}}$$

$$NH_{3(g)} + HCl_{(aq)} \longrightarrow NH_4\,Cl_{(aq)}$$

$$NH_{3(g)} + HNO_{3(aq)} \longrightarrow NH_4\,NO_{3(aq)}$$

(4) Reaction With Chlorine (Cl_2):

When ammonia reacts with chlorine, it first reduces chlorine to produce hydrogen chloride and nitrogen. Then hydrogen chloride reacts with excess of ammonia to produce dense white fumes of ammonia chloride.

(a) $2NH_{3(g)} + 3Cl_{2(g)} \longrightarrow N_{2(g)} + 6HCl_{(g)}$

(b) $6NH_{3(g)} + 6HCl_{(g)} \longrightarrow \underset{\text{white fumes}}{6NH_4Cl_{(s)}}$

The over all reaction can be described as:

$$8NH_{3(g)} + 3Cl_{2(g)} \longrightarrow \underset{\text{ammonium chloride}}{6NH_4Cl_{(s)}} + N_{2(g)}$$

If chlorine is in excess then nitrogen trichloride (NCl_3) would be produced which is an oily liquid and is dangerously explosive.

$$NH_{3(g)} + 3Cl_{2(g)} \longrightarrow NCl_{3(l)} + 3HCl_{(g)}$$

(5) As Reducing Agent:

Ammonia is not a strong reducing agent. However it reduces heated copper oxide (CuO) to free copper metal with the evolution of N_2 gas and water.

$$3CuO_{(s)} + 2NH_{3(g)} \xrightarrow{heat} 3Cu_{(s)} + N_{2(g)} + 3H_2O_{(l)}$$

(6) Reaction With Carbon Dioxide (CO_2):

Ammonia reacts with CO_2 at high temperature about 150^0C under pressure to produce Urea $(NH_3)_2$ CO, which is an important fertilizer.

$$2NH_{3(g)} + CO_{2(g)} \xrightarrow[\text{high pressure}]{150^0 C} \underset{\text{urea}}{(NH_2)_2CO_{(s)}} + H_2O_{(l)}$$

Uses:

1- Aqueous ammonia is used in softening of temporary hard water.
2- It is used as solvent in launderies for removing grease and oil stains.
3- Liquid ammonia is used as cooling agent in some refrigerators.
4- Ammonia is used in the manufacture of nitric acid in Ostwald's method and in the manufacture of sodium carbonate (Washing soda) by solvay process.
5- The biggest use of ammonia is in the manufacture of nitrogenous fertilizers, like urea, ammonium sulphate, ammonium nitrate, ammonium phosphate etc.

2- Nitric Acid: (HNO_3)

Nitric acid is a very important acid which is used extensively in the laboratories and in industries. It was first prepared by Glauber in 1685 from sulphuric acid and Potassium nitrate. The early al-chemists used the acid for separating gold from silver, silver being soluble in this acid while gold is insoluble. As a result of corrosive action on many metals, the acid was previously known as **aqua fortis** meaning strong water.

Preparations:

(1) Laboratory Preparation:

Nitric acid is prepared in the laboratory by heating solid Potassium nitrate (KNO_3) with conc. sulphuric acid.

$$KNO_{3(s)} + H_2SO_{4(aq)} \xrightarrow{heat} \underset{\text{potassium hydrogen sulphate}}{KHSO_{4(aq)}} + \underset{\text{nitric acid}}{HNO_{3(g)}}$$

Note that all glass apparatus must be used in this preparation because vapours of nitric acid formed will rapidly attack corcks, rubber and other materials.

(2) Industrial Preparation:

Ostwald's method:

Nitric acid is manufactured on large scale by the catalytic oxidation of ammonia in Ostwald's method. In this method ammonia is allowed to react with excess of air in the presence of platinum, catalyst at 600°C to produce nitric oxide (NO) gas and steam in the catalytic chamber or converter. The catalyst is used in the form of gauze. About 96% of ammonia is converted into nitric oxide.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{pt/600^0C} 4NO_{(g)} + 6H_2O_{(1)} \ ; \ \Delta H = -95.5\ KJ/mol.$$

Since the reaction is exothermic, so once started, the heat released during the reaction maintains the catalytic action at the required temperature. The nitric oxide formed is cooled by passing through coolers upto 150°C.

Nitric oxide is then mixed with excess of air in oxidation chamber to produce nitrogen dioxide i.e. nitrogen peroxide (NO_2).

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

Nitrogen peroxide (NO_2) produced is directly dissolved in water to produce nitric acid, liberating nitric oxide gas in the absorption chamber. Nitric oxide gas thus obtained is recycled to get more nitric acid.

$$3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)} + NO_{(g)}$$

Nitric acid obtained from this process is 68% concentrated which can be concentrated further by passing over conc H_2SO_4 up to 98%.

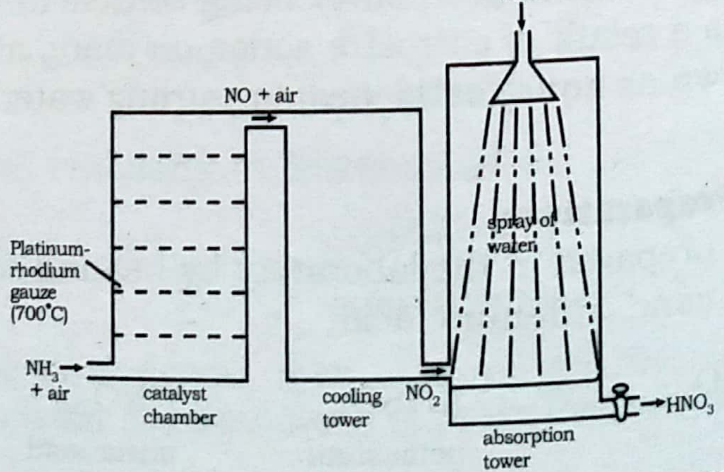


Fig13.4 Ostwald's method for the manufacture of HNO_3

Physical Properties:

1- Nitric acid is a colourless fuming liquid with sharp chocking smell. It has sour taste. Although it is colourless when pure, it tends to turn yellowish after sometimes due to decomposition of some acid into NO_2 which then dissolves in the acid and turns it yellowish.

2- The boiling point of pure nitric acid is 83^0C while its freezing point is -41.6^0C. The density of pure nitric acid is $1.52 g/cm^3$. 65% ordinary nitric acid has specific gravity 1.41 and boils at 121^0C.

3- It is miscible in water in all proportion.

conc. nitric acid is unstable and decomposes in sunlight or on heating.

$$4HNO_{3(conc)} \xrightarrow{heat} 4NO_{2(g)} + O_{2(g)} + 2H_2O_{(l)}$$

Chemical Properties:

(1) **As an acid:** Nitric acid is a strong monobasic acid in its aqueous solution ionizes completely in water as:

$$HNO_3 + H_2O \rightleftharpoons \underset{\text{hydronium ion}}{H_3O^+} + NO^-_3$$

It reacts with alkalies, metal oxides and metal carbonates to form nitrate salts and water.

$$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow NaNO_{3(aq)} + H_2O_{(l)}$$

$$HNO_{3(aq)} + KOH_{(aq)} \longrightarrow KNO_{3(aq)} + H_2O_{(l)}$$

$$CaO_{(s)} + 2HNO_{3(aq)} \longrightarrow Ca(NO_3)_{2(aq)} + H_2O_{(l)}$$

$$PbO_{(s)} + 2HNO_{3(aq)} \longrightarrow Pb(NO_3)_{2(aq)} + H_2O_{(l)}$$

$$CaCO_{3(s)} + 2HNO_{3(aq)} \longrightarrow Ca(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$\underset{\text{Sodium bicarbonate}}{NaHCO_{3(s)}} + HNO_{3(aq)} \longrightarrow NaNO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$$

There are some metals like Mg and Mn which react with nitric acid to form their nitrate salts with the liberation of H_2 gas.

$$Mg_{(s)} + 2HNO_{3(aq)} \longrightarrow Mg(NO_3)_{2(aq)} + H_{2(g)}$$
$$Mn_{(s)} + 2HNO_{3(aq)} \longrightarrow Mn(NO_3)_{2(aq)} + H_{2(g)}$$

(2) As oxidizing agent:

Nitric acid acts as a powerful oxidizing agent because it is an electron acceptor and has nitrogen at its highest oxidation state (+5) and can undergo reduction in many ways.

The oxidizing property of nitric acid depends upon the following factors.

(i) Concentration of the acid.
(ii) Nature of the reducing agent.
(iii) Temperature.

Due to these factors nitric acid gives variety of reduction products, such as NO_2, NO, N_2O, N_2, HNO_2, NH_4NO_3 etc.

(a) Reaction with non-metals:

Hot conc. nitric acid reacts with many non-metals and oxidizes them into their oxides or oxy-acids and itself is reduced to NO_2 gas.

Reaction with Carbon: Carbon oxidizes to liberate CO_2 gas on heating with conc HNO_3.

$$C_{(s)} + 4HNO_{3(aq)} \xrightarrow{hot} CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$$

Similarly silicon (Si) oxidizes to SiO_2

$$Si_{(s)} + 4HNO_{3(aq)} \xrightarrow{hot} SiO_{2(s)} + 4NO_{2(g)} + 2H_2O_{(l)}$$

Reaction with Sulphur: sulphur oxidizes first into SO_2 gas and then to sulphuric acid, on heating with conc. nitric acid.

$$S_{(s)} + 4HNO_{3(aq)} \xrightarrow{hot} SO_{2(g)} + 4NO_{2(g)} + 2H_2O$$

i.e $$S_{(s)} + 6HNO_{3(aq)} \xrightarrow{hot} \underset{\text{sulphuric acid}}{H_2SO_{4(aq)}} + 6NO_{2(g)} + 2H_2O_{(l)}$$

Reaction with Phosphorous: Red phosphorous oxidizes to phosphoric acid on heating with conc nitric acid.

$$P_{(s)} + 5HNO_{3(aq)} \xrightarrow{hot} \underset{\text{phosphoric acid}}{H_3PO_{4(aq)}} + 5NO_{2(g)} + H_2O_{(l)}$$

Reaction with Iodine: Iodine is oxidized to hydroiodic acid (HIO_3) when heated with nitric acid.

$$I_{2(s)} + 10HNO_{3(aq)} \xrightarrow{hot} 2HIO_{3(aq)} + 10NO_{2(g)} + 4H_2O$$

(b) Reaction with Metals:

Conc. as well as dil. nitric acid oxidizes many metals. Conc. HNO_3 liberates NO_2 gas, while the reaction of dil. HNO_3 depends upon the nature of the reducing agent.

Reaction with Copper:

$$Cu_{(s)} + 4HNO_{3(conc)} \xrightarrow{hot} Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

$$3Cu_{(s)} + 8HNO_{3(dil)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O$$

Reaction with Lead:

$$Pb_{(s)} + 4HNO_{3(conc)} \xrightarrow{hot} Pb(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

$$3Pb_{(s)} + 8HNO_{3(dil)} \longrightarrow 3Pb(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

Reaction with Zinc:

$$Zn_{(s)} + 4HNO_{3(conc)} \xrightarrow{hot} Zn(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

$$4Zn + 10HNO_{3(dil)} \longrightarrow 4Zn(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3H_2O_{(l)}$$

Reaction with Some Reducing Agents:

Nitric acid which is a strong oxidizing agent also undergoes redox reactions with some common reducing agents like, H_2S, $FeSO_4$ and SO_2 etc.

Reaction with H_2S:

Conc. nitric acid oxidizes H_2S to sulphur while itself is reduced to NO_2 gas.

$$H_2S_{(g)} + 2HNO_{3(aq)} \longrightarrow S_{(s)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

Reaction with $FeSO_4$:

Ferrous sulphate reacts with conc. nitric acid and oxidizes to ferric sulphate in the presence of sulphuric acid. While HNO_3 is reduced to NO gas.

$$6FeSO_{4(aq)} + 2HNO_{3(aq)} + 3H_2SO_{4(aq)} \longrightarrow \underset{\text{ferric sulphate}}{3Fe_2(SO_4)_{3(aq)}} + 2NO_{(g)} + 4H_2O_{(l)}$$

Reaction with SO_2:

Sulphur dioxide oxidizes to sulphuric acid on heating with conc. HNO_3.

$$SO_{2(g)} + 2HNO_{3(conc)} \xrightarrow{hot} H_2SO_{4(aq)} + 2NO_{2(g)}$$

(3) Nitration Reaction (as nitrating agent):

Hot conc. nitric acid reacts with organic compounds like benzene (C_6H_6) to replace hydrogen atom by the nitro ($-NO_2$) group to form substituted product, nitro benzene ($C_6H_5NO_2$). The substitution of $-NO_2$ group in organic compound is called nitration.

$$\underset{\text{Benzene}}{C_6H_{6(l)}} + HNO_{3(conc)} \xrightarrow[450^0C]{hot} \underset{\text{Nitro benzene}}{C_6H_5NO_{2(l)}} + H_2O_{(l)}$$

AQUA REGIA:

The noble metals are like gold and platinum which are not soluble in conc. nitric acid. However they are dissolved in a mixture of conc. HNO_3 and conc. HCl taken in the ratio of 1:3. This mixture is called aqua regia or royal water. Aqua regia dissolves gold due to liberation of nascent chlorine which forms gold chloride with it, which is soluble.

$$HNO_{3(conc)} + 3HCl_{(conc)} \longrightarrow \underset{\text{nitrosyl chloride}}{NOCl} + 2H_2O_{(l)} + \underset{\text{nascent or atomic chloride}}{2Cl}$$

$$NOCl \longrightarrow NO+Cl$$

$$Au_{(s)} + 3Cl \longrightarrow \underset{\text{gold chloride}}{AuCl_3}$$

Uses:

Nitric acid is an important chemical compound.

1- Large amount of nitric acid is used in the manufacture of fertilizers. Such as NH_4NO_3, $NaNO_3$, KNO_3 etc.
2- It is used in the manufacture of cellulose, lacquers and smokeless gun powder.
3- It is used in the manufacture of dyes and explosives such as nitroglycerol and trinitrotoluene (T.N.T) which are powerful explosives.
4- It is used as a powerful oxidizing agent in the production of important polymers like nylon and terylene.
5- It is used as laboratory reagent.
6- It is used as nitrating agent and in the formation of aqua regia which dissolves noble metals and also for producing etching designs on copper plates.

SUMMARY

1. Nitrogen is present up to 78% by volume in the earth's atmosphere. It is chemically unreactive. Free nitrogen in air is of great importance because it dilutes oxygen in the air to the point where combustion, respiration and oxidation processes are comparatively slow. It is mainly used in the manufacture of ammonia.
2. Ammonia is manufactured by the direct combination of nitrogen and hydrogen gases by the Haber's process. Ammonia can be obtained in the laboratory by heating ammonium salts with a base specially with slaked lime; $Ca\,(OH)_2$
3. Oxygen is the most abundant element on the earth. It occurs in nature both, in the free as well as in the combined state. In the free state oxygen (O_2) is present in the earth's atmosphere upto 21% by volume. In the combined state oxygen accounts for nearly about 50% by mass of the earth's crust. Water contains oxygen about 88.8% by mass and it is the most abundant compound on the earth. Oxygen is essential and vital for life on earth.
4. Nitrogen and oxygen are isolated by the fractional distillation of liquid air. At-196^0C nitrogen gas boils out from liquid air while at -183^0C oxygen gas boils out from liquid air.
5. In addition to respiration, combustion, oxygen is also used for water purification, steel manufacturing and for bleaching purposes. Oxygen combines with other elements except noble gases to form oxides.
6. Oxides are classified on the basis of oxidation states or valence numbers of oxygen into four categories, namely **normal oxides, peroxides, super oxides** and **sub oxides**. Normal oxides are further classified on the bases of their chemical characteristics into basic, acidic, amphoteric and neutral oxides. Most of the metallic oxides are basic, oxides of non-metals are acidic, oxides of certain metals like zinc, aluminium and tin are amphoteric in nature i.e possessing both basic and acidic characteristics. Some oxides of non-metals are neutral, having neither basic nor acidic characteristics, such as water (H_2O), nitric oxide (NO), nitrous oxide (N_2O) and carbon monoxide (CO).
7. Oxygen combines with hydrogen to form not only water (H_2O), but also peroxide; H_2O_2 hydrogen peroxide. Hydrogen peroxide is obtained by the action of dilute sulphuric acid over barium peroxide (BaO_2). On large scale H_2O_2 is produced by the oxidation of isopropyl alcohol with oxygen under reduced pressure. Hydrogen peroxide is a pale blue syrupy liquid. Its solution in water is slightly acidic. It decomposes

easily in air to literate O_2 gas with the formation of H_2O. Its decomposition is slowed down in the presence of glycerine. Hydrogen peroxide is a powerful oxidizing agent as well as a bleaching agent. It is used as antiseptic, as bleaching agent for restoring paintings. It is used as fuel component in space rockets and submerged submarines.

8. The reactions in which oxidation and reduction occur simultaneously are called oxidation-reduction reactions or redox reactions. A substance that accepts or gains electrons is known as oxidizing agent but it itself is reduced. A substance that loses or donates electrons is known as the reducing agent but it itself is oxidized.

9. Ozone is allotropic form of oxygen with molecular formula O_3. It is a pale blue poisonous gas. Ozone is formed from atmospheric oxygen by lightening flashes but it is very unstable. It exists at a height of about 20 kilometer above the earth, where it protects earth surface from ultra violet radiations of the sun. Ozone has a characteristic sharp, irritating small like chlorine. Ozone is a powerful oxidizing agent and oxidizes many chemical compounds.

10. Ammonia is used to make fertilizers which are mostly the ammonium salts. It is also used to produce urea and nitric acid.

11. Nitric acid is manufactured on the large scale from ammonia by the Ost wald's process. In this process ammonia reacts with oxygen in the presence of platinum catalyst to form nitric oxide (NO), which is mixed with oxygen to produce nitrogen peroxide (NO_2). NO_2, is then dissolved or absorbed in water to form nitric acid. In the laboratory nitric acid is obtained by heating potassium nitrate with conc sulphuric acid.

12. Nitric acid is a powerful oxidizing agent and also very corrosive. It decomposes in light. It is used to make nitrogenous fertilizers, explosives, dyes, smokeless gun powder etc.

EXERCISE

1. (a) Fill in the blanks.

(i) The yellow colour of nitric acid is due to dissolved ______ gas.

(ii) When ______ mole of N_2 gas is mixed with ______ moles of H_2 gas, 2 moles of NH_3 gas are produced.

(iii) Nitric acid on the large scale is produced by ________ method from ammonia.

(iv) Ammonia on the large scale is produced by _________ process.

(v) Ozone is an ______ form of ______ with molecular formula ________.

(vi) The powerful ultra violet radiation of the sun are screened by _________ layer.

(vii) The process which takes place by the loss of electrons is called __________.

(viii) In peroxides the oxidation state of oxygen is ___________.

(ix) The oxides that show acidic and basic characters are known as _________ oxides.

(x) Nitrogen boils out from the liquid air at temperature ______ ^{0}C.

(b) Point out True or False in the following statements:

(i) Oxygen is separated from the liquid air before nitrogen.

(ii) Air contains about 21% O_2 gas by volume.

(iii) Nitric acid acts as a powerful oxidizing agent.

(iv) Hydrogen peroxide decomposes to liberate O_2 gas on exposure.

(v) Ammonia gas is insoluble in water.

(vi) Ozone exists at the height of about 20 Kilometers above the earth.

(vii) The substance that accepts or gains electrons acts as reducing agent.

(viii) Haber's process is used for the production of nitric acid.

(ix) Nitrogen in HNO_3 is in its highest oxidation state of +5.

(x) Nitrogen belongs to VIA group of the periodic table.

(c) Pick up the correct answer from the following:

(i) When ammonium chloride is heated with a base, the gas liberated is:

(a) ammonia (b) oxygen (c) nitrogen (d) nitric oxide (NO).

(ii) The catalyst used for the catalytic oxidation of NH_3 in Ostwald's method is:

(a) nickel (b) chromium (c) platinum (d) vanadium penta oxide.

(iii) The metal that liberates H_2 gas when treated with dil. HNO_3 is:
(a) copper (b) aluminium (c) zinc (d) magnesium.

(iv) The boiling point of liquid oxygen is:
(a) -196^{0}C (b) -183^{0}C (c) -200^{0}C (d) -187.5^{0}C

(v) Select the redox reaction from following reactions.

(a) $Cl + Cl \longrightarrow Cl_{2(g)}$

(b) $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(s)}$

(c) $2FeCl_3 + H_2S_{(s)} \longrightarrow 2FeCl_2 + 2\ HCl + S$

(d) $N_2 \longrightarrow N^* + N^*$

(vi) The air we breathe in, usually contains a higher proportion of:
(a) nitrogen (b) oxygen (c) carbon dioxide (d) water vapours.

(vii) Which one of the following is the easy way to distinguish ozone from oxygen.
(a) by comparing their solubilities.
(b) by comparing their oxidizing properties.
(c) by comparing allotropic forms.
(d) by comparing their odours.

(viii) The most abundant element found in nature is:
(a) oxygen (b) silicon (c) nitrogen (d) hydrogen.

(ix) Urea is produced by heating carbon dioxide (CO_2) with,
(a) nitric acid (b) ammonia (c) hydrogen (d) potassium nitrate.

(x) Hydrogen peroxide is produced in the laboratory by heating sulphuric acid with:
(a) sodium peroxide (b) potassium peroxide
(c) barium peroxide (d) storntium peroxide.

2. (a) The first step in the manufacture of nitric acid from NH_3 involves the exothermic oxidation of NH_3 to nitric oxide (NO) and steam.

(i) Write the equation for the reaction of ammonia with O_2 to form NO.

(ii) Predict the conditions of temperature for the maximum yield of NO in the equilibrium mixture. What is the percentage conversion of NH_3 into NO.

(iii) Describe with equations, how nitric oxide produced is changed into nitric acid.

(b) What happens when nitric acid is reacted with:
(i) $CaCO_3$ (ii) NaOH (iii) Mg

(iv) C (v) Zn (conc and dilute HNO_3)
(vi) $FeSO_4$ (vii) H_2S (viii) C_6H_6 (Benzene).

3. (a) What is aqua regia? How does it dissolve gold?
(b) What is the result, when potassium nitrate is heated with conc. sulphuric acid? Give the correct equation.
(c) Give the industrial preparation of ammonia by Haber's process. With an example, show that ammonia acts as
(i) a base (ii) a reducing agent.
(d) Explain why ammonia is used in (i) refrigerators (ii) laundries (iii) fertilizers.

4. (a) Nitrogen is one of the major components of air. How can you get nitrogen from the atmospheric air. Give two uses of nitrogen.
(b) Describe the laboratory preparation of oxygen. How is oxygen industrially produced from liquid air.
(c) Give the action of oxygen on the following:
(i) carbon (ii) phosphorous (iii) carbon monoxide (CO)
(iv) Mg metal (v) nitric oxide (NO) and (vi) ammonia (NH_3)

5. (a) What are oxides? How are they classified? Describe normal oxides in detail.
(b) Give the preparation and properties of hydrogen peroxide and its uses.
(c) Explain what happens when H_2O_2 is added to the followings:
(i) hydrogen sulphide (H_2S)
(ii) acidified potassium iodide (KI)
(iii) chlorine (Cl_2)
(iv) potassium permanganate ($KMnO_4$) in the presence of H_2SO_4.

6. (a) Define the followings in terms of electron transfer:
(i) oxidation (ii) reduction (iii) oxidizing agent
(iv) radox reaction (v) reducing agent.
(b) Classify the following normal oxides on the basis of their acidic, basic, amphoteric and neutral nature.
(i) CaO (ii) CO_2 (iii) Al_2O_3 (iv) Na_2O (v) NO
(vi) CO (vii) ZnO (viii) SO_2.
(c) Give the reactions of ZnO with HCl and NaOH.

7. (a) What is ozone? How ozone is produced in the atmosphere? How ozone can be obtained from oxygen? What is the structure of ozone?

(b) Describe the reactions of ozone with: (i) PbS (ii) SO_2 (iii) KI in acidic medium.

(c) Why ozone is important in the upper atmosphere? What is its importance?

8. Complete the following reactions. Give the balanced equations.

(i) $H_2S_{(g)} + O_{3(g)} \longrightarrow$

(ii) $NH_{3(g)} + Cl_{2(g)\ (excess)} \longrightarrow$

(iii) $NH_{3(g)} + CO_{2(g)} \longrightarrow$

(iv) $NH_{3(g)} + O_{2(g)\ (excess)} \longrightarrow$

(v) $NO_{2(g)} + H_2O_{(l)} \longrightarrow$

(vi) $PbO_{(s)} + HNO_{3(aq)} \longrightarrow$

(vii) $C_6H_6 + HNO_3 \longrightarrow$

(viii) $NH_4\ NO_{2(s)} \longrightarrow$

(ix) $HNO_3 + HCl \longrightarrow$

(x) $CO_{2(g)} + NaOH_{(aq)} \longrightarrow$

CHAPTER-14

SULPHUR AND ITS COMPOUNDS

You will learn in this chapter about:

- Sulphur and its allotropic forms,Rhombic,Monoclinic and plastic sulphur, their preparations and properties.
- Occurrence and extraction of sulphur by Frasch process.
- Manufacture of sulphuric acid by contact process.
- Physical and chemical properties of H_2SO_4, uses of sulphuric acid.

Introduction

Sulphur is the second member of VIA group of the periodic table and has symbol "S". It's atomic number is 16 while atomic mass is 32 a.m.u. Sulphur has been known for its medicinal and germicidal effect from very ancient time before 1000 B.C, but its chemical nature remained unknown until 1787 when Lavoiser recognized it as an element.

14.1 SULPHUR AND ITS ALLOTROPIC FORMS

The existence of an element in two or more different forms in the same physical state is called allotropy, while different forms are known as allotropic modifications or allotropes.

Sulphur exists in several allotropic forms, out of which the three forms are,

(i) Rhombic sulphur ($\propto$ - sulphur)
(ii) Monoclinic sulphur (β or Prismatic sulphur)
(iii) Plastic sulphur (γ - sulphur)

Allotropic forms have similar chemical properties but different physical properties due to different structures.

These allotropes of sulphur are discussed below with their physical properties and structures.

(i) Rhombic Sulphur ($\propto$- Sulphur):

It is the most stable crystalline form of sulphur at ordinary condition. Free sulphur exits in nature as rhombic sulphur. It is obtained as pale-yellow crystals, giving lemon-yellow powder. Its melting point is 113°C and its density is 2.08g/cm³ at 20°C. It is insoluble in water but dissolves in carbon disulphide (CS_2), benzene, disulphur dichloride (S_2Cl_2), turpentine etc.

Preparation: Rhombic sulphur is prepared by slow evaporation of the solution of ordinary sulphur in carbon disulphide or S_2Cl_2, which is filtered first to remove insoluble impurities present in sulphur. The filterate on evaporation produces octahedral crystals of rhombic sulphur.

Structure: Rhombic sulphur consists S_8 molecules. These S_8 molecules consists of 8 sulphur atoms bound to each other through single covalent bonds. The shape of rhombic sulphur is given in fig. 14.1(a).

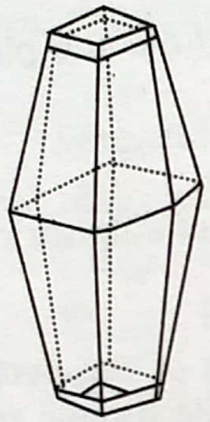


Fig 14.1 (a) Crystal of Rhombic sulphur

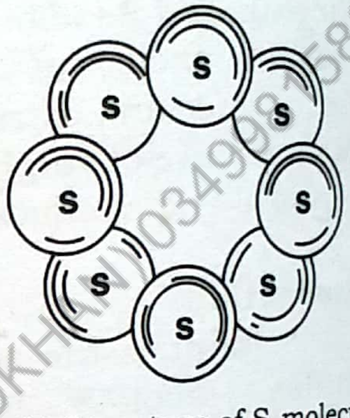


Fig 14.1 (b) Structure of S_8molecules

(ii) Monoclinic Sulphur (β or Prismatic Sulphur):

Monoclinic sulphur is another crystalline form of sulphur. It is stable between 96 to 119°C and hence it changes slowly to rhombic sulphur at ordinary temperature. It consists of dark yellow transparent needle-like crystals. On standing the crystals become opaque, brittle and lemon yellow in colour. Its melting point is 119°C. Its density is 1.96 g/cm^3. It is soluble in carbon disulphide (CS_2) but insoluble in water. The transformation of monoclinic sulphur to rhombic sulphur is reversible and can be described as:

$$\text{Rhombic sulphur} \xrightleftharpoons{96^{0}\text{C}} \text{Monoclinic sulphur}$$

Below 96°C, the rhombic sulphur is stable and above 96°C, monoclinic sulphur is stable. Thus the temperature at which both forms coexist in equilibrium is called as **transition temperature**. The transition temperature of sulphur is 96°C.

Preparation: Monoclinic sulphur is obtained by slow cooling molten sulphur until a crust is formed on the surface of the molten sulphur. Pierce two holes through the crust and pour off the remaining molten sulphur from inside on removing the crust the long needle shaped crystals of monoclinic sulphur are formed on the sides of the dish.

Structure: Monoclinic sulphur also consists of sulphur atoms of S_8 molecules. The only difference is the shapes of the crystals. The monoclinic sulphur, the S_8 molecule unite together to give long, needle-shaped crystals as given in fig 14.2.

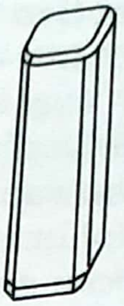


Fig. 14.2 Crystal of monoclinic sulphur

(iii) Plastic Sulphur (γ - Sulphur):

Plastic sulphur is a super cooled form of sulphur. It is the non-crystalline allotrope of sulphur.

When ordinary sulphur is heated carefully upto its boiling point about 444.6°C and then the molten sulphur is poured into very cold water, a soft rubber like mass is obtained which looks as if it is made of plastic material. Plastic sulphur is generally not considered to be a true allotrope of sulphur because it is unstable and reverts to rhombic sulphur on standing. It has zig-zag arrangements of sulphur atoms as shown in fig. 14.3.

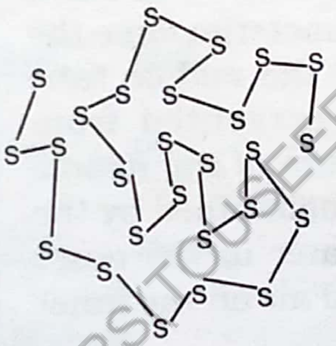


Fig. 14.3 Model of Plastic sulphur

14.2 OCCURRENCE AND EXTRACTION OF SULPHUR

Occurrence:

Sulphur is non-metal and makes up about 0.1% of the earth's crust. It is found in the free state in sicily, Mexico and in USA. In USA large deposits of sulphur are found in Louisiana and Texas. It is also found in the free state in Japan and Newzealand. In the combined state, it is largely found, as sulphides of iron, zinc, lead, copper and mercury and also as sulphates of magnesium, calcium and barium.

In Pakistan some deposits of sulphur occur in Koh-i-sultan and in Kalat.

In addition to this, sulphur is an essential constituent of many organic substances of the plants and animal origins such as proteins, eggs, onions, garlic and mustard etc.

Extraction of Sulphur (Frasch Process):

Most of the world's sulphur is obtained from underground deposits which may be more than 200 metres below the surface of the earth. About 60-70% native sulphur occur deep below the earth's surface. For this reason sulphur can not be dug out directly by ordinary mining. For the extraction of sulphur an ingenious method was discovered by Herman Frasch, an American engineer, known as Frasch Process.

In this process a hole about 30cm in diameter is drilled through the soil layers to the sulphur bed. Three concentric iron pipes are sunk into the bore or hole. The outer most pipe. (20 cm diameter) is sunk up to the deposits and the next inner pipe (10 cm diameter) is held a little above the surface of the sulphur deposits. Super heated water at about 170^0C and 100 atmospheric pressure is forced through the outermost pipe to the sulphur bed to melt sulphur (m.p $=115^0C$) of the sulphur bed. Hot compressed air at a pressure of 15 atm is then flown down the inner most pipe (5cm diameter)to force the molten sulphur up through the middle tube or pipe. This sulphur is prevented from solidifying by high temperature of the middle pipe whose temperature is maintained by the heat of the super-heated water in the outer side and also hot compressed air on the inner side.

The molten sulphur is continuously pumped into a receptacle at the surface where it is allowed to solidify in large wooden tanks. The sulphur obtained is about 99.5% pure. Fig. 14.4.

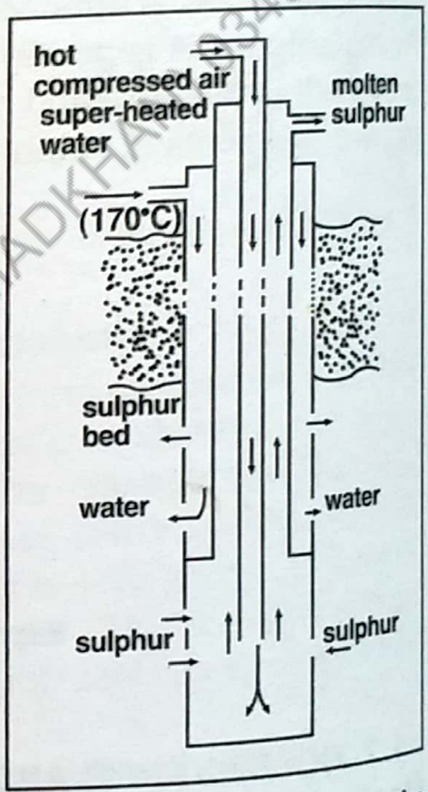


Fig. 14.4 Frasch process for the extraction of sulphur

14.3 PROPERTIES OF SULPHUR

Physical Properties:

1. Sulphur is a yellow solid. It is insoluble in water but soluble in carbon disulphide (CS_2).
2. It is a non-metal. It is bad conductor of heat and electricity.

3. When sulphur is heated, it melts at a temperature between 113°C to 119°C, into an amber coloured liquid. The colour darkens as the temperature increases. Its boiling point is about 444°C.

When the vapours of sulphur at its boiling point are condensed on a cold surface, a fine powder, which forms a **flowers pattern** is obtained. It is known as **flowers of sulphur**.

Chemical Properties:

1. Reactions with metals:

Sulphur combines with many metals directly to form their respective sulphides. Reactive metals like sodium, potassium may even react with sulphur spontaneously without much more heating, when both are in finely divided form.

(i) $2Cu_{(s)} + S_{(s)} \xrightarrow{heat} Cu_2S_{(s)}$ **(Cupperous sulphide)**

(ii) $Fe_{(s)} + S_{(s)} \xrightarrow{heat} FeS_{(s)}$ **(Ferrous sulphide)**

(iii) $Zn_{(s)} + S_{(s)} \xrightarrow{heat} ZnS_{(s)}$ **(Zinc sulphide)**

(iv) $Pb_{(s)} + S_{(s)} \xrightarrow{heat} PbS_{(s)}$ **(Lead sulphide)**

(v) $2Na_{(s)} + S_{(s)} \xrightarrow{heat} Na_2S_{(s)}$ **(Sodium sulphide)**

2. Reaction with Non-Metals:

Many non-metals react with sulphur at different conditions.

(a) **With Oxygen:** Sulphur burns in oxygen of the air with a bright blue flame to form sulphur dioxide.

$$S_{(s)} + O_{2(g)} \xrightarrow{Ignition} SO_{2(g)}$$

(b) **With Hydrogen:** At high temperature about 600-660°C, Sulphur combines with hydrogen slowly to form hydrogen sulphide (H_2S) gas. The reaction is more rapid if hydrogen is bubbled through molten sulphur.

$$H_{2(g)} + S_{(s)} \xrightarrow{600-660^0 C} H_2S_{(g)}$$

(c) With Carbon: Sulphur combines with coke in an electric furnace to form a colourless liquid, carbon disulphides (CS_2). This vapourizes readily forming poisonous and highly inflammable fumes. CS_2 is used as solvent for waxes, gums and sulphur.

$$C_{(s)} + 2S_{(s)} \xrightarrow{\text{Electric furnace}} CS_{2(l)}$$

(d) With Chlorine: Sulphur combines with chlorine on heating to high temperature, forming disulphur dichloride (S_2Cl_2).

$$2S_{(s)} + Cl_{2(g)} \xrightarrow{\text{high temperature}} S_2Cl_{2(l)}$$

(e) With fluorine: Sulphur combines with fluorine on heating to form sulphur hexa fluoride (SF_6)

$$S_{(s)} + 3F_{2(g)} \xrightarrow{\text{heat}} SF_{6(l)}$$

3. Reaction with Acids:

Sulphur is readily oxidized when warmed with conc. sulphuric acid to produce SO_2 gas and also with conc nitric acid to produce NO_2 gas.

(i) $S_{(s)} + 2H_2SO_{4(conc)} \xrightarrow{\text{Hot}} 3SO_{2(g)} + 2H_2O_{(l)}$

(ii) $S_{(s)} + 6HNO_{3(conc)} \xrightarrow{\text{Hot}} H_2SO_{4(aq)} + 6NO_{2(g)} + 2H_2O_{(l)}$

Uses of Sulphur:

1. Sulphur is used in the manufacture of sulphuric acid, sulphur dioxide and carbon disulphide.
2. It is used for the manufacture of calcium and magnesium hydrogen sulphates and also used for bleaching wood-pulp.
3. Sulphur is used in volcanizing rubber.
4. It is used for disinfecting houses and for dirty vines. It also helps to kill the fungi and insects.

14.4 SULPHURIC ACID (H_2SO_4)

Sulphuric acid is one of the most important chemical compounds known. It is commonly used in the laboratory and in industries in many processes.

Industrial Preparations of Sulphuric Acid:

On the large scale sulphuric acid is manufactured by two methods, the contact process and the lead-chamber process. The contact process is the most recent one and gives sulphuric acid of highest purity.

14.4.1 The Contact Process

This method was developed in Germany in the early 19th century but came into operation from 1912. Now-a-days sulphuric acid is mostly manufactured by contact process.

In Pakistan sulphuric acid is also manufactured by this process and hence contact method is described here.

In this method SO_2 is produced mainly by burning sulphur in dry air or iron pyrite in pyrite burners.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$\underset{\text{Iron pyrite}}{4FeS_{2(s)}} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

It is very important that in contact process SO_2 and air must be very pure, free from all sorts of impurities which poison the catalyst; so the mixture of SO_2 and air is passed through special dust filters. The solid particles settle down in the dust chamber. Then SO_2 is passed through the washing or scrubing chamber. Here steam is injected from the top of the chamber. Solid particles from droplets with steam and settle down. The moist mixture of SO_2 and air is passed through the drying towers in which conc. H_2SO_4 is sprayed from the top.

This washed, dried and purified mixture of SO_2 and air is passed through contact tower i.e. Catalytic chamber. In this tower SO_2 is oxidized to SO_3 in the presence of catalyst venadium pentaoxide (V_2O_5) or Pt. The catalyst is arranged in contact tower in such a way that it exposes the maximum possible surface area, for the reacting gaseous mixture. Since Pt is very expensive, so it is replaced by finely divided, V_2O_5 which is less expensive and more resistant to impurities. The reaction occurs as:

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)} \quad ; \quad \Delta H = -197 \text{ K.J/mol.}$$

Since the reaction is reversible and exothermic, the favourable conditions for obtaining maximum yield of SO_3 are (a) low temperature (b) high pressure (c) excess of O_2.

In actual practice the optimum temperature chosen in the presence of catalyst is 450°C; while the optimum pressure should be 1.5-1.7 atmosphere.

The sulphur trioxide (SO_3) produced in contact tower is not directly dissolved in water, because it is less soluble in it. Therefore, SO_3 is absorbed first in 97% conc. sulphuric acid producing a very thick liquid called **Oleum** i.e. Pyrosulphuric acid in the absorption tower.

$$SO_{3(g)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{Oleum}}{H_2S_2O_{7(aq)}}$$

Oleum is then diluted with appropriate amount of water to get sulphuric acid of desired concentration.

$$H_2S_2O_{7(aq)} + H_2O_{(l)} \longrightarrow \underset{\text{Sulphuric acid}}{2H_2SO_{4(aq)}}$$

Sulphuric acid obtained by the contact process is about 100% pure. The continuous nature of this process is shown diagrammatically in fig 14.5.

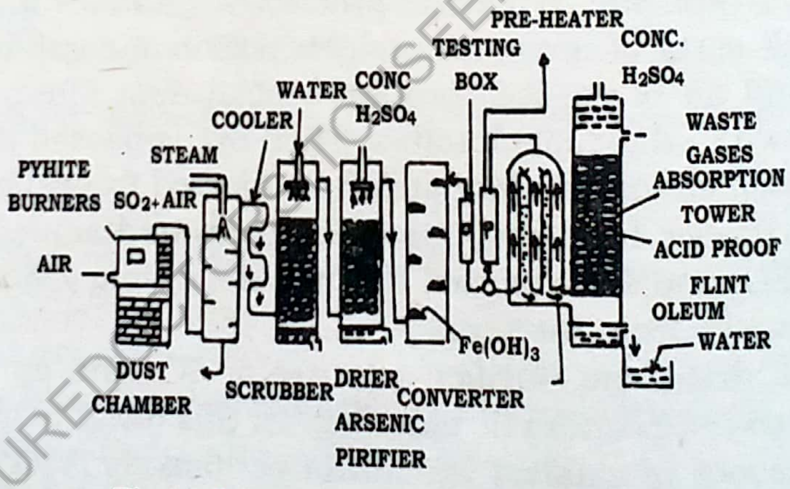


Fig 14.5 Contact process to prepare H_2SO_4

Physical Properties:

(1) Pure conc.sulphuric acid is a colourless, odourless, viscous oily liquid, often known as **oil of vitriol**.

(2) Its melting point is 10.5°C while its boiling point is 338°C.

(3) Conc.H_2SO_4 (98.3%) has specific gravity about 1.84, while dilute 65% sulphuric acid has specific gravity about 1.55.

(4) It is corrosive and is hygroscopic as it absorbs water vapours from the surroundings and becomes dilute. It is therefore used as drying agent.

Chemical Properties:

Sulphuric acid behaves in three different ways.

(1) as an acid, (2) as an oxidizing agent

(3) as drying or dehydrating agent.

(1) As an Acid:

Sulhpuric acid is a strong dibasic acid and ionizes in water in two stages.

(a) $H_2SO_{4(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+_{(aq)}} + \underset{\text{Hydrogen sulphate ion}}{HSO^-_{4(aq)}}$

(b) $HSO_4{}^{1-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Sulphate ion}}{SO^{2-}_{4(aq)}}$

Sulphuric acid reacts with alkalis (bases) to give two types of salts: hydrogen sulphate and sulphate.

(1) $NaOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{(Sodium hydrogen sulphate)}}{NaHSO_{4(aq)}} + H_2O_{(l)}$

(2) $NaHSO_{4(aq)} + NaOH_{(aq)} \longrightarrow \underset{\text{(Sodium sulphate)}}{Na_2SO_{4(aq)}} + H_2O_{(l)}$

Sulphuric acids also react with metal oxides (basic oxides) like MgO to form salts and water.

$$MgO_{(s)} + H_2SO_{4(aq)} \longrightarrow MgSO_{4(aq)} + H_2O_{(l)}$$

(2) As an Oxidizing Agent:

Sulphuric acid acts as oxidizing agent. The oxidizing properties of H_2SO_4 depend upon (i) concentration of the acid (ii) nature of the metal or reducing agent (iii) temperature.

Oxidation of Metal:

Less electropositive metals like Zn, Fe, Al react with dilute sulphuric to liberate H_2 gas and forming their sulphates.

$$Zn_{(s)} + H_2SO_{4(aq)} \xrightarrow{\text{dilute}} ZnSO_{4(s)} + H_{2(g)}$$

$$Fe_{(s)} + H_2SO_{4(aq)} \xrightarrow{\text{dilute}} FeSO_{4(aq)} + H_{2(g)}$$

$$2Al_{(s)} + 3H_2SO_{4(aq)} \xrightarrow{\text{dilute}} Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$$

Hot conc.sulphuric acid oxidizes some metals to their sulphates liberating SO_2 gas.

$$Cu_{(s)} + 2H_2SO_{4(aq)} \xrightarrow[\text{Hot}]{\text{Conc.}} CuSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$

$$Pb_{(s)} + 2H_2SO_{4(aq)} \xrightarrow[\text{Hot}]{\text{Conc.}} PbSO_{4(s)} + SO_{2(g)} + 2H_2O_{(l)}$$

$$2Al_{(s)} + 6H_2SO_{4(aq)} \xrightarrow[\text{Hot}]{\text{Conc.}} Al_2(SO_4)_{3(aq)} + 3SO_{2(g)} + 6H_2O_{(l)}$$

Reactive metals with conc H_2SO_4 form different products. Zinc reacts with 90% conc. H_2SO_4 to liberate H_2S gas.

$$4Zn_{(s)} + 5H_2SO_{4(aq)} \xrightarrow{90\%} 4ZnSO_{4(s)} + H_2S_{(g)} + 4H_2O_{(l)}$$

Oxidation of Non-Metals:

Hot conc. sulphuric acid oxidizes some non-metals like C,S and P into their oxides or oxyacids.

$$C_{(s)} + 2H_2SO_{4(aq)} \xrightarrow[\text{Hot}]{\text{Conc.}} CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$$

$$S_{(s)} + 2H_2SO_{4(aq)} \xrightarrow[\text{Hot}]{\text{Conc.}} 3SO_{2(g)} + 2H_2O_{(l)}$$

$$2P_{(s)} + 3H_2SO_{4(aq)} \xrightarrow[\text{Hot}]{\text{Conc.}} 2H_3PO_{4(aq)} + 3SO_{2(g)}$$

Phosphoric acid

Oxidation of other Compounds:

Conc. sulphuric acid oxidizes hydrogen sulphide (H_2S) which is oxidized to sulphur and HI is oxidized to liberate vapours of I_2.

$$H_2S_{(aq)} + H_2SO_{4(aq)} \xrightarrow{\text{Conc.}} S_{(s)} + SO_{2(g)} + 2H_2O_{(l)}$$

$$2HI_{(aq)} + H_2SO_{4(aq)} \xrightarrow{\text{Conc.}} I_{2(g)} + SO_{2(g)} + 2H_2O_{(l)}$$

(3) As Drying or Dehydrating Agent:

Conc H_2SO_4 has great affinity for water, so conc. H_2SO_4 is able to remove hydrogen and oxygen in the form water from the compounds like sugar, ethanol, formic acid, oxalic acid etc. Thus hot conc. H_2SO_4 acts as powerful drying or dehydrating agent. This process of removing water from a compound is called dehydration. Conc. H_2SO_4 also removes water of crystallization from hydrated ionic compound to make the compound anhydrous.

$$C_{12}H_{22}O_{11(s)} \xrightarrow[\text{hot}]{\text{conc}H_2SO_4} 12C_{(s)} + 11H_2O_{(l)}$$

Sugar — Charred mass

$$CH_3\text{-}CH_2\text{-}OH_{(l)} \xrightarrow[170^0C]{\text{conc}H_2SO_4} CH_2 = CH_{2(g)} + H_2O_{(l)}$$

Ethanol — Ethene

$$HCOOH_{(l)} \xrightarrow{\text{conc}H_2SO_4} CO_{(g)} + H_2O_{(l)}$$

Formic acid

$$\begin{array}{l}COOH\\|\\COOH\end{array}_{(s)} \xrightarrow{\text{conc.}H_2SO_4} CO_{(g)} + CO_{2(g)} + H_2O_{(l)}$$

Oxalic acid

$$CuSO_4.5H_2O_{(s)} \xrightarrow{\text{conc}H_2SO_4} CuSO_{4(s)} + 5H_2O_{(g)}$$

Blue (hydrate) — White (anhydrous)

Uses of Sulphuric Acid:

Sulphuric acid is the most important chemical compound and is extensively used in industries. The progress and the prosperity of any nation can be estimated in terms of the amounts of sulphuric acid consumed annually. It is therefore, barometer of industrial and economical progress of a country. It's important uses are as follows:

(1) It is used in the manufacture of fertilizers, about one quarter of sulphuric acid produced in the world is consumed for the production of two main fertilizers; dihydrogen calcium phosphate (super phosphate) $Ca(H_2PO_4)_2$ and ammonium sulphate. $(NH_4)_2\ SO_4$.

(2) It is used in the manufacture of Rayon, paper, plastics and detergents.

(3) It is used in the manufacture of paints and pigments.
(4) It is used in the making cellulose film and all kinds of main-made fabrics.
(5) It is used in the steel pickling and cleaning.
(6) It is used in the dehydrating, drying reactions, also oxidizing reactions.
(7) It is used in the motor batteries and lead accumulators and in refining of metals by electrolysis.
(8) It is used for refining of petroleum.

SUMMARY

1. Sulphur exists in different allotropic forms, including rhombic sulphur, monoclinic sulphur and plastic sulphur. Rhombic sulphur is octahedral crystalline solid, while monoclinic sulphur is needle-like crystalline solid. Both are formed from S_8 molecules of sulphur. The melting point of rhombic sulphur is $113^{0}C$ and that of monoclinic sulphur is $119^{0}C$. Rhombic sulphur is a stable form of sulphur at ordinary condition. Both forms co-exist in equilibrium at $96^{0}C$ which is knwon as transition temperature. Rhombic sulphur exists below $96^{0}C$. while monoclinic sulphur exist between $96\text{-}119^{0}C$. Plastic sulphur is non-crystalline form of sulphur.
2. Sulphur is extracted from its deposits deep in the earth by Frasch process. In this method, compressed air and hot water at $170^{0}C$ are forced down through centre pipe into the sulphur deposit underground, molten sulphur is then forced up to the surface by another pipe.
3. Sulphur combines with metals and non-metals to form sulphides, it burns in air with blue flame forming sulphur dioxide gas. Sulphur also reacts with conc. HNO_3 and conc. H_2SO_4 to get oxidized.
4. Sulphuric acid is manufactured on large scale by the contact process. In this process SO_2 is oxidized to SO_3 in the presence of catalyst and then SO_3 is absorbed in conc. H_2SO_4 to form oleum ($H_2S_2O_7$) which is dissolved in water to get sulphuric acid of desired concentration.
5. Sulphuric acid is a strong dibasic acid. Dilute H_2SO_4 dissolves some metals liberating H_2 gas. With alkalis, sulphuric acid may form two types of salts, hydrogen sulphates and sulphates.
6. Sulphuric acid acts as powerful oxidizing agent, oxidizes metals, non metals and some chemical compounds and it self reduces to produce SO_2 gas. It is also a drying or dehydrating agent.

7. Sulphuric acid has great industrial importances and is used to get fertilizers, plastics, paints, pigments, fabrics, cellulose film etc. It is also used in motor batteries.

EXERCISE

1. Fill in the blanks.
   (i) Rhombic sulphur is the most ________ form of sulphur.
   (ii) Monoclinic sulphur has ________ structure.
   (iii) CS_2 is a good solvent for ________.
   (iv) The melting point of monoclinic sulphur is ________.
   (v) Pure sulphuric acid on large scale is manufactured by the ________ process.
   (vi) Phosphorous with hot conc. H_2SO_4 oxidizes to ________.
   (vii) Ethene gas evolves when ________ is dehydrated by hot conc. H_2SO_4.

2. Tick true or false for the following statements:
   (i) Plastic sulphur is hard.
   (ii) Monoclinic sulphur is stable above 96°C
   (iii) Sulphur is extracted by the direct mining from the earth's deposits.
   (iv) Conc. sulphuric acid has greater affinity for water.
   (v) Conc. sulphuric acid reduces to SO_2 when acts as oxidizing agent.
   (vi) In the manufacture of sulphuric acid, SO_3 is directly dissolved in water to produce oleum.
   (vii) Conc. H_2SO_4 removes water from sugar to leave charred mass.

3. Pick up the correct answer:
   (i) The formula of iron pyrite for getting SO_2 from pyrite burner is:
   (a) FeS (b) Fe_2S_3 (c) FeS_2 (d) Fe_2S_2
   (ii) The non crystalline form of sulphur is
   (a) Plastic sulphur (b) Rhombic sulphur,
   (c) Monoclinic sulphur (d) Ordinary sulphur.
   (iii) The specific gravity of 98.3% conc. H_2SO_4 is:
   (a) 1.5 (b) 1.84 (c) 1.80 (d) 1.91.

(iv) The density of rhombic sulphur is:
(a) 1.96 (b) 1.92 (c) 2.4 (d) 2.08.

(v) Rhombic sulphur has structure of shape:
(a) Square planar (b) Octahedral
(c) Tetrahadral, (d) Prismatic.

(vi) The Optimum condition of temperature for the maximum yield of SO_3 in contact process is:
(a) 350°C (b) 450°C (c) 1700°C (d) 900°C.

(vii) Sulphur burns in oxygen with blue flame to produce:
(a) SO_3 (b)H_2S (c) S_2Cl_2 (d) SO_2.

4. (a) What is allotropy? Describe different allotropic forms of sulphur.
(b) What is plastic sulphur? Why is it elastic?
(c) What is the action of sulphur on heating with.
(i) Cu (ii) C (iii) Cl_2 (iv) Na.
(d) Give four uses of sulphur.

5. (a) Describe and explain, how sulphur is extracted from underground deposits by Frasch process.
(b) Describe what happens when:
(i) Sulphur is heated in the absence of air.
(ii) Sulphur is heated in the presence of air.
(c) Complete the following reactions with balanced equations.

(i) $FeS_{2(s)} + O_{2(g)} \longrightarrow$

(ii) $Fe_{(s)} + S_{(s)} \longrightarrow$

(iii) $S_{(s)} + H_2SO_{4(aq)} \xrightarrow{Hot}$

(iv) $S_{(s)} + HNO_{3(conc)} \xrightarrow{Hot}$

(v) $SO_{3(g)} + H_2SO_{4(conc)} \xrightarrow{Hot}$

6. (a) Discuss various stages in the manufacture of sulphuric acid by the contact process, giving equations of the reactions involved. What is the catalyst used in the process?

(b) Explain why SO_2 is purified before it is passed into the contact tower for its oxidation to SO_3.

(c) Show that sulphuric acid acts as:

(i) oxidizing agent (ii) dehydrating agent.

(d) With the acid of equation, describe the action of conc. sulphuric acid on:

(i) Al metal (ii) C

(iii) $C_{12}H_{22}O_{11}$ (iv) Blue crystals of $CuSO_4.5H_2O$.

(e) Give the importance of sulphuric acid and its uses.

CHAPTER-15

HALOGENS

You wil learn in this chapter about:

- Occurrence, sources of halogens and importance of halogens in daily life.
- Chlorine and preparations of chlorine, laboratory and commercial preparations of cholrine.
- Physical,chemical properties and uses of chlorine,compounds of chlorine,hydrochloric acid,its preparation,properties and its uses.
- Bleaching powder, its preparation and importance.
- Silver nitrate test for the presence of Cl^-,Br^- and I^- ions.

15.1 INTRODUCTION

Halogens are the elements of VII A group of the periodic table. These elements are Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and Astatine (At). These elements are known as halogens-a name derived from Greek words meaning **Salt producing** (Halo means Salt, Gene means Producing), because these elements combine readily with metals to form salts.

Generally speaking halogens are the most reactive group of non-metals. These are strong oxidizing agents. The last member of the family Astatine is radioactive, shows different behaviour and is rather unstable (astatos=unstable). They exhibit various oxidation states in their compounds except fluorine which shows an oxidation state-1, which is a common oxidation state for all the halogens. Halogens exist as diatomic molecules, F_2, Cl_2, Br_2 and I_2.

Halogens belong to VII A group in the periodic table because all these elements contain seven electrons in their valence shells. All the halogens are oxidizing agents due to their ability to gain electron. However oxidizing power decreases from F_2 to I_2.

Fluorine and chlorine are gases, F_2 is of pale yellow in colour, Cl_2 is of greenish yellow gas or pale green in colour. Bromine (Br_2) is volatile reddish brown liquid. Iodine (I_2) is shiny black solid that sublimes readily giving violet vapours.

Some of the physical properties of halogens are summarized in the table 15.1

Table 15.1

Element	Fluorine(F)	Chlorine(Cl)	Bromine(Br)	Iodine (I)
Atomic number	9	17	35	53
Electronic configuration	2,7	2,8,7	2,8,18,7	2,8,18,18,7
Outer Shell (E.C)	$2s^2\ 2p^5$	$3s^2\ 3p^5$	$4s^2\ 4p^5$	$5s^2\ 5p^5$
State at 20^0C	Gas	Gas	Liquid	Solid
Colour	Pale yellow	Pale green	Redish brown	Black
Atomic size (A^0)	0.71	0.99	1.14	1.33
Ionic size ($\overline{x}$) (A^0)	1.33	1.81	1.96	2.20
First ionization energy (K.J/mol)	1681	1257	1140	1008
Electron affinity(K.J/mol)	-328	-349	-325	-295
Electro negativity	4.0	3.0	2.8	2.5
Melting point (^0C)	-220	-101	-7	113
Boiling point (^0C)	-188	-35	59	183
X-X single bond energy (KJ/mol)	155	242	193	151
Reduction potential (volt)	2.87	1.36	1.07	0.56
Solubility in water (g/100g water) $\frac{1}{2}X_2 + e^- \longrightarrow X^-_{(aq)}$	Reacts readily with water	0.5g (Reacts partially with water)	3.6g	0.018g

Occurrence or Sources:

The halogens are so reactive that they can not exist in the free state in nature. Halogens always occur naturally as compounds with metals. In these compounds they are present as their negative ions i.e, Flouride (F^-), chloride (Cl^-), bromide (Br^-) and iodide (I^-). Chlorine, bromine and iodine are found as halides, in sea water and in salt deposits. The concentration of iodine in these sources is very small. However it is concentrated in seaweeds. Fluorine and chlorine are abundant elements.

Fluorine occurs in the minerals, the most widely spread compounds of fluorine are fluorspar (CaF_2), cryolite ($Na_3 AlF_6$) and fluorapatite {$3Ca_3 (PO_4)_2 CaF_2$}.

Chlorine is abundant in oceans and salt deposits as sodium chloride i.e, rock salt(NaCl). Each kilogram of sea water contains about 30g of NaCl (3%). The large salt deposits in Pakistan are at khewra near Jhelum.

Bromine is less abundant and is found as bromide (Br) of Na and K in sea water. Sea water contains very small concentration of bromide, about 70 parts per million by mass, however this amount is still feasible for its extraction.

Iodine is even less abundent than bromine. Sea water contains traces of iodide (0.05 part per million by mass), however it concentrates in seaweeds is present upto 800 parts per million by mass and can be extracted from seaweeds. Iodine is also present as sodium iodide (NaI) in certain oil-wells and also as sodium iodate ($NaIO_3$), found along with chile salt peter ($NaNO_3$).

Astatine does not occur naturally. It is very unstable radioactive element.

Importance of Halogens in Daily Life:

Except chlorine, the halogens have limited uses, however their compounds are extensively used in industries, agriculture, medicines and homes.

Small quantity of fluorine is used in rocket propulsion, fluorine is used to make wide range of fluoro carbon compounds which are used as refrigerants, aerosol propellants, anaesthetics and fire-extinguisher fluids. One of the most important fluoro carbon is (poly tetra fluoroethane) PTFE, which is excellent electrical insulator and is used for wire coverings. PTFE which is commonly called as Teflon has very low co-efficient of friction and has non stick property, so it is also used to prepare non-sticking sauce pans, cooking stainless steel non-sticking utensils etc. Stannous fluoride (SnF_2) is used in tooth pastes for preventing tooth decay HF torches produce temperature upto 4000°C and is used in weldings.

The production and consumption of chlorine on large scale make it one of the most important product of chemical industry and national economy. This means chlorine is an important building block in the chemical industry. It is used in the manufacture of organic compounds like CCl_4 and $CHCl_3$ which are very good organic solvents. It is used in the manufacture of vinyl chloride which is used extensively in the preparation of PVC (Polyvinyl chloride) plastic. It is used in the productions of chlorocarbon, DDT (dichloro diphenyl trichloroethane), hexachloro-cyclohexane etc which are effective pesticides and in various synthetic products such as rubber etc.

Most of the drinking water is treated with chlorine to distroy bectaria i.e. drinking water is stirlized by chlorine, also disinfecting drainages. Swimming pools are rendered safe by chlorine treatment. All pathogenic organisms can be destroyed by chlorine.

You know sodium chloride (NaCl) is one of the most important compound of our daily diet. It is known as common salt or table salt. It has great importance. Na^+ ions of NaCl are important assistants in our body's communication systems and are key figures. Cl^- ions of NaCl have an equally vital function as Na^+ ions but in quite different region of the body. Cl^- ions form hydrochloric acid (HCl) in the stomach. However, its concentration is 0.5 percent, which is sufficient to destroy all the germs that smuggle into our body with the food.

The recent studies have shown that chlorine also plays an important role in the daily battle of the body's defense system against countless invisible enemies: bacteria, viruses, fungi and toxins. Many diseases are successfully controlled by chlorine. Chlorine fights against cholera. This shows chlorine plays a vital role in our health. Roughly 40 percent of all pharmaceutical products are based on chemical processes involving chlorine. For example chloroquine is the most effective medicine against malaria. Millions of malaria sufferers survive, thank to chlorine.

Inspite of all the importance in the daily life, chlorine has still come under fire and is described as **satanic element**. This is just because of its compounds which are considered to be dangerous and pose a threat to our health and environment, such as DDT (Dichloro diphenyl - trichloro ethane), PCBs (Poly chlorinated biphenyls), CFCs (Chloro fluoro carbons) etc are dangerous compounds. But chlorine has its benefits and we want to make use of its compounds.

Organo bromine compounds are used as Pharmaceuticals, dyes, fumigants and pesticides. Bromine compounds are also used in fire-extinguishers and fire retardants. An important inorganic compound of bromine which is silver bromide (AgBr) is used in photographic films, being light sensitive.

Iodine is of less importance than Cl_2 and Br_2, although iodine and its compounds do have applications as catalysts in medicine and in photographic films emulsion (AgI). Iodine and its compounds have uses in analytical chemistry. Iodide ion is used in thyroid glands to synthesise thyroxin, a substance that helps to regulate metabolism. An iodide ion deficiency leads to an enlargement of thyroid gland, a condition called **goiter**. Goiter is prevented by the use of iodized salt, a product that is mainly NaCl but includes a small quantity of NaI or KI. Iodine dissolved in ethyl alcohal, commonly known as **Tincture of Iodine**, is used as mild antiseptic for cuts and scratches. Iodine when mixed with detergents is used in cleaning dairy equipments.

15.2 CHLORINE

Chlorine is the second member of halogen family i.e. of VIIA group of the periodic table. Chlorine is the most abundant and very important member of VIIA group elements. Chlorine was discovered by C.W. Scheele a Swedish chemist by the action of hydrochloric acid on mangnese dioxide (MnO_2). The name chlorine to the gas was suggested in 1810 by Sir Humphry Davy from Greek word. **Chloros** means pale green, because the colour of the gas was pale green. We smell chlorine sometimes in our drinking water, in swimming pools, whose smell is slightly irritating and disagreeable.

PREPARATION OF CHLORINE

(1) Laboratory Method:

Chlorine is usually prepared in the laboratory from hydrochloric acid, which is a convenient source of chlorine. When concentrated hydrochloric acid is gently heated with oxidizing agent, such as MnO_2, $KMnO_4$ or $KClO_3$, chlorine gas is produced.

Reaction:

(i) $MnO_{2(s)} + 4HCl_{(conc)} \xrightarrow{\text{Heat}} MnCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$

(ii) $2KMnO_{4(s)} + 16HCl_{(conc)} \xrightarrow{\text{Heat}} 2KCl_{(aq)} + 2MnCl_{2(aq)} + 8H_2O_{(l)} + 5Cl_{2(g)}$

In this method MnO_2 is taken in round bottom flask, as shown in the figure 15.1, fitted with a cork, containing a delivery tube. Concentrated hydrochloric acid is added in the flask over MnO_2. On gentle heating greenish yellow chlorine gas comes out which is collected by the upward displacement of air in a gas jar through the delivery tube. Since it is a poisonous gas so efficient ventilation in the laboratory is necessary.

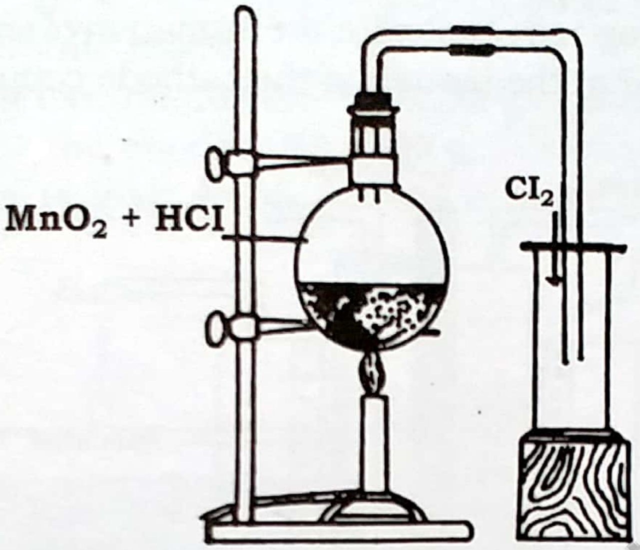


Fig.15.1 Laboratory preparation of chlorine

Chlorine in the laboratory can also be obtained by heating common salt (NaCl) with conc. H_2SO_4 in the presence of MnO_2.

$$2NaCl_{(s)} + 2H_2SO_{4(conc)} + MnO_{2(s)} \xrightarrow[\text{slow}]{\text{heat}} Na_2SO_{4(aq)} + MnSO_{4(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$$

Relatively pure chlorine in the laboratory is produced by heating potassium dichromate ($K_2Cr_2O_7$) with conc. HCl.

$$K_2Cr_2O_{7(s)} + 14HCl_{(conc)} \xrightarrow{\text{Heat}} 2KCl_{(aq)} + 2CrCl_{3(aq)} + 7H_2O_{(l)} + 3Cl_{2(g)}$$

(2) Industrial or Commercial Methods:

Chlorine on large scale is manufactured by the electrolysis of sodium chloried solution. For this purpose two cells are used which are described below:

(a) From Nelson's Cell:

Nelson's cell consits of a U-shaped perforated steel vessel, which acts as cathode. The graphite anode is dipped in the salt solution, taken in the U-shaped vessel. The U-tube is separated from anode by asbestos layer or diaphragm, deposited on the inner wall of the perforated U-tube, as shown in the figure 15.2. Through the diaphragm the salt solution slowly seeps. The U-tube is known as anode compartment and this U-tube is fixed in an outer compartment, known as cathode compartment. On passing electric current through the salt solution, chlorine gas is produced at anode, which rises into the dome at the top of the anode and is drawn away. Na metal is produced at cathode which interacts with water of the solution seeping through the diaphragm to release hydrogen (H_2) gas with the formation of sodium hydroxide solution which is collected at the bottom of the cathode compartment.

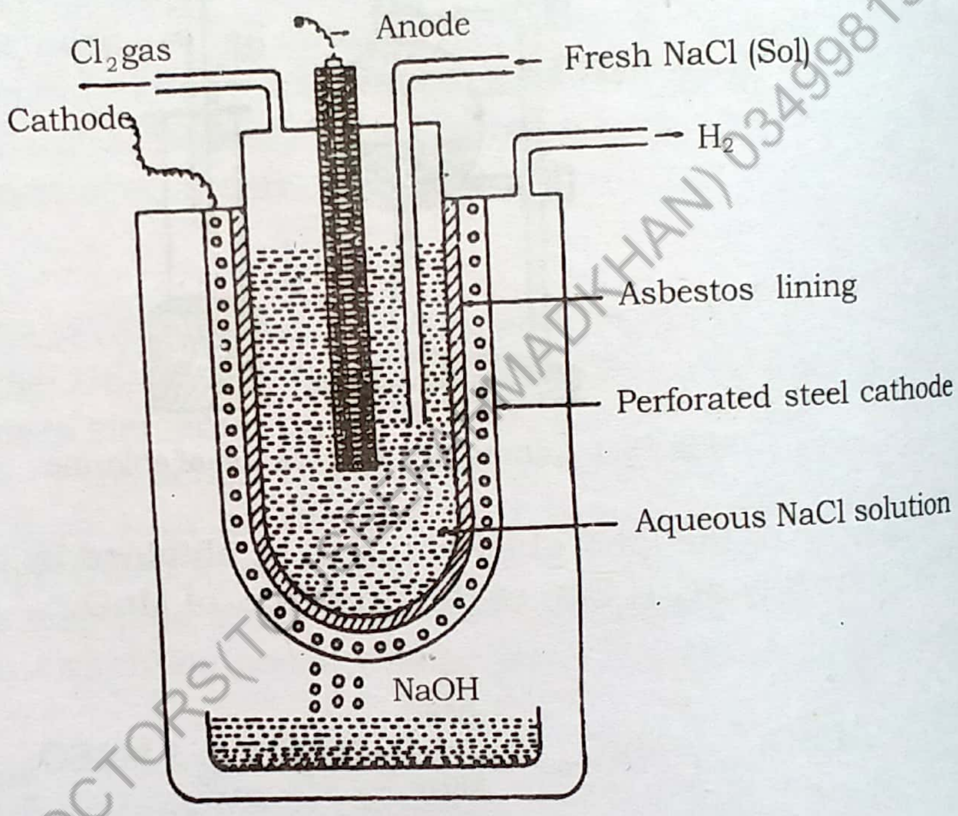


Fig. 15.2 Manufacture of chlorine from Nelson's Cell

Reactions:

(1) Ionization reaction:

$$2NaCl \xrightleftharpoons{\text{aqueous}} 2Na^{+}_{(aq)} + 2Cl^{-}_{(aq)}$$

(2) (i) Reaction at anode

$$2Cl_{(aq)} \longrightarrow Cl_{2(g)} + 2e^{-}$$

(ii) Reaction at cathode

$$2Na^{+}_{(aq)} + 2e^{-} \longrightarrow 2Na_{(s)}$$

$$2Na + 2H_2O \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

(b) From Castner-Kellner's Cell:

This cell has cathode consisting of moving mercury layer at the bottom of the cell. Mercury flows from right to left as this upper cell is slightly tilted. Saturated solution of NaCl also flows through the cell along with the Hg. Anodes are titanium plates dipped in the saturated solution of NaCl. There is also a lower cell known as **Soda cell** or denuder which is packed with graphite blocks.

On passing electric current chlorine gas is released at anodes and is collected outside the anodes. Na^+ ions are discharged at cathode which is moving mercury to form Na metal which at once forms sodium amalgam with mercury.

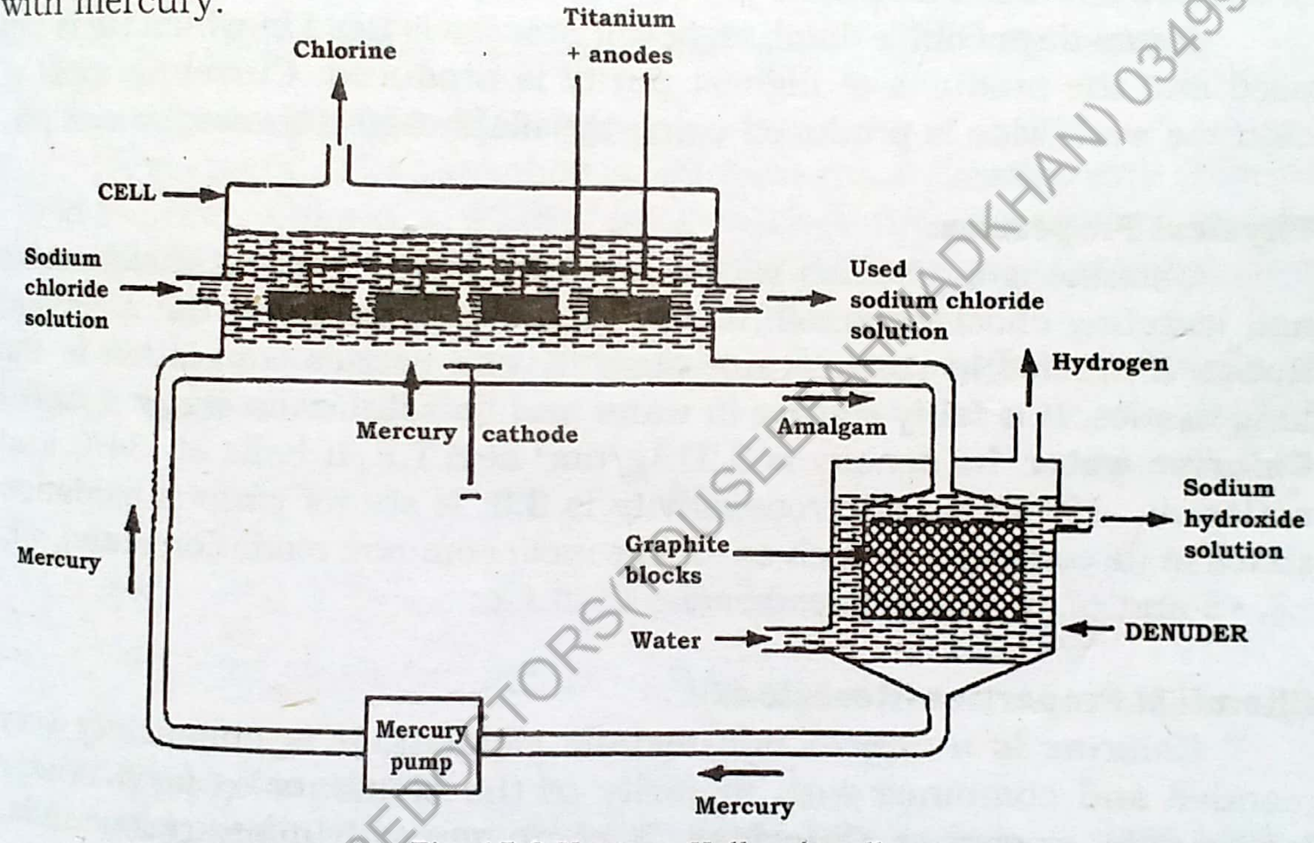


Fig. 15.3 Kastner-Kallner's cell

Reactions:

$$2NaCl \underset{}{\overset{\text{aqueous}}{\rightleftharpoons}} 2Na^+_{(aq)} + 2Cl^-_{(aq)}$$

Reaction at anode:

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$$

Reaction at cathode (Hg):

$$2Na^+_{(aq)} + 2e^- \longrightarrow 2Na$$

$$2Na + 2Hg \longrightarrow 2NaHg_{(l)} \text{ (sodium amalgam)}$$

Sodium amalgam is then carried to soda cell, where it is allowed to react with water to produce NaOH, liberating H_2 gas, while free mercury obtained is recycled in the upper cell to act as cathode.

$$2NaHg_{(l)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)} + 2Hg_{(l)}$$

The problem in this process is that mercury vapours escapes into the environment which are toxic, even small amount of mercury contaminates sea water, as a result mercury becomes the parts of tissues of aquatic animals and plants producing the pollution of food chains.

Now a days Gibb's diaphragm cell process is used in which Hg is not used and the products of highest purity is produced. Currently most of chlorine worldwide is produced using the diaphragm process.

Physical Properties:

Chlorine is a greenish yellow gas, with sharp pungent disagreeable and irritating chocking smell. It produces inflammation in the nose and throat, if inhaled in considerable quantity and causes congestion in the lung tissues. It is fairly soluble in water and its solution in water is called **Chlorine water**. Its density is 3.214g/dm^3 at S.T.P. It boils at -34°C and melts at -101°C. Its electronegativity is 3.0. It shows various oxidation states in its compounds such as -1 (the most common oxidation state), +1, +3, +5 and +7. It is 2.5 times heavier than air.

Chemical Properties (Reactions):

Chlorine is a typical non-metalic element. It is chemically very reactive and combines with majority of the elements to form binary compounds, known as **Chlorides**. It combines with many compounds, displacing other elements such as oxygen, bromine, iodine, hydrogen etc. It also adds in many chemical compounds.

(1) Reactions with Hydrogen:

Chlorine combines with hydrogen in the presence of sunlight or on heating quickly to form hydrogen chloride.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow[\text{or heat}]{\text{Sun light}} 2HCl_{(g)}$$

(2) Reactions with Metals:

Practically all metals combine with chlorine on heating to form their chlorides.

(i) $2Na_{(s)} + Cl_{2(g)} \xrightarrow{heat} 2NaCl_{(s)}$

(ii) $Zn_{(s)} + Cl_{2(g)} \xrightarrow{heat} ZnCl_{2(s)}$

(iii) $2Sb_{(s)} + 3Cl_{2(g)} \xrightarrow{heat} 2SbCl_{3(s)}$ (Antimony chloride)

(iv) $2Fe_{(s)} + 3Cl_{2(g)} \xrightarrow{heat} 2FeCl_{3(s)}$ (Ferric chloride)

(v) $Sn_{(s)} + 2Cl_{2(g)} \xrightarrow{heat} SnCl_{4(s)}$ (Stannic chloride)

(3) Reactions with Non- Metals:

Non - metals like phosphorus, sulphur etc. on heating with chlorine, produce their chlorides. Phosphorus catches fire in chlorine, forming phosphorus trichloride (PCl_3) a colourless liquid, in excess of chlorine forms phosphorus pentachloride (PCl_5) a pale yellow solid.

Chlorine combines with hot sulphur, forming sulphur monochloride (S_2Cl_2), a yellowish liquid.

(i) $2P_{(s)} + 3Cl_{2(g)} \xrightarrow{heat} 2PCl_{3(l)}$

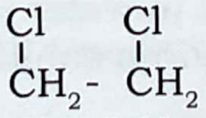
(ii) $2P_{(s)} + 5Cl_{2(g)} \xrightarrow[excess]{heat} 2PCl_{5(s)}$

(iii) $2S_{(s)} + Cl_{2(g)} \xrightarrow{heat} S_2Cl_{2(l)}$

(4) Addition Reactions:

Chlorine directly combines with many compounds to form addition products.

(i) $CH_2 = CH_{2(g)} + Cl_{2(g)} \longrightarrow$



$\overset{Cl}{\overset{|}{CH_2}}-\overset{Cl}{\overset{|}{CH_2}}$

Ethane

1,2 - dichloro ethane

(ii) $CO_{(g)} + Cl_{2(g)} \longrightarrow COCl_{2(g)}$

Phosgene gas; a poisonous gas and is used as chemical weapon in warefare.

(iii) $SO_{2(g)} + Cl_{2(g)} \longrightarrow SO_2Cl_2$

Sulphuryl chloride

(5) Substitution Reactions:

Chlorine replaces one or more atoms from other compounds such reactions are called substitutions reactions.

(i) $H_2S_{(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)} + S_{(s)}$

(ii) $2KBr_{(s)} + Cl_{2(g)} \longrightarrow 2KCl_{(s)} + Br_{2(g)}$

(iii) $2KI_{(s)} + Cl_{2(g)} \longrightarrow 2KCl_{(s)} + I_{2(g)}$

(iv) $CH_{4(g)} + Cl_{2(g)} \xrightarrow{h\nu} CH_3Cl_{(l)} + HCl$

(v) $CH_3Cl + Cl_{2(g)} \xrightarrow{h\nu} CH_2Cl_2 + HCl$

(6) Oxidation and Bleaching Action:

Chlorine in the presence of water acts as powerful oxidizing and bleaching agent due to the formation of hypochlorous acid, Cl_2 reacts with water and under go auto oxidation-reduction forming hypochlorous acid and hydrochloric acid.

$$Cl_2^0 + H_2O \longrightarrow H\text{–}Cl + \underset{\text{Hypochlorous acid.}}{HOCl}$$

It oxidize green coloured ferrous chloride ($FeCl_2$) to yellow coloured ferric chloride ($FeCl_3$).

$$\underset{\text{Green}}{2FeCl_{2(aq)}} + Cl_2\text{(water)} \longrightarrow \underset{\text{Yellow}}{2FeCl_{3(aq)}}$$

Solution of chlorine in water is a strong oxidizing agent and oxidizes sulphurous acid (H_2SO_3) into sulphuric acid (H_2SO_4).

$$H_2SO_3 + Cl_2 + H_2O \longrightarrow H_2SO_4 + 2HCl$$

The reaction proceeds as,

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl + HOCl$$
$$HClO \longrightarrow HCl + [O]$$
$$H_2SO_3 + [O] \longrightarrow H_2SO_4$$

(7) Reactions of Chlorine with Alkalies:

When Cl_2 gas is passed through caustic soda solution (NaOH) in cold, then sodium hypochlorite and chlorides are formed.

$$Cl_2 + 2NaOH_{(aq)} \xrightarrow{\text{cold}} NaCl_{(aq)} + NaClO + H_2O$$

i.e sod hypochlorite
or sodium chlorate (I)

If excess of Cl_2 gas is passed through hot solution of NaOH, sodium chlorate (v) is produced, by the decomposition of sodium hypochlorite.

$$3Cl_{2(g)} + 6NaOH_{(aq)} \xrightarrow{\text{hot}} 5NaCl_{(aq)} + NaClO_3 + 3H_2O$$

Sodium chlorate (v)

Or $$3NaClO \xrightarrow[\text{excess of } Cl_2]{\text{hot}} NaClO_{3(aq)} + 2NaCl_{(aq)}$$

Sodium chlorate(I) Sodium chlorate (v)

(8) Reaction with Ammonia:

Chlorine reacts with ammonia violently to form nitrogen and hydrogen chloride, hydrogen chloride then combines with excess of NH_3 to produce white fumes of NH_4Cl.

(i) $$2NH_{3(s)} + 3Cl_{2(g)} \longrightarrow N_{2(g)} + 6HCl_{(g)}$$

(ii) $$6NH_{3(g)} + 6HCl_{(g)} \longrightarrow 6NH_4Cl \text{ (white fumes)}$$

In this reaction ammonia must be in large excess otherwise nitrogen trichloride (NCl_3) would be produced which is highly explosive compound.

(9) Reaction with Lime Water:

Chlorine reacts with lime water in three ways:

(i) With cold and dilute lime water in excess.
When Cl_2 is reacted with excess of cold and dil. lime water, calcium chlorate (I) is produced.

$$2Ca(OH)_2 + 2Cl_2 \xrightarrow{\text{cold}} Ca(OCl)_2 + CaCl_2 + 2H_2O$$

Ca-hypochlorite

(ii) With hot lime water in excess of chlorine.

When excess of Cl_2 is reacted with hot lime water calcium chlorate (v) is produced.

$$6Ca(OH)_2 + 6Cl_2 \xrightarrow{hot} \underset{\text{Ca-chlorate}}{Ca(ClO_3)_2} + 5CaCl_2 + 6H_2O$$

(iii) Passing Cl_2 gas over dry slaked lime.

When Cl_2 gas is passed over dry slaked lime at about 40^0C, bleaching powder is produced.

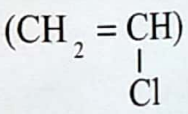
$$\underset{\text{Dry}}{Ca(OH)_{2(s)}} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl_{(s)}} + 2H_2O$$

Uses Of Chlorine:

The production and consumption of chlorine on large scale make it one of the most important chemicals of chemical industry and national economy.

(i) It is used in the manufacture of chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) which are very good organic solvents and in the production of sulphur monochloride (S_2Cl_2), a volcanizing agent.

(ii) It is used in the preparation of Vinyl Chloride



$\left(CH_2 = \underset{\underset{Cl}{|}}{CH}\right)$

which is used in the manufacture of PVC (Poly Vinyl Chloride), a common plastic.

(iii) It is used in the chloro-carbon preparations such as D.D.T, hexachloro cyclohexane which are effective pesticides.

(iv) It is used in the preparation of bleaching powder which is used in bleaching cotton, linen cloths.

(v) It is used for sterilizing drinking water and disinfecting drainages and sewers to kill bacteria.

(vi) It is used in the production of some poisonous gases of warfare such as phosgene, $COCl_2$, Chloropicrin; CCl_3 NO_2 and mustard gas, $(C_2H_4Cl)_2S$.

(vii) Chlorine is used extensively in the production of dyes, drugs, explosives etc.

(viii) It is also used in the layer test for the identification of bromine and iodine.

15.3 COMPOUNDS OF CHLORINE

(1) Hydrochloric Acid; HCl (Hydrogen Chloride):

Hydrochloric acid was sometimes called as muriatic acid.

Laboratory preparation:

The oldest laboratory method for the preparation of hydrochloric acid, is by the action of Conc. H_2SO_4 on common salt (NaCl).

$$NaCl_{(s)} + H_2SO_{4(conc)} \xrightarrow{150^0 C} \underset{\text{Sodium hydrogen sulphate}}{NaHSO_{4(aq)}} + HCl_{(g)}$$

In this method, common salt (NaCl) is placed in a round bottom flask, fitted with a thistle funnel and a delivery tube fig 15.4. Concentrated H_2SO_4 is added from the thistle funnel over common salt, thistle funnel should be dipped in the acidic mixture. The reaction starts at once with effervescence to liberate HCl gas and when HCl gas evolution slakens, the flask is gently heated to get faster supply of HCl gas, which is collected through the delivery tube in gas jar by the upward displacement of air. The gas is highly soluble in water and dissolves to form hydrochloric acid. This acid is usually yellow due to impurities.

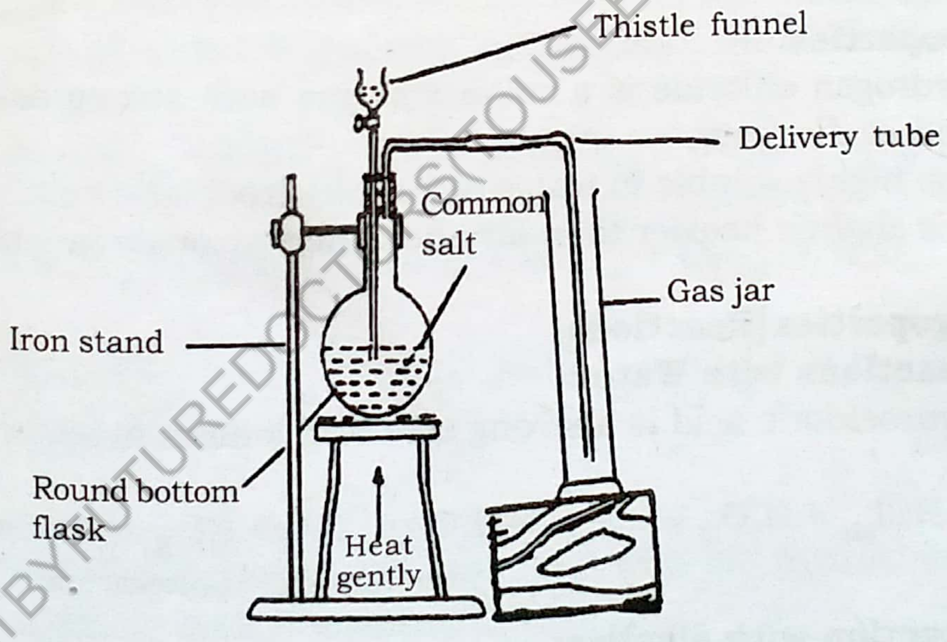


Fig.15.4 Laboratory preparation of hydrochloric acid

Industrial Preparations:

(i) Hydrochloric acid is commercially prepared in the pure state by the direct combination of hydrogen and chlorine gas.

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)} \quad ; \Delta H = -44.12 \text{ KJ/mol}$$

The reaction is strongly exothermic. The gas mixture is burnt in brick lined furnace; using water cooled iron nozzle. A small excess of H_2 gas is usually used to minimize corrosion. Gases from the furnace are absorbed in water. Hydrochloric acid is much in demand in Pakistan.

Today, however most of hydrochloric acid is obtained as a by product during the chlorination of hydrocarbons.

(ii) Hydrochloric acid from the chlorides of non-metals, such as PCl_3 is obtained by the action of PCl_3 with water.

$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow \underset{\text{Phosphorus acid}}{H_3PO_{3(aq)}} + 3HCl_{(g)}$$

(iii) Hydrochloric acid can also be obtained by the action of chlorine over hydrogen compounds.

(a) $H_2S_{(g)} + Cl_{2(g)} \longrightarrow S_{(s)} + 2HCl_{(g)}$

(b) $2H_2O_{(l)} + 2Cl_{2(g)} \longrightarrow 4HCl_{(aq)} + O_{2(g)}$

Physical Properties:

(i) Hydrogen chloride is a colourless gas with strong acidic odour and acidic taste.

(ii) It is highly soluble in water to form hydrochloric acid.

(iii) It is slightly heavier than air and fumes strongly in moist air.

Chemical Properties (Reactions)

(i) Reactions with Water:

Hydrochloric acid is a strong acid and ionizes in water as,

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{hydronium ion}}{H_3O^+_{(aq)}} + \underset{\text{Chloride ion}}{Cl^-_{(aq)}}$$

(ii) Reaction with alkalies:

Hydrochloric acid reacts with alkalies like NaOH solution or KOH solution to produce salt and water.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$$KOH_{(aq)} + HCl_{(aq)} \longrightarrow KCl_{(aq)} + H_2O_{(l)}$$

(iii) Reaction with ammonia:

Hydrochloric acid react with ammonia (NH_3) to produce ammonium chloride; white fumes of NH_4Cl is observed.

$$NH_3 + HCl \longrightarrow NH_4Cl \text{ (White fumes)}$$

(iv) Reaction with less electropositive metals:

Less electropostive metals like Mg, Zn, Al etc. react with dilute hydrochloric acid to liberate hydrogen gas with the formation of their chlorides.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}\uparrow$$

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}\uparrow$$

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}\uparrow$$

(v) Reaction with metal corbonates and bicarbonates:

Metal carbonates and bicarbonates react with dilute hydrochloric acid to liberate CO_2 gas with effervescence with formation of metal chlorides.

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + CO_{2(g)}\uparrow + H_2O_{(l)}$$

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + CO_{2(g)}\uparrow + H_2O_{(l)}$$

$$\underset{\text{sod-bicarbonate}}{NaHCO_{3(s)}} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + CO_{2(g)}\uparrow + H_2O_{(l)}$$

(vi) Reaction with $AgNO_3$ and $Pb(NO_3)_2$

Silver nitrate and lead nitrate react with dil- hydrochloric acid to precipitate their chlorides.

$$AgNO_{3(aq)} + HCl_{(aq)} \longrightarrow \underset{\text{White precipitate}}{AgCl_{(s)}} + HNO_{3(aq)}$$

$$Pb(NO_3)_{2(aq)} + 2HCl_{(aq)} \longrightarrow \underset{\text{White precipitate}}{PbCl_{2(s)}} + 2HNO_{3(aq)}$$

Uses:

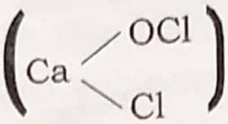
(i) Hydrochloric acid is used for the pickling of iron and steel that is to remove the rust from the metal surface.

(ii) It is used in the manufacture of dyes, plastics, medicine, rubber, chlorides etc.

(iii) It is used as chemical reagent in the laboratory.

(iv) It is used to remove $CaCO_3$ deposits from sanitary wares and floors.

2- Bleaching Powder:

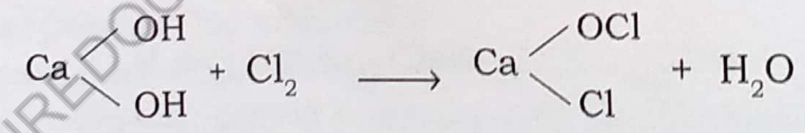
Bleaching powder is a mixed salt of calcium with chloride and oxychloride. Professor Odling suggested the formula of bleaching powder as Ca(OCl) Cl or $CaOCl_2$  on the basis of the available percentage of chlorine.

Preparation:

(i) Laboratory Preparation:

In the laboratory bleaching powder is prepared by shaking a small quantity of slaked lime; $Ca(OH)_2$ with chlorine in a jar, a white powder is produced.

$$Ca(OH)_{2(aq)} + Cl_{2(g)} \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)Cl_{(s)}} + H_2O_{(l)}$$



$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + H_2O$$

(ii) Commercial Preparation:

On large scale bleaching powder is prepared by Hasenclever process. The Hasenclever plant consists of four, iron cylinders 2 to 3 meter long in which chlorine gas is passed in the opposite direction to come in contact with slacked lime which is blown from top of the cylinders by means of compressed air and is allowed to fall. Chlorine is completely absorbed in the upper cylinders where fresh slacked lime enters. The reaction occurs to form bleaching powder.

Reaction:

$$Ca(OH)_2 + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_{2(s)}} + H_2O$$

An off white amorphous powder (bleaching powder) with the smell of chlorine is removed, dried and packed in wooden vats and kept in the dark for sometimes. It is stored in well-ventilated rooms.

Physical Properties:

Bleaching powder is a white amorphous powder which strongly smells like chlorine. It is frequently called as **Bleach**.

Chemical Properties:

(i) Reaction with water:

Bleaching powder is generally used with reasonable quantity of water. In water, it liberates Cl_2 gas on reaction.

$$Ca(OCl)Cl_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + Cl_{2(g)}$$

It also decomposes into $CaCl_2$ and $Ca(OCl)_2$ in presence of excess of water and acts as strong bleaching agent.

$$2Ca(OCl)Cl \xrightarrow{H_2O(excess)} CaCl_{2(aq)} + \underset{\text{Calcium hypochlorite}}{Ca(OCl)_{2(aq)}}$$

(ii) Reaction with strong acids:

Bleaching powder reacts with strong acids like HCl to liberate Cl_2 gas.

$$Ca(OCl)Cl + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + Cl_{2(g)} + H_2O_{(l)}$$

(iii) Reaction with CO_2 in the presence of moisture (with weak carbonic acid):

Bleaching powder reacts slowly with carbon dioxide of air in the presence of moisture in the air to hypochlorous acid (HClO) which oxidizes and destroys impurities in the surrounding atmosphere.

$$2Ca(OCl)Cl + CO_{2(g)} + H_2O \longrightarrow CaCO_{3(s)} + CaCl_{2(aq)} + 2HOCl_{(aq)}$$

(iv) Reaction with ammonia:

When bleaching powder is treated with solution of ammonia, N_2 gas evolves.

$$3Ca\,(OCl)Cl + 2NH_3 \longrightarrow 3CaCl_{2(aq)} + N_{2(g)} + 3H_2O_{(l)}$$

Uses:

(i) Bleaching powder is used for sterlization of drinking water and disinfecting drainages and sewers.

(ii) It is used for bleaching of cotton, linen and paper pulp.

(iii) It is used for the quick preparation of Cl_2 gas which is a powerful oxidizing agent.

(iv) It is also used to prepare hypochlorous acid (HClO)

15.4 TESTS FOR HALIDE IONS (Silver Nitrate Test)

All common metallic halides, such as NaCl, K Br, Mg I_2 etc are soluble in water except halides of Ag and Pb. For the detection of Cl^-, Br^- and I^- ions silver nitrate test is performed which gives the precipitates of AgCl, AgBr and AgI. For this purpose, the aqueous solution of the common metallic halides are treated with the solution of silver nitrate ($AgNO_3$) to give the precipitate of AgCl, AgBr and AgI which helps us for the inference of Cl^-, Br^- and I^- ions.

Experiment	Observation	Inference
Original solution + $AgNO_3$	(i) If white ppt of AgCl, soluble in dilute and conc. NH_3 solution. **or** white ppt of AgCl turns purple grey in sunlight	Cl^- is present
	(ii) If light yellow or cream precipitate of AgBr, which is partially soluble in dilute NH_3 solution but insoluble in conc. NH_3. cream ppt of AgBr turns green yellow in sunlight.	Br^- is present
	(iii) If bright yellow ppt of AgI which is insoluble in dil. and conc. NH_3 solution. Yellow ppt of AgI has no effect of sunlight.	I^- is present

Reactions:

(i) $NaCl_{(aq)} + AgNO_{3(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$
white ppt

(ii) $NaBr_{(aq)} + AgNO_{3(aq)} \longrightarrow AgBr_{(s)} + NaNO_{3(aq)}$
light yellow
or cream ppt

(iii) $NaI_{(aq)} + AgNO_{3(aq)} \longrightarrow AgI_{(s)} + NaNO_{3(aq)}$

SUMMARY

1- The halogens are VIIA group elements in the periodic table and are reactive non metals. They are powerful oxidizing agents because of their tendency to gain electron.

2- The halogens show remarkable similarities in their properties and reactions. However with the increasing atomic number, the reactivity becomes less.

3- The halogens due to their greater chemical reactivites, never occur in the free state in nature. They occur naturally in the combined states that is only in their compounds.

4- The halogens exist as diatomic molecules. Such as F_2, Cl_2, Br_2 and I_2. Their atoms have seven electrons in their valence shells.

5- In nature chlorine occurs mostly as sodium chloride which is found as salt deposits in the ground and also in the sea water.

6- Chlorine is prepared in the laboratory by the action of conc. hydrochloric acid on mangnese dioxide. Commercially, it is produced by the electrolysis of aqueous sodium chloride (brine).

7- Chlorine is used for bleaching, disinfecting drinking water, drainages, sewers and in the chemical industry.

8- Hydrogen chloride is prepared in the laboratory by the action of conc. sulpuric acid over common salt (NaCl). On large scale, it is prepared by the direct combination of hydrogen (H_2) and chlorine (Cl_2) gases. It is a gas which is highly soluble in water to form strong hydrochloric acid.

9- Bleaching powder is commonly known as **bleach** and is prepared on large scale by Hasenclever process by the interaction of slaked lime;

$Ca(OH)_2$ and Cl_2 gas. It is a white amorphous powder which smells chlorine.

10- Sodium iodide when treated with silver nitrate, bright yellow precipitate of AgI is obtained which is insoluble in ammonia.

EXERCISE

1. (a) Fill in the blank:

(i) __________ is the dark brown volatile liquid.

(ii) __________ is the black shining low melting solid.

(iii) __________ can replace all other halogens from the solutions of their salts.

(iv) I_2 dissolved in alcohol is called __________.

(v) Cl_2 gas is liberated by the action of __________ over water.

(b) Write True or False in the following statements:

(i) In the electrolysis of sodium chloride solution, chloride ions are discharged at the anode.

(ii) Hydrochloric acid reacts with many metals to release H_2 gas.

(iii) Bleaching powder is a powerful reducing agent.

(iv) All halogens contain six electrons in the outer shell.

(v) Astatine the last member of halogens is unstable and radioactive.

(vi) Br_2 can displace chlorine from KCl.

(c) Pick up the correct answers:

(i) In the process of electrolysis:

(a) Oxidation takes place at cathode.

(b) Reduction takes place at anode.

(c) Cations are discharged at cathode.

(d) Anions are discharged at cathode.

(ii) Which one of the following will release chlorine from hydrochloric acid?

(a) Na (b) MnO_2 (c) KOH (d) $CuSO_4$.

(iii) When chlorine atom combines with hydrogen atoms, which type of the bond is formed?

(a) Ionic bond (b) Co ordinate covalent

(c) Polar covalent (d) Non-Polar covalent.

(iv) Chlorine gas prepared in the laboratory is collected in the gas jar by:
(a) Upward displacement of water
(b) Upward displacement of air
(c) Downward displacement of air
(d) Downward displacement of water.

(v) The most abundant and useful halogen is:
(a) Bromine (b) Fluorine (c) Iodine (d) Chlorine.

2. Complete the following reactions:

(i) $MnO_{2(s)} + HCl_{(conc)} \longrightarrow$

(ii) $NaHg_{(l)} + H_2O_{(l)} \longrightarrow$

(iii) $KI_{(s)} + Cl_{2(g)} \longrightarrow$

(iv) $NaOH_{(aq)} + Cl_{2(g)}\ \text{(excess)} \xrightarrow{\text{hot}}$

(v) $AgNO_{3(aq)} + HCl_{(aq)} \longrightarrow$

(vi) $Ca(OCl)Cl_{(s)} + HCl_{(aq)} \longrightarrow$

(vii) $KBr_{(aq)} + AgNO_{3(aq)} \longrightarrow$

(viii) $K_2Cr_2O_7 + HCl_{(conc)} \longrightarrow$

3. (a) What are halogens? Why are they placed in VII A group in the periodic table? Describe the state of each member of the family and also their colours.

(b) What are the sources of halogens? Describe the importance of Cl_2, Br_2 and I_2 in our daily life.

4. (a) How is chlorine prepared in the laboratory?

(b) Describe the commercial preparation of chlorine by the electrolysis of aqueous NaCl solution in Nelson's cell.

(c) What happens when chlorine reacts with: (i) Sn (ii) H_2S (iii) CO (iv) P (v) $FeCl_2$ (vi) H_2O. Give reactions and equations.

(d) Discuss the uses of chlorine.

5. (a) Give the preparation of hydrogen chloride (HCl) in the laboratory by the action of conc. H_2SO_4 over common salt (NaCl).

(b) How is hydrogen chloride is manufactured commercially by direct combination of H_2 and Cl_2 gases.

(c) What is the action hydrochloric acid (HCl) on

(i) NaOH (ii) $NaHCO_3$ (iii) $Pb(NO_3)_2$
(iv) MnO_2 (v) $KMnO_4$

6. (a) What is bleaching powder? How is it manufactured commercially by Hasenclever process? Give the uses of bleaching powder.

(b) What is the action of bleaching powder over:

(i) water (ii) excess of water (iii) H_2CO_3 (weak acid)
(iv) ammonia (NH_3), (v) HCl.

7. (a) Describe silver nitrate test for the presence of Cl^- ion in a salt of chloride. Give the reaction.

(b) Identify the following:

(i) A pale green gas that dissolves in aqueous NaOH solution give a solution used as a bleach.
(ii) A gas with pungent smell, acidic taste, highly soluble in water to form a strong acid.
(iii) White amorphous solid which reacts with water to liberate chlorine gas.
(iv) The deficiency of this leads to the enlargement of thyroid gland.
(v) A pale yellow gas, very unstable in water.
(vi) A non-sticking material, having very low coefficient of heat.

CHAPTER-16

METALS AND THEIR EXTRACTION

You will learn in this chapter about:

- Metals and non-metals and their physical,chemical differences between metals and non-metals.
- Minerals and ores, occurrence of metals like Fe,Cu,Al and Cr.
- Metallurgy, primary preparations of ores.
- Metallurgy of iron i.e extraction of iron from haematite (Fe_2O_3).
- Pig iron,cast iron,wrought iron and steel. Difference between iron,steel and tempering.
- Extraction of copper metal from copper pyrite and refinning of blister copper.
- Extraction of aluminium metal from its bauxite ore. Alloys and some common alloys like bronze, brass and nichrome.

16.1 METALS AND NON-METALS

Elements in the periodic table are classified mainly as metals and non-metals. In early days, metals were identified from non-metals by their physical characteristics. Some of the physical characteristics of metals and non-metals are given below.

Physical Differences Between Metals and Non-Metals:

Metals:

1. All metals except mercury are solids with high melting points and boiling points.
2. Metals have characteristic lusture, known as metallic lusture and can be polished.
3. They on hitting with hammer give off notes i.e they are **Sonorous.**
4. Metals are malleable and ductile that is they can be converted into sheets and wires.
5. Metals have great tensile strength and can withstand stress and strain.
6. They have relatively high densities.
7. They are good conductors of heat and electricity. Some common metals are Iron (Fe), Copper (Cu), Aluminium (Al) and Chromium (Cr).

Non-Metals:

1. Non-metals have low melting and boiling points, about half of the non-metals are gases.
2. Non-metals do not have lusture like metals and can not be polished.
3. They are not sonorous and break on hitting.
4. They are usually brittle and break easily when subjected to stress or strain.
5. They are neither malleable nor ductile.
6. They are generally bad conductors of heat and electricity.
7. They have relatively low densities. Some examples of non-metals are Sulphur (S), Carbon(C), Oxygen (O_2), Nitrogen (N_2) and Chlorine (Cl_2).

There are few exceptions to the statements about metals and non-metals, for instance, mercury (Hg) is a liquid metal with very low melting point about - 39^{0}C. Metals like sodium and potassium are very light metals and also soft. They can be cut by knife and have relatively low melting points about 98^{0}C and 63^{0}C respectively. Similarly in case of non-metals like diamond (carbon) which is very hard and has very high melting point about 3500^{0}C, while its allotrope graphite (carbon) is a shiny solid, having dull metallic lusture and is a good conductor of heat and electricity.

Chemical Differences Between Metals and Non-Metals

Metals and non-metals not only differ in their physical properties but also show characteristic differences in their chemical properties. The most outstanding differences are in their oxides formations.

Metals combine with oxygen on burning to yield basic oxides i.e the oxides of metals are basic in character. When dissolved in water they form alkaline solution that turns red litmus blue. On the other hand, non-metals combine with oxygen on burning to yield acidic oxides i.e the oxides of non-metals are acidic in character. When dissolved in water they form acidic solutions that turn blue litmus red.

However, our present day knowledge about the structures of atoms, shows that the essential difference between metals and non-metals is in their electronic arrangements i.e electronic configurations. Their physical differences are due to their basic atomic structures i.e the arrangements of their atoms, while chemical differences are due to the number of electrons in their valence shells.

So metals and non-metals may be re-defined as:

Metal is an element which ionizes by the loss of electrons to form positive ion easily, while non-metals is an element which ionizes by the gain of electrons easily to form negative ion.

Metals have few electrons in their valence shells so have greater tendency to lose electrons during chemical reactions to form electrovalent i.e ionic compounds and are electropositive elements to produce positive ions i.e cations.

For Example:

$\underset{(2,8,1)}{Na} \rightarrow \underset{(2,8)}{\overset{+1}{Na}} + 1\overset{-}{e}$ (univalent cation)

$\underset{(2,8,2)}{Mg} \rightarrow \underset{(2,8)}{\overset{2+}{Mg}} + 2\overset{-}{e}$ (divalent cation)

$\underset{(2,8,3)}{Al} \rightarrow \underset{(2,8)}{\overset{3+}{Al}} + 3\overset{-}{e}$ (trivalent cation)

On the other hand non-metals have more electrons in their valence shells, usually four to seven electrons in their valence shells. So they have either the tendency to accept or gain electrons in chemical reactions to form ionic or electrovalent compounds and form negative ions i.e anions. Or they share electrons during chemical reactions to form covalent compounds. The number of electrons gained per atom of non-metal is the valency of the non-metal.

For Example:

$\underset{(2,8,7)}{Cl} + 1\overset{-}{e} \rightarrow \underset{(2,8,8)}{\overset{-}{Cl}}$ (univalent negative ion)

$\underset{(2,8,6)}{S} + 2\overset{-}{e} \rightarrow \underset{(2,8,8)}{\overset{2-}{S}}$ (divalent negative ion)

The important differences in the chemical properties of metals and non-metals are due to their ability to lose or gain or share electrons respectively.

1. Reactions With Acids:

Metals which are more electropositive than hydrogen react with dilute acids to liberate H_2 gas, forming their salts by the loss of electrons.

$$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

$$Mg_{(s)} + 2HNO_{3(aq)} \longrightarrow Mg(NO_3)_{2(aq)} + H_{2(g)}$$

$$2Al_{(s)} + 3H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$$

Non-metals do not react with dilute acids, however, with hot concentrated acids, some of the non-metals get oxidized into their oxides or some oxy-acids.

For Example:

$$C_{(s)} + 4HNO_{3(conc)} \xrightarrow{hot} CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$$

$$S_{(s)} + 6HNO_{3(conc)} \xrightarrow{hot} H_2SO_{4(aq)} + 6NO_{2(g)} + 2H_2O_{(l)}$$

$$S_{(s)} + 2H_2SO_{4(conc)} \xrightarrow{hot} 3SO_{2(g)} + 2H_2O_{(l)}$$

2. Reducing And Oxidizing Agents:

Metals are generally reducing agents because they have greater tendency to donate their electrons readily during chemical reactions. On the other hand, non-metals are generally oxidizing agents because of their tendency to accept electrons readily during chemical reactions.

For Example:

$$\underset{\text{metal}}{2\overset{0}{Na}} + \underset{\text{non-metal}}{\overset{0}{Cl_2}} \rightarrow 2\overset{+1}{Na}\overset{1-}{Cl}$$

$$\underset{\text{metal}}{2\overset{0}{Al}} + \underset{\text{non-metal}}{3\overset{0}{S}} \xrightarrow{heat} \overset{3+}{Al_2}\overset{2-}{S_3}$$

3. Nature of Chlorides:

Metallic chlorides are electrovalent i.e ionic compounds. They are non-volatile crystalline solids and are good electrolytes. They have high melting points and are generally soluble in water.

For example:

$$\overset{+}{Na}\overset{-}{Cl}\left(Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow \overset{+}{Na}\overset{-}{Cl}_{(s)}\right)$$

On the other hand non-metals form covalent chlorides by the sharing of electrons, which are usually volatile liquids, easily hydrolysed in water in most of the cases.

For Example:

$$PCl_{3(l)}(2P_{(s)}+3Cl_{2(g)} \longrightarrow 2PCl_{3(s)}$$

For example PCl_3 is hydrolyzed in water to form phosphorous acid and HCl.

$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow \underset{\text{Phosphorous acid}}{H_3PO_{3(aq)}} + 3HCl_{(aq)}$$

4. Nature of Hydrides:

Metals form very few compounds with hydrogen. However very electropositive metals like Na, K, Ca etc. combine with hydrogen to form ionic hydrides by the transfer of electrons such as Na^+H^-, K^+H^-, $Ca^{2+}H^{1-}_2$ etc.

For Example:

$$\overset{+}{Na}\overset{-}{H}_{(s)}\left(Na_{(s)}+\frac{1}{2}H_{2(g)} \rightarrow \overset{+}{Na}\overset{-}{H}_{(s)}\right)$$

These metallic hydrides are salt-like ionic solids. They are good electrolytes, soluble in water, but they react with water to liberate H_2 gas. This is a hydrolysis reaction.

$$\overset{2+}{Ca}\overset{1-}{H}_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + 2H_{2(g)}\uparrow$$

On the other hand, non-metals combine with hydrogen to form stable covalent hydrides by the sharing of electrons, such as NH_3, H_2S, HCl etc.

They are mostly gases and are generally non-electrolytes.

16.2 MINERALS AND ORES (Occurrence of Metals like Fe, Cu, Al and Cr)

Only few least reactive metals, such as gold and platinum are found in the free state i.e in the uncombined state in nature, while the majority of metals are usually found in combined states.

The combined forms of metals with less definite chemical impurities are known as **minerals.** Often these minerals are found mixed with earthy materials, known as **ores**. Thus those minerals which are considered worth minning commercially for the extraction of one or more metals are called ores. Ores mostly consist of a mixture of minerals with worthless rocky materials. These rocky materials present in ores are called **gangue particles.**

For example, the most important ore of iron is Fe_2O_3 (haematite).

Occurrence of Iron:

Iron has been known and used by mankind for very long time. Today it is one of the best known metal in the world because of its great industrial importance.

Iron is the second most abundant metal after aluminium found in the earth crust. Iron is generally found in the combined states. The most common ores of iron are:

(i) Haematite : Fe_2O_3

(ii) Magnetite : Fe_3O_4

(iii) Iron pyrite : FeS_2

(iv) Siderite or Spathic : $FeCO_3$

(v) Limonite : $Fe_2O_3 . 3H_2O$ (Hydrated)

Iron is also present in clay soils as iron silicate. Iron is an important part of haemoglobin, present in the red blood cell.

In Pakistan large deposits of high grade iron ores are found in Chitral, Kohistan and in Baluchistan. Presently these ores are not commercially utilized in Pakistan.

Occurrence of Copper:

Copper has been known since the **Bronze Age.** The ancient Egyptians, Romans and Greeks used copper for their metal works. It is less abundant in earth as compared to iron, but it is very useful and an important metal. It is less reactive and can be found in the free state. However, the important ores of copper are:

(i) Copper pyrite : $CuFeS_2$

(ii) Cuperite : Cu_2O

(iii) Chalcocite : Cu_2S

(iv) Malochite : $CuCO_3 . Cu(OH)_2$ (green colour)

(v) Azurite : $[2CuCO_3 . Cu(OH)_2]$ (blue colour)

(vi) Bornite : $Cu_2S . CuS . FeS.$

The most important ore of copper is copper pyrite ($CuFeS_2$). Copper ores are present in Baluchistan in Pakistan.

Occurrence of Aluminium:

Aluminium is the third most abundant element after oxygen and silicon found in the earth's crust. It is the most abundant metal present in the earth's crust. It is found in the combined state. Aluminium generally occurs as alumino-silicate minerals. The important ores of Aluminium are:

1. SILICATE ORES (i) Kaolin : $Al_2O_3 . 2SiO_2 . 2H_2O$
(ii) Potash Felspar : $K_2O . Al_2O_3 . 6SiO_2$
(iii) Potash mica : $K_2O . 3Al_2O_3 . 6SiO_2 . 2H_2O$

2. FLUORIDE ORE (i) Cryolite : $Na_3 AlF_6$

3. SULPHATE ORE (i) Alunite : $K_2SO_4 . Al_2(SO_4)_3 . 4Al(OH)_3$

4. OXIDE ORES (i) Bauxite : $Al_2O_3 . nH_2O$(or $Al_2O_3.2H_2O$)
(ii) Diaspore : $Al_2O_3 . H_2O$
(iii) Corrundum : Al_2O_3

The chief ore for the extraction of Al-metal is bauxite. Bauxite is found in Pakistan near the village Khilla; Muzaffarabad (Azad Kashmir), village Gian and Salhan of Tehsil Kohli, near Rawalpindi at Margalla hills, Surge of District Attock and in Tharparkar and Dadu Districts of Sindh.

Occurrence of Chromium:

Chromium is a silvery white metal and is well-known for its corrosion and rusting property. The main ore of chromium is chromite or chrome iron; $FeO. Cr_2O_3$. Chromite ore is found in Baluchistan and in Malakand at NWFP.

16.3 METALLURGY

The majority metals are found in nature in the combined states with other chemical substances, known as minerals. The minerals are often mixed with earthy materials, called as **ores**. The metal contents in ores are very low. The extraction of metal from its ore is termed as **metallurgy**. Thus metallurgy is the science and technology of extracting metals from their natural sources i.e ores and making them for practical use. Metallurgy usually involves some simple processes such as:

(i) Minning (ii) Concentration of the ore i.e making it suitable for further treatment (iii) Reduction of the ore to get free metal (iv) Refining or purification of the metal (v) Mixing of the metal with other elements to modify its strength. The last process is to produce an alloy of the metal.

Preliminary Preparations:

After being mined, an ore is usually crushed and grinded for the preliminary preparations.

(1) Concentration of The Ore:

Concentration of the ore is performed only for sulphide ores. A more sophisticated technique of the concentration of the ore is the **froth floatation process**. Froth floatation process involves the mixing of finely divided ore with impurities with water and oil, specially pine oil or creosote oil. Air is blown in the mixture and the oil, forming froth which floats on the surface and then the froth is skimmed off that contains the sulphide ore, while the gangue particles present in the ore sink at the bottom. The froth is washed and dried, and is known as **Concentrated Ore**.

Another common method is to pass the ore through magnetic separator, as in case of copper ore. The ores which have high metallic contents are deflected into a pile, while the earthy impurities pass straight on.

(2) Roasting of The Concentrated Ore:

The concentrated ore is roasted in a furnace in air to remove the sulphur, carbon and other impurity contents from the ore. Sulphur and carbon are removed as SO_2 and CO_2 gases respectively, leaving behind the oxides of the metals. Arsenic and antimony present are also burnt off in the process of roasting. The oxides are easier to deal with as compared to sulphides and carbonates.

For Example:

$$4CuFeS_{2(s)} + 5O_{2(g)} \xrightarrow{\text{roasting}} 2Cu_2S_{(s)} + 2FeO_{(s)} + 2FeS_{(s)} + 4SO_{2(g)}$$

(3) Smelting of The Ore:

In this process of smelting, the roasted ore is mixed with sand i.e silica (SiO_2) and coke (C). The ore is now heated strongly until it melts. The remaining impurities present react with silica to form **Slag** of molten **Silicates**. The slag is removed from the top of the molten mass and is discarded. The remaining molten mass left is called **matte**.

(4) Reduction:

In order to get free metals, reduction process is applied, in which a reducing agent or electron donor must be present to supply electrons to the metallic ions. The reduction can be brought by three main methods, depending upon the nature of the particular metal (a) Chemical reduction (b) Thermal reduction and (c) Electrolytic reduction.

(a) Chemical Reduction:

The less electropositive metals like Pb, Fe, Sn, Zn etc. are usually obtained by reducing their oxides with coke or carbon monoxide, which are cheaply available. For example in case of zinc, its ore zinc blend (ZnS) is first oxidized or converted into its oxide in the process of roasting. The oxide of zinc is then reduced by heating it with coke.

(i) $2ZnS_{(s)} + 3O_{2(g)} \xrightarrow[\text{(heat)}]{\text{roasting}} 2ZnO_{(s)} + 2SO_{2(g)}$

(ii) $ZnO_{(s)} + C_{(s)} \xrightarrow{\text{heat}} Zn_{(s)} + CO_{(g)}\uparrow$

(b) Thermal Reduction:

Some metals are reduced from their ores by direct heating for example; mercury is obtained by simply heating its ore mercuric sulphide (HgS) in air.

$$HgS_{(s)} + O_{2(g)} \longrightarrow Hg_{(l)} + SO_{2(g)}$$

(c) Reduction by Electrolysis:

More electropositive metals like Na, K, Ca, Mg etc. form compounds which are very stable and difficult to reduce chemically. The reduction of these metals occurs by electrolytic reduction process by passing electric current through their molten salts specially chloride salts, for example, sodium metal is obtained by the electrolytic reduction of molten NaCl, when electric current is passed through the molten mixture of NaCl and $CaCl_2$. Electrolytic reduction process is expensive and is applied when chemical method is not applicable.

$$2\overset{+}{Na}\overset{-}{Cl} \rightleftharpoons 2\overset{+}{Na}_{(l)} + 2\overset{-}{Cl}_{(l)}$$

At Cathode $2N\overset{+}{a} + 2\overset{-}{e} \longrightarrow 2Na_{(s)}$

16.4 METALLURGY OF IRON

Metallic iron has been known and used by the mankind for a very long time. Today it is considered as one of the best known metals in the world because of its usefulness in the service of mankind. Our modern life style is mostly based on the use of machineries whose major components are made from iron and its alloys.

Extraction of Iron:

The most important raw materials or ores from which iron metal is extracted, are oxide ores i.e haematite (Fe_2O_3) or limonite ($Fe_2O_3 \cdot 3H_2O$).

The first stage involved in the manufacture of iron is the reduction of oxide ores in a blast furnace as given in fig. 16.1. This involves the crushing of the oxide ore to produce lumps. These lumps are then pre-heated using hot gases from the blast furnace. This removes water and other volatile impurities present in the ore.

In the second stage the roasted iron ores are charged with coke and lime stone ($CaCO_3$) which are fed from the top of the furnace, while a blast of hot air is introduced into it from the bottom through small pipes known as **tayeres**.

The temperature inside the furnace varies from about 2000°C near the bottom to about 200°C at the top. The blast of hot air oxidizes the coke to carbon dioxide with the liberation of lot of heat.

$$C_{(s)}+O_{2(g)} \longrightarrow CO_{2(g)};\ \Delta H=-394\ KJ/mol$$

The reaction is highly exothermic. This raises the temperature. As CO_2 gas rises up the furnace, it reacts with more coke, forming CO gas.

$$CO_{2(g)}+C_{(s)}+heat \longrightarrow 2CO_{2(g)}\ ;\ \Delta H=+173\ \ KJ/mol$$

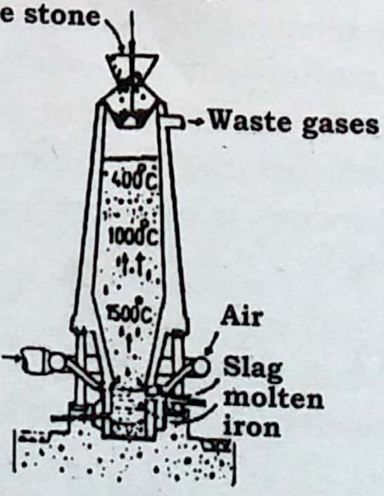


Fig: 16.1 Diagrammatic representation of a blast furnace

Carbon monoxide (CO) gas, thus produced then reduces the iron oxide ores to free iron metal in the upper parts of the furnace. Here temperature is between 477°C to 727°C.

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(l)} + 3CO_{2(g)}$$

The lime stone which has been introduced together with coke, decomposes at high temperature to yield calcium oxide (CaO) which then combines with silica (SiO_2) and aluminium oxide (Al_2O_3), present as impurities to form calcium silicate ($CaSiO_3$) and calcium aluminate ($Ca\,Al_2O_4$).

$$\underset{\text{Lime stone}}{CaCO_{3(s)}} \xrightarrow{\text{high temp}} CaO_{(s)} + CO_{2(g)}$$

(i) $CaO + SiO_2 \longrightarrow Ca\,SiO_{3(l)}$

(ii) $CaO + Al_2O_3 \longrightarrow CaAl_2O_{4(l)}$

The mixture of $CaSiO_3$ and $Ca\,Al_2O_4$ which remains molten at the furnace temperature is known as **slag**. The molten free iron runs downward to the bottom of the furnace and is withdrawn through a tap hole at short intervals. The slag being lighter floats on top of the molten iron and is run off. The slag is not wasted and is a useful bye-product. It is used as a road making material, for cement manufacturing and for making light weight building materials.

The gas leaving the furnace is known as flue gas. It contains nitrogen, carbon monoxide, carbon dioxide and fine solid particles including carbon particles. The emission of flue gas is a source of environmental pollutions.

The molten iron metal, obtained from the blast furnace is run into sand moulds where it cools down to solid blocks called **Pig Iron.** Pig iron is hard but brittle and melts at 1227°C. Pig iron may also be used directly to make steel. Pig iron is about 96% iron (Fe) and 4% carbon (C), with small amounts of other impurities such as silica, sulphur, phosphorous and mangnese as shown in the table 16.1.

TABLE 16.1 THE MAIN COMPONENTS OF PIG IRON

COMPONENT	PERCENTAGE
Iron	**94 - 96%**
Carbon	**3.5 - 4%**
Silica (Silicon)	**1.2%**
Sulphur	**0.05 - 0.1%**
Phosphorous	**0.05 - 1.5%**
Mangnese	**0.05 - 1.0%**

Pig iron is re-melted, mixed with scrap steel and cooled in mould to form cast iron. This has much the same properties as pig iron and can be used for items such as gates, pipes, lamp posts, engine blocks, stoves etc. The presence of impurities makes cast iron brittle and difficult to weld.

Activity:

Take small pieces of iron. Spread on a table. Take a magnet and touch iron pieces with the magnet. See, what happens?

Types of Iron:

(1) Pig Iron:

Pig iron is the iron which is obtained directly from the blast furnace and is quite impure. The impurities are mentioned in the table 16.1. It contains upto 4% carbon which is present both as graphite and iron carbide (Fe_3C) together with other impurities of Si, S, P and Mn in varying proportions depending on the nature of the ores used and the operating temperature. The presence of these impurities lowers the melting point of iron from 1530°C to 1200°C. Pig iron is hard and brittle and therefore has limited industrial uses.

(2) Cast Iron:

Cast iron is obtained from pig iron which is re-melted with some scrap steel and then cooled in moulds of required shapes. Cast iron has a slightly lower percentage of impurities than pig iron and almost has the same physical properties. It is brittle and can not be welded or forged. It is used for machinery objects which do not require greater tensile strength; for example: tools, lamp posts, gates, pipes, railings, the base of Bunsen burners, engine blocks etc.

(3) Wrought Iron:

Wrought iron is the purest commercial iron. It contains only about 0.1% carbon. Wrought iron is obtained by heating cast iron in a furnace with haematite (Fe_2O_3). During this process, carbon and sulphur are oxidized and are removed as CO_2 and SO_2 respectively.

$$2Fe_2O_{3(s)} + 3C_{(s)} \longrightarrow 4Fe_{(l)} + 3CO_{2(g)}$$

$$2Fe_2O_{3(s)} + 3S_{(s)} \longrightarrow 4Fe_{(l)} + 3SO_{2(g)}$$

At the same time phosphorous and silicon present are converted into phosphate and silicates of iron which can be removed as a slag from the semi-molten mass of iron.

Wrought iron is almost pure iron. Therefore it is soft but very tough and malleable. It can be shaped by hammering at about 500°C to 1000°C before its melting point. It can easily be welded and forged. It is used for making nails, chains, iron rods, sheets and horse shoes.

(4) Steel (Conversion of Iron into Steel):

Most of the pig iron manufactured now-a-days is used for the production of steel. About 90% of the pig iron is converted into steel. Steel is an alloy of iron with carbon and other elements such as mangnese, nickel, chromium, tungston and vanadium.

The main impurities in pig iron and in mild steel is given in table 16.2.

TABLE 16.2

Impurity	Percent Impurity in Pig Iron	Percent Impurity in Steel
Carbon	3-5	0.15
Silicon	1-2	0.03
Sulphur	0.05-0.10	0.05
Phosphorous	0.05-1.5	0.05
Mangnese	0.50-1.0	0.50

There are several methods of making steel. During the last 50 years, the technique of steel productions have undergone vast changes. New processes have also been developed to keep pace with the demands of quantity and quality. The more important methods are:

(1) The basic oxygen process.
(2) Open hearth process.
(3) The electric arc process.

However, they are all based on the same general principle of removing the impurities of C, Si, S, P and Mn from the molten pig iron and to obtain steel of desired compositions.

Difference Between Iron and Steel:

As compared to iron, steel is hard, tough and strong. Its properties depend on its carbon content, the heat treatment it receives (tempering and the presence of other metals). If carbon content in steel is greater than in iron, then hardness and brittleness increase. For example mild steels which are the commonest steels contain 0.1-0.25% of carbon and are soft, malleable and ductile. Medium steels contain 0.6-1.5% carbon are harder than mild steels. They are used for making tools and most alloy steels.

Medium and hard steels can be heat-treated to produce steels with different degree of hardness and tensile strength. This is done by heating the steel to red hot and cooling it suddenly. The steel obtained is very hard and brittle. To remove brittleness and to increase tensile strength, the steel is re-heated to certain carefully regulated temperatures and allowed to cool slowly. This process is known as **tempering**.

Alloy steels vary widely in compositions. The presence of Ni and Cr gives stainless steels which resist corrosion or rusting and are used in making cutleries, scissors, surgical instruments and machineries. The presence of cobalt gives highly magnetic steel, used for making permanent magnets. Tungsten gives very hard steel for making cutting, drilling tools.

Some Common Stainless Steels:

There are three main types of stainless steels which have different percentage of base metals and are as follows:

1. Stainless steel containing 13% Cr and 0.1-0.4% C
2. Stainless steel containing 17% Cr and 2% Ni
3. Stainless steel containing 18% Cr and 6% Ni

16.5 COPPER

Occurrence:

Copper occurs naturally in few places. Copper is very useful and important metal. It is relatively un-reactive. In combined state, it is found as its naturally occurring compounds as ores. The most important ores of copper are:

(i) Copper pyrite : $CuFeS_2$
(ii) Copper glance : CuS
(iii) Chalcocite : Cu_2S
(iv) Cuperite : Cu_2O
(v) Malachite : $CuCO_3 . Cu(OH)_2$ (green)
(vi) Azurite : $[2CuCO_3 . Cu(OH)_2]$ (blue)

Extraction of Copper (Metallurgy of Copper):

Copper metal is usually extracted from its sulphide ores, such as copper pyrite ($CuFeS_2$) which contains about 6% copper.

The extraction of copper from copper pyrite involves the following processes.

(1) Concentration of the ore.
(2) Roasting of the concentrated ore.
(3) Smelting of the roasted ore.
(4) Reduction to produce blister copper.
(5) Refining of blister copper (electrical refining).

(1) Concentration of The Ore:

Copper metal is mainly extracted from copper pyrite which is low grade and contains about 6% copper. In this process the pyrite ore is first purified by concentration. Froth floatation process is used for concentrating the ore. In this process the ore is crushed and is mixed with water and pine oil or creosote oil. Air is blown into the mixture, oil forms froth with sulphide ore, which floats to the surface. The gangue particles in ore, settle down. The sulphide ore particles tend to get coated with oil and are carried to the surface along with the froth. The froth along with the mineral particles is skimmed off and is dried to get concentrated ore. The gangue particles are left behind (Fig. 16.2)

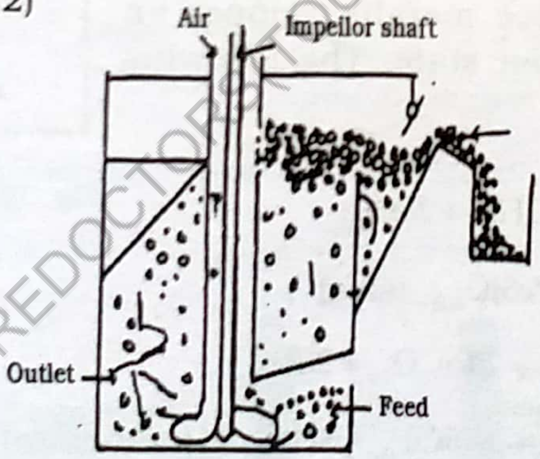


Fig. 16.2 Concentration of an ore by a froth floatation process

(2) Roasting:

The enriched concentrated ore is then roasted on an open-hearth furnace in air. Part of sulphur and other impurities like arsenic and antimony are burnt off and are removed as their oxides.

$$4CuFeS_{2(s)} + 5O_{2(g)} \xrightarrow{\text{roasted}} 2Cu_2S_{(s)} + 2FeO_{(s)} + 2FeS_{(s)} + 4SO_{2(g)}$$

(3) Smelting:

The roasted ore is then charged into a blast furnace together with a little coke and silica (SiO_2). In the process of smelting sulphide ore is oxidized to oxide of iron which combines with silica to form slag as iron silicate ($FeSiO_3$). The slag is removed which floats on the surface at regular intervals and is discarded.

$$2FeS_{(s)} + 3O_{2(g)} \longrightarrow 2FeO + 2SO_{2(g)}$$

$$FeO + SiO_2 \longrightarrow FeSiO_{3(l)} \quad \text{(slag)}$$

The molten mass below the slag comprises of cuperous sulphide (Cu_2S), mixed with some ferrous sulphide (FeS), known as **matte**.

(4) Reduction:

The molten copper matte i.e Cu_2S with some unreacted FeS is carried out to a converter called Bessemer converter where it is treated with some silica by blowing hot air. The iron sulphide that escapes during smelting is oxidized to FeO, forming a slag with silica by blowing hot air. The blast of hot air converts Cu_2S partially to Cu_2O which then reacts with remaining Cu_2S to give metallic copper on reduction in the molten state. The following reactions take place.

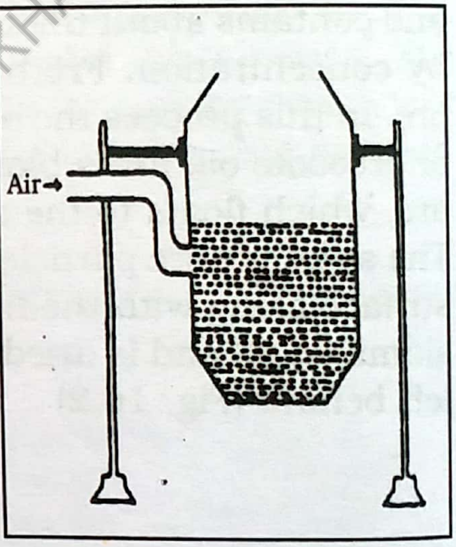


Fig. 16.3 Bessemer converter

$$2FeS + 3O_{2(g)} \longrightarrow 2FeO + 2SO_{2(g)}$$

$$FeO_{(l)} + SiO_2 \longrightarrow FeSiO_{3(l)} \quad \text{(slag)}$$

$$2Cu_2S_{(l)} + 3O_{2(g)} \longrightarrow 2Cu_2O_{(l)} + 2SO_{2(g)}$$

$$2Cu_2O_{(l)} + Cu_2S_{(l)} \longrightarrow 6Cu_{(l)} + SO_{2(g)} \quad \text{(reduction)}$$

The molten copper is poured into sand moulds. On cooling, thus solidified in sand moulds and is known as **blister copper**. The blisters are produced during solidification on cooling due to the escape of dissolved $S0_2$ gas. Blister copper is about 98% pure copper. Blister copper contains impurities of iron, zinc, lead, silver, gold etc. Due to presence of impurities, blister copper is not suitable for electrical work. It is then further refined by electrolytic process.

(5) Refining of Blister Copper:

Blister copper contains Fe, Zn, Pb, Ag, Au as impurities which reduce the conductivity of copper, so blister copper is refined by the electrolytic process.

In this process blocks of impure copper (blister copper) are used as anodes and very thin sheets of pure copper act as cathodes. The anodes and cathodes are suspended in copper sulphate solution ($CuSO_4$), acidified with little amount of dilute sulphuric acid (H_2SO_4).

The electrolysis is carried out at 50°C by passing electric current of 1.3 volt, which helps to deposit pure copper metal at cathode by dissolving impure (blister) copper anodes forming Cu^{2+} ions. The impurities of less active metals like Zn, Ag, Au etc are left over un-dissolved and fall at bottom of the cell as **anode mud** (Fig. 16.4).

Reactions:

At Anodes:

$$\underset{\text{Blister copper}}{Cu_{(s)}} \longrightarrow Cu^{2+}_{(aq)} + 2\bar{e}$$

At Cathode:

$$Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow \underset{\text{Pure copper metal}}{Cu_{(s)}}$$

The electrically refined copper is 100% pure.

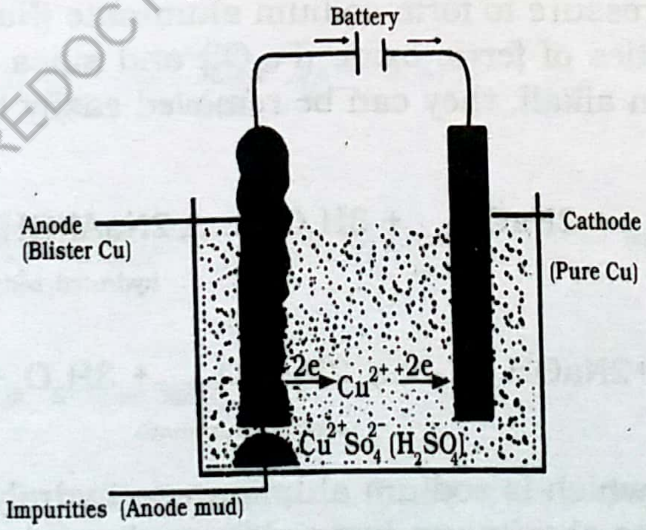


Fig. 16.4 Electrolytic refining of copper (Electrolysis of blister copper)

16.6 ALUMINIUM (Al)

Occurrence:

Al is the only common metal in III A group. Al is less reactive than alkali and alkaline earth metals. It is not found in the free state in nature. Its compounds are wide spread. Aluminium is the third most abundant element (after oxygen and silicon), found in the earth's crust. It is present up to 7.6% in the earth's crust. It is found abundantly as silicates in rocks and clays.

Extraction of Aluminium:

Economically the most important ore for the extraction of aluminium metal is **bauxite** (impure hydrated aluminium oxide, $Al_2O_3 \cdot 2H_2O$), from which Al metal is obtained.

The industrial process invented independently in 1886 by C.M. Hall and L.T. Heroult was introduced for the extraction aluminium metal from bauxite, known as Hall-Heroult process.

The extraction of Al metals by this process proceeds in two stages. In the first stage the crude bauxite is treated and purified to yield pure anhydrous alumina (Al_2O_3), which is then electrolysed in the second stage to get aluminium metal.

(1) Purification of Bauxite:

The bauxite ore contains major impurities of ferric oxide (Fe_2O_3) and silica (SiO_2). These impurities should be removed from bauxite in order to get aluminium metal of highest quality.

In this step the bauxite ore is grinded and crushed to finely divided bauxite ore. It is then heated with concentrated caustic soda (NaOH) solution under pressure to form sodium aluminate ($NaAlO_2$) or $NaAl(OH)_4$. Since the impurities of ferric oxide (Fe_2O_3) and silica (SiO_2) do not react with or dissolve in alkali, they can be removed easily by filteration and is called a sludge.

$$\underset{\text{bauxite}}{Al_2O_3 \cdot 2H_2O_{(s)}} + 2NaOH_{(aq)} + 3H_2O \longrightarrow \underset{\text{hydrated sodium aluminate}}{2NaAl(OH)_{4(aq)}} + \text{impurities}_{(s)}$$

or

$$Al_2O_3 . 2H_2O_{(s)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{sodium aluminate}}{2NaAlO_{2(aq)}} + 3H_2O_{(l)} + \text{impurities}$$

The filterate which is sodium aluminate is hydrolysed with excess of water to precipitate aluminium hydroxide or aluminium oxide trihydrate ($Al_2O_3 \cdot 3H_2O$), which is filtered, washed and dried.

$$2NaAlO_2 + 4H_2O \longrightarrow Al_2O_3 \cdot 3H_2O_{(s)} + 2NaOH_{(aq)}$$

or

$$2NaAl(OH)_4 \longrightarrow 2Al(OH)_{3(S)} + 2NaOH_{(aq)}$$

$Al_2O_3 \cdot 3H_2O_{(s)}$ or $Al(OH)_{3(S)}$ obtained is strongly heated upto 1500°C to yield pure alumina (Al_2O_3) on dehydration.

$$2Al(OH)_{3(S)} \xrightarrow{1500^0 C} \underset{\text{Pure alumina}}{Al_2O_{3(S)}} + 3H_2O_{(g)}$$

or

$$Al_2O_3 \cdot 3H_2O_{(s)} \xrightarrow{1500^0 C} \underset{\text{Pure alumina}}{Al_2O_{3(S)}} + 3H_2O_{(s)}$$

(2) Electrolysis of Pure Alumina:

The electrolysis of alumina is carried in a steel tank lined inside with graphite which acts as cathode, while anodes are the graphite rods dipped in the molten mixture of pure alumina dissolved in molten cryolite (Na_3AlF_6) with some fluorspar (CaF_2). Cryolite lowers the melting point of pure alumina upto 950°C and maintains the temperature through out the electrolysis, while fluorspar increases the fluidity of molten Al-metal. Al^{3+} ions would be discharged at cathode.

On passing the electric current the reactions take place as:

Ionization Reactions:

$$2Al_2O_3 \underset{950^0C}{\overset{\text{cryolite}}{\rightleftharpoons}} 4Al^{3+} + 6O^{2-}$$

At Cathode

$$4Al^{3+} + 12e^- \xrightarrow{950^0 C} 4Al_{(l)}$$

At Anode

$$6O^{2-} \longrightarrow 3O_{2(g)} + 12\bar{e}$$

Molten Al metal is produced at cathode which flows down the cell and is tapped off from the outlet at the bottom of the cell periodically.

Oxygen (O_2) gas is liberated at anode which interacts with the carbon of anode to form oxides of carbon. As a result the anodes are gradually burnt away and must be replaced from time to time. Fig. 16.5.

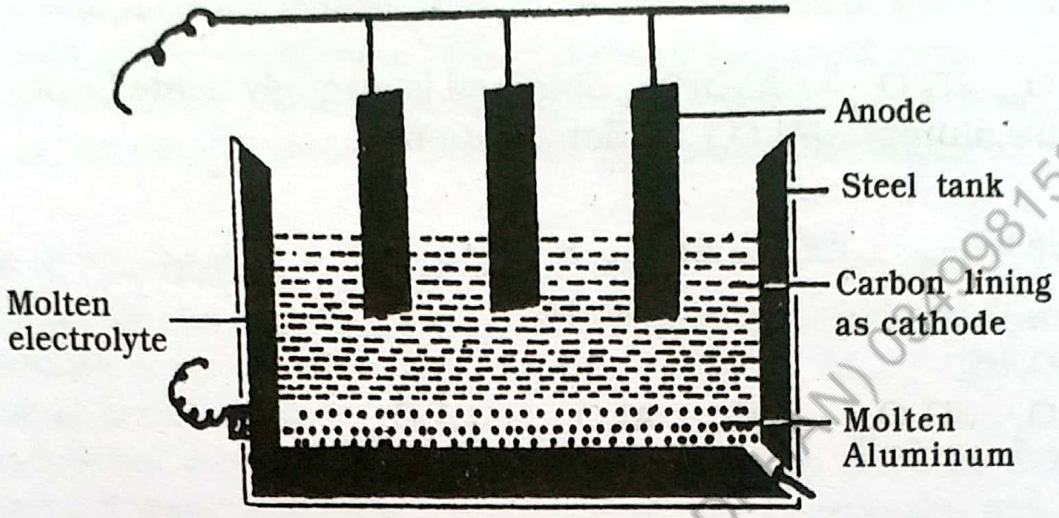


Fig. 16.5 Electrolysis of pure alumina.

16.7 ALLOYS

An alloy is a substance prepared by adding other metals or non-metals to a baser metal, so as to obtain certain desirable qualities.

An alloy can be considered as a uniform mixture of two or more metallic elements or non-metallic elements like carbon or silicon. The component elements do not undergo any chemical changes during the process of alloying. The percentage composition of the component elements may vary according to the quality desired.

Metals readily form alloys since metallic bond is non-specific. The presence of small quantities of a second element in the metal, frequently increases its strength. The uses of a particular metal are governed by its chemical and physical properties. In most cases, a pure metal does not posses all the desired properties necessary. These short comings of the metal are usually eliminated by alloying the metal with one or more other substances (usually metals or carbon) for example, pure iron is soft and is useless for many purposes. If however it is alloyed with Si, C, Mn, Cr, Ni or V etc., the resultant alloys are very useful.

Some Common Alloys:

(1) Bronze:

This is a very common alloy of baser metal, copper. Bronze contains 90-95% copper and 5-10% Tin.

It is strong and shows greater resistance to chemical attack. In appearance it is quite attractive. It is used for making coins, medals, scalptures and also for general metallic work.

(2) Brass:

This is also an alloy of baser metal copper. It contains 60-80% copper and 20-40% Zn.

Brass is stronger and more malleable than copper. It is of yellow colour. It has low melting point and is more attractive in appearance. It is used for making moving parts of clocks and watches, nut and bolts, rods, tubes, musical instruments, ornaments, household utinsils and also for general metal work.

(3) Nichrome:

Nichrome is an alloy that contains 60% nickel, 25% iron and 15% chromium.

Nichrome is heat resistance and also electrical resistance. It is used in the making of wires.

SUMMARY

1. Metals and non-metals were identified by their appearances and physical characteristics such as their states, melting points, boiling points, conductivities and densities.
   Metal oxides are generally basic, while the oxides of non-metals are acidic in nature.
   Metals are defined as the elements that ionize by the loss of electrons forming cations, while non-metals are the elements that ionize by the gain of electrons forming anions. The hydrides of metals are generally water soluble ionic solids. While the hydrides of non-metals are mostly volatile liquids or gases and they are covalent in nature.

2. The combined forms of metals with less definite chemical impurities are known as "minerals". Minerals when mixed with earthy materials are called as "Ores". An ore is considered as a mixture of minerals with worthless rockey materials. These rockey materials present in ores are called "gangue particles".

3. Iron is one of the most important metal and is the second most abundant metal after aluminium found in the combined state in the earth crust. The important ores of iron are haematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($Fe_2O_3 . 3H_2O$), iron pyrite (FeS_2) and siderite ($FeCO_3$). Copper is also an important metal and is found in combined states as copper pyrite ($CuFeS_2$), cuperite (Cu_2O), Chalcocite (Cu_2S) and malochite [$CuCO_3 . Cu(OH)_2$].

Aluminium is the most abundant metal found in the earth crust. It is third most abundant element after oxygen and silicon present in the earth crust. It is found in the earth crust in combined states as silicates, fluoride, sulphate and oxide ores. The chief ore of aluminium is bauxite ($Al_2O_3 . 2H_2O$).

Chromium is found in nature as chromite or chrome iron ($FeO . Cr_2O_3$).

4. Majority of metals are extracted from their ores in the free state. The extraction of metals from their ores is termed as metallurgy. Metallurgy is the science and the technology of extracting metals from their natural sources that is ores. Different processes are involved for the extraction of different metals.

5. Iron is usually extracted from its oxide ore; haemetite which is heated in a blast furnace with coke and limestone, sand i.e silica, the common impurities present, combine with the limestone and is removed as slag. The iron obtained from the blast furnace is impure and is called as "pig iron". Wrought iron and steel are obtained from pig iron by reducing the impurities. Iron rusts when exposed to moist air. The composition of rust is $Fe_2O_3 . H_2O$.

   Iron can be alloyed easily with other elements to produce different steels with great variety of properties and uses.

6. Copper is usually extracted from its sulphide ore i.e from copper pyrite ($CuFeS_2$). The extraction of copper from its ore involves four stages.

   (i) The concentration of copper pyrite by froth floatation process.
   (ii) The roasting of the concentrated ore to remove part of sulphur impurities.
   (iii) The smelting of the roasted ore after mixing with silica and coke to remove major impurities of iron as slag and to get matte.
   (iv) Reduction of the Cu_2O formed with copper sulphide present to form blister copper which is about 98% pure.
   (v) Blister copper is then refined by the electrolysis process.

7. Aluminium metals are extracted from its bauxite ore which is purified first by removing the impurities of ferric oxide (Fe_2O_3) and silica (SiO_2).

In this process the finely divided bauxite is treated with 45% NaOH solution to dissolve aluminium oxide from bauxite forming sodium aluminate, leaving behind the impurities undissolved. Sodium aluminate is re-changed into pure alumina (Al_2O_3).

Aluminum metal is obtained by the electrolysis of pure alumina (Al_2O_3) in molten cryolite. Aluminium metal is a silvery white metal and is widely used in the making of light alloys for the transport industries and also in the making of electric cables.

8. Metals readily form alloys by the presence of other elements, metals or non-metals which increases the strength of a metal. An alloy is therefore a substance prepared by adding other metals or non-metals to a baser metal, so as to obtain certain desireable qualities. Some common alloys are stainless steel, bronze, brass, duralumin, nichrome etc.

EXERCISE

1. Fill in the blanks by the correct answer:
   (i) Aluminium is the member of group ______ of the periodic table.
   (ii) During the extraction of Al, bauxite is purified by dissolving in ______ solution, the insoluble impurities are removed by ______.
   (iii) Elements in the periodic table are classified mainly as ______ and ______.
   (iv) Metals are good conductors of ______ and ______.
   (v) Metals have greater tendency to ______ electrons and generally are ______ agents.
   (vi) The combine forms of metals with less definite chemical impurities are known as ______, with more earthy impurities are called ______.
   (vii) The formula of haematite is ______.
   (viii) Na_3AlF_6 is the formula of ______.
   (ix) $CaO + SiO_2 \longrightarrow$ ______.
   (x) Bronze contains 90-95% copper and ______ tin.

2. Write True or False for the following statements:
   (i) Blister copper is refined by electrolytic process.
   (ii) Ore is the pure form of a metal oxide.

(iii) The chief ore of iron is magnetite.
(iv) Pig iron is hard and brittle.
(v) Brass is of silvery white colour.
(vi) $CaSiO_3$ and $FeSiO_3$ are known as slags.
(vii) Metals are usually soft and brittle.
(viii) Non-metals can not be polished like metals.
(ix) An ore can be concentrated also by magnetic separator.
(x) Impurities of Au, Ag & Zn are removed from blister copper by roasting.

3. Tick the correct answer.

(i) The formula of iron rust is:
(a) Fe_2O_3 (b) Fe_3O_4 (c) $Fe_2O_3 . H_2O$ (d) FeO.

(ii) The most important ore of copper is:
a) Cu_2O (b) $Cu FeS_2$ (c) Cu_2S (d) $Cu CO_3 . Cu (OH)_2$

(iii) The formula of potash mica is:
(a) $K_2O . 3Al_2O_3 . 6SiO_2 . 2H_2O$
(b) $Al_2O_3 . 2SiO_2 . 2H_2O$.
(c) $K_2O . Al_2O_3 . 6SiO_2$ (d) Al_2O_3

(iv) Chromite is found in Pakistan at:
(a) Azad Kashmir (b) Punjab
(c) Sindh (d) Baluchistan.

(v) Iron metal obtained from blast furnace is impure and is called as:
(a) Cast iron (b) Pig iron (c) Steel (d) Wrought iron.

(vi) Stainless steel is an alloy of iron with:
(a) Cr and Mn (b) Ni and Cr (c) Mn and S (d) C and S.

(vii) Which one is the reduction reaction in the manufacture of blister copper:
(a) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_{2(g)}$
(b) $FeO + SiO_2 \longrightarrow FeSiO_3$
(c) $2Cu_2S + Cu_2S \longrightarrow 6Cu + SO_{2(g)}$
(d) $4Cu FeS_2 + 5O_2 \longrightarrow 2Cu_2S + 2FeO + 2FeS + 4SO_{2(g)}$

(viii) The chief ore of Al has the formula:
(a) $Al_2O_3 . 2H_2O$ (b) Al_2O_3 (c) $Al_2O_3 . H_2O$ (d) $Na_3 AlF_6$.

(ix) Nichrome is an alloy that contains major percentage of:
(a) Cr (b) Fe (c) Ni (d) Zn.

(x) The medal given at third position in any event is made up of:
(a) Bronze (b) Brass (c) Nichrome (d) Copper.

4. (a) Define the following terms.
(i) Minerals (ii) Ores (iii) Metallurgy
(b) Write down the preliminary operations or preparations involved in the metallurgy of metals from their ores. Discuss only concentration of the ore and the roasting of the concentrated ores.
(c) What happens when metals Zn, Mg and Al react with dilute HCl and H_2SO_4. Give reactions.
(d) Give the reactions of the followings with water.
(i) PCl_3 (ii) CaH_2 (iii) NH_3.

5. (a) What are the chief ores of iron? How is iron obtained by the blast furnace?
(b) What are the main components of pig iron?
(c) Differentiate between wrought iron and steel.

6. (a) What is rusting? How is rusting controlled?
(b) Before the extraction of a metal begins, ores must be purified and concentrated. Mention two different processes by which it is done.
(c) Why does in metal extraction often slag is produced?

7. (a) What are the different ores of copper? Name some of the chief ore of copper from which copper is extracted.
(b) How copper ore is concentrated by froth floatation process?
(c) Discuss various steps involved in obtaining blister copper.
(d) How is blister copper further purified? Write down the process of purification of blister copper.

8. (a) What are different ores of aluminium? What is the percentage of Al-compounds present in the earth crust?
(b) Describe the extraction of aluminium metals from its bauxite ore? Give details including purification and electrolysis of pure alumina.
(c) Write down the formula of the followings:
(i) Lime stone (ii) Iron silicate (iii) Alumina.
(iv) Iron pyrite (v) Copper pyrite (vi) Chromite.

9. (a) What do you mean by alloy? Describe the composition and applications of important alloys of copper.
(b) What is nichrome?
(c) Give the physical characteristics of copper metal.
(d) What are three common stainless steel and their compositions?

CHAPTER-17

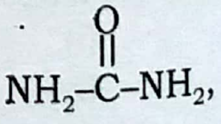
ORGANIC CHEMISTRY

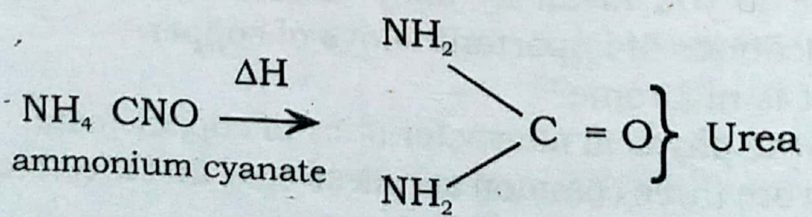
You will learn in this chapter about:

- * Organic chemistry and its definition.
- * Natural sources of organic compounds,animals,plants,coal,natural gas and petroleum.
- * Fractional distillation of petroleum i.e refinning of petroleum and reforming of petrol.
- * Cracking.
- * Homologous series,isomerism.
- * Functional groups.
- * Hydrocarbons and their classifications as saturated and un-saturated hydrocarbons.
- * Alicyclic and Aromatic hydrocarbons and compounds.
- * Alkanes,alkenes and alkynes and the names of first ten(10) hydrocarbons.
- * Preparations and properties of methane(CH_4).
- * Preparations and properties of Ethene ($CH_2=CH_2$) and ethyne($CH\equiv CH$).

17.1 INTRODUCTION

Early chemists called substances produced by living organisms, as organic compounds. Substances from minerals or non-living sources were called as inorganic compounds. This classification was based on source but not on composition. For these reasons, chemists believed that there was **vital force**, which came only from life, was necessary for the synthesis of organic compounds, in living organisms and it was impossible to synthesize organic compounds from inorganic sources in the laboratories.

But in 1828 Wohler converted an inorganic compound ammonium Cyanate [NH_4CNO] into an organic compound urea  $NH_2-\overset{\overset{O}{||}}{C}-NH_2$, (a constituent of urine) by control heating.



By this chemical conversion the vital force theory, that organic compounds could not be synthesized in laboratory was rejected.

In 1845 Kolbe also synthesized acetic acid (CH_3COOH) a chief component of vinegar, by the combination of carbon, hydrogen and oxygen..

Soon after the conversion of Wohler, chemists began to make organic compounds in laboratories. However all these compounds obtained from living sources or prepared in laboratory were alike in that they contained the element, carbon. Hence the present definition of organic chemistry, is the chemistry of carbon compounds, *apart from few compounds such as carbon dioxide, carbon mono-oxide, metal carbonates, bicarbonate and carbides which are regarded as inorganic, all other carbon compounds are grouped together in separate branch of chemistry i.e. organic chemistry.*

17.2 NATURAL SOURCES OF ORGANIC COMPOUNDS

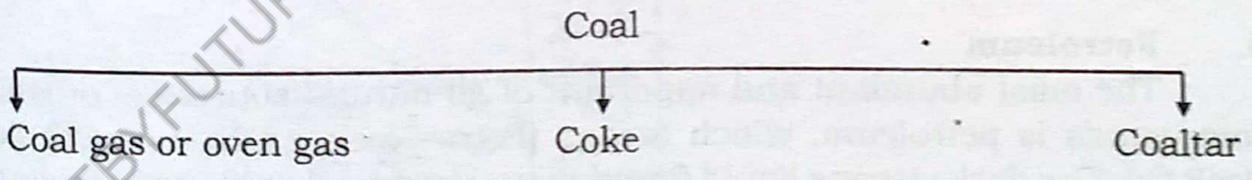
The principal source of organic compounds is living organisms i.e., animals and plants. Coal, natural gas and petroleum are the major mineral sources of organic compounds. They are described as under:

1. Animal and Plant kingdom:

Animals produce, fats, proteins, urea, uric acid, vitamins, harmones etc. Plants synthesize numerous organic chemicals, e.g., sugar, starch, cellulose, citric acid, oxalic acid, tartaric acid, oils and vitamins.

2. Coal:

Coal is a complex material. It is composed of mainly carbon, but it also contains small percentage of other elements. The quality of coal as an energy source is based on its carbon contents. The ranking runs from low grade peat and lignite to high grade anthracite. Soft (bituminous) coal is much more plentiful than hard coal anthracite, which contains considerable quantities of complex compounds. When coal is heated in absence of air in an oven it undergoes destructive distillation into three main products.



(i) Coal gas or oven gas mainly contains hydrogen methane and CO_2 gas.
(ii) Coke is pure carbon and is used in metallurgy of iron and steel, and for the manufacture of the calcium carbide.
(iii) Coaltar a black viscous liquid and is rich in aromatic hydrocarbons. The fractional distillation of coaltar gives so many hydrocarbons. **For example,** coaltar on fractional distillation upto 170°C yields light oil (Naptha) which mainly gives benzene, toluene, xylenes etc. Over

215 aromatic hydrocarbons are isolated from coaltar. Coaltar is also, used in carpeting roads.

2. Natural gas:

Natural gas is found wherever oil and coal occur. Natural gas largely contains methane (CH_4) along with small quantities of ethane, propane, butane and also contains carbon dioxide, nitrogen and occasionally helium (He).

Natural gas is piped from gas wells for use as fuel in homes, industries and into thermal electric power stations. Certain components such as propane and butane may be separated from the gas at the wells. Bottled in tanks under pressure and sold as bottled gas also called liquified petroleum gas (LPG), where natural gas lines are not available.

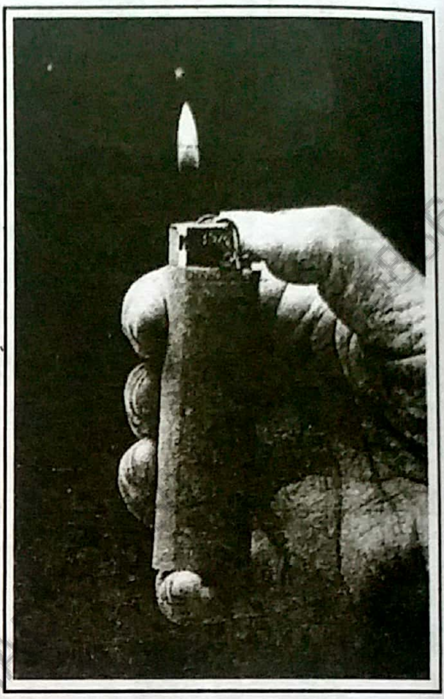


Fig. 17.1 Butane Lighter. The lighter contains liquified butane under pressure. When the valve is pressed, the pressure is released and butane gas escapes.

Natural gas is also used as a raw material for making many important organic and inorganic compounds. It is source of hydrogen (H_2) for making ammonia (NH_3). Methyl and ethyl alcohol are made from natural gas. Carbon black used in printers, ink and tires is also made from natural gas by incomplete combustion. Natural gas is a better industrial and domestic fuel than coal gas.

In Pakistan, it is largely found at Sui in Baluchistan, called Sui-gas. In Sindh at various places like, Khairpur, Mari (Mari gas) in Badin. It is also found in Punjab at Dhodak and Radho, district Dera Ghazi Khan and as well as at Pir-Koh in Mari-bugti.

4. Petroleum

The most abundant and important of all natural sources of organic compounds is petroleum, which means (Petra=Rock + Oleum = Oil) i.e, Rock Oil. The dark viscous liquid found in underground deposits in various parts of earth at different depths. Petroleum is extremely complex mixture of gaseous, liquid and solid hydrocarbons ranging from (C_1 - C_{40}), together with the varying amounts of compounds containing oxygen, sulphur and nitrogen.

In petroleum, there are two types of hydrocarbons i.e. paraffins and cyclo paraffins (cyclohexane, C_6H_{12}).

It is generally believed to have been formed from the remains of plants and animals which lived in the warm inland and oceans millions of years ago. The chemical effects of pressure, temperature and bacteria have converted these remains into petroleum.

In Pakistan, the important petroleum reserves are in Meyal and Tut in Pothohar areas of Punjab and some places in District Badin, Dadu and Hyderabad of Sindh.

17.2.1 Fractional Distillation of Petroleum (Refining of Petroleum):

In this process, the petroleum or crude oil is heated to above 400^0C to vapourize. The resulting vapours are then carried to a fractionating column, having different temperature zones i.e. fractionating column is divided into several compartments, each compartment has a specific range of temperature. As the petroleum vapours ascend the column, several fractions condense and separate in these compartments.

More than five hundred hydrocarbons are separated from petroleum.

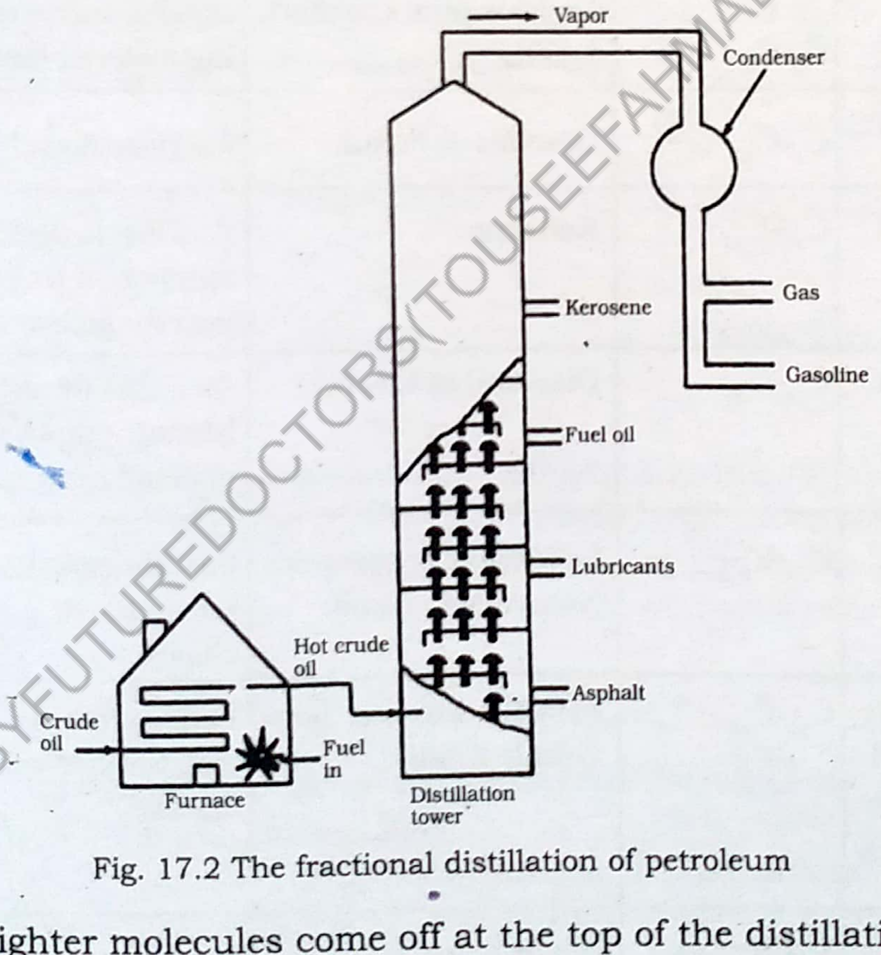


Fig. 17.2 The fractional distillation of petroleum

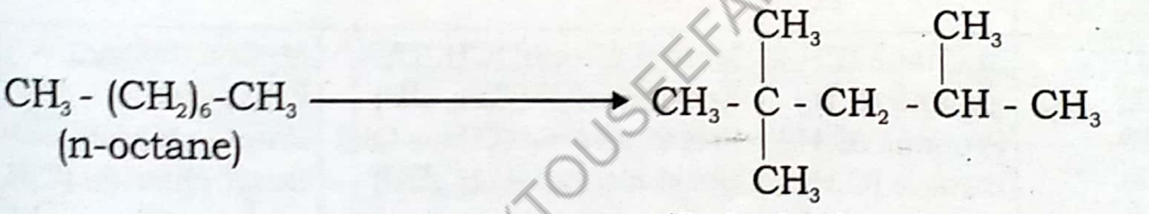
The lighter molecules come off at the top of the distillation column, the heavier at the bottom. Before the development of automobile, the most important product from petroleum was Kerosene oil. It was used for lighting. Now gasoline is the most important product, with diesel fuel, heavy oils and various lubricants also in a great demand. Petroleum is becoming increasingly important as a source of energy and for the preparations of hundreds of diverse organic compounds. One of the main operation in refining is to separate the petroleum into useful fractions, following is the typical list of such fractions, separated at different temperature zone (Table 17.1).

Table 17.1 Petroleum Fractions

Boiling range	Range of carbon atoms per molecule	Name of the fractions	Uses
Below 20^{0}C	C_1-C_4	Petroleum gases mixture of methane ethane, propane and butane.	Fuels for homes and industries for heating and cooking. In the manufacture of petrochemicals.
20^{0}C-60^{0}C 60^{0}C-120^{0}C	C_5-C_6 C_6-C_7	Petroleum Ether (liquids). Light naptha (ligroin); liquids.	Both the products are used as organic solvents and as a cleaning material for textile fabrics.
40^{0}C-200^{0}C	C_6-C_{10}	Gasoline or Petrol.	Fuel for automobile engines.
175^{0}C-325^{0}C	C_{11}-C_{18}	Kerosene.	As a fuel in domestive stoves, for lighting, in jet engines, as a solvent for grease and paints.
250^{0}C-400^{0}C	C_{14}-C_{25}	Diesel oil or Gas oil.	As a fuel for diesel engines, for heating purposes and as a raw material for cracking.
Above 400^{0}C	C_{20}-C_{higher}	Lubricating or heavy oils Non-volatile liquid.	For lubrication as grease in moving parts of engines and machines.
Obtained by vacuum distillation of the remaining fractions.	C_{20}-C_{40}	Paraffin wax i.e. non-volatile solids.	Packing material, making of candles, water, proof materials, polish, vaseline.
Solid residue left behind.	Solid carbon	Bitumen (pitch) asphalt.	For surfacing roads and airfields, roofing material, in protective paints and pipe coatings etc.

17.2.2 Reforming of Petroleum:

Petrol or gasoline is a mixture of hydrocarbons generally consisting of six to ten carbon atoms per molecule. It is a volatile liquid which is a common fuel. Gasoline is reformed to prevent fuel knock in the motor engine. Knocking is caused by the rapid and uneven burning of straight chain hydrocarbons and generally leads to loss of power or demage to the engine. Reforming is a process similar to the process of cracking by which octane-rating i.e octane number of gasoline can be increased. The quality of petrol is measured in terms of its octane-rating. By the process of reforming the straight chain hydrocarbons are converted into branched chain hydrocarbons. Knock inhibitor like tetraethyl. Lead; $(Pb(C_2H_5)_4$ is also added but lead being poisonous, produces pollution. So petrol is heated in the presence of silicate catalyst to convert straight chain hydrocarbons into branched chain hydrocarbons. For example, when n-octane is heated in the presence of silicate catalyst, it is converted into 2, 2, 4-trimethyl pentane, thus producing the higher grade gasoline.



$$\underset{\text{(n-octane)}}{CH_3-(CH_2)_6-CH_3} \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

. (2, 2, 4 trimethyl pentane)

17.2.3 Cracking:

The yield of petrol is increased by catalytic thermal cracking of heavy molecules of hydrocarbons. If the alkanes of large molecular mass are heated to high temperature in the absence of air, the molecules breakup (cracks) into several smaller and more valuable of fragments.

An example is.

$$C_{16}H_{34} \xrightarrow{\text{Cracking}} C_8H_{18} + C_8H_{16}$$

Molecules with 16 carbon atoms cannot be used as gasoline but molecules with 8 carbon atoms can.

A second example is, when propane is heated, at high temperature of 700 – 800°C in absence of oxygen, it cracks into propene, ethene, methane and hydrogen.

$$\underset{\text{Propane}}{2(CH_3-CH_2-CH_3)} \xrightarrow[\text{Absence of air}]{700-800^0C} \underset{\text{Propene}}{CH_3-CH{=}CH_2} + \underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{Methane}}{CH_4} + H_2$$

17.3 HOMOLOGOUS SERIES

In Greek, **Homo** means **same** and **logous** means **ratio**. Organic compounds can be classified into series (families)whose members are closely related in molecular structure and properties.

The formula in which any member differs from that of proceeding one in the series by the increment ($>CH_2$) called methylene group, such a series is called a **homologous series** and each member of it is the homolog of preceeding one.

Definition: *A homologous series is a family of similar organic compounds which follows a regular structural pattern, in which each successive member has a difference of* ($>CH_2$) *group.*

For example: The alkanes, alcohols and alkyl halides listed in the table below, show the difference of methylene group e.g. ($>CH_2$) and are thus homologous series.

No. of carbon	Alkanes (R-H)	Alcohols (R - OH)	Alkyl halides (R-X)
01	Methane (CH_4)	Methyl alcohol (CH_3-OH)	Methyl chloride (CH_3-Cl)
02	Ethane (C_2H_6)	Ethyl alcohol (C_2H_5-OH)	Ethyl chloride (C_2H_5-Cl)
03	Propane (C_3H_8)	Propyl alcohol (C_3H_7 - OH)	Propyl chloride (C_3H_7-Cl)
04	Butane (C_4H_{10})	Butyl alcohol (C_4H_9-OH)	Butyl chloride (C_4H_9-Cl)
.	.	.	.
.	.	.	.
.	.	.	.
n	$C_nH_{2n}+_2$	$C_nH_{2n+1}OH$	C_nH_{2n+1}-X

Homologous series are a common feature of organic chemistry.

17.3.1 Isomerism

In Greek **Iso** means **same** and **mers** means **part** or **units**. The compounds which possess the same percentage, composition and molecular weight i.e.; the same molecular formula but different structures are known as isomers and the phenomenon is called isomerism.

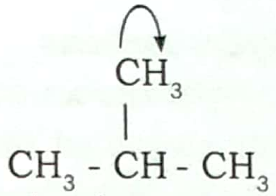
Definition: *Isomerism is the existence of two or more compounds, having same molecular formula but different molecular structure.*

For example: n-butane, and iso-butane have the same molecular formula M.F. (C_4H_{10}) but different structures, so they differ in physical properties, despite the fact that they have the same molecular formula, C_4H_{10}.

(i) $CH_3-CH_2-CH_2-CH_3$

n-butane

(C_4H_{10})

(ii) 

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

iso-butane

(C_4H_{10})

n-Butane and isobutane are thus isomers.

The above compounds possess the same molecular formula (C_4H_{10}) but different arrangement of carbon atoms in the hydrocarbon chain. This type of isomerism is called chain or skeletal isomerism, and this type of isomerism always occurs among the alkanes.

17.3.2 Functional Group

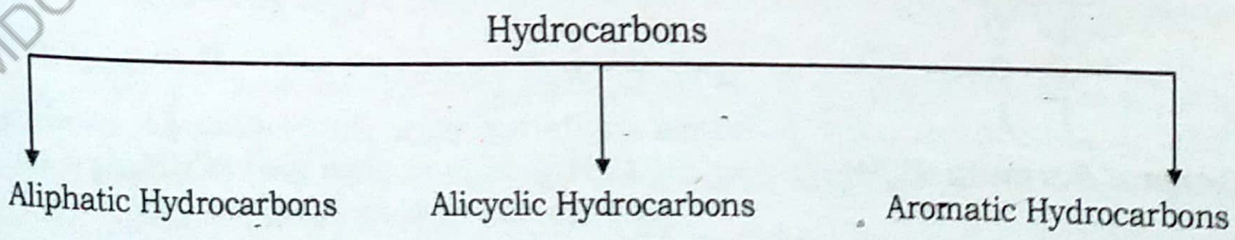
A functional group is an atom or group of atoms present in a molecule, which gives the molecules unique character and the properties and is therefore referred as functional group.

The functional groups of some important compounds are given below:

Types of compounds	General formula	Functional group	Example	Name of example
Organic acids	$R-\overset{\overset{O}{\parallel}}{C}-OH$	$-\overset{\overset{O}{\parallel}}{C}-OH$ (carboxyl group)	$CH_3-\overset{\overset{O}{\parallel}}{C}-OH$	Acetic acid
Alcohols	R-OH	-OH (Hydroxyl group)	CH_3-OH	Methyl alcohol
Alkyl halides	R-X	-X (Halide group)	C_2H_5-Cl	Ethyl chloride

17.4 HYDROCARBONS

Compounds containing only two elements C and H are known as hydrocarbons. In terms of structural concept, they are further classified into three classes.



1. Aliphatic Hydrocarbons

Aliphatic Hydrocarbons are composed of open chains of carbon atoms, they are further classified into two classes, i.e., saturated hydrocarbon and unsaturated hydrocarbon.

(i) Saturated Hydrocarbons:

Saturated hydrocarbons contain only single bonds, between the carbon atoms, it means the valency of carbon is fully utilized. Alkanes are the example of saturated hydrocarbons e.g. CH_4, C_2H_6, C_3H_8.

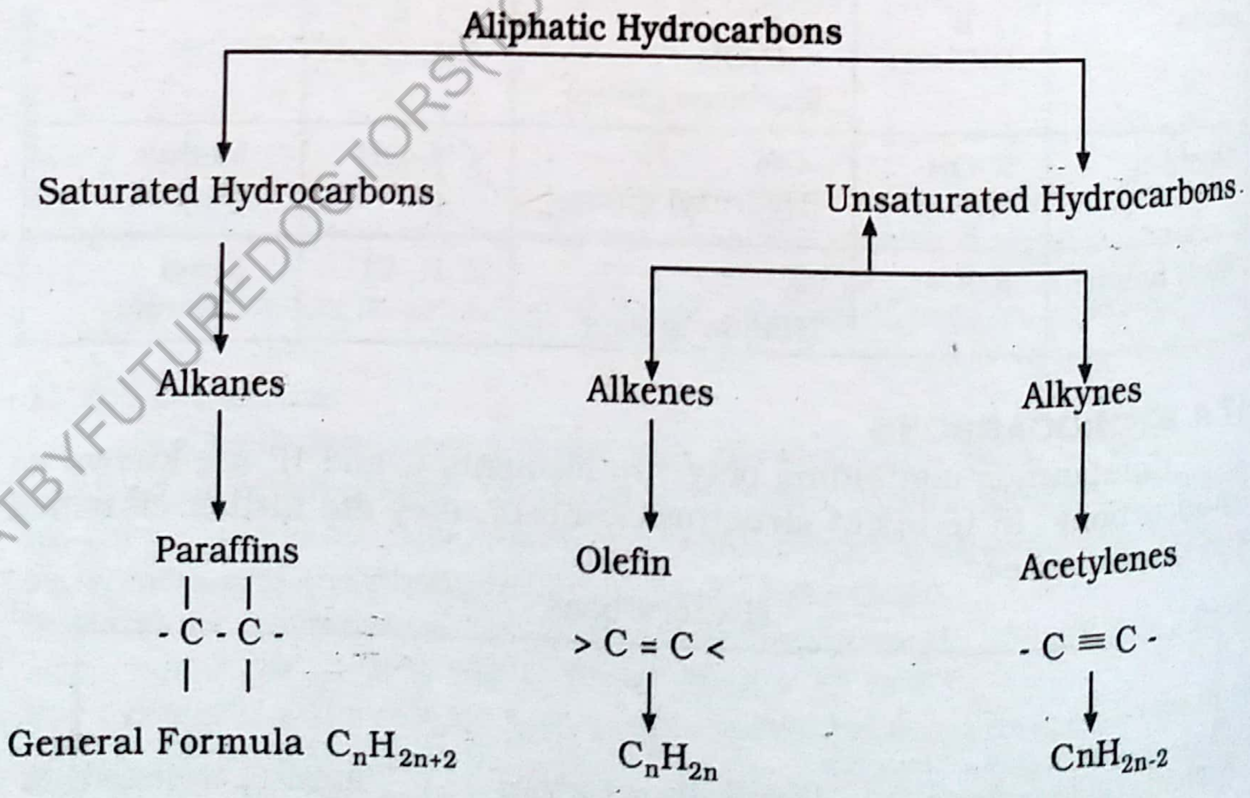
(ii) Unsaturated Hydrocarbons:

Unsaturated hydrocarbons, are those which contain one or more double or triple bonds. It means that the valency of carbon is not fully utilized.

Those which contain double bond are called alkenes and which contain triple bond are called alkynes.

The common examples of Alkenes and Alkynes are:

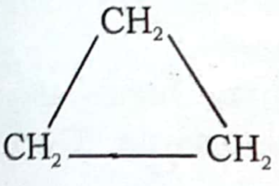
C_2H_4 $(CH_2 = CH_2)$ Ethylene or (Ethene)	C_2H_2 $(HC\equiv CH)$ Acetylene or (Ethyne)



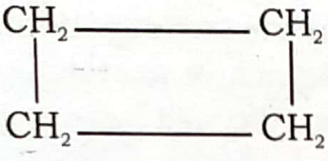
2. Alicyctic Compounds:

Aliphatic-cyclic hydrocarbons, are the compounds in which carbon atoms are arranged in rings.

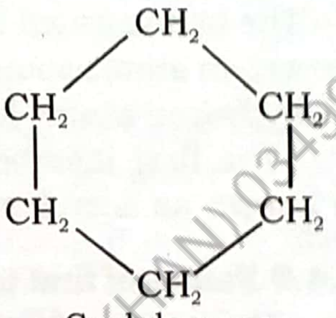
The cyclo alkanes have two fewer hydrogen atoms than alkanes, thus have the General formula ($C_n H_{2n}$). They are named by pre-fixing cyclo to the name of corresponding alkane, having the same number of carbon atoms, in the ring e.g.



Cyclopropane



Cyclobutane

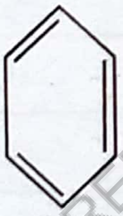


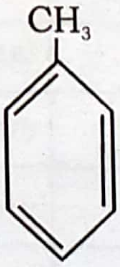
Cyclohexane

3. Aromatic Compounds:

Aromatic hydrocarbons, contain six membered ring (Benzene ring) into which, there are three carbon-carbon alternate double bonds.

Now–a-days, aromatic hydrocarbons are suitably defined, that the hydrocarbons which contain benzene ring and the compounds that resemble benzene in chemical behaviour.


C_6H_6
Benzene



$C_6 H_5 - CH_3$
Toluene

17.4.1 Alkanes, Alkenes, Alkynes:

1. Alkanes:

Alkanes are saturated hydrocarbons in which the various carbon atoms are linked by single covalent bonds to adjacent carbon atoms forming chains.

Alkanes have the general formula (C_nH_{2n+2}) which show that all the valencies of carbon are fully satisfied, hence all alkanes are stable and unreactive. For this reason they are called paraffins (from the Latin **Para** means **little** and **ffins** means **attraction**).

2. Alkenes:

The unsaturated hydrocarbons which contain one double bond, joining two carbon atoms somewhere in molecule are called alkenes, they contain two hydrogen atoms less than the corresponding alkanes.

The first member of alkenes is ethylene or ethene, hence alkenes are known as olefins (oil making). Alkenes have a general formula, of ($C_n H_{2n}$)

3. Alkynes:

The unsaturated hydrocarbons, which contain one triple bond joining two carbon atoms somewhere in molecule, are called alkynes. They contain four hydrogen atoms less than the corresponding alkane.

The first member of alkynes is acetylene or ethyne hence alkynes are known as acetylene series. Alkynes have a general formula, ($C_n H_{2n-2}$).

17.4.2 Names of first ten Hydrocarbons (i.e. Alkanes, Alkenes and Alkynes):

The names of first ten hydrocarbons are given in the following chart. The ending for all of the names of alkanes is **ane**, alkenes is **ene** and for alkynes is **yne**.

The first four members retain their original names. After butane (Greek or Latin) numeral prefixes, indicate the number of carbons in the molecule. Thus one, two, three, four, five becomes meth, eth, prop, but, pent.

No. of carbon	Molecular formula of alkane	Name of alkane	Molecular formula of alkene	Name of alkene	Molecular formula of alkyne	Name of alkyne
01 Meth	CH_4	methane	—	—	—	—
02 Eth-	C_2H_6	ethane	C_2H_4	ethene	C_2H_2	ethyne
03 Prop-	C_3H_8	propane	C_3H_6	propene	C_3H_4	propyne
04 But-	C_4H_{10}	butane	C_4H_8	butene	C_4H_6	butyne
05 Pent-	C_5H_{12}	pentane	C_5H_{10}	pentene	C_5H_8	pentyne
06 Hex-	C_6H_{14}	hexane	C_6H_{12}	hexene	C_6H_{10}	hexyne
07 Hept-	C_7H_{16}	heptane	C_7H_{14}	heptene	C_7H_{12}	heptyne
08 Oct-	C_8H_{18}	octane	C_8H_{16}	octene	C_8H_{14}	octyne
09 Non-	C_9H_{20}	nonane	C_9H_{18}	nonene	C_9H_{16}	nonyne
10 Dec-	$C_{10}H_{22}$	decane	$C_{10}H_{20}$	decene	$C_{10}H_{18}$	decyne

These first ten members of straight chain alkanes are named by prefixing n-(for normal) however in the absence of any qualifying prefixes, the hydrocarbon is considered to be 'normal' or unbranched.

For example:

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

Pentane or n-Pentane

In common system, the first three are unbranched alkanes i.e. straight chain alkanes.

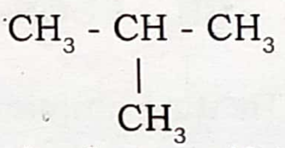
e.g. CH_4 methane $CH_3 - CH_3$ ethane $CH_3 - CH_2 - CH_3$ propane

From the fourth carbon, there is possibility of branched chain. In case of branched chain alkanes, the prefixes, iso, and neo are adequate to differentiate various butanes and pentanes, however, naming of organic compound is done now-a-days by a system called IUPAC system.

In butane (C_4H_{10}) there are two isomers, called n-butane and iso-butane.

$$CH_3 - CH_2 - CH_2 - CH_3$$

n-butane (C_4H_{10})



$$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - CH_3$$

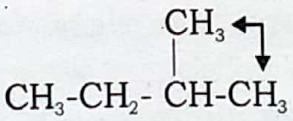
Iso-butane (C_4H_{10})

The common names of the three isomers of pentane (C_5H_{12}) are n-pentane, iso-pentane and neo-pentane

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

n-pentane

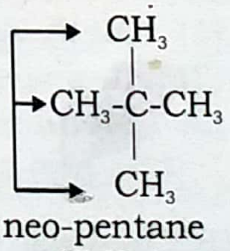
(C_5H_{12})



$$CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}CH_3$$

iso-pentane

(C_5H_{12})



$$CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-}CH_3$$

neo-pentane

(C_5H_{12})

The prefix n-is for normal i.e. unbranched chain, where as prefix iso – is reserved for two methyl groups ($-CH_3$) on any corner of the basic chain and prefix neo- is reserved for three methyl groups ($-CH_3$) on any corner of the basic chain.

17.5 PREPARATION AND PROPERTIES OF METHANE (CH_4)

Introduction: Methane is simplest known stable compound of alkane with a molecular formula, CH_4. Methane is an end product of decay of plants, and is found at marshy places so is called **Marsh gas**. Methane (CH_4) is a major component (94%) of natural gas. It is largely found in Sui at Baluchistan in Pakistan and is known as sui gas.

In coal mines, mixture of methane (CH_4) and air forms a dangerous fire damp (Ger: damp = vapours) which explodes on contact with flame. Hence it is also called **Fire-damp.**

17.5.1 Preparation:

In laboratory methane is prepared by the following two methods.

i. From Sodium acetate (CH_3-COONa).
ii. By hydrolysis of aluminium carbide.

i. Heating anhydrous sodium acetate with soda lime, (NaOH + CaO) produces methane.

$$CH_3-COONa_{(aq)} + NaOH_{(aq)} \xrightarrow[\text{heat}]{\text{CaO}} CH_{4(g)} + Na_2\,CO_{3(aq)}$$

ii. Heating aluminum carbide with water, produces methane.

$$\underset{\text{Aluminium carbide}}{Al_4\,C_3} + 12H_2O \xrightarrow{\text{heat}} 3CH_{4(g)} + \underset{\text{Aluminium hydroxide}}{4Al\,(OH)_{3(aq)}}$$

17.5.2 Physical Properties:

(1) Methane is light-colourless, tasteless gas, odourless gas.
(2) It is sparingly soluble in water (5ml in 100mls).
(3) Methane is symmetrical, and have no dipole, moment, hence it is non-polar.

17.5.3 Chemical Properties:

Methane does not react with aqueous solution of acids, alkali, $KMnO_4$ or other oxidizing agents, because of non-polar character.

In methane, all the four valencies of carbon are fully satisfied, hence it is saturated and can not give addition reaction, but it forms a derivative only by substitution. Its important substitution reaction is halogenation.

Besides it also burns in open air or oxygen the reaction is termed as combustion.

Halogenation:

The reaction in which one or more atoms are replaced by other atoms is known as substitution reaction. If the substitution occurs by halogens the reaction is known as halogenation.

Methane may be chlorinated or brominated by treatment, with Cl_2 or Br_2 in the presence of sun light (S. L)or ultra violet light (U.V.L.).

If the mixture of methane and Cl_2 is exposed to (S.L.) or (U.V.L.), reaction occurs with the progressive replacement of the hydrogen atoms by (Cl) atoms and the mixture of the following four products is obtained.

$$Cl_2 \xrightarrow[U.V.L]{S.L} 2Cl^0$$

$$CH_4 + Cl_2 \xrightarrow[U.V.L]{S.L} CH_3 - Cl + HCl$$

Methyl chloride (Chloro methane)

$$CH_3 - Cl + Cl_2 \xrightarrow{S.L} CH_2 - Cl_2 + HCl$$

Methylene chloride (Di-chloro methane)

$$CH_2 - Cl_2 + Cl_2 \xrightarrow{S.L} CHCl_3 + HCl$$

Chloroform (Tri-chloromethane)

$$CH - Cl_3 + Cl_2 \xrightarrow{S.L} CCl_4 + HCl$$

Carbon tetra chloride (Tetra chloro methane)

Combustion or Oxidation:

CH_4 on complete oxidation or combustion at high temperature yields CO_2, water and much heat, for this CH_4 is to be considered important, industrial and domestic fuel than coal gas.

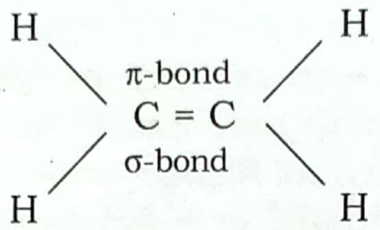
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O; \ \Delta H = -890 \text{ KJ/mole.}$$

Uses of Methane:

1. Methane is used as an important industrial and domestic fuel.
2. It is mostly used in the preparation CH_3OH, $CHCl_3$, CCl_4 pure carbon and as a source of H_2 for the production of fertilizers.

17.6 PREPARATION AND PROPERTIES OF ETHENE (Ethylene) ($CH_2 = CH_2$)

Introduction: The first member of alkene series is ethene, more commonly called ethylene. It is unsaturated because it contains one double bond between two carbon atoms.



It is produced by cracking of petroleum and is therefore, called **Petrochemical**.

Preparation:

Mostly the ethene is prepared by dehydration of ethyl alcohol (ethanol). Ethyl alcohol on dehydration (removal of water molecule) yields ethene. Dehydration of ethyl alcohol can be carried out in the presence of dehydrating agents, such as H_2SO_4, and Al_2O_3 at high temperatures.

(i) $CH_3\text{-}CH_2\text{-}OH + H_2SO_4 \xrightarrow[-H_2O]{160^0C-180^0C} H_2C = CH_2 + H_2O$

(ii) $CH_3\text{-}CH_2\text{-}OH + Al_2O_3 \xrightarrow[-H_2O]{300^0C-350^0C} CH_2 = CH_2 + H_2O$

17.6.1 Physical Properties:

(1) Ethylene is colourless gas having pleasant smell.
(2) It is slightly lighter than air, and burns with luminous flame.
(3) It is slightly soluble in water (1ml in 4ml) and is soluble in common organic solvents.
(4) When inhaled, it produces an anesthesia.

17.6.2 Chemical Properties:

The presence of double bond, in ethene makes it more reactive than ethane, which possess only strong sigma (σ) bonds. The fact that (π) electrons forming the second bond are more loosely held, and seek to form strong sigma bonds with other atoms by addition reactions. The most important addition reactions of ethene are,

1. Addition of H_2
2. Addition of X_2
3. Addition of HX

1. Addition of H_2:

Ethene adds H_2, in presence of catalysts, such as Ni, Pt or Pd to form ethane:

$$CH_2 = CH_2 + H_2 \xrightarrow[300^0 C]{Ni} CH_3 - CH_3$$

Such reactions are called catalytic reductions or hydrogenations.

2. Addition of X_2 (Br_2):

Ethylene adds a bromine molecule (Br_2) to form ethylene dibromide or 1, 2 dibromoethane.

$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{\text{1, 2 - dibromoethane}}{Br - CH_2 - CH_2 - Br}$$

In this test the colour of bromine solution is discharged proving that ethene is unsaturated. The presence of one double bond is called one unsaturation.

The test is known as bromine water test, and is used for the presence of double bond.

3. Addition of HX:

Ethene adds HX, to form ethyl halide,

For example: When ethene is reacted with H-Br, ethyl bromide is formed.

$$CH_2 = CH_2 + H - Br \longrightarrow CH_3 - CH_2 - Br$$

Besides, addition reactions of ethene, the other important reactions are as under:

i. Combustion
ii. Polymerization

(i) Combustion:

Like CH_4, ethene burns in open air, and produces CO_2, water and heat.

$$CH_2 = CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + Heat$$

(ii) Polymerization or Formation of Polyethene:

With a suitable catalyst ethylene can be made to add itself or polymerizes, according to the reaction.

$$n\,(CH_2{=}CH_2) \xrightarrow{0.01\%\ \text{oxygen}} \underset{\text{Polythene}}{(\text{-}CH_2\text{-}CH_2\text{-})_n}.$$

The product is given the name polyethylene and the trade name **Polythene**.

17.6.3 Uses of Ethene or Ethylene:

1. Ethylene is used as starting material for the production of alcohol, glycol, ethyl chloride.
2. It is used in welding and cutting metals, because of the intense heat of oxy-ethylene flame.
3. It is used to give the appearance of ripeness to the fruit.
4. An ethylene – oxygen mixture which is used as an excellent, general anaesthetic.
5: For manufacture of plastic, called polythene.

17.7 PREPARATION AND PROPERTIES OF ETHYNE (Acetylene $HC \equiv CH$)

Introduction: The first member of alkyne series is ethyne. It is more unsaturated than ethene, because it contains one triple bond between two carbon atoms.

$$H - C \equiv C - H$$

It is found in natural gas and petroleum. Traces of acetylene are present in the incomplete combustion of coal gas and in bunsen burner.

17.7.1 Preparation:

Ethyne is conveniently prepared by the action of water on calcium carbide (CaC_2).

$$CaC_2 + 2(H - OH) \longrightarrow \underset{\text{Ethyne}}{C_2H_2} + Ca\,(OH)_{2(aq)}$$

17.7.2 Physical Properties:

1. Acetylene is colourless gas with garlic odour.
2. It is very slightly soluble in water, some what more in alcohol and ether.

3. Liquid acetylene explodes violently by shock or heat.
4. It is lighter than air.

17.7.3 Chemical Properties:

Acetylene mostly gives addition reaction, because of two (π) bonds, present in it.

Acetylene, therefore adds: →

1) H_2 2) X_2 3) HX

Acetylene also burns in open air and the reaction is termed as combustion. Acetylene also adds oxygen in presence of catalyst, the reaction is known as oxidation.

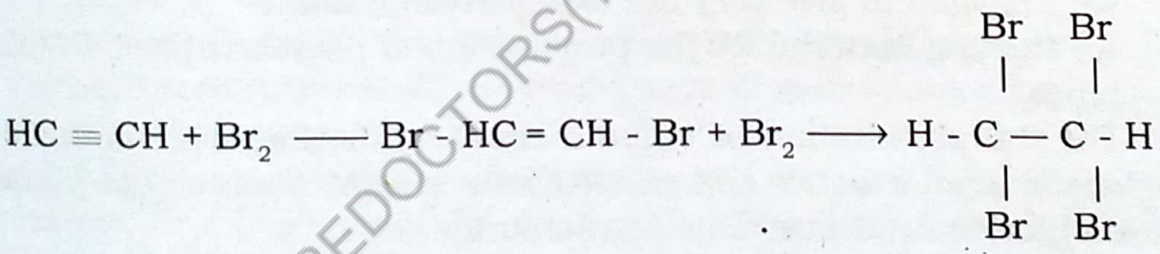
1. Addition of H_2 (Hydrogenation):

In presence of catalysts, such as Ni, Pt, or Pd, ethyne reacts with H_2 to give first ethene and then ethane.

$$HC \equiv CH + H_2 \xrightarrow[200^0 C]{Ni} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[300^0 C]{Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

2. Addition of x_2(Halogens):

With Br_2 and Cl_2, acetylene reacts to give first acetylene dibromide or dichloride and then acetylene tetrabromide or tetrachloride.



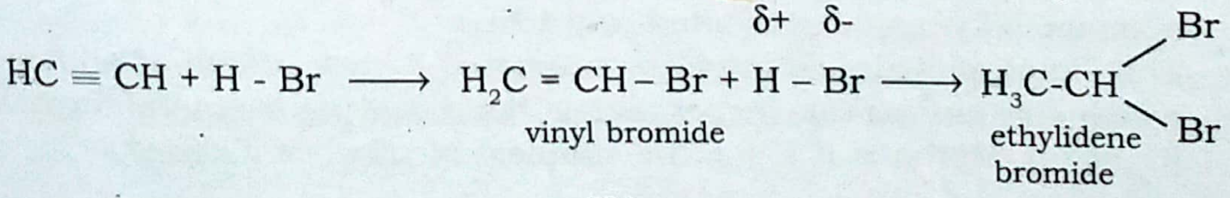
$$HC \equiv CH + Br_2 \longrightarrow Br - HC = CH - Br + Br_2 \longrightarrow H - \underset{\displaystyle Br}{\overset{\displaystyle Br}{C}} - \underset{\displaystyle Br}{\overset{\displaystyle Br}{C}} - H$$

But ethyne adds only one molecule of (I_2) in presence of catalyst ethanol and form acetylene diiodide.

$$HC \equiv CH + I_2 \xrightarrow{Ethanol} I - HC = CH - I$$

3. Addition of Hx:

Acetylene adds two molecules of H-Br and first forms vinyl bromide and then ethylidene bromide.



Combustion:

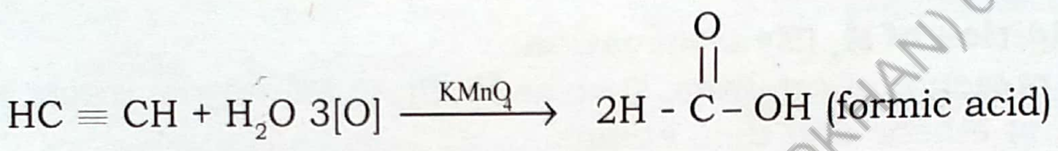
Acetylene also burns in open air and the reaction is termed as combustion.

$$2(CH \equiv CH) + 5O_2 \longrightarrow 4CO_2 + 2H_2O + heat$$

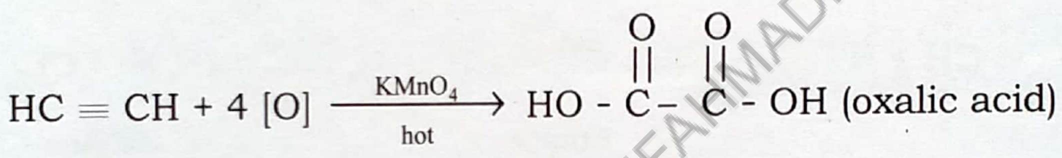
When pure oxygen is used, the very hot oxy-acetylene flame is produced. This flame is enough hot and a temperature of 3000°C is reached. So, it is used for cutting and welding of metals.

Oxidation:

Acetylene is oxidized to formic acid in presence of aqueous $KMnO_4$ solution, with an alkaline $KMnO_4$, it is oxidized to oxalic acid

(1)


$$HC \equiv CH + H_2O\ 3[O] \xrightarrow{KMnO_4} 2H - \overset{\overset{O}{||}}{C} - OH \text{ (formic acid)}$$

(2)


$$HC \equiv CH + 4\,[O] \xrightarrow[hot]{KMnO_4} HO - \overset{\overset{O}{||}}{C} - \overset{\overset{O}{||}}{C} - OH \text{ (oxalic acid)}$$

Uses of Acetylene:

1. Acetylene is used as illuminant.
2. It is used in welding, cutting iron and steel, when combines with oxygen to give very hot oxy-acetylene flame.
3. As starting material for the preparation of plastic rubber, P.V.C. pipes..
4. For the preparation of organic compounds, like acetaldehyde, acetic acid, ethanol and as excellent solvent such as acetylene dichloride, and acetylene tetrachloride.

SUMMARY

1. Organic chemistry is the study of carbon containing compounds. Compounds consisting of only carbon and hydrogen, are known as hydrocarbons. There are five major kinds of hydrocarbons, alkanes, alkenes, alkynes, alicyclic and aromatic.
2. The simplest hydrocarbons are saturated hydrocarbons or alkanes, which contain carbon-carbon single bond, having a general formula ($C_n H_{2n+2}$). Methane (CH_4) is the simplest member of alkanes.

3. Alkenes and alkynes are unsaturated hydrocarbons, because they possess the multiple bonds in molecules. Alkenes are the hydrocarbons that contain one double bond in molecules, having a general formula ($C_n H_{2n}$). Ethylene ($H_2C = CH_2$) is the simplest member of alkenes. Alkynes are the hydrocarbons that contain one triple bond in molecules, having a general formula $C_n H_{2n-2}$. Acetylene ($HC \equiv CH$) is the simplest member of alkynes.
4. Alicyclic hydrocarbons (cycloalkanes) are the sub-family of Alkanes, whose carbon atoms are joined in a ring. Alkanes and cycloalkanes are saturated hydrocarbons.
5. Compounds that contain one or more benzene rings are called aromatic hydrocarbons.
6. Unsaturated hydrocarbons (alkenes and alkynes) undergo addition reactions, such as hydrogenation (addition of hydrogen) and halogenation (addition of halogens). Polyethylene or polythene, is an addition polymer consisting of many ethylene units.
7. An Alkyl group (R) is a group of atoms, obtained by removing one hydrogen atom from an alkane.
8. A functional group is an atom or group of atoms, that is largely responsible for chemical behaviour of the molecules, for example alcohols (R-OH) contain (-OH) group, the carboxylic acids or organic acids (R-COOH) contain (–COOH) group and alkyl halides (R-X) contain (–x) group, as functional groups.
9. A series of similar compounds which can form to a general formula, where each member differs from the next member by a constant ratio i.e. methylene group ($>CH_2$) is called homologous series.
10. A fuel is any substance which burns and supplies heat. Practically all liquid fuels are obtained from petroleum. Petroleum is a complex mixture of hydrocarbons, that it must be refined into different fractions before it can be used. The first step in the refining or (processing) of petroleum is to separate it into fractions on the basis of their boiling points.
11. The fraction consists of 5 to 10 carbons, per molecule boiling range (20°C-150°C) is straight-run gasoline, the fraction consists of 10 to 13 carbons per molecule, boiling range is (150°C-230°C) is a kerosene, and the fraction consisting of 14 to 21 carbons, boiling range (230°C- 400°C) is gas oil. Further distillation under reduced pressure yields lubricating oils and waxes and leaves a tarry residues of asphalt (coke), natural gas consists largely methane (CH_4) but also contains ethane, propane and butane.

12. Chemicals made from petroleum are called petrochemicals.
13. Petroleum fractions undergo cracking, a process that breaks large molecules into smaller ones.
14. Thermal cracking (pyrolysis) is one at high temperatures, calytic cracking uses a catalysts at low temperatures, in catalytic reforming alkanes and cyclo alkanes are converted into aromatic compounds.
15. The octane number of gasoline is a measure of its resistance to knock. The octane rating of gasoline is improved by adding certain compounds called antiknock agents.

EXERCISE

1. Explain the old and new concept of organic chemistry?
2. Explain the main sources of organic compounds?
3. What are the hydrocarbons? How they are classified?
4. Define the following terms?
   i. Alkanes.
   ii. Alkenes.
   iii. Alkynes.
   iv. Alicyclic compounds.
   v. Aromatic compounds.
5. What is meant by each of the following,
   i. Refining of petroleum.
   ii. Reforming of petroleum.
   iii. Cracking.
6. Define and give an example of homologous series.
7. How methane is prepared? Give its properties.
8. How ethene is prepared from ethyl alcohol?
9. Give equation for the preparation of acetylene from CaC_2 and give its uses?
10. What are the general formulas for:
    (i) The alkane series (ii) The alkene series and (iii) The alkyne series
11. Explain the chain Isomerism? Give an example?
12. Draw the structural formulas for the three isomers of pentane.
13. A hydrocarbons contain 6 carbon atoms? Give its molecular formula M. F, if it is (i) An alkane (ii) An alkene and (iii) An alkyne.
14. Write the balanced equation for the complete combustion of (i) Methane (ii) Ethene and (iii) Acetylene.

15. What is meant by term functional group? Give some examples of functional groups?
16. Why alkanes are said to be saturated?
17. What is the name of the straight chain alkane having seven carbon atoms?
18. What is the name of alkyl group obtained by removing an end hydrogen atom from propane?
19. Bromine adds to ethylene? What is the chemical reaction? How can be bromine used as a test for multiple bonds?
20. What is the range of carbon atoms in heavy oil? And give it uses?
21. What is the paraffin-wax, give the range of carbon atoms per molecule and also mention its uses?
22. What is the boiling range of coke? Give range of carbon atoms in a molecule and also its uses?

Tick the Correct Answer:

1. The branch of chemistry, which deals with the compounds of carbon is called:
   (a) Physical chemistry. (b) Inorganic chemistry.
   (c) Organic chemistry. (d) Analytical chemistry.
2. The first synthetic organic compound is:
   (a) Methane. (b) Ethane.
   (c) Urea . (d) Acetic acid.
3. Which is pure carbon:
   (a) Coaltar. (b) Coal gas.
   (c) Coke. (d) None of these.
4. Residue left after fractional distillation of coaltar:
   (a) Coke. (b) Matte
   (c) Pitch. (b) None of these.
5. Natural gas mainly consists of:
   (a) Methane. (b) Ethane.
   (c) Propane. (d) Butane.
6. Fraction of petroleum containing 10-13carbons, and its boiling range 150°C-230°C:
   (a) Natural gas. (b) Gasoline.
   (c) Kerosene. (d) Light oil.
7. Fraction of petroleum containing $C_{21} - C_{40}$ and boiling range is above 400°C, is:
   (a) Light oil. (b) Heavy oil.
   (c) Praffin wax. (d) Bitumen.

8. The oils that have been carefully purified and decolourized, act as mild laxative are:

(a) Gasoline. (b) Kerosene.
(c) Light oil. (d) Heavy oil.

9. The process in which the octane rating of gasoline can be increased, is called:

(a) Cracking. (b) Refining.
(c) Reforming. (d) isomerism.

10. A series of compounds, in which each member differs from the preceeding one by a constant ratio of (>CH_2) methylene group, is called:

(a) Monologous series. (b) Homologous series.
(c) Isomerism. (d) None of these.

11. Isomerism in which the compounds possess the same molecular formula but different arrangement of carbon atoms in the hydrocarbon Chain is called:

(a) Chain isomerism. (b) Functional isomerism.
(c) Position isomerism. (d) Metamerism.

12. A process that breaks large molecules into smaller one, is called:

(a) Refining. (b) Reforming.
(c) Cracking. (d) None of these.

13. Compounds which contain only carbon and hydrogen elements, are called:

(a) Carbohydrates. (b) Hydrocarbons.
(c) Halides. (d) None of these.

14. The hydrocarbons which contain one or more double or triple bonds, are called:

(a) Saturated hydrocarbons (b) Unsaturated hydrocarbons.
(c) Paraffin. (d) Halogous.

15. The first member of alkene series is:

(a) Methane. (b) Ethane.
(c) Ethene. (d) Ethyne.

16. The hydrocarbons in which carbon atoms are arranged in rings, are called:

(a) Aliphatic. (b) Aromatic.
(c) Ali cyclic. (d) None of these.

17. The quality of petrol is measured by:

(a) Cracking. (b) Reforming.
(c) Octane number. (d) Decane number.

18. General formula for alkane is:

(a) $C_n H_{2n+2}$ (b) $C_n H_{2n}$

(c) $C_n H_{2n-2}$ (d) $C_n H_{2n+1}$

19. the first member of Alkyne series is:

(a) Methane. (b) Ethane.

(c) Ethene. (b) Acetylene.

20. The number of isomers in butane is:

(a) 1 (b) 2 (c) 3 (d) 4

21. An atom or group of atoms present in a molecule and is responsible for chemical behaviour is called:

(a) Alkyl group. (b) Alkenyl group.

(c) Functional group. (d) Aryl group.

22. Iso-butane possesses:

(a) Position isomerism (b) Functional isomerism.

(c) Metamerism. (d) Chain isomerism.

23. Preparation of ethene from ethyl Alcohol is an example of:

(a) Dehydration. (b) Hydration.

(c) Dehalogenation. (d) Halogenation.

24. The Hydrocarbons which possess double bond in their molecules are called:

(a) Alkanes. (b) Alkenes.

(c) Alkynes. (d) Paraffins.

25. The alkanes are also called:

(a) Olefins. (b) Alkynes.

(c) Paraffins. (d) Acetylenes.

26. Which is the functional group of alcohols:

(a) -X (b) -COOH

(c) -OH (d) $> C = O$

27. Which of the following molecules is alkane:

(a) C_5H_8 (b) C_5H_{10}

(c) C_5H_{12} (d) C_5H_{14}

28. Methane is also known is:

(a) Oil gas. (b) Kerosene.

(c) Gasoline. (d) Marsh gas.

CHAPTER-18

CHEMICAL INDUSTRIES

You will learn in this chapter about:

* Chemical industries i.e soda industries.
* Industrial preparation of sodium hydroxide (NaOH),(Caustic soda).Its properties and uses.
* Industrial preparations of sodium bicarbonate($NaHCO_3$) and sodium carbonate (Na_2CO_3), their properties and uses, washing soda ($Na_2CO_3.10H_2O$).
* Soaps and their preparations (Saponification). Types of soaps, functions of soaps. Detergents, their compositions and functions of detergents.
* Plastics,classification of plastics,structures and uses of common plastics.
* Paints, composition of paints or enamels. Distempers varnishes, compositions and their uses or applications.
* Polishes,black shoe polish,dark brown shoe polish.Preparations of shoe polish.
* Inks,types of inks, preparations of some inks.
* Food preservation,causes of food spoilage,food preservation method.

18.1. INTRODUCTION

Chemical industries are generally installed in the country to get variety of useful and profitable products on large scale from the raw materials which are available in the country, through chemical processings. Hence the industry where useful products or chemical compounds are produced, is called chemical industry.

There are several chemical products which have assumed the status of integral part of our every day life. These include sodium compounds such as sodium hydroxide i.e. caustic soda, sodium carbonate, sodium bicarbonate or baking soda etc.

The other daily useful products are soaps, detergents, plastics, paints varnishes, polishes and inks. Apart from that the rising need of food with the population growth round the world, has made it necessary to preserve and store the food items. This need has therefore paved the way for the establishment of industries which serve the purpose of food preservation.

18.1.1 Soda Industries:

The term soda industries relates to the products manufactured from sodium compounds. These include caustic soda i.e sodium hydroxide, (NaOH) soda ash (anhydrous sodium carbonate. Na_2CO_3), baking soda (sodium bicarbonate), ($NaHCO_3$) washing soda (decahydrated sodium carbonate), ($Na_2CO_3 .\ 10H_2O$) etc.

These products play very important role in our daily life. Sodium hydroxide is used in manufacture of soap, in petroleum industry and in the manufacture of artificial silk. Washing soda is used as a domestic cleaning agent. Baking soda is employed to enhance the cooking process. Soda ash apart from being used in paper industry and for washing fabrics, and has special place in the manufacture of glass products.

18.1.2 Industrial Preparation of Sodium Hydroxide:

Sodium hydroxide (NaOH) is one of the most important chemicals of industrial use. It is commonly called as caustic soda, because it is caustic i.e corrosive to touch and causes harmful burns.

Due to its great commercial importance sodium hydroxide therefore is required to be manufactured on large scale.

Electrolytic Process: Mercury cathode process (Castner-Kellner Cell).
Raw material: 25% w/w solution of sodium chloride.
Construction of the cell: The construction of the cell is shown in figure 15.3. In this cell anode is made of a number of titanium plates and cathode is a stream of flowing mercury. When electric current is passed through sodium chloride solution, Na metal is discharged at cathode, while Cl_2 gas at anode.

$$\text{Ionization} \quad 2NaCl_{(aq)} \rightleftharpoons 2Na^+_{(aq)} + 2Cl^-_{(aq)}$$

Reaction at anode.

$$2Cl^-_{(aq)} \xrightarrow{-2e^-} Cl_{2(g)}$$

Reaction at cathode.

Sodium ions are easily discharged over mercury cathode, producing sodium metal via sodium amalgum as shown by chemical equation.

(i) $2Na^+ + 2e^- \longrightarrow 2Na_{(s)}$

(ii) $Na_{(s)} + Hg_{(l)} \longrightarrow Na/Hg$ (sodium amalgum)

(iii) $2Na/Hg + 2H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)} + Hg_{(l)}$

The mercury set free in this cell is recycled to utilize as cathode.

18.1.3 Properties of Sodium Hydroxide:

(a) Physical Properties:

(i) It is a white crystalline solid.
(ii) It melts at 318°C to a clear liquid, and at 322°C, it decomposes.
(iii) Its density is 2.13g/ml.
(iv) It is highly soluble in water and liberate large amount of heat.

(b) Chemical Properties:

The chemcial reactions of NaOH are following:

(i) Reaction with acids:

It reacts with acids like sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid to form corresponding salts of sodium i.e. sodium sulphate, sodium chloride and sodium nitrate.

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow \underset{\text{Sodium sulphate}}{Na_2SO_{4(aq)}} + H_2O_{(l)}$$

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow \underset{\text{Sodium chloride}}{NaCl_{(aq)}} + H_2O_{(l)}$$

$$NaOH_{(aq)} + HNO_{3(aq)} \longrightarrow \underset{\text{Sodium nitrate}}{NaNO_{3(aq)}} + H_2O_{(l)}$$

(ii) Reaction with ammonium chloride:

When NaOH reacts with ammonia salt i.e. ammonium chloride, it librates ammonia gas on warming.

$$NaOH_{(aq)} + NH_4Cl_{(aq)} \longrightarrow NaCl_{(aq)} + NH_{3(g)} + H_2O_{(l)}$$

(iii) Reaction with carbon dioxide:

It reacts with carbon dioxide to produce sodium carbonate and water.

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow \underset{\text{Sodium carbonate}}{Na_2CO_{3(aq)}} + H_2O_{(l)}$$

(iv) Reaction with chlorine gas:

The reaction of sodium hydroxide with chlorine gas results in the formation of sodium salt of oxy acids such as,

$$2NaOH_{(aq)} + Cl_{2(g)} \longrightarrow \underset{\text{Sodium chlorate(1)}}{NaOCl_{(aq)}} + NaCl_{(aq)} + H_2O_{(l)}$$

(v) Reaction with metals:

Sodium hydroxide reacts with certain metals like zinc, tin, aluminium etc to produce sodium zincate, sodium stannite, and sodium aluminate with the liberation of hydrogen gas.

$$2NaOH_{(aq)} + Zn_{(s)} \xrightarrow{heat} \underset{\text{Sodium zincate}}{Na_2ZnO_{2(aq)}} + H_{2(g)}$$

$$2NaOH_{(aq)} + Sn_{(s)} \xrightarrow{heat} \underset{\text{Sodium stannite}}{Na_2SnO_{2(aq)}} + H_{2(g)}$$

$$2NaOH_{(aq)} + Al_{(s)} + 2H_2O_{(l)} \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_{2(aq)}} + 3H_{2(g)}$$

18.1.4 Uses of Sodium Hydroxide:

(i) It is used in the manufacture of soap and petroleum industry.
(ii) It is used in textile and paper industries.
(iii) It is used in bleaching and dyeing process as well as for mercerizing the cotton cloth.
(iv) It is used in purification of bauxite.
(v) It is used in manufacture of artificial silk.

18.2 PREPARATION OF CARBONATE AND BI-CARBONATE OF SODIUM

Anhydrous sodium carbonate, hydrous sodium carbonate and sodium bi-carbonate are generally prepared by ammonia solvay process. The reagents in the process used are, sodium chloride (NaCl), lime stone ($CaCO_3$) and ammonia (NH_3) gas. The formation of these products involves the steps described below.

18.2.1 Industrial Preparation of Sodium Bi-carbonate:

A saturated solution of sodium chloride known as brine is treated with ammonia to form ammoniated brine.

Ammoniated brine is allowed to trickle down a carbonating tower called **Solvey tower** which meets an upward current of carbon dioxide gas obtained by heating lime stone, $CaCO_3$.

$$CaCO_{3(s)} \xrightarrow{heat} CaO_{(s)} + CO_{2(g)}$$

The carbon dioxide and ammonia of ammoniated brine react in the presence of water to give ammonium carbonate $(NH_4)_2CO_3$.

$$2NH_{3(g)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow (NH_4)_2CO_{3(aq)}$$

The ammonium carbonate formed in this way react further reacts with CO_2 and H_2O to produce ammonium bicarbonate.

$$(NH_4)_2\,CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \longrightarrow 2NH_4HCO_{3(aq)}$$

The ammonium bicarbonate then reacts in the form of NH_4^+ and HCO_3^- ions with Na^+ and Cl^- ions of brine to precipitate $NaHCO_3$ beside leaving ammonium chloride (NH_4Cl) in the aqueous solution, at low temperature.

$$\overset{+}{N}a\,Cl^-_{(aq)} + NH_4^+HCO^-_{3(aq)} \xrightarrow[15^0C]{} NaHCO_{3(s)} + NH_4Cl_{(aq)}$$

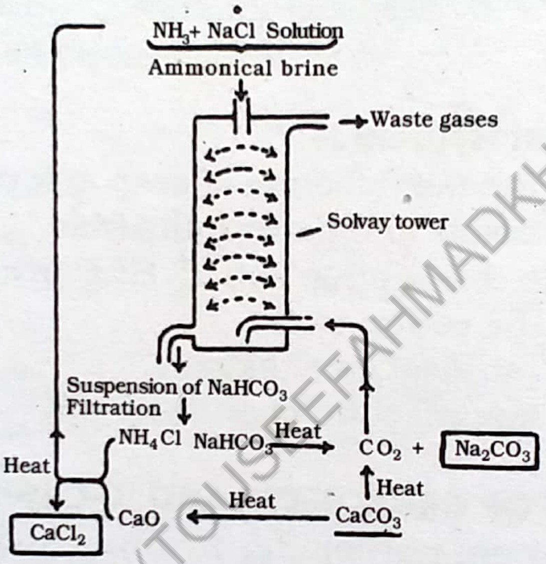


Fig: 18.1 Ammonia Solvay process

The precipitated product, $NaHCO_3$ is separated immediately by vacuum filtration and NH_4Cl is washed away.

The overall reaction may be summarized as:

$$CO_{2(g)} + H_2O_{(l)} + NH_{3(g)} + NaCl_{(aq)} \xrightarrow{15^0C} NaHCO_{3(s)} + NH_4Cl_{(aq)}$$

To recover ammonia for its reuse, the ammonium chloride formed is treated with calcium hydroxide ($Ca(OH)_2$) which is obtained from the lime stone calcium oxide, (CaO).

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$$

$$Ca(OH)_{2(aq)} + 2NH_4Cl_{(aq)} \xrightarrow{heat} CaCl_{2(aq)} + 2NH_{3(g)} + 2H_2O_{(l)}$$

18.2.2 Properties of Sodium Bi-carbonate:

(a) Physical Properties:

(i) It is a white crystalline compound.
(ii) It is bitter in taste.
(iii) Its density is 2.11g/ml.
(iv) It is sparingly soluble in water at room temperature.

(b) Chemical Properties:

(i) Action of heat: Sodium bicarbonate loses carbon dioxide and water to give sodium carbonate on heating.

$$2NaHCO_{3(s)} \xrightarrow{heat} Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$

(ii) Reactions with acids: Sodium bicarbonate reacts with acids such as hydrochloric acid to form its salt (sodium chloride) with the liberation of carbon dioxide gas.

$$NaHCO_{3(s)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

18.2.3 Uses of Sodium Bi-carbonate:

(i) Sodium bicarbonate is largely used in baking powder for which it is called baking soda.
(ii) It is used in the preparation of effervescent drinks and fruit salts.
(iii) It is used in fire extinguisher.
(iv) It is used in medicine as antacid to neutralize the acidity in the stomach.
(v) It is used in the textile, tanning, paper, ceramics industries.

18.2.4 Industrial Preparation of Sodium Carbonate:

Sodium carbonate (Na_2CO_3) can be prepared directly from sodium bicarbonate or by using the raw material adapting the method described for the preparation of sodium bicarbonate. By both means sodium bicarbonate is heated to give an hydrous sodium carbonate (soda ash).

$$2NaHCO_{3(s)} \xrightarrow{heat} \underset{\text{Soda ash}}{Na_2CO_{3(s)}} + H_2O + CO_{2(g)}$$

18.2.5 Properties of Sodium Carbonate:

(a) Physical Properties:

(i) It is a white amorphous solid.
(ii) It metls at 852°C.
(iii) It is highly soluble in water at room temperature with evolution of heat.

(b) Chemical Properties:

(i) Decomposition by acids: Sodium carbonate is decomposed by acids with the evolution of carbon dioxide.

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$
$$Na_2CO_{3(s)} + H_2SO_{4(aq)} \longrightarrow Na_2\ SO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$$

(ii) Reaction with non-alkali metals salts: It forms carbonates of non-alkali metal salts such as magnesium chloride ($MgCl_2$) and zinc sulphate ($ZnSO_4$).

$$Na_2CO_{3(aq)} + MgCl_{2(aq)} \longrightarrow MgCO_{3(s)} + 2NaCl_{(aq)}$$
$$Na_2CO_{3(aq)} + ZnSO_{4(aq)} \longrightarrow ZnCO_{3(s)} + N_2SO_{4(aq)}$$

(iii) Reaction with carbon dioxide: Aqueous sodium carbonate reacts with carbon dioxide to give sodium bicarbonate.

$$Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \longrightarrow 2NaHCO_{3(s)}$$

(iv) Fusion with sand: When fused with sand (silicon dioxide, SiO_2) sodium carbonate forms sodium silicate (Na_2SiO_3) i.e water glass.

$$Na_2CO_{3(s)} + SiO_{2(s)} \xrightarrow[\text{fusion}]{} Na_2SiO_{3(s)} + CO_{2(g)}$$

18.2.6 Uses of Sodium Carbonate:

(i) Sodium carbonate is used domestically as cleansing agent.
(ii) It is used for softening hard water.
(iii) It is used in manufacturing of soap.
(iv) It is used in manufacture of glass and ceramics.
(v) It is used in manufacture of papers, cement and paints.

18.2.7 Hydrous Sodium Carbonate. Na_2CO_3. $10H_2O$ (washing Soda):

Preparation:

(i) When calculated amount of water is added in soda ash then it crystallizes into hydrous sodium carbonate, a decahydrate.

$$Na_2CO_3 + 10H_2O \longrightarrow Na_2CO_3.\ \ 10H_2O_{(s)}$$

Sodium carbonate decahydrate (Na_2CO_3. $10H_2O$) is commonly known as washing soda, which is used for washing purposes.

18.3 SOAPS

The sodium and potassium salts of fatty acids used for cleansing purpose are called soaps. The acid components employed are usually stearic acid, $C_{17}H_{35}$ COOH; oleic acid, $C_{17}H_{33}$ COOH and palmitic acid, $C_{15}H_{31}$ COOH. The fatty acid part is usually comprised of C_{16} to C_{18} chain carboxylate group.

18.3.1 Raw Material:

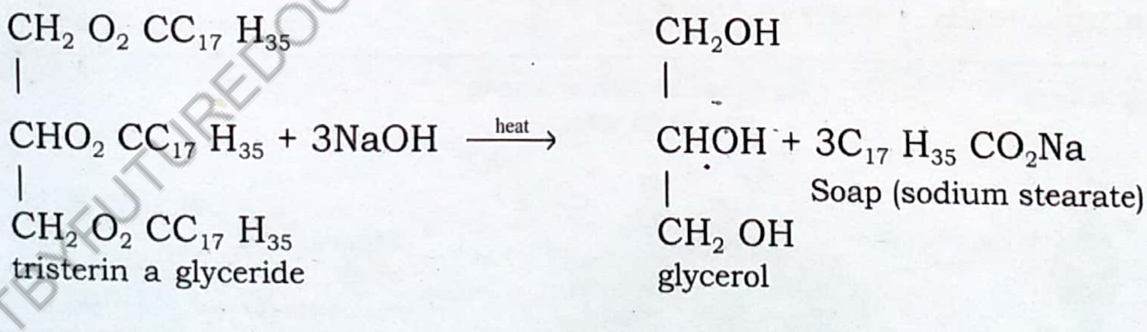
(i) The Natural source of the above fatty acids is either vegetable oils such as coconut oil and palm oil or animal fats such as beef tallow.

(ii) The alkali metal (sodium and potassium) sources are sodium hydroxide (NaOH) and potassium hydroxide (KOH).

18.3.2 Preparation of Soap (Saponification):

The equation of the reaction for the preparation of soap may be shown by taking stearic acid in the form of tristearin as an example. In the reaction it reacts with sodium hydroxide to form sodium stearate, a soap and glycerol (glycerine). Glycerol is separated out from the product mixture by a process, the common salt i.e. sodium chloride is added to the mixture. Glycerine by this way dissolve in the salt solution. Being heavier than soap it settles down and drained off from the bottom of the container from which glycerol is recovered as a by-product. This process is known as salting out the soap.

The chemical process for the preparation of soap is called **saponification**. The reaction is represented by the following equation.



$$\begin{array}{l} CH_2\,O_2\,CC_{17}\,H_{35} \\ | \\ CHO_2\,CC_{17}\,H_{35} \\ | \\ CH_2\,O_2\,CC_{17}\,H_{35} \\ \text{tristerin a glyceride} \end{array} + 3NaOH \xrightarrow{\text{heat}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2\,OH \\ \text{glycerol} \end{array} + \underset{\text{Soap (sodium stearate)}}{3C_{17}\,H_{35}\,CO_2Na}$$

18.3.3 Types of Soaps and their Composition:

(i) Toilet Soaps:

These are prepared from 80 to 90% tallow oil and 10 to 20% coconut oil. Beef tallow consists of stearic and oleic acids. Palmitic acid is found in vegetable oils. To this type of soaps the desired colour and perfumes are added.

(ii) Laundry Soaps:

The soap prepared by using ordinary fat is further heated with resin and caustic soda and their molten mixture is solidified. During solidification, sodium silicate, washing soda and sodium phosphate are added to increase the cleansing ability of the soap. This type of soap is used for washing all types of clothes.

(iii) Kitchen Soaps:

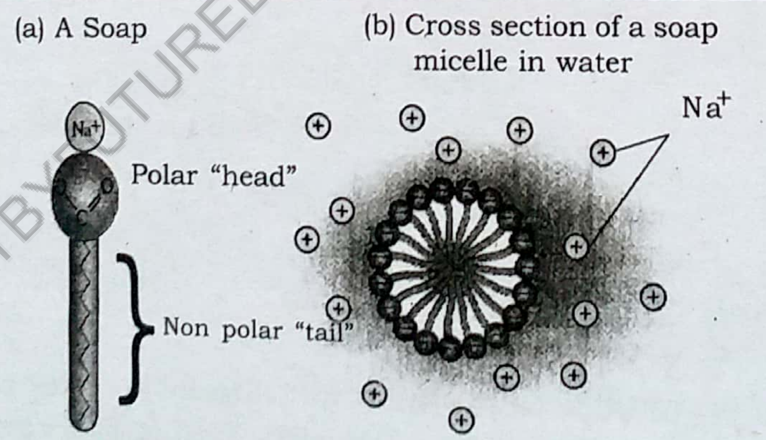
The soaps prepared for washing/cleansing utensils are called kitchen soaps. These are prepared by adding finely divided sand and washing soda.

(iv) Shaving Soaps:

The soaps for shaving purpose are prepared by the saponification of good quality animal fat or edible oil with potassium hydroxide (caustic potash). In these soaps stearic acid is used in excessive amount to prevent them from drying.

18.3.4 Function of Soaps:

Soaps serve their functions as dirt remover. Most dirt particles (on skin or cloth) become surrounded by a layer of an oil or fat. Water molecules alone are unable to disperse these greasy globules because they are unable to penetrate the oily layer and separate the individual particles from each other or from the surface to which they are stuck. Soap solutions however are able to separate the individual particles because their hydrocarbon chain of the carboxylate part can dissolve the oily layer. The process is diagramatically shown in the fig. 18.2.



(a) A Soap

(b) Cross section of a soap micelle in water

Figure 18.2
Soap micelles (a) A sodium soap molecule (b) Non polar (hydrophobic) hydrocarbon chains are clustered in the interior of the micelle and polar (hydrophilic) carboxyiate groups are on the surface of the micelle. Soap micelles repel each other because of their negative surface charges.

18.3.5 Detergents:

The cleansing agents used for cleaning a solid surface are called detergents. Actually detergents are soapless cleansing agents. These are salts of organic sulphonic acids having general formula $R\text{-}SO_3^- Na^+$ or $R\text{-}O\text{-}SO_3^-Na$.

18.3.6 Composition of Detergents:

The detergents consist of two parts; a hydrocarbon and a sulphonate ($-SO_3^-$) or a sulphate ($-OSO_3^-$) group. These molecules are made usable by converting them into a water soluble sodium salts.

A simple example of these compounds is sodium lauryl sulphate, $C_{12}H_{25}OSO_3^-Na^+$, a sodium salt of a long chain hydrocarbon attached to a sulphate group. The detergents available having this composition are usually used for washing a variety of utensils.

The detergents closely related to soaps and used for house-hold laundry belong to the sulphonates such as sodium -p- dodecyl benzene sulphonate. The structure of such molecule contain a benzene ring between sulphonate and alkyl group.

Sodium-p- dodecyl benzene sulphonate.

The detergents of this type are used for washing various kinds of clothes.

18.3.7 Function of Detergents:

Detergents function in the same way as soaps. They offer an advantage over soaps by functioning well in hard water, that is water containing calcium (Ca^{2+}), farrous (Fe^{2+}), ferric (Fe^{3+}) and magnesium (Mg^{2+}) ions. Calcium, iron and magnesium salts of alkane sulphonates and alkyl hydrogen sulphonates are largely water soluble. A detergent removes dirt very easily. There is a large variety of detergents which are used as washing powders and washing liquids.

18.4 PLASTICS

Plastics are one of the types of polymers. The compounds built up of a large number of smaller molecules that have reacted with one another are called **polymers**. Polymers occur in nature as well as synthesized. Plastics belong to the synthetic polymers. The essential ingredients of these compounds are organic substances of various types.

18.4.1. Sources:

The common basic raw material for synthesizing plastics are coal, petrochemicals, cotton, wood, gas, salt and water.

18.4.2 Applications:

Plastics have a large number of applications, because of their toughness, water resistance, corrosion resistance, ease of fabrication and remarkable colour range. When properly selected, they can be used with the same degree of assurance as metals and alloys e.g. steel.

18.4.3 Classification:

Plastics are classified as:
(a) Thermoplastic, (b) Thermosetting plastics.

(a) Thermoplastic:

Synthetic resins formed by addition polymerization are thermoplastic. They softens on heating and hardens on cooling. The repetition of the process does not affect the properties of these types of plastics. They can easily be moulded into variuos shapes. Cellulose nitrate, cellulose acetate and vinyl polymers are examples of this class.

(b) Thermosetting plastics:

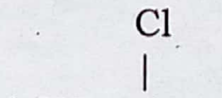
The plastics belonging to this class can only be heated once before they set on cooling. The process cannot be repeated in this case as they do not soften on reheating. The examples of this class are phenol formaldehyde (formica, bakelite), epoxy resins (araldite, and adhesive).

18.4.4 Sturcture and Uses of Some of the Common Plastics:

(a) Polythene (Polyethylene) $(-CH_2 - CH_2 -)n$.

It is a polymer of ethylene molecules $(CH_2 = CH_2)$ most commonly used in the preparation of polythene bags for carrying fruits, vegetables etc., and plastic bottles.

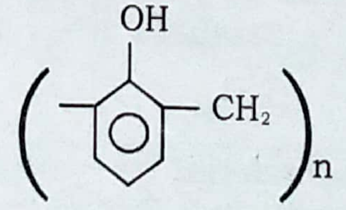
(b) Polyvinyl chloride (PVC):



$(-CH_2 - \overset{\overset{\displaystyle Cl}{|}}{CH})_n$

It is a polymer of vinyl chloride $(CH_2 = CHCl)$ used in the manufacture of electrical cable coverings, suit cases, gramophone records etc.

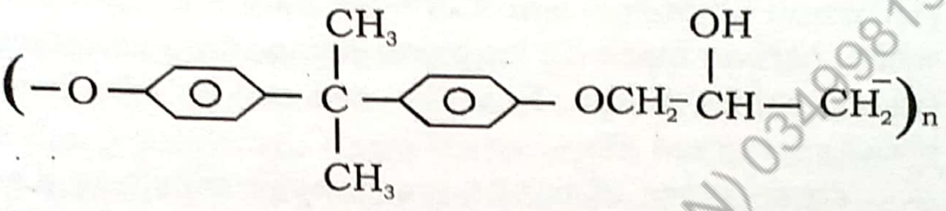
(c) Bakelite (Phenol- formaldehyde polymer)



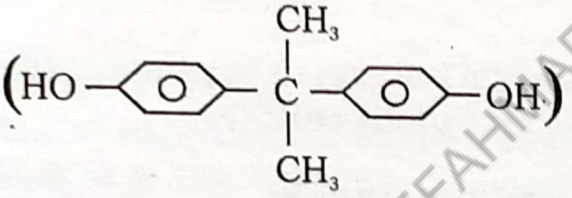
It is formed by polymerization of phenol () and formaldehyde (HCHO).

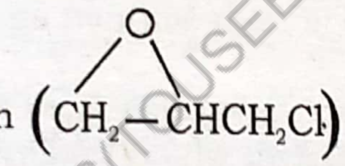
Switches, electric board sheets, cameras, radio, telephone etc components are manufactured by this type of plastic.

(d) Exposy resin:



It is formed by polymerization of biphenol A



and epichlorohydrin 

A well known adhesive araldite is an example of this plastic material.

18.5 PAINTS

Paints are fluids containing a colouring material (pigments) dispersed in organic liquid. Their application to a surface of walls, windows, doors, wooden and iron furniture etc. and exposure to the air to dryness results into a hard adherent protective and decorative layer. Paints may either be oil based or water based.

18.5.1Composition of oil Paints or Enamels:

The oil based paint is composed of following main components. Linseed oil, pigments, a thinner, a resin and a drier.

The linseed oil serves as a protective layer on the painted surface. Pigments provide colours. A thinner is turpentine or other volatile liquid. The resins act as binders. A drier accelerates drying or hardening of linseed oil. Fillers such as china clay and barium sulphate ($BaSO_4$) are added to the pigments to increase the durability of paints.

These type of paints are usually called oil paints or synthetic enamels and are applied over wooden or iron surfaces.

18.5.2 Composition of Water Paints or Distemper:

Water based paints are available in the form of emulsion. Such paints usually consists of an emulsion of hydrocarbons, butadiene and styrene, polymers polyvinyl acetate or acrylic resins in water.

The pigments used as colouring material are usually titanium dioxide (TiO_2) and lithopone, zinc sulphide, ZnS, and barium sulphate ($BaSO_4$) for white, carbon black (C) for black colour, chrome yellow ($PbCrO_4$) for yellow colour, oxides of iron, Fe_2O_3 for red and FeO for brown; chromium oxide (Cr_2O_3) for green etc.

These types of paints are usually called as distemper and plastic emulsion, and are applied over walls especially the interior ones.

18.6 VARNISHES

Varinish is a colloidal solution used without pigments as a protective and decorative coating for various surfaces.

18.6.1 Composition and Application:

Varnish is composed of clear solution and consists of resins, volatile organic solvent and driers.

When applied to a surface, varnish dries to a tough adherent film by the drying oil used is linseed oil which undergoes evaporation, **oxidation** and polymerization.

Varnishes are used without pigments therefore these are less resistant to damage by light than are paints. The transparent film furnished by varnishes accentuates the texture of the surface coated.

The resinous component of varnishes now-a-days in use are mostly comprised of synthetic alkyl and urethane resins because of their greater durability, less yellowing, ease of application and beauty. Alkyl resins are formed by the reaction of polyhydric alcohols and polybasic acids. Urethane resins are ethly carbonate molecules.

18.7 POLISHES

Certain articles such as shoes, furniture, cars, motorcycles, floor of the houses etc if left untreated tend to be damaged. They need to be protected by applying a protective layer upon their surface. That layer is called **polish**.

Here the polishes meant only for applying on the shoes are described such as black shoe, dark brown shoe polishes.

18.7.1 Constituents of Black Shoes Polish:

The black shoes polish is comprised of powdered animal charcoal, bees wax, carnauba wax, turpentine oil, nigrosine oil, sodium hydroxide and soap.

18.7.2 Constituents of Dark Brown Shoe Polish:

The dark brown shoe polish is mainly made up of bismarck brown, pearl ash (potassium carbonate), turpentine oil, palm oil or soap.

18.7.3 Functions of the Constituents of Polish:

Animal charcoal and bismarck brown provide black and dark brown colours respectively to the polishes. The waxes maintain the required softness and provide shine to the shoes. Turpentine oil beside keeping the shoes soft, prevent them from drying and helps in the absorption of the polish in leather from which shoes are manufactured.

18.7.4 Preparation of Shoes Polish:

Pure bees wax is melted by heating on the water bath. Soon after that turpentine oils is added to it. The mixture is homogenized and cooled with stirring. Meanwhile in another container caustic soda (NaOH) is heated in a minimum quantity of water to make a strong alkaline solution, lye. This lye is added to the above mixture with vigorous stirring. When it becomes thick, nigrosine oil is added to it and stirring is continued till it gains the desired thickness.

A powdered animal charcoal is added to give the polish black colour, and a concentrated solution of bismarck brown and pearl ash (potassium carbonate) in water is added when a brown polish is required.

18.8 INKS

Inks are deeply coloured liquids of varied composition used for writing or printing. They contain a protective substance such as gum arabic to make them more durable.

18.8.1 Types of Inks:

The inks of different colours are meant for various purposes which are given below alongwith their constituents.

(i) Black ink:

It is a mixture of an infusion of gall nuts with ferrous sulphate and a certain proportion of hydrochloric acid. Gall nuts are excrescences from the oak plant.

(ii) Blue ink: It can be prepared by dissolving prussian blue in a dilute solution of oxalic acid.

(iii) Marking ink: It consists either of silver nitrate solution coloured and thickened with gum or of dyes.

(iv) Printing inks: These are made by incorporating a pigment into a suitable varnish medium with driers and appropriate accessories. For printing of good quality a polymerized linseed oil is generally used together with resin oil and various pigments. The pigment is usually ground finely in a mixture of mineral oil and resins.

(v) Red ink: It is prepared normally from Brazil wood or by dissolving carmine in aqueous ammonium hydroxide. The dyestuff eosin is also used as a constituent of red ink.

(vi) Type writing inks: These are prepared by employing dyes in conjuction with the other materials which include certain proportion of glycerol.

(vii) Blue black ink: It is made up of tannic acid, gallic acid, ferrous sulphate, hydrochloric acid (dilute), gum arabic, carbolic acid, phenol blue and water.

(viii) Royal blue ink: It is composed of ink blue colour methyl violet, ethylene glycol, acetone, phenol and carboxy methyl cellulose.

(ix) Stamp pad ink: It is prepared with aniline dye, glycerine, tug, soyabean oil, water and alcohol.

18.8.2 Preparation of Common Inks:

Blue black and royal blue fountain pen inks are widely used in our routine work, hence the constituents required and methods of preparation of inks is kept confined here to these types of inks.

18.8.3 Preparation of Blue Black Ink:

Tannic acid (75g) and gallic acid (30g) are dissolved in 150cm^3 of warm water. In another container ferrous sulphate (100g) along with gum arabic (60g) is dissolved in 600cm^3 of distilled water. Mix the two solutions by adding 75ml of dilute hydrochloric acid (15g), phenol blue (15g) and water is added to produce 3dm^3 solution. The contents to be kept aside for a fornight and then filtered.

18.8.4 Preparation of Royal Blue Ink:

First of all the carboxy methyl cellulose is dissolved in minimum quantity of distilled water. In another pot, ink blue (15g) and methyl violet (5g) colours are dissolved in 200cm^3 warm distilled water and the solution is filtered. This solution is mixed with the earlier prepared carboxy methyl cellulose solution and the remaining ingredients i.e. Ethylene glycol (20cm^3), accetone (10cm^3) and phenol (1g) are added. The combined solution to be stirred well and kept for 10 days. Afterwards filtered to get the royal blue ink ready for use.

18.9 FOOD PRESERVATION

Foods whether grown on trees e.g. fruits, in the ground as plants e.g. vegetables, cereals etc. or as animals e.g. mutton, beef etc., above the ground do not last for ever. Fruits, vegetables and cereal grains begin to deteriorate once they are harvested. Similarly meat begins to deteriorate in quality soon after slaughter of the animal.

In this modern world, the food needs to be stored or supplied to distant areas, it is therefore necessary to prevent the food from being destroyed or spoiled.

18.9.1 Causes of Food Spoilage:

The food may subject to several decay mechanisms. These inculde moisture, biological attack by pests, disease or decay micro-organisms, senescence, chemical reactions and physical changes. The producer and processor therefore want to prevent or minimize chances of spoilage of the foods.

(i) **Moisture:** The agricultural products of low moisture contents such as corn and soyabean when exposed to higher humidity take up enough moisture contents to permit the growth of moulds and bacteria.

(ii) **Microbial activities:** There are several kinds of food which tend to spoil by microbial attack. Fish, poultry and dairy products are specifically spoiled by microbial growth.

(iii) **Chemical Changes:** The chemical changes brought by enzymes are responsible for food spoilage. These enzymes may have their origin in the food material or may be produced by yeast, moulds and bacteria which contaminate the product. The chemical and biochemical changes renders the fats and oils rancid and are also responsible for browning of fruits and vegetables.

18.10 FOOD PRESERVATION METHODS

There are numerous methods of preservation of foods. Some of the most widely used ones are described here.

(a) Removal of moisture:

This method of preservation of food relates with removal of water or drying process. The products that needs to be dried are the various pastes, milk, coffee and tea, some vegetable, fruits, meat and eggs.

Dried foods are easy to store or transport because they occupy only about one tenth the volume of fresh food. The use of this technique controls the growth of microorganisms, which render the food to spoil.

(b) Addition of salt and sugar:

As a means of chemical preservation, sugar and salt are added to many sausages to increase their shelf life. The sugar and salt bind the water, which helps the microorganisms to grow. The inhibition in growth of microbes by this way retards the process of food spoilage. The water binding agents are known as humectants.

(c) Temperature control:

One of the controlling factor for preservation of food is temperature. Environmental conditions related to temperature though not destroy organisms however it prevents their growth. Refrigeration and freezing of foods in this respect lowers the environmental temperature to levels which do not allow the growth of many destructive organisms.

(d) Preservation by Storage:

Many types of fresh foods such as fruits, vegetables, meats, fish etc. when required to be stored for long term are preserved by heat treatment employing various methods. Amongst these methods canning and irradiation are noteworthy.

(i) Canning: The preservation of food by sealing into air tight containers is called canning. This method is widely used for food perservation. The containers may be metal which is often plastic-lined aluminium or special strength glass. The raw food is packed into the container sealed and the whole package is then treated with heat in a steam pressure used to cook the food and sterilize both the container and the contents.

(ii) Irradiation: The process of passing radiation through any substance is called irradiation. The radiation is comprised of alpha (α), beta (β) and gamma (γ) rays.

Radiation can be used to preserve food such as meat, potatoes and onions etc. without causing undesirable protein denaturation or appreciably altering the taste. The process leaves no residual radioactivity in the food. There is a little loss of vitamins in all foods by the recommended doses than that seen with canning, freezing or drying.

(e) Preservation by Chemical addition:

Certain chemical substances are added in small proportions to preserve food. In this regard commonly used food additions are salts of calcium, magnesuim, potassium and sodium. The use of sodium sulphite and potassium meta-bi-sulphite are used to prevent the growth of micro-organisms.

Sodium dihydrogen phosphate is incorporated to improve the texture and magnesium hydroxide reduce the acidity in foods.

Addition of common salt preserves meat and fish items.

Propanoic acid, benzoic acid and their salts prevents the bread and cheese from moulds and yeasts.

Dry fruits, Jam and jellies are preserved by addition of sulphur dioxide or salts of sulphurous acid.

SUMMARY

1. Sodium hydroxide is an important member of soda industries which is commonly known as caustic soda.
2. Electrolyte process is very useful method of preparation of sodium hydroxide.
3. Sodium hydroxide when dissolved in water, liberates large amount of heat.
4. A wide range of chemical reagents react with sodium hydroxide to produce a variety of products.
5. In the industries such as soap, textile, paper etc. sodium hydroxide has a key role to play.
6. Sodium hydrogen carbonate is used in the preparation of effervescent drinks and fruit salts.
7. Sodium carbonate have an important role in paper, soap, tanning, cement, glass and ceramic industries.

8. Washing soda is used as domestic cleaning agent; baking soda is employed to enhance the cooking process and soda ash is used in paper industry, washing fabrics as well as in the manufacture of glass products.
9. Bicarbonates and carbonates of sodium are soda ash, baking soda and washing soda.
10. Bicarbonates and carbonates of sodium are manufactured by ammonia solvay process.
11. The raw material used in ammonia solvay process are sodium chloride, lime stone and ammonia.
12. The saturated solution of sodium chloride is called a brine.
13. Baking soda ($NaHCO_3$) on heating gives anhydrous sodium carbonate (Na_2CO_3).
14. Sodium and potassium salts of fatty acids used for cleansing purposes are called soaps.
15. The fatty acid component used for soaps preparation are usually stearic acid, oleic acid and palmitic acid.
16. The natural sources of above fatty acids are either vegetable oils such as coconut oil, palm oil or animal fats such as beef-tallow.
17. Toilet soaps such as lux, capri are prepared fom 80-90% tallow-oil and 10-20% of coconut oil.
18. Plastics belong to the synthetic polymers.
19. The common basic raw material for synthesizing plastics are coal, petrochemicals, cotton, wood, gas, salt and water.
20. Plastics tend themselves to an acceedingly large number of applications, because of their toughness, water resistance, corrosion resistance, remarkable colour range etc.
21. Thermoplastic plastics are synthetic resins which soften on heating and hardens on cooling.
22. Thermosetting plastics can only be heated once before they set on cooling.
23. The polymer of ethylene molecules are most commonly used for preparation of bags to carry fruits, vegetables etc.
24. Electrical cable covering, suit cases etc are manufactured from polymer of vinyl chloride.
25. Bakelite is prepared by polymerization of phenol and formaldehyde. It is used in the manufacture of switches, cameras, radio etc.
26. Paints are applied to the surface of walls, windows, doors, iron articles etc to form a protective and decorative layer.

27. The oil based paint is composed of linseed oils, pigments, a thinner, a resin and a drier.
28. Water based paints usually consist of emulsion of hydrocarbons, butadiene and styrene, polyvinyl acetate etc in water.
29. The pigments used for red colour are oxides of iron, Fe_2O_3.
30. Varnishes are clear solutions made up from resins, volatile organic solvent, containing driers.
31. Polish when applied on the surface of shoes, furniture, cars, floor of houses etc, it serves to protect these articles.
32. One of the ingredients of polishes, wax, maintain the required softness and provide shine to the shoes.
33. Blue inks are prepared by dissolving prussian blue in a dilute solution of oxalic acid.
34. The food may be spoiled by biological attack by pests, disease or decay through microorganisms and chemical reactions.
35. Removal of moisture controls the growth of microorganisms, which renders the food to spoil.
36. Refrigeration and freezing of foods lower the environmental temperature to levels which do not allow the growth of many destructive organisms.
37. Canning and irradiation methods are used to store many types of fresh foods such as fruits, vegetables, meats, fish etc.

EXERCISE

Fill in the blanks:

(i) Sodium hydroxide causes harmful burns to the skin, therefore it is commonly called ________.

(ii) Sodium hydroxide produces a large amount of ________ of when dissolved in water.

(iii) When sodium hydroxide is treated with ________ it forms sodium sulphate salt.

(iv) The reactions of sodium hydroxide with ________ result in liberation of hydrogen gas.

(v) The molecular formula for baking soda is ________.

(vi) Sodium carbonate, washing soda and ________ are generally prepared by ammonia solvay process.

(vii) The chemical process for the preparation of soap is called ______

(viii) The detergents are usually consists of two parts, a ______ and a sulphonate or a sulphate.

(ix) Compounds made up of large number of smaller molecules are called ______

(x) The plastics belong to ________ class can only be heated once before they set on cooling.

(xi) P.V.C is the abbriviation (Short form) for ________.

(xii) Paints are fluids containing ________ dispersed in organic liquid.

(xiii) Linseed oil, pigments resin etc are main components of ______ paints.

(xiv) A thinner is turpentine or other ______ liquid.

(xv) Water based paints are available in the form of ________

(xvi) ________ are used without pigments to furnish the transparent film on the surface coated.

(xvii) Marking ink consists of ________ solution thickened with gum or of dyes.

(xviii) The removal of moisture controls the growth of ______ which renders the food to spoil.

(xix) The water binding agents used in the preservation of food are known as ________.

(xx) The preservation of food by sealing into tight containers is called________.

(xxi) ________ is used in the preparation of effervescent drinks and fruit salts.

(xxii) Sodium carbonate when fused with ________ it forms sodium silicate (glass).

(xxiii) ________ is used for softening hard water.

(xxiv) The colour of black shoe polish is due to ________.

(xxv) Turpentine oil beside keeping the shoes ________ prevent then from drying and helps in is absorption in the leather.

Tick the correct answers

1. Sodium hydroxide is prepared at large scale by the following methods.
   (a) Electrolytes process. (b) Saponification method.
   (c) Hydrolysis.
2. Sodium hydroxide at 318°C:
   (a) Melts with decomposition. (b) Does not melt.
   (c) Melts to a clear liquid. (d) Converts to gas.

3. Carbon dioxde and sodium hydroxide react to give.
(a) Sodium carbonate and water. (b) Sodium carbonate only.
(c) Sodium metal and water. (d) Sodium and carbon monoxide.

4. When sodium hydroxide reacts with ammonium chloride it liberates gas:
(a) Carbon dioxide. (b) Hydrogen.
(c) Oxygen. (d) Ammonia.

5. Sodium hydrogen carbonate used in medicine which of the effects it cause in the stomach?
(a) Increase the basicity. (b) Increase the acidity.
(c) Neutralize the acidity. (d) Decrease the basicity.

6. The product/ products obtained by reaction of sodium carbonate with carbon dioxide in aqueous medium is / are:
(a) Sodium hydroxide. (b) Sodium hydrogen carbonate.
(c) Sodium carbonate and water. (d) Sodium oxide.

7. Carbonates and bicarbonate of sodium are manufactured by:
(a) Contact method . (b) Ammonia solvay process.
(c) Ostwald's process. (d) Haber's method.

8. Detergents are cleansing agents prepared from:
(a) Water soluble sodium salts. (b) Hydrocarbons only.
(c) Hydrocarbon and a sulphonate. (d) Sulphonate only.

9. The material which softens on heating and hardens on cooling come under the class:
(a) Thermosetting palstic. (b) Thermoplastic.
(c) Formica. (d) Bakelite.

10. The class of plastic that can only be heated once before they set on cooling is:
(a) Thermoplastic. (b) Cellulose nitrate.
(c) Cellulose acetate. (d) Themosetting plastic.

11. The polymer which is used in the manufacture of bags for shopping purpose is:
(a) Poly vinyl chloride. (b) Poly ethylene.
(c) Epoxy resin. (d) Araldite

12. Cameras, radios, telephone sets, etc are prepared from:
(a) Polyethene. (b) Poly vinyl chloride.
(c) Bakelite. (d) Cellulose nitrate.

13. The pigments used to produce white colour are:
(a) Oxides of iron. (b) Chromium oxide.
(c) Zinc sulphide. (d) Ferric oxide.

14. Varnishes are used:
(a) With pigments. (b) Without dirers.
(c) With out pigments. (d) Without resins.

15. Which of the following constituents of shoe polish is used to provide shining to the shoes:
(a) Bees wax. (b) Sodium hydroxide.
(c) Pearl ash. (d) Soap.

16. The common ingredients used in black and brown shoe polishes is,
(a) Nigrosine oil. (b) Pearl ash.
(c) Animal Charcoal. (d) Turpentine oil.

17. A mixture of infusion of gall nuts with ferrous sulphate and certain proportion of hydrochloric acid produces:
(a) Black ink. (b) Printing ink.
(c) Marking ink. (d) Blue ink.

18. Red ink is normally prepared from:
(a) Oak plant. (b) Linseed oil.
(c) Silver nitrate. (d) Brazil wood.

19. Addition of salts and sugar:
(a) Decreases the shelf life of food. (b) Preserve the food.
(c) Spoil the food. (d) Help to grow micro-organisms.

20. The radiation paned through food to preserve it are comprised of:
(a) α- rays only. (b) γ-rays.
(b) α and β-rays only. (d) α, β and γ-rays.

Answers the following questions:

1. (a) Give the industrial preparation of sodium hydroxide.
   (b) Give the reactions of NaOH with:
   (i) HCl (ii) Al (iii) CO_2 (iv) NH_4Cl (v) Cl_2
   (c) Describe the uses of NaOH.

2. (a) Describe ammonia solvay process for the manufacture of sodium hydrogen carbonate.
   (b) Complete the following reactions:

(i) $NH_4Cl + Ca(OH)_2 \longrightarrow$

(ii) $NaHCO_{3(s)} \xrightarrow{heat}$

(iii) $Na_2CO_3 + CO_2 + H_2O \longrightarrow$

(iv) $NaOH + CO_2 \longrightarrow$

3. (a) What do you mean by saponification?
   (b) What are different types of soap? and what is the funciton of soap?

4. (a) What do you understand by a detergent? Give the composition of detergent and its function.
   (b) Differentiate between thermoplastic and thermosetting plastic. Describe the structures of some of the plastics.
   (c) Describe composition and application of varnishes.

5. (a) Differentiate between oil paints and water paints.
   (b) What are polishes? Give in details about the composition and preparations of different types of polishes.
   (c) Write notes on food preservation.

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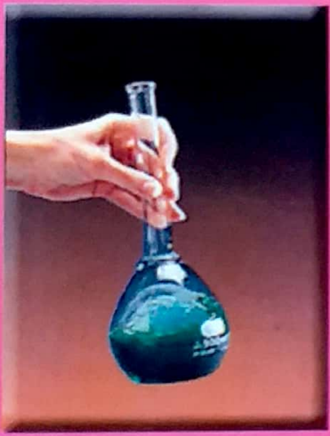

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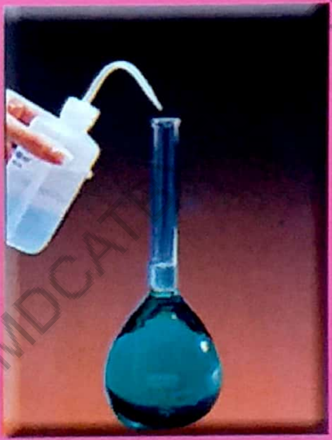

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