

# Chemistry of Selected Non-Metals and their Compunds

# LEARNING OBJECTIVE

Upon completion of this topic, learners will:

- Describe the metallurgy, properties as well as uses of Al, Fe, Cu, Au and Sn
- Discuss alloys including the common uses of brass, bronze, steel, and duralumin and
- Analyze the production processes of cement and uses.

# 6.1 CARBON AND ITS COMPOUNDS

Carbon is the first element of group 14 of the periodic table. Its electronic configuration  $(1s^22s^22p^2)$  shows that it has four electrons in the outermost shell. It exhibits some unique properties because of its small size in comparison to the other elements of the group. It shows maximum tendency of catenation (self linking property) in comparison to any other element in the periodic table. Carbon forms extensive range and variety of compounds. In fact, the number of compounds of carbon is more than those of any other element except hydrogen. The chemistry of carbon compounds is treated as separate branch of chemistry called organic chemistry. However, the compounds of carbon with metals, metalloids, non-metals and those which do not contain C–H bonds are traditionally regarded as inorganic compounds.

# TERRESTRIAL ABUNDANCE AND DISTRIBUTION

Carbon is widely distributed in nature both in *free* as well as in combined state.

In free state, it occurs as *diamond*, *graphite* and *coal*.

In **combined state**, it occurs as:

(*i*) *Carbonates* in many minerals like

*Malachite*  $CuCO_3 \cdot Cu(OH)_2$ ;

Dolomite  $CaCO_3 \cdot MgCO_3$ 

Calcite  $CaCO_3$ ;

(*ii*) *Hydrocarbons* in the form of *crude oil* and *natural gas*. (*iii*) *Carbon dioxide* in air (about 0.03%).

It is also important constituent of all the living systems in the form of carbohydrates, proteins, fats, vitamins, harmones, nucleic acids, etc.

## **ISOTOPES OF CARBON**

Naturally occurring carbon contains two stable isotopes  ${}^{12}$ C (98.9%) and  ${}^{13}$ C (1.1%) along with traces of  ${}^{14}$ C isotope which is radioactive with half life period of 5770 years.  ${}^{14}$ C isotope is used in *radiocarbon dating* to determine the age of archaeological specimens. The isotope  ${}^{12}$ C is the international standard for atomic mass measurement and has been assigned a mass of 12,00000*u*.

# IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest to the members of its group. It is due to its *smaller size, higher electronegativity, higher ionization enthalpy and non-availability of d-orbitals.* 

- 1. In carbon, only *s* and *p* orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This limits the maximum covalence to four whereas other members of the group can expand their covalence due to the presence of vacant *d*-orbitals in their valance shells.
- 2. Carbon also has unique ability to form  $p\pi$ - $p\pi$  multiple bonds with itself and with other atoms because of its small size and high electronegativity. Few examples of multiple bonding are: C=C, C=C, C=O, C=S and C=N.
- 3. Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. *This property is called catenation.* This is because C—C bonds are very strong. Down the group as the atomic size increases and the electronegativity decreases, therefore, the tendency to show catenation decreases.

The order of catenation is:

 $C >> Si > Ge \approx Sn$ 

Lead does not show catenation.

Due to property of catentation and  $p\pi$ - $p\pi$  bond formation, carbon is able to show different allotropic forms.

### Allotropic forms of Carbon

Allotropy is a phenomenon of existence of different forms of an element, having different physical properties. The various form are called **allotropes** or **allotropic forms**. Carbon exists as crystalline as well as amorphous allotropes.

## Crystalline Allotropes

The important **crystalline allotropes** of carbon are *diamond*, *graphite* and *fullerenes*.

## Diamond

It is the purest form of carbon. It occurs in nature as such and is also artificially prepared.

### Main uses of diamond are:

- 1. Diamond is the hardest naturally occurring substance. Due to its extreme hardness, it is used for making **tools for cutting and grinding** other hard material and also in oil-well drills for drilling holes through the earth's rocky layers.
- 2. It is used in dies for the manufacture of tungsten filaments for electric light bulbs.
- 3. Diamond is transparent and has very high refractive index. It possesses extraordinary brilliance. Because of these properties it is used *for making jewellery*.
- 4. Sharp-edged diamonds are *used by eye surgeons to remove cataract from eyes* with high precision.
- 5. Because of its extraordinary sensitivity to heat rays, it is used *in high precision thermometers*.
- 6. It is used *in protective windows for space probes* as it can keep out harmful radiations.

The value of diamond depends upon its weight and freedom from impurities. Weight of diamond is expressed in terms of *carats*. One *carat* is equal to 0.2 g or 200 mg.

### Graphite

It occurs in nature and can also manufactured artificially by heating coke to 3275–3300 K in an electric furnace. The process in known as Acheson's process.

Main uses of graphite are:

- 1. Graphite is used *as lubricant* either as a powder or as a dispersion in oil or water.
- 2. Mixed with clay it is used in 'lead' pencils.

- 3. Since, it is good conductor of electricity and is inert, it is used *for making carbon electrodes* in electrolytic cells and in dry cells.
- 4. Because of its high melting point it is used *for making graphite crucibles.* Crucibles made of graphite are not attacked by dilute acids or fused alkalies.
- 5. It is a component of *printers' ink*.
- 6. Graphite is used *as moderator* in nuclear reactors.
- 7. Graphite under the effect of high temperature and high pressure can be converted into diamond.

# Comparison of Properties of Diamond and Graphite *Diamond*

- 1. Due to its high refractive index, it is a transparent substance.
- 2. It has high density  $(3.51 \text{ g cm}^{-3})$ .
- 3. It is very hard.
- 4. It is bad conductor of heat and electricity.
- 5. It possesses three dimensional network structure.
- 6. Chemical reactivity is low.

## Graphite

- 1. Although it is black and opaque, yet it has metallic lustre.
- 2. It has relatively low density (2.26 g cm<sup>-3</sup>).
- 3. It is soft.
- 4. It is good conductor of heat and electricity.
- 5. It possesses a sheet type structure.
- 6. Chemical reactivity is high.

# Amorphous forms of Carbon

*Coke, charcoal* and *carbon-black* are the amorphous allotropes of carbon. These forms are briefly described as follows:

## 1. Coke

It is a greyish black solid. It is obtained by destructive distillation of coal (*heating out of contact of air*). It is mainly **used** as *fuel* and also as a reducing agent in metallurgical operations.

## 2. Charcoal

It is obtained in three forms by different processes. These are *wood charcoal, animal charcoal* and *sugar charcoal*.

*Wood charcoal* is obtained by heating wood in limited supply of air.

**Animal charcoal** is obtained by destructive distillation of bones. It is mainly used for decolourisation of sugar and other organic matter. It contains 10% of carbon approximately and rest being calcium phosphate.

*Sugar charcoal* is obtained by the action of concentrated sulphuric acid on sugar.

 $C_{12}H_{22}O_{11} + \text{conc. } H_2SO_4 \longrightarrow 12C(s) + 11H_2O$ 

Sugar charcoal

## 3. Carbon black or Lamp black

It is obtained when substances rich in carbon content, like kerosene oil, petroleum, terpentine oil, etc., are burnt in limited supply of air. The soot obtained is made to stick on wet blankets. After drying, the soot is removed from the blankets. The soot so formed is known as *lamp black* or *carbon black*. It is **used** in making black ink, shoepolishes, and also in manufacture of tyres.

# IMPORTANT COMPOUNDS OF CARBON AND SILICON

## **Oxides of Carbon**

Carbon forms two main oxides, *carbon monoxide* (CO) and *carbon dioxide* (CO<sub>2</sub>) by direct combination with oxygen.

## Carbon Monoxide (CO) or Carbon (II) Oxide

## Preparation

Some of the methods of preparation of CO are given below:

## 1. By heating carbon in limited supply of oxygen

Carbon monoxide is formed by incomplete combustion of carbon or carbon containing compounds (such as hydrocarbons) in the limited supply of oxygen.

$$C + \frac{1}{2} O_2 \longrightarrow CO$$

# 2. By heating formic acid with $H_2SO_4$

Carbon monoxide is considered as *anhydride* of formic acid and thus, can also be prepared by dehydration of formic acid with conc.  $\rm H_2SO_4$ 

HCOOH  $\xrightarrow{\text{H}_2\text{SO}_4}$  H<sub>2</sub>O + CO

## Properties of Carbon Monoxide

**1.** Physical nature. It is a *colourless, odourless* gas with very *small solubility in water.* It is *neutral* in nature.

**2. Toxic nature.** It is quite *poisonous* because it combines with the haemoglobin of the red blood cells to form a complex *carboxyhaemoglobin* which is about 300 times more stable than oxygen-haemoglobin complex. Thus, it destroys the capacity of the blood to carry oxygen from lungs to the various parts of the body and ultimately results in death of a person.

**3. Combustibility.** It is highly *combustible.* Its combustion in air produces carbon dioxide alongwith lot of heat.

 $2CO(g) + O_2(g) \longrightarrow 2CO_2(g) + heat$ 

**4. Reducing nature.** It is a very *good reducing agent* due to its ability to get oxidised to  $CO_2$ . It reduces almost all metal oxides other than those of the group-1 and group-2 metals, aluminium and a few transition metals, to metals.

 $\begin{array}{c} \operatorname{Fe}_2\operatorname{O}_3 + 3\operatorname{CO} & \xrightarrow{823\operatorname{K}} & 2\operatorname{Fe} + 3\operatorname{CO}_2 \\ \operatorname{ZnO} + \operatorname{CO} & \longrightarrow & \operatorname{Zn} + \operatorname{CO}_2 \end{array}$ 

**5.** Formation of metal carbonyls. It combines with many of the transition metals like Ni, Fe, Co, Mn, etc., to form metal carbonyls.

Ni + 4CO  $\xrightarrow{335K}$  Ni (CO)<sub>4</sub> Tetracarbonyl nickel (0) Fe + 5CO  $\longrightarrow$  Fe (CO)<sub>5</sub>

Pentacarbonyl iron (0)

**6.** Reaction with chlorine. It reacts with chlorine in the presence of sunlight to form another poisonous gas, phosgene.

 $CO(g) + Cl_2(g) \xrightarrow{\text{Sunlight}} COCl_2$ 

Phosgene or (Carbonyl chloride)

## Uses of Carbon Monoxide (CO)

1. CO is an important industrial fuel. It is one of the components of fuel gases which are commonly used as industrial fuels as *water gas* and *producer gas*.

Carbon monoxide in water gas or producer gas can undergo combustion forming carbon dioxide with the liberation of heat.

- 2. It is used as a reducing agent in many metallurgical processes.
- 3. It is used in purification of nickel by Mond's process.
- 4. It is used in the manufacture of methanol, formic acid, etc.

## Carbon Dioxide (CO<sub>2</sub>)

## Preparation

Some common methods of preparation of  $CO_2$  are :

## 1. Combustion of carbon and carbon containing fuels

Combustion of carbon and carbon containing fuels in the presence of excess of air gives carbon dioxide.

 $\mathrm{C} + \mathrm{O}_2 \longrightarrow \mathrm{CO}_2$ 

 $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ 

2. By decomposing carbonates and hydrogencarbonates

It can also be prepared in the laboratory by the reaction of carbonates or hydrogencarbonates with acids.

 $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$ 

 $NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$ 

## Properties of Carbon Dioxide

- 1. Carbon dioxide is a *colourless, odourless* gas.
- 2. It is *heavier* than air.
- 3. Unlike CO, it is *not poisonous* but it does not support life in animals and humans.
- 4.  $CO_2$  is *acidic* in nature and is fairly soluble in water.

The solubility of  $CO_2$  in water increases with increase in pressure. Soda water and other aerated drinks are prepared by dissolving  $CO_2$  in water under pressure.

*Carbonic acid*  $(H_2CO_3)$  is a weak *dibasic acid* and forms two series of salts, the *hydrogencarbonates*  $(HCO_3^{-})$  and *carbonates*  $(CO_3^{2-})$ . Only alkali metals form stable hydrogencarbonates.

5. Reaction with lime water.  $CO_2$  reacts with lime water to form insoluble  $CaCO_3$  which makes it milky. However, if  $CO_2$  is bubbles through lime water for a longer time milkiness disappears due to the formation of soluble calcium hydrogenearbonate

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$
  
Lime water Milkiness

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$
  
Excess

6. **Photosynthesis.** Carbon dioxide is absorbed by plants in the presence of *chlorophyll* and sunlight. The absorbed  $CO_2$  combines with  $H_2O$  to form glucose and starch (carbohydrates) which are used as food by the plants. This process is called *photosynthesis*.

$$6\text{CO}_2 + 12\text{H}_2\text{O} \xrightarrow[\text{Chlorophyll}]{\text{sunlight}} \xrightarrow{\text{Chlorophyll}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + 6\text{H}_2\text{O}_6$$

7. Reaction with alkalis. Since  $CO_2$  is acidic in nature, it reacts with alkalis to form carbonates.

2NaOH + CO<sub>2</sub>  $\longrightarrow$  Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O

8. Action of ammonia. When  $CO_2$  is reacted with liquid ammonia at 453—473 K under a pressure of 220 atmospheres, it first forms ammonium carbamate which subsequently decomposes to give urea.

 $\begin{array}{c} \text{CO}_2 + 2\text{NH}_3 & \xrightarrow{\text{Pressure}} & \text{NH}_2\text{COO}^-\text{NH}_4^+ \\ & \text{Ammonium carbamate} \\ & \xrightarrow{\text{Heat}} & \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}. \end{array}$ 

Urea

Uses of Carbon Dioxide (CO<sub>2</sub>)

- 1. Dry ice (solid  $CO_2$ ) is used as a refrigerant for ice-cream and frozen food.
- 2. Gaseous  $\mathrm{CO}_2$  is used extensively to prepare carbonated soft drinks.
- 3. One of the major use of  $\text{CO}_2$  is in the manufacture of urea by its reaction with ammonia.
- 4. Being heavy and non-supporter of combustion, it is also used as fire extinguisher.
- 5. For artificial respiration as mixture of 95%  $O_2$ , 5%  $CO_2$  under the name **Carbogen** especial for the victims of CO poisoning.
- 6. In the recent years,  $CO_2(l)$  in the form of super critical fluid (a substance above its critical pressure) has been used as solvent to extract organic compounds from their natural source (*e.g.*, caffine from coffee beans; perfumes from flowers).

# 6.2 COAL

Coal is a combustile black or brownish-black sedimentary rock with a high amount of carbon and hydrocarbons. Coal is classified as a non-renewable energy source because it takes millions of years to form. Coal contains the energy stored by plants that lived hundreds of millions of years ago in swampy forests.

Layers of dirt and rock coverred the plants over millions of years. The resulting pressure and heat turned the plants into the substance we call coal.

## Types of Coal

Coal is classified into four main types, or ranks: anthracite, bituminous, sub-bituminous, and lignite. The ranking depends on the types and amounts of carbon the coal contains and on the amount of heat energy the coal can produce. The rang of a coal deposit is determined by the amount of pressure and heat that acted on the plants over time.

Anthracite contains 86%-97% carbon and generally has the highest heating value of all ranks of coal. Anthracite accounted for less than 1% of the coal mined in the United States in 2020. All of the antracite mines in the United States are in northeastern Pennsylvania. In the United States, anthracite is mainly used by the metals industry.

**Bituminous** coal contains 45-86% carbon. Bituminous coal in the United States is between 100 million and 300 million years old. Bituminous coal is the most abundant rank coal found in the United States, and it accounted for about 44% of total U.S, coal production in 2020. Bituminous coal is use to generate electricity and is an important fuel and raw material for making coal or use in the iron and steel industry. Bituminous coal was produced in at least 18 states in 2020, but five states accounted for about 74% of total bituminous production.

**Subbituminous** coal typically contains 35-45% carbon, and it has a lower heating value than bituminous coal. Most subbituminous coal in the United States is at least 100 million years old. About 46% of total U.S. coal production in 2020 was subbituminous and about 88% was produced in Wyoming and 8% in Montana. The remainder was produced in Alaska, Colorado, and New Mexico.

**Lignite** contains 25-35% carbon and has the lowest energy content of all coal ranks. Lignite total deposits tend to be relatively young and were not subjected to extreme heat or pressure. Lignite is crumbly and has high moisture content, which contributes to its low heating value. Lignite accounted for 9% of toal U.S. coal production in 2020. About 54% was mined in North Dakota and about 39% was mined in Texas. The other 7% was produced in Louisiana, Mississippi and Montana. Lignite is mostly used to generate electricity. A facility in North Dakota also converts lignite to synthetic natural gas that is sent in natural gas pipelines to consumers in the eastern United States.

## **Destructive Distillation of Coal**

The process of heating coal in the absence of air is called the destructive distillation of coal. Coal contains a number of elements such as carbon, hydrogen, oxygen, nitrogen and sulphur. When coal is heated in the absence of air, a number of products are obtained.



Fig. 6.1 Fractional distillation

The main products obtained by the destructive distillation of coal are as follows:

- 1. Coke: Coke contains 98% carbon. It is porous, tough, black and the purest form of coal. Like charcoal, it is a good fuel and burn without smoke. It is largely employed as a reducing agent in the extraction of metals from their ores. It is also used in making fuel gases like water gas and producer gas.
- **2. Coal tar (liquid):** Coal tar is a mixture of different carbon compounds. It thick, black liquid with unpleasant smell. The fractional distillation of coal tar gives many chemical substances

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which are used in the preparation of dyes, explosives, paints, synthetics fibers, drugs and pesticides. Some of these chemical substances are benzene, toluene, phenol and aniline. Naphthalene balls used to repel moth and other insects are also obtained from coal tar.

**Note:** These days bitumen a petroleum product is used in place of coal tar for metalling the roads.

**3.** Coal gas. Coal gas is mainly a mixture of hydrogen, methane and carbon monoxide. The gases present in coal gas are combustible and hence, it is an excellent fuel. It has high calorific value. It was used for lighting houses, factories and streets in Mumbai until 1950. It was also used for cooling earlier.

### Uses of Coal

Coal is primarily used as fuel to generate electric power. In coal-fired power plants, bituminous coal, sub-bituminous coal, or lignite is burned. The heat produced by the combustion of the coal is used to convert water into high-pressure steam, which drives a turbine, which produces electricity. In 2019, about 23 percent of all electricity in the United States was generated by coal-fired power plants, according to the **U.S. Energy Information Administration**.

Certain types of bituminous coal can also be used in making steel. Coal used for steel making needs to be high in carbon content and low in moisture, ash, sulfur and phosphorous content. Coal that meets these specifications is known as metallurgical coal. Coal also has a myriad of other uses, including in cement production, carbon fibers and foams, medicines, tars, synthetic petroleum-based fuels, and home and commerical heating.

# 6.3 COKE

A mixture of carbon and hydrogen gas is made by heating a solution of limestone, chalk or dolomite, producing coke. Coke is used as a fuel, to make glass and bricks, and as a drying agent in the chemical industry. It can also be used to produce electricity and heat energy.

## **Features of Coke**

Coke can only be produced from coal. The process of turning coal into coke is called cooking and the temperatures are in excess of  $600^{\circ}$ C. Carbon from within the coal is released as gas and left to cool down.

Coke can appear as a friable, porous mass that contains a large amount of graphite (carbon) and ash content about 6,000 BTU per pound.

#### Difference between Coal and Coke

Coal is fossilized material found on the earth.

Coke is produced from coal through the coking process.

Coke can only be used as a fuel by making it into coke and injecting it into furnaces to give heat energy.

Coal can be used to produce heat energy in furnaces or to generate electricity through the burning of coal.

Coke has slightly more than half the carbon content of a standard bag of coal, but still contains some carbon and other minerals that make up the rock, such as sulphur and nitrogen.

Coke also has a higher amount of ash content than coal.

Coke is rich in carbon, with a calorific value of about 6,000 BTU per pound.

It gives off energy at temperatures exceeding  $3,800^{\circ}$ C when burning. Coal contains around 30-60% carbon but produces carbon dioxide and soot when it burns

Coal's calorific value is around 3,800-5,500 BTU per pound

Coke in dense, blakc and has high carbon content, lending to its high calorific value – about 6,000 BTU per pound

Coal is a good fuel as it produces a lot of heat when burned.

Coke contains a higher ash content than coal, which makes it less valuable as a consumer product. However, it is still a high-temperature fuel

Coke can be used in blast furnaces for smelting and purifying iron ore

Coke is more expensive than coal because it takes more of the raw material to produce the same amount of coke

Coke has been used as an ingredient in cigarettes to add flavour and nicotine to the tobacco blend

It has also been used in armour plating and military weapons like grenades

Coke is produced by heating a solution of limestone or other carbonate-bearing materials temperatures above 600 degree celsius  $(1,112^{\circ}F)$ 

### Synthesis Gas and Its Production

Syngas is a valuable flammable gas which is mainly a mixture of hydrogen and carbon monoxide.

Syngas is the short name for a gasification product, mostly from waste biomasses, known as "synthesis gas", consisting of a mixture of  $H_2$ , CO and  $CO_2$  that could be used as a potential intermediate in the conversion of biomass into fuel. The primary use of syngas is in the production of other fuels, namely methanol and diesel fuel. In some industrial setting (steel milling, petroleum refining, etc.) large amounts of waste gas with these characteristics are produced.

The production of diesel fuel from syngas relies on the Fischer-Tropsch process, a series of chemical reactions converting CO and  $H_2$ into **liquid hydrocarbon**. Methane from landfills could serve as feedstock for producing diesel fuel, technically considered **biodiesel** because it is not derived from fossil fuels. A novel use of syngas is to directly power **hydrogen fuel** cells; hydrogen is simply captured from the gas, and refined for use in fuel cells. Of course, this tends to defeat the "zero-emissions" aim of fuel cells and so is not widely used beyond research.

Syngas has been used as domestic and industrial fuel, but its low energy per unit volume makes it unattractive if it has to be pumped to a distanct consumer. For such applicatin, the gas can be **enriched** by transforming it into methane. This is the basis of many **coal glassification** processes. Observe that the preceding **syngas** is dangerously poisnous owing to the carbon monoxide it contains.

An important use of syngas is as a **feedstock** for the production of an amazing number of chemicals. Many of these have H : C ratio substantially larger than that of syngas. For this reason, and for its use in low temperature fuel cells, a hydrogen enriching step may be needed. This is known as a **shift** reaction.

## **Syngas Production**

**Syngas** could be produced from solid carboaceous fuel as well as from natural gas (> 80% CH<sub>4</sub>) using a steam-metahne-reforming reaction. The reforming reaction is, however, not strictly gasification but a molecular rearrangement:

 $CH_4 + H_2O(catalyst) \rightarrow CO + 3H_2 + 206,000 \text{ kJ/kmol}$ 

**Partial oxidation** of natural gas or methane is an alternative route for production of **syngas**. In contrast to the reforming reaction, **partial oxidation** is exothermic.

Partial oxidation of fuel oil also produces syngas:

 $CH_4 + 1/2O_2 \rightarrow CO + 2H_2 - 36,000 \text{ kJ/k mol}$ 

#### **Gasification of Biomass**

Synthesis gas (syngas in brief) is a gas mixture of predominantly **CO** and  $H_2$ . Gasification of biomass **feedstocks** produces **syngas** through **partial oxidation**. **Syngas** quality largely depends on the compositions of biomass **feedstock**, gasifier types, and the gasifying agents. Other than the major constituents – CO and  $H_2$ , gasification of biomass also produces methane (CH<sub>4</sub>), nitorgen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), water vapor, trace amounts of sulfur containing compounds, tar, higher hydrocarbons such as ethane (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>) and paritculate matter.

Gasifiers are mainly divided into two categories, namely, fixed-bed and fludizied-bed **gasifiers**. The fixed-bed gasifiers are characterized by the stationary reaction zone. Typically, in these gasifiers, biomass is fed from the top. Depending on the direction of biomass feeding and the oxidant employed, fixed-bed gasifiers are further divided into updraft and downdraft gasifiers. Fluidized-bed gasifiers use sand, ash, or char as moving media to increase the heat transfer and the gasification efficiency. Generally, the gasification of biomass takes place at high temperatures (fludized bed: 750-900°C).

## 6.4 DINITROGEN, N<sub>2</sub>

#### Preparation of Dinitrogen

#### Laboratory Preparation

In the **laboratory**, dinitrogen is prepared by heating aqueous solution of ammonium chloride with sodium nitrite.

 $NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{Heat} N_2(g) + 2H_2O(l) + NaCl(aq)$ 

Small amounts of NO and  $\text{HNO}_3$  are also formed in this reaction ; these impurities can be removed by passing the gas through aqueous sulphuric acid containing some potassium dichromate.

#### Industrial Preparation

**Commercial preparation** of dinitrogen is carried out by liquefaction of air and its subsequent fractional distillation. Dinitrogen (b.p. 77.2 K) distills over first leaving behind liquid dioxygen (b.p. 90 K). Dinitrogen derived from air does contain some traces of noble gases and dioxygen.

## Physical Properties of dinitrogen

- 1. It is a *colourless*, *tasteless* and *odourless gas*.
- 2. It is non-toxic.
- 3. It has very low solubility in water (23.2  $\text{cm}^3$  per litre of water at 273 K and 1 bar pressure)
- 4. Its freezing point and boiling point are 63 K and 77.2 K respectively.

## **Test for Nitrogen**

Burning magnesium with nitrogen to form magnesium nitride

$$3Mg(s) + N_2 \implies Mg_3N_2$$

Magnesium nitride react with water to liberate ammonia

$$Mg_3N_2(g) + 6H_2O \longrightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

The evolved gas pass over the red litmus paper, then turn blue, due to presence of ammonia gas.



Fig. 6.2 Testing the gas evolved from magnesium nitride and water

# USES OF DINITROGEN

- 1. The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen such as: calcium cyanamide.
- 2. It also finds use where the presence of an inert atmosphere is required. For example, in iron and steel industry.
- 3. Liquid nitrogen is used as refrigerant to preserve biological materials, in freezing food articles and in cryosurgery.

# **Example 6.1.** Why is $N_2$ less reactive at room temperature?

**Solution.** Nitrogen molecule has a triple bond between the two nitrogen atoms and hence the bond dissociation energy of  $N_2$  (941.4 kJ mol<sup>-1</sup>) is very high. Therefore, nitrogen is less reactive at room temperature.

### Ammonia (NH<sub>3</sub>)

Ammonia is hydride of nitrogen. It is present in small quantities in air and soil where it is formed by the decay of nitrogeneous organic matter such as urea

 $\underset{\text{Urear}}{\text{NH}_2\text{CONH}_2} \longrightarrow 2\text{H}_2\text{O} \longrightarrow (\text{NH}_4)_2\text{CO}_3 \rightleftharpoons 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$   $\underset{\text{Carboate}}{\text{Ammonium}}$ 

#### Preparation of Ammonia

Some common methods of preparation of ammonia are:

**1. By heating ammonium salts with strong** bases such as sodium hydroxide, potassium hydroxide or calcium hydroxide either in the solid state or dissolved in water.

 $(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2NH_3$ 

 $\begin{array}{c} \mathrm{NH_4Cl} + \mathrm{KOH} & \stackrel{\Delta}{\longrightarrow} \mathrm{KCl} + \mathrm{H_2O} + \mathrm{NH_3} \\ \mathrm{2NH_4Cl} + \mathrm{Ca(OH)_2} & \longrightarrow \mathrm{2NH_3} + \mathrm{CaCl_2} + \mathrm{2H_2O} \end{array}$ 

2. By the action of water on metal nitrides

 $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$ Mag. nitride

 $\underset{\text{nitride}}{\text{AIN}} + 3\text{H}_2\text{O} \longrightarrow \text{Al(OH)}_3 + \text{NH}_3$ 

**3. Laboratory method of preparation.** Ammonia is prepared in the laboratory by heating a mixture of slaked lime and ammonium chloride.

 $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$ 

A mixture of ammonium chloride and slaked lime (1:3) is heated in a round bottomed flask. Ammonia thus produced is collected by downward displacement of air since it is lighter than air.

#### Manufacture of Ammonia

Ammonia is generally manufactured by **Haber's process** which involves the direct combination of nitrogen and hydrogen.

 $N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g); \Delta_I H^{\ominus} = -46.1 \text{ kJ/mol.}$ 

We find that the forward reaction is exothermic and proceeds with decrease in the number of gaseous moles. Therefore, according to the

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Le-Chatelier's principle, the *conditions favourable for the forward process* are:

low temperature, high pressure and presence of catalyst.

At low temperature, the rate of the reaction becomes very slow. Therefore, in practice, the optimum *temperature of about 750 K* is used. High *pressure of about 200*  $10^5 Pa - 900$   $10^5 Pa$  (about 200–900 atm) is employed to favour the forward reaction. Since the operating temperature is fairly low (750 K), the rate of reaction is increased by using a **catalyst** which consists of *finely divided iron* containing *molybdenum as promoter* or *iron oxide with small amounts of K*<sub>2</sub>O and  $AI_2O_3$ . The flow chart for the manufacture of ammonia by Haber's process is shown in Fig. 6.3.



Fig. 6.3 Haber's process for the manufacture of ammonia.

## Physical Properties of Ammonia

- 1. Ammonia is a *colourless gas* with a characteristic pungent smell called *ammoniacal smell*. It causes tears in eyes.
- 2. It is lighter than air.
- 3. It is extremely soluble in water. One volume of water can dissolve about 1000 volumes of the gas at 273 K.
- 4. Its freezing point is 198.4 K and boiling point is 239.7 K.
- 5. It liquefies on cooling under pressure to liquid ammonia. On evaporation, it produces intense cooling.

## Chemical Properties of Ammonia

## 1. Basic nature

Aqueous solution of ammonia is basic in nature and turns red litmus blue. Its basic character is due to the formation of  $OH^-$  ions in aqueous solution.

$$NH_3 + H_2O \implies NH_4^+ + OH^-.$$

#### 2. Formation of ammonium salts

It reacts with both weak and strong acids to form salts.

 $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ 

 $2NH_3(g) + H_2SO_4(l) \longrightarrow (NH_4)_2SO_4(s)$ 

3. Precipitation of heavy metal ions from the aqueous solutions of their salts

Metal ions like  $Fe^{3+}$ ,  $Al^{3+}$ ,  $Cr^{3+}$ , etc., are precipitated as hydroxides from their aqueous salt solutions on reaction with aqueous ammonia.

 $\operatorname{FeCl}_{3}(aq) + \operatorname{3NH}_{4}\operatorname{OH}(aq) \longrightarrow \operatorname{Fe}_{2}\operatorname{O}_{3}.x\operatorname{H}_{2}\operatorname{O}(s) + \operatorname{3NH}_{4}\operatorname{Cl}(aq)$  (Brown ppt.)

 $AlCl_3(aq) + 3NH_4OH(aq) \longrightarrow Al(OH)_3 + 3NH_4Cl(aq)$ (White *ppt.*)

### 4. Complex formation

Ammonia acts as a *Lewis base* due to the presence of a lone pair of electrons on nitrogen and hence, forms a number of complexes with metal ions. This complex forming property finds application in qualitative analysis of metal ions such as  $Cu^{+2}$ ,  $Ag^+$ :

 $\begin{array}{c} \text{AgCl} + 2\text{NH}_{3} \rightleftharpoons [\text{Ag}(\text{NH}_{3})_{2}\text{Cl}] \\ \text{(white ppt.)} \\ \text{(colourless soluble complex)} \end{array}$ 

 $\underbrace{\operatorname{Cu}^{2+}_{(blue)} + 4\operatorname{NH}_3}_{(blue)} \rightleftharpoons \underbrace{\operatorname{[Cu}(\operatorname{NH}_3)_4]^{2+}}_{(deep \ blue)}$ 

#### 5. Ammonia as solvent

Just like water, ammonia also undergoes *self-ionisation* in liquid state and is used as solvent

 $2\mathrm{NH}_{3} \Longrightarrow \mathrm{NH}_{4}^{+} + \mathrm{NH}_{2}^{-}$  $2\mathrm{H}_{2}\mathrm{O} \Longrightarrow \mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{OH}^{-}$ 

for dissolving many polar compounds and also for carrying out many reactions in non-aqueous medium.

### Uses of Ammonia

1. Ammonia is used mostly to produce various nitrogeneous fertilizers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate);

- 2. In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid, and sodium carbonate
- 3. Liquid ammonia is used as a refrigerant.
- 4. It is used as a reagent in the laboratory.

# TESTS OF AMMONIA

- 1. It turns moist turmeric paper brown.
- 2. It gives brown precipitate with Nessler's reagent.
- 3. It gives dense white fumes with a drop of HCl.
- 4. It gives a deep blue solution with solution of copper (II) sulphate due to the formation of  $[Cu(NH_3)_4]SO_4$ .
- 5. It gives yellow precipitate with chloropla-tinic acid.

 $\begin{array}{ccc} \mathrm{H}_{2}\mathrm{PtCl}_{6} + 2\mathrm{NH}_{3} & \longrightarrow & (\mathrm{NH}_{4})_{2}\mathrm{PtCl}_{6} \\ \mathrm{Amm. chloroplatinate} \\ & (Yellow \ ppt.) \end{array}$ 

# Nitric Acid (HNO<sub>3</sub>)

It is one of the most important oxoacids of nitrogen.

# Laboratory Preparation

In the laboratory, nitric acid can be prepared by heating  $NaNO_3$  or  $KNO_3$  with concentrated sulphuric acid to about 425–475 K in a glass retort. The vapours of  $HNO_3$  formed are condensed.

 $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ 

Acid, thus, produced contains some water as impurity. Anhydrous nitric acid can be obtained by distillation of concentrated aqueous nitric acid with  $P_4O_{10}$ .

# Manufacture

In this method,  $HNO_3$  is manufactured by oxidation of ammonia. The outlines of the plant are illustrated in Fig. 6.4. The main steps in this process are:

(*i*) *Catalytic oxidation of ammonia by atmospheric oxygen*. Using platinum or rhodium gauze heated electrically to about 500 K and 9 bar pressure.

$$4\mathrm{NH}_{3} + \underbrace{5\mathrm{O}_{2}}_{(air)} \xrightarrow{\mathrm{Pt/Rh \ gauge \ catalyst}}_{500 \ \mathrm{K}, \ 9 \ \mathrm{bar}} \rightarrow 4\mathrm{NO} + 6\mathrm{H}_{2}\mathrm{O}$$
$$\Delta_{*}\mathrm{H} = -90.2 \ \mathrm{kJ}$$

(*ii*) *Oxidation of nitric oxide*. The nitric oxide obtained above is cooled and passed through a spacious chamber called *oxidising chamber*. The nitric oxide is oxidised to nitrogen dioxide.

$$2NO(g) + O_2(g) \implies 2NO_2(g)$$

(*iii*) Absorption tower. Nitrogen dioxide is dissolved in water in the absorption tower which is packed with acid proof stones. It gives about 60% nitric acid.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$
$$4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(aq)$$

NO formed is recycled. The aqueous  $HNO_3$  can be concentrated by distillation upto about 68% by mass. Further concentration of nitric acid can be done to 98% acid by dehydration with concentrated sulphuric acid.



Fig.6.4 Ostwald process for manufacture of acid.

## **Physical Properties of Nitric Acid**

- 1. When pure, it is a colourless liquid. The impure acid is generally yellow due to the presence of nitrogen dioxide as impurity. Conc. nitric acid containing dissolved nitrogen dioxide is known as *fuming nitric acid*.
- 2. It has corrosive action on skin and produces painful blisters.
- 3. It forms a constant boiling mixture with water which contains 68% of the acid. Consequently, dilute nitric acid cannot be concentrated beyond 68% by distillation.
- 4. Pure acid has a specific gravity of 1.504. It boils at 355.6 K and freezes to a white solid (m.p. 231.4 K).

## **Chemical Properties of Nitric Acid**

## 1. Acidic nature

Nitric acid is one of the strongest acids. In aqueous solutions it gets almost completely ionised to form  $H_3O^+$  ions and  $NO_3^-$  ions.

 $HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$ 

Therefore, nitric acid gives the usual reactions of acids as given below:

- It turns blue litmus red.
- It reacts with bases to form salts and water. For example:  $NaOH(aq) + HNO_3(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$

 $Ca(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2H_2O(I)$ 

- It decomposes carbonates to give carbon dioxide.
- $Na_2CO_3(s) + 2HNO_3(aq) \longrightarrow 2NaNO_3(aq) + CO_2(g) + H_2O(I)$
- 2. Action of heat

On heating strongly, nitric acid decomposes to liberate nitrogen dioxide and oxygen.

 $4\text{HNO}_3(l) \longrightarrow 4\text{NO}_2(g) + \text{O}_2(g) + 2\text{H}_2\text{O}(l)$ 

## 3. Reaction with metals

When nitric acid reacts with metals, different products are formed depending upon *the concentration of the acid* and *activity of the metal*.

(a) Reaction with dilute nitric acid. Magnesium and manganese are the only metals which liberate hydrogen from very dilute nitric acid ( $\approx 2\%$ ).

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

*More active metals* such as *zinc*, *react with cold dilute nitric acid to form ammonium nitrate.* 

 $4\text{Zn}(s) + 10\text{HNO}_3(aq) \longrightarrow 4\text{Zn}(\text{NO}_3)_2(aq) + \text{NH}_4\text{NO}_3(aq) + 3\text{H}_2\text{O}(l)$ 

However, with *hot dilute nitric acid* the ammonium nitrate, so formed gets decomposed resulting in the production of  $N_2O$  as:

 $4\text{Zn}(s) + 10\text{HNO}_3(aq) \longrightarrow 4\text{Zn}(\text{NO}_3)_2(aq) + \text{N}_2\text{O}(g) + 5\text{H}_2\text{O}(l)$ 

*Less active metals like copper, react with dilute nitric acid to liberate nitric oxide NO as*:

 $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$ 

(b) Reaction with concentrated nitric acid. Metals such as copper and zinc, form nitrogen dioxide on reaction with conc.  $HNO_3$ 

 $\operatorname{Cu}(s) + 4\operatorname{HNO}_3(aq) \longrightarrow \operatorname{Cu}(\operatorname{NO}_3)_2(aq) + 2\operatorname{NO}_2(g) + 2\operatorname{H}_2\operatorname{O}(l)$ 

 $Zn(s) + 4HNO_3(aq) \longrightarrow Zn(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$ 

*Metals,* such as *iron, aluminium, chromium,* and *nickel* are rendered passive by concentrated nitric acid.

*Noble metals* like *gold* and *platinum* do not react with nitric acid. However they dissolve in *aqua regia (mixture of one part of conc. HNO<sub>3</sub> and 3 parts of conc. HCl)* forming respective chlorides.

 $\begin{array}{ccc} \operatorname{HNO}_{3} + \operatorname{3HCl} & \longrightarrow & \operatorname{NOCl}_{\operatorname{Nitrosyl}} + 2\operatorname{H}_{2}\operatorname{O} + 2\operatorname{Cl}_{\operatorname{Nitrosyl}}\\ & & \operatorname{Aqua\ regia} & & \operatorname{Aut\ + 3Cl} \longrightarrow \operatorname{AuCl}_{3}\\ & & \operatorname{Pt\ + 4Cl} \longrightarrow \operatorname{PtCl}_{4} \end{array}$ 

#### 4. Oxidising nature

It is a very strong oxidising agent and oxidises many non-metals and compounds.

#### Brown Ring Test for Nitrates

The brown-ring test for nitrates depends on the ability of  $Fe^{2+}$  to reduce nitrates to nitric oxide which reacts with  $Fe^{2+}$  ions to form a brown coloured complex. The test is usually carried out by adding freshly prepared dilute ferrous sulphate to an aqueous solution suspected of containing nitrate ion, followed by careful addition of concentrated sulphuric acid along the sides of the test-tube so that a seperate layer is formed. A brown ring at the interface between the solution and sulphuric acid indicates the presence of nitrate ions in solution.

#### **Uses of Nitric Acid**

1. The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.

- 2. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.
- 3. Other major uses are in the pickling of stainless steel and etching of metals.
- 4. As an oxidizer in rocket fuels.

# 6.5 DIOXYGEN, O<sub>2</sub>

Oxygen is the most abundant element on the surface of the earth. In free state, it occurs in air and constitutes 21% by volume of air and 23.2% by weight. In the combined state, it constitutes 89% by mass of water and 50% by mass of earth's solid crust. In earth's solid crust, it is mainly present as silicates, carbonates, aluminates and oxides of metals.

## Preparation of Dioxygen

The general methods of preparation are:

1. From oxygen rich salts. Certain oxygen rich salts such as chlorates, permanganates, peroxides and *nitrates* on heating decompose to give dioxygen gas.

Heat  $\rightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$  $2\text{KClO}_3(s)$  – MnO<sub>2</sub> Potassium chlorate Heat  $\rightarrow$  K<sub>2</sub>MnO<sub>4</sub>(s) + MnO<sub>2</sub>(s) + O<sub>2</sub>(g) 2KMnO<sub>4</sub>(s) Potassium Potassium permanganate manganate Heat  $\rightarrow 2$ KNO<sub>2</sub> + O<sub>2</sub>

```
2KNO_3
Pol. nitrate
```

2. Laboratory preparation of Dioxygen. Dioxygen is prepared in the laboratory by any of the following two methods:

By Heating potassium chlorate. Mixture of KClO<sub>3</sub> and MnO<sub>2</sub> in the mass ratio of 4 : 1 is heated in hard glass tube in the apparatus as shown in Fig. 6.5.



Fig. 6.5 Preparation of O<sub>2</sub> from KClO<sub>3</sub>.

 $2\text{KClO}_3 \xrightarrow{\text{MnO}_2} 2\text{KCl} + 3\text{O}_2$ 

The dioxygen gas so liberated is collected by downward displacement of water.

Function of MnO<sub>2</sub>

(*i*) It lowers the m.p. of KClO<sub>3</sub> from 630 K to 500 K.
(*ii*) It acts as a catalyst.

### Manufacture of Dioxygen

The large scale preparation of dioxygen is carried out from the following two sources:

- (*i*) From air. The most economical method for commercial preparation of dioxygen involves *liquefaction of air followed by fractional distillation of the liquid air thus obtained*. During this process, dinitrogen ( $N_2$ ) with lower boiling point (77 K) distils over in the gaseous form leaving behind dioxygen with higher boiling point (90 K) in the liquid state which can be separated.
- (*ii*) **From water.** Dioxygen can also be prepared by the electrolysis of water containing a small amount of a mineral acid or an alkali.

 $2H_2O(I) \xrightarrow{\text{Electrolysis}} 2H_2(g) + O_2(g)$ 

Dioxygen is collected at the anode while dihydrogen is liberated at the cathode.

The world's total production of dioxygen is over 100 million tonnes per year.

# Pure dioxygen can be prepared by electrolysis of a solution of $Ba(OH)_2$ using Ni or Pt electrode.

### **Properties of Dioxygen**

- (i) Dioxygen is colourless, tasteless and odourless gas.
- (*ii*) It is *slightly soluble in water.* Its solubility being approximately 30.8 cm<sup>3</sup> per litre of water at 293 K. Its slight solubility in water is responsible for sustaining the life of aquatic animals and also for the degradation of organic wastes in water bodies.
- (iii) It liquefies at 90 K and freezes at 55 K.
- (*iv*) It is appreciably soluble in alkaline pyrogallol solution.
- (*v*) Liquid oxygen is unique in being, paramagnetism, inspite of having even number of electrons.

### **Chemical Reations**

Dioxygen has small chemical reactivity at room temperature because of the high value of bond dissociation enthalpy (493.4 kJ mo $\Gamma^1$ ) of (O = O) bond. However, at higher temperatures cleavage of O = O bond causes dissociation of dioxygen molecule. Therefore, most of the chemical reaction of dioxygen occur at elevated temperatures. Some important chemical reactions are given below :

1. Action with litmus. It is neutral to litmus.

2. **Reaction with metals.** Dioxygen directly reacts with nearly all metals and non-metals except some metals like Au, Pt and some noble gases. Active metals like Na, Ca, etc. react at room temperature forming the respective oxides

 $4Na(s) + O_2(g) \longrightarrow 2Na_2O_2(s)$ Sodium peroxide

 $2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$ 

Metals like Mg burn in dioxygen to form magnesium oxide.

 $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$ 

Metals like iron and aluminium combine with dioxygen on heating to form their respective oxides.

 $4\mathrm{Fe}(s) + 3\mathrm{O}_2(g) \longrightarrow 2\mathrm{Fe}_2\mathrm{O}_3(s).$ 

 $4\mathrm{Al}(s) + 3\mathrm{O}_2(g) \xrightarrow{\mathrm{Heat}} 2\mathrm{Al}_2\mathrm{O}_3$ 

Less active metals like gold and platinum do not react with dioxygen.

**3. Reaction with non-metals.** The chemical reactions of some non-metals with dioxygen have been summarised as follows :

**4. Reaction with compounds.** Dioxygen oxidises various compounds. Some of the important reactions are given below:

Hydrogen chloride ;

 $\begin{array}{l} 4\mathrm{HCl}(g) + \mathrm{O}_{2}(g) \xrightarrow{700 \mathrm{K}}_{\mathrm{CuCl}_{2}} \rightarrow 2\mathrm{H}_{2}\mathrm{O}(l) + 2\mathrm{Cl}_{2}(g) \\ \textbf{Sulphur dioxide ;} \\ 2\mathrm{SO}_{2}(g) + \mathrm{O}_{2}(g) \xrightarrow{\mathrm{Pt}}_{725 \mathrm{K}} \rightarrow 2\mathrm{SO}_{3}(g) \\ \xrightarrow{\mathrm{Sulphur}}_{\mathrm{trioxide}} \\ \textbf{Zinc sulphide ;} \\ 2\mathrm{ZnS} + 3\mathrm{O}_{2} \longrightarrow 2\mathrm{ZnO} + 2\mathrm{SO}_{2} \\ \textbf{Ammonia ;} \\ 4\mathrm{NH}_{3}(g) + 5\mathrm{O}_{2}(g) \xrightarrow{\mathrm{Pt}}_{1075 \mathrm{K}} \rightarrow 4\mathrm{NO}(g) + 6\mathrm{H}_{2}\mathrm{O}(l) \\ \xrightarrow{\mathrm{Nitric}} \end{array}$ 

#### **Uses of Dioxygen**

Some of the important uses of dioxygen are :

(*i*) In the oxy-hydrogen or oxy-acetylene torches, which are used for cutting and welding of metals.

oxide

- (*ii*) In the metallurgical processes for the removal of metallic impurities by oxidation. For example, oxygen is used for the manufacture of steel.
- (iii) In the manufacture of phenol, ethylene oxide, etc.
- (*iv*) A mixture of carbon dust and liquid oxygen is used as explosive for coal mining.
- (v) Liquid oxygen is used as a fuel for rockets and missiles.
- (*vi*) For artificial respiration in case of pneumonia or gas poisoning. Mountaineers and pilots need oxygen at very high altitudes.

#### **Simple Oxides**

The binary compound of oxygen with various elements are called *oxides*. There are many elements which form more than one compounds with oxygen. However, they differ widely with regards to their properties and nature of bonding. Oxides can be classified into different categories depending upon their acid base characteristics.

**1. Acidic oxides.** These are generally formed by combination of *non-metals* and *oxygen.* Some examples are:  $P_4O_{10}$ ,  $SO_3$ ,  $CO_2$ ,  $N_2O_5$ ,  $Cl_2O_7$ ,  $B_2O_3$ , etc. These oxides are generally, *covalent compounds, which are volatile in nature and dissolve in water to give acidic solutions.* For examples:

$$\begin{split} & \operatorname{P_4O_{10}(s)} + \operatorname{6H_2O(l)} \longrightarrow \begin{array}{l} & \operatorname{4H_3PO_4(aq)} \\ & \operatorname{Phosphoric\ acid} \\ & \operatorname{SO_3(g)} + \operatorname{H_2O(l)} \longrightarrow \operatorname{H_2SO_4(aq)} \\ & \operatorname{N_2O_5(g)} + \operatorname{H_2O(l)} \longrightarrow \operatorname{2HNO_3(aq)} \\ & \operatorname{Cl_2O_7(g)} + \operatorname{H_2O(l)} \longrightarrow \operatorname{2HClO_4(aq)} \\ & \operatorname{Perchloric\ acid} \end{split}$$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character *e.g.*  $Mn_2O_7$ ,  $CrO_3$ ,  $V_2O_5$ .

2. Basic oxides. These are generally formed by the combination of oxygen with highly electropositive metals. Some examples are: MgO, K<sub>2</sub>O, CaO, BaO, Na<sub>2</sub>O. They are *generally ionic compounds with high melting and boiling points. They dissolve in water to give basic solutions.* 

 $BaO(s) + H_2O(l) \longrightarrow Ba(OH)_2(aq)$  $Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$ 

**3.** Amphoteric oxides. These are generally formed by the elements which are on the borderline between the metals and nonmetals. Some common examples are:  $Al_2O_3$ ,  $SiO_2$ , ZnO, PbO, etc. They are the oxides of intermediate characteristics. *They react with acids as well as alkalies to form salts.* 

 $Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \longrightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$  $Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[Al(OH)_6](aq)$ 

**4. Neutral oxides.** These oxides are neutral to litmus and they do not react with acids or bases. Some examples are  $N_2O$ , CO, NO etc.

# 6.6 SULPHUR

**In free state,** sulphur occurs in the volcanic regions of Sicily, Italy, South America, Japan and Russia. The largest deposits of sulphur have been found in Louisiana and Taxas (USA). In India, it has been found at Jawalamukhi in Kangra district.

In combined state, sulphur occurs mainly as the *sulphides* and *sulphates.* 

#### Allotropic forms of Sulphur

Like many other non-metals, sulphur also exhibit the phenomenon of allotropy. Various allotropic forms of sulphur are: *rhombic sulphur, monoclinic sulphur* and *plastic sulphur*. Some of their characteristics are given below:

- (a) Rhombic Sulphur (α-sulphur)
  - (*i*) It is a most stable and common form of sulphur.
  - (*ii*) It is also called  $\alpha$ -Sulphur.
  - (iii) It has bright yellow colour having m.p. of 385.8 K.
  - (*iv*) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in  $CS_2$ .
  - (v) Its density is  $2.06 \text{ g cm}^{-3}$
  - (*vi*) It exists as  $S_8$  molecule.
- (b) Monoclinic Sulphur (β-sulphur)
  - (*i*) It is stable only above 369 K and transforms into  $\alpha$ -sulphur below it. At 369 K both forms are stable ( $\alpha$  and  $\beta$ ). This temperature is called **transition temperature**.
  - (ii) It is dull yellow in colour with specific gravity of 1.98.
  - (*iii*) It is also called  $\beta$ -sulphur.
  - (*iv*) It is soluble in carbon disulphide but insoluble in water.
  - (v) It has a long needle shaped crystals.
  - (vi) It slowly changes into rhombic sulphur.
  - (vii) It also exist as  $S_8$  molecules which have puckered ring structure. It however, differs from the rhombic sulphur in the symmetry of the crystals.

(*c*) **Plastic Sulphur** ( $\gamma$ -*sulphur*). It is obtained by pouring molten sulphur in cold water.

- (*i*) It is amorphous form of sulphur.
- (*ii*) It is also called  $\gamma$ -sulphur and does not have sharp melting point.
- (iii) On standing, it also slowly gets converted to rhombic sulphur.
- (*iv*) Its density is  $1.95 \text{ g cm}^{-3}$ .
- (*v*) It is insoluble in water as well as carbon disulphide.

The chain polymers of sulphur called **catena**- $S_n$  (n = 2 - 5) are also known.

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# COMPOUNDS OF SULPHUR

#### Sulphur dioxide (SO<sub>2</sub>)

#### Preparation

The following reactions can be used for the preparation of sulphur dioxide.

(a) By burning sulphur in air or oxygen

 $S(s) + O_2(g) \longrightarrow SO_2(g)$ 

(b) By heating sulphur with concentrated sulphuric acid

 $S(s) + 2H_2SO_4(aq) \xrightarrow{Heat} 2H_2O + 3SO_2$ 

### **Physical Properties**

- (a) It is a colourless gas with a pungent, suffocating odour.
- (b) It is heavier than air.
- (c) It is highly soluble in water.
- (*d*) It can be easily liquefied to a colourless liquid at 10 C and into a snowlike solid at 76 C.

### **Chemical Properties**

**1. Combustibility.** It neither burns nor it helps in burning. However, burning magnesium, potassium and carbon continue to burn in its atmosphere.

$$\begin{array}{rcl} & \operatorname{BMg} + \operatorname{SO}_2 & \longrightarrow & 2\operatorname{MgO} + \operatorname{MgS} \\ & & \operatorname{4K} + 3\operatorname{SO}_2 & \longrightarrow & \operatorname{K}_2\operatorname{SO}_3 + \operatorname{K}_2\operatorname{S}_2\operatorname{O}_3 \\ & & \operatorname{C} + \operatorname{SO}_2 & \longrightarrow & \operatorname{CO}_2 + \operatorname{S} \end{array}$$

**2. Thermal decomposition:** It decomposes at 1200°C producing sulphur trioxide and sulphur.

 $3SO_2 \longrightarrow 2SO_3 + S$ 

**3. Acidic nature:** It is an *acidic oxide*. It dissolves in water forming sulphurous acid.

 $SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulphurous acid)

**4.** Bleaching action:  $SO_2$  in presence of moisture, acts as a bleaching agent. This is due to the reducing nature of  $SO_2$ .

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

Coloured matter + H  $\longrightarrow$  Colourless matter.

The bleaching is temporary. The bleached matter when exposed to air regains its colour due to oxidation.

#### Uses

- (*i*) It is used in the manufacture of sulphuric acid and paper from wood pulp (use of bisulphites).
- (*ii*) It is used as a bleaching agent for delicate articles like wool, silk and straw.
- (*iii*) It is used in refining of petroleum and sugar.
- (*iv*) As a disinfectant for killing disease germs, fungi and certain moulds.
- (v) As a refrigerant in the form of liquid  $SO_2$ .
- (*vi*) It is used as an antichlor for removing chlorine from a fabric after bleaching.
- (*vii*) Liquid  $SO_2$  is used as a solvent to dissolve a number of organic and inorganic chemicals.

## Sulphuric Acid (H<sub>2</sub>SO<sub>4</sub>)

It is the most important oxyacid of sulphur and is known from ancient times. It is called '*oil of vitriol*' because in early days it has been prepared from ferrous sulphate crystals (green vitriol) and has an oily appearance. It occurs in certain minerals and springs. Because of its large applications in industries it is also known as the "*king of chemicals*".

Manufacture of sulphuric acid. Sulphuric acid is manufactured by contact process. The process involves the following steps:

**1**. *Production of sulphur dioxide.* It is carried out by burning powdered sulphur or roasting of sulphur rich ores.

 $S_8 + 8O_2 \longrightarrow 8SO_2$  $4FeS_2 + 11O_2 \longrightarrow 2FeO_3 + 8SO_2.$ 

2. Oxidation of sulphur dioxide

 $2\mathrm{SO}_2(g) + \mathrm{O}_2(g) \xrightarrow{\mathrm{V}_2\mathrm{O}_5} 2\mathrm{SO}_3; \Delta_{I}\mathrm{H}^{\ominus} = -196.6 \text{ kJ}.$ 

This step is the key step on the manufacture of  $H_2SO_4$ .

The reaction in exothermic, reversible and the forward reaction leads to decrease in volume. Therefore, low temperature and high pressure are favourable conditions for maximum yield.

3. Conversion of  $SO_3$  into  $H_2SO_4$ .  $SO_3$  is absorbed in conc.  $H_2SO_4$  to get oleum

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

Oleum may then be diluted with calculated quantity of water to get  $H_2SO_4$  of required concentration.

 $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ 

The flow sheet of the **plant used** has been shown in Fig. 6.6. **Brief Discription of Plant** 

In practice, the plant is operated at a pressure of 2 bar and a temperature of 700–720 K.

1. Sulphur Burner. Here, sulphur dioxide is produced.

**2. Purification Unit.** This unit is an assembly of various parts like,

(a) Dust precipitator, which removes dust from the gases.

(b) Scrubber, which removes soluble impurities.

(c) Drying tower, which removes moisture from the gases.

(d) Arsenic purifier, which removes impurities of  $As_2O_3$ , etc.



Fig. 6.6 Flow sheet for the manufacture of sulphuric acid.

The gases coming out of the purification unit are passed through the **testing box** to make sure that they are completely free from the impurities. If impurities are still present, these are recirculated again through the purification unit.

The pure gases coming from the testing box are preheated to  $720\,\text{K}$  in a  $\,\text{preheater.}$ 

**3. Catalyst Convertor.** The hot gases are then passed through the catalyst chamber where  $SO_2$  is oxidised to  $SO_3$ .

**4.** Absorption Tower.  $SO_3$  from contact tower is introduced at the base of the absorption tower from the top of which conc.  $H_2SO_4$  is

showered. As  $SO_3$  gas moves up it is dissolved in sulphuric acid forming oleum which may be drawn out from the base of the tower.

 $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ Oleum

Oleum is then diluted with water to get  $H_2SO_4$  of the desired concentration.

 $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ 

 $SO_3$  is not absorbed in water directly to form sulphuric acid because it results in the formation of mist of acid particles in air which does not condense easily. Hence, the operation becomes difficult to handle.

The sulphuric acid obtained by contact process is 96–98% pure.

## Physical Properties of sulphuric Acid

1. Pure  $\rm H_2SO_4$  is colourless but commercial acid is yellow in colour due to presence of impurities.

2. Highly concentrated  $H_2SO_4$  (98%) has a specific gravity of 1.84 and high b.pt. of 621 K. The high b.pt. shows that  $H_2SO_4$  has associated structure due to hydrogen bonding.

3. Conc.  $H_2SO_4$  has a great affinity for water. Its dissolution in water is highly exothermic in nature. When water is added to acid spurting takes place because of lot of heat produced during the process. Therefore, for dilution of the acid, always add acid to  $H_2O$  slowly, and not water to acid.

4. On coming in contact with the skin it produces severe burns, therefore, it must be carefully handled.

### **Chemical Properties**

**1. Dissociation.** On heating strongly it dissociates into  $SO_3$  and  $H_2O$ .

 $H_2SO_4 \rightleftharpoons H_2O + SO_3$ 

**2.** Acidic Nature. It is a typical acid and turns blue litmus red because it produces  $H^+$  ion according to following ionizations:

 $H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq); Ka_1 = 1 \quad 10^3$  $HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{-2-}(aq); Ka_2 = 1.2 \quad 10^{-2}$ 

The larger value of  $Ka_1$  ( $Ka_1 > 10$ ) means that  $H_2SO_4$  is largely dissociated into  $H^{\dagger}$  and  $HSO_4^{-}$ .

Thus, it forms two series of salts *sulphates* and *bisulphates*. For example,

 $NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$ Sodium bisulphate

 $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$ Sodium sulphate

**3.** As a Dehydrating Agent. Sulphuric acid has a strong affinity for water. Therefore, conc.  $H_2SO_4$  is a powerful dehydrating agent. Its dehydrating nature is shown by the following properties:

- (*i*) *Drying of gases.* Certain gases (which don't react with H<sub>2</sub>SO<sub>4</sub>) like CO<sub>2</sub>, SO<sub>2</sub>, Cl<sub>2</sub>, HCl etc., may be dried by passing through conc. H<sub>2</sub>SO<sub>4</sub>.
- (*ii*) *Charring.* Conc.  $H_2SO_4$  reacts with sugar, wood, paper, etc., to form black mass of carbon. The phenomenon is called **charring.**

$$\underset{\text{Sugar}}{\text{C}_{12}\text{H}_{22}\text{O}_{11}} \xrightarrow{\text{Conc.H}_2\text{SO}_4} 11\text{H}_2\text{O} + 12\text{C}$$

**4.** Oxidising Action. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to  $SO_2$ . Some of the oxidising reactions are:

(i) Carbon is oxidised to  $CO_2$   $H_2SO_4 \longrightarrow H_2O + SO_4 + O] 2$   $C + 2O \longrightarrow CO_2$  $\overline{C + 2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + CO_2}$ 

(ii) Sulphur is oxidised to  $SO_2$   $H_2SO_4 \longrightarrow H_2O + SO_2 + O] 2$  $\frac{1}{8}S_8 + 2O \longrightarrow SO_2$ 

 $\frac{1}{8}S_8 + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$ 

(iii) HBr is oxidised to  $Br_2$ 2HBr + H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  2H<sub>2</sub>O + SO<sub>2</sub> + Br<sub>2</sub> (iv)  $H_2S$  is oxidised to sulphur

 $H_2S + H_2SO_4 \longrightarrow 2H_2O + S + SO_2$ 

(v) **Metals** are oxidised first to their oxides and then to their sulphates.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

## Uses of H<sub>2</sub>SO<sub>4</sub>

Sulphuric acid is used in large number of industries. It is called the **"King of chemicals".** Its important uses are:

- (*i*) As an acid in laboratories and industries.
- (ii) In storage batteries and lead accumulators.
- (*iii*) In chemical industries for the preparation of hydrochloric acid, nitric acid, sulphates, ether, dyes and paints.
- (iv) As a dehydrating agent.
- (*v*) In fertilizers, for the preparation of ammonium phosphate, ammonium sulphate, superphosphate of lime, etc.
- (vi) As a laboratory reagent in mixture analysis and drying of gases.
- (vii) In metallurgy, for electrolytic refining of metals.
- (viii) For pickling i.e., cleaning of metal surfaces before electroplating.

# 6.7 THE HALOGENS

The non-metallic elements *fluorine* (F), *chlorine* (Cl), *bromine* (Br), *iodine* (I) and *astatine* (At) are grouped together to form group 17 of the Periodic Table. Their salts are present in sea-water and hence they are collectively known as **halogens** (Greek, *Halos* means *sea salt producers*). The group collectively is called *halogen family*. All halogens precede the noble gases in the periodic table. Their atoms contain one electron less than the electronic configuration of the inert gas. They have very strong tendency to acquire stable inert gas configuration by accepting one electron. For this reason halogens exhibit non-metallic behaviour. Astatine the last member of halogen family is a radioactive element with a very short life. All other halogens are abundant in nature in the combined state.

### **Physical Properties of Halogens**

1. Physical State. The halogens are all diatomic and exist as  $F_2$ ,  $Cl_2$ ,  $Br_2$  and  $I_2$ . The intermolecular forces are very weak in halogens. The nature of forces is van der Waals' and their magnitude increases down the group.

Thus,  ${\rm F_2}$  and  ${\rm Cl_2}$  are gases, bromine is a volatile liquid and iodine is a volatile solid.

2. Colour. Halogens are coloured.

The colour of different halogens are as follows:

Halogen	Fluorine	Chlorine	Bromine	Iodine
Colour	Pale yellow	Greenish yellow	Reddish orange	Dark
				violet

Thus, the colour deepens down the group.

**3.** Melting and Boiling Points. Melting and boiling points increase with increase in atomic number. This indicates that the strength of intermolecular forces of attraction between the molecules increases with the increase in atomic number.

The intermolecular forces in halogens are van der Waal's forces which increase with the size of the molecule.

- **4. Ionization Energies.** Ionization energies of all the halogens are very high. Therefore, they have a less tendency to lose electron. However, this tendency increases down the group.
- **5. Electronegativity.** The halogens have very high electronegativity. Halogens are the most electronegative elements in their respective periods. Electronegativity decreases on descending the group. Fluorine is the most electronegative element in the Periodic Table.
- **6.** Non-metallic Character. All the halogens have very high values of ionization energies and exhibit non-metallic character. The non-metallic character, however, decreases down the group. Iodine shows some distinct metallic properties *e.g.*, it possesses metallic lustre and forms positive ions like I<sup>+</sup>, I<sup>3+</sup>, etc.

# Laboratory Preparation and Tests of Halogens

# Activity

- Take solid  $\rm MnO_2$  in a test tube and add about 2 mL of concentrated hydrochloric acid.
- Heat the mixture on a flame of Bunsen burner. *Observe the colour of the gas evolved.*
- Bring a moist starch iodide paper near the mouth of the test tube and observe what happens.
- Record your observation and draw inferences.

In the laboratory **chlorine** can be prepared by the oxidation of concentrated hydrochloric acid with manganese dioxide or potassium permanganate.

 $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$ 

 $2KMnO_4 + 16HCl \longrightarrow 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2$ 

## **Tests for Chlorine**

- 1. Chlorine is a greenish yellow gas.
- 2. It turns moist starch iodide paper blue.
- 3. It bleaches litmus solution.

## Activity

- Take a small amounts of KBr and  $MnO_2$  (about 1 g each) in a test tube and add concentrated sulphuric acid.
- Heat the contents and observe what happens.
- Bring a moist starch paper and a moist starch-iodide paper near the mouth of the test tube.

What do you observe?

Record your observations, interpret and draw conclusions.

**Bromine** can be prepared in the laboratory by heating a mixture of potassium bromide, and manganese dioxide with concentrated sulphuric acid.

 $2\text{KBr} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Br}_2$ 

Bromine evolves as deep orange red vapours.

Bromine can also be prepared by adding chlorine water to the solution of some bromide.

 $2\text{KBr}(aq) + \text{Cl}_2(aq) \longrightarrow 2\text{KCl}(aq) + \text{Br}_2(aq)$ 

## **Tests for Bromine**

- 1. Bromine may be identified by its deep orange red colour and pungent smell.
- 2. It turns starch paper yellow and starch iodide paper blue.
- 3. It may be distinguished from nitrogen dioxide by the fact that it does not turn  $FeSO_4$  solution black.

# **Comparative Study of Chemical Properties of Halogens**

All the halogens are very reactive but amongst them fluorine is the most reactive. As we move down the group, reactivity decreases.

All the elements of the halogen family have a tendency to acquire noble gas electronic configuration by either accepting an electron resulting in the formation of monovalent anion or by sharing one electron with those of other elements. Thus, they show an oxidation state of -1 or +1 depending on whether the element combining with halogens is less electronegative or more electronegative than halogen.

## **Reaction of Halogens with Water**

The reaction of halogens with water shows the decrease in oxidizing power on going down the Group 17. Fluorine reacts with water and oxidizes it to oxygen.

 $2F_2(g) + 2H_2O(l) \longrightarrow O_2(g) + 4HF(aq)$ 

Chlorine reacts with water by disproportionation to form hydrochloric acid and hypochlorous acid

 $Cl_2(g) + H_2O(l) \implies HCl(aq) + HOCl(aq)$ 

Due to the presence of these two acids in solution, the solution turns blue litmus red in the begining and then HOCl bleaches it.

Bromine interacts slightly with water to give an acidic solution. Bromine solution is prepared by adding a few drops of liquid bromine to water and shaking. A light yellow solution is produced.

## Reaction of Halogens with Alkalis

All the halogens react with alkalis potassium hydroxide or sodium hydroxide. However, different products are formed under different conditions of temperature and concentration of the alkali. Fluorine reacts with cold and hot alkali solution as follows:

 $2F_2(g) + 2NaOH(aq) \longrightarrow 2NaF(aq) + OF_2(g) + H_2O(l)$ Cold, dilute

$$2F_2(g) + 4NaOH(aq) \longrightarrow 4NaF(aq) + O_2(g) + 2H_2O(l)$$
  
Hot, concentrated

Chlorine, bromine and iodine react with alkali in essentially the same way with only slight differences of products.

$$Cl_2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaClO(aq) + H_2O(I)$$
Cold, dilute

 $3\text{Cl}_2(g) + \underset{\text{Hot, concentrated}}{6\text{NaOH}(aq)} \longrightarrow 5\text{NaCl}(aq) + \text{NaClO}_3(aq) + 3\text{H}_2\text{O}(I)$ 

#### **Reaction of Halogens with Metals and Non-Metals**

Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.

 $Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$ 

With metals like Na, K, Mg, etc., having low ionization energies, the halogens react to form ionic halides which have high boiling and melting points.

The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is a monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example,  $SnCl_4$ , PbCl<sub>4</sub>, are more covalent than  $SnCl_2$ , PbCl<sub>2</sub>, respectively.

#### **Uses of Halogens**

(a) **Fluorine.** It is mainly used for the manufacture of  $UF_6$  for nuclear power generation.

Some of the uses of HF are in the glass industry as an *etching agent* and in the manufacture of fluoride salts. Prominent among the fluorides is NaF used for the fluorination of water; one part per million level fluoride in drinking water prevents tooth decay.

(b) Chlorine. The chief uses of chlorine are:

- (*i*) production of organic compounds like polyvinyl chloride, chlorinated hydrocarbons, pharmaceuticals, herbicides, pesticides, etc.
- (*ii*) bleaches the paper pulp and textiles and disinfectant for sterilizing drinking water.
- (*iii*) production of inorganic compounds like HCl,  $PCl_3$ ,  $PCl_5$  sodium hypochlorite (NaOCl), bleaching powder (CaOCl<sub>2</sub>) etc.

(*c*) **Bromine.** The main use of bromine is in the preparation of ethylene bromide which is used as an additive to *leaded* petrol. Bromine is also used to make AgBr for photography.

(*d*) Iodine. Some important uses of iodine are:

- (*i*) Iodine is used as an anticeptic in the form of an alcoholic solution, which is known as *tincture of iodine*.
- (*ii*) It is also used for the preparation of iodoform and potassium iodide.
- (*iii*) Iodide ion is necessary for the normal functioning of the thyroid gland. Insufficient iodide in the diet leads to *goitre*

(enlargement of thyroid gland). Hence, sodium or potassium iodide is added to table salt and this type of salt is known as *"iodized"* salt.

# 6.8 CHLORINE

Chlorine was discovered by **Scheele** in 1774 by the action of HCl on  $MnO_2$ . In 1810, **Davy** established its elementary nature and named it chlorine on account of its greenish-yellow colour (Greek, chloros = greenish-yellow).

## Laboratory Preparation

By the action of HCl on  $KMnO_4$ . This is a convenient method to prepare chlorine in the laboratory. It consists the addition of cold concentrated HCl on potassium permanganate crystals.

 $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 3Cl_2$ The apparatus used is shown in Fig. 6.7.





A small quantity of potassium permanganate is placed in the flatbottom flask fitted with a dropping funnel and a delivery tube. HCl is added drop by drop from the dropping funnel. A brisk reaction occurs and yellowish-green gas is evolved. It is passed through water and conc.  $H_2SO_4$  and finally, dry and pure chlorine is collected in a jar by upward displacement.

## **Physical Properties of Chlorine**

- (*a*) Chlorine is a yellowish-green gas with a pungent suffocating smell.
- (*b*) It is heavier than air and oxygen. It is 2.5 times heavier than air.

- (c) It is poisonous in nature. It produces headache if inhaled in small quantity. It affects throat, nose and lungs. Large quantities prove fatal.
- (*d*) It can be easily liquefied by cooling under pressure. The liquid chlorine is a yellow liquid (b.p. 239 K and m.p. 171 K).
- (*e*) It is fairly soluble in water. The aqueous solution is called chlorine water. It has yellow colour and smells of chlorine. At 0  $^{\circ}$ C, crystals of chlorine hydrate Cl<sub>2</sub>.8H<sub>2</sub>O are formed.

#### **Chemical Properties of Chlorine**

1. Action on litmus. Dry chlorine has no action on litmus paper. In the presence of moisture chlorine turns blue litmus red. It is because  $Cl_2$  reacts with water to form HCl and HClO

 $Cl_2 + H_2O \longrightarrow NCl + HClO$ 

**2.** Combustibility. Chlorine does not burn and also does not help in burning.

**3.** Combination with elements. It combines with all the nonmetals *except nitrogen, oxygen, carbon and inert gases.* 

(*i*) It *combines with hydrogen* in light (but not in dark) with explosion to form HCl. However, in presence of charcoal as a catalyst, the reaction is safe.

 $H_2 + Cl_2 \xrightarrow{sunlight} 2HCl$ 

(*ii*) *Combination with non-metals.* On heating with chlorine, Arsenic, sulphur, phosphorus (red). etc., combine with chlorine to form trichlorides.



Yellow phosphorus readily catches fire in chlorine.

(*iii*) **Combination with metals.** Most of the metals directly react with chlorine to form corresponding chlorides. *Alkali metals* burn brilliantly in chlorine. *Iron, copper, aluminium, magnesium, zinc*, etc., when heated in chlorine form corresponding chlorides. A trace of moisture always catalyse the reaction.

 $2Na + Cl_2 \xrightarrow{\Delta} 2NaCl$ ;  $2Fe + 3Cl_2 \xrightarrow{\Delta} 2FeCl_3$ 

 $2\text{Al} + 3\text{Cl}_2 \xrightarrow{\Delta} 2\text{Al}\text{Cl}_3; \quad \text{Cu} + \text{Cl}_2 \xrightarrow{\Delta} \text{Cu}\text{Cl}_2$ 

 $Mg + Cl_2 \xrightarrow{\Delta} MgCl_2; \qquad Zn + Cl_2 \xrightarrow{\Delta} ZnCl_2$ 

**4. Affinity for hydrogen.** It has great affinity for hydrogen. It decomposes several hydrogen compounds forming HCl.

(*i*) *Turpentine* burns in chlorine forming HCl and carbon.

 $C_{10}H_{16} + 8Cl_2 \longrightarrow 10C + 16HCl$ 

(ii) It reacts with water in the presence of sunlight and forms  $O_2$ .

 $2H_2O + 2Cl_2 \longrightarrow 4HCl + O_2$ 

Chlorine water loses its yellow colour on exposure to sunlight, This is due to the formation of HCl.

(*iii*) It removes hydrogen from  $H_2S$ 

 $H_2S + Cl_2 \longrightarrow 2HCl + S$ 

(*iv*) Reaction with ammonia. It reacts with ammonia under two conditions:

• *When ammonia is in excess:* The products are nitrogen and ammonium chloride.

 $2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$ 

 $[NH_3 + HCl \longrightarrow NH_4Cl]$  6

 $8NH_3 + 3Cl_3 \longrightarrow N_2 + 6NH_4Cl$ 

• *When chlorine is in excess:* The products are nitrogen trichloride and HCl.

 $NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl_3$ 

5. Displacement reactions

It displaces bromine and iodine from bromides and iodides respectively.

 $\begin{array}{ccc} 2\text{KBr} + \text{Cl}_2 & \longrightarrow & 2\text{KCl} + \text{Br}_2 \\ 2\text{KI} + \text{Cl}_2 & \longrightarrow & 2\text{KCl} + \text{I}_2 \end{array}$ 

**6.** Oxidising and bleaching nature. In presence of moisture, chlorine acts as an oxidising and a bleaching agent.

 $Cl_{2} + H_{2}O \longrightarrow HCl + HClO$  $HClO \longrightarrow HCl + O$  $Cl_{2} + H_{2}O \longrightarrow 2HCl + O$ 

Coloured matter + Nascent oxygen  $\longrightarrow$  colourless matter

*The bleaching action is permanent*. The delicate articles should not be bleached with chlorine.

7. Action of alkalies. When passed into cold dilute solution of alkalies, it forms chlorides and hypochlorites.

 $2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$ 

2KOH + Cl<sub>2</sub>  $\longrightarrow$  KCl + KClO + H<sub>2</sub>O

 $2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$ 

Cold and dilute

With hot concentrated alkali solutions, chlorates are formed.

6NaOH + 3Cl<sub>2</sub>  $\longrightarrow$  5NaCl + NaClO<sub>3</sub> + 3H<sub>2</sub>

6KOH + 3Cl<sub>2</sub>  $\longrightarrow$  5KCl + KClO<sub>3</sub> + 3H<sub>2</sub>O

 $6Ca(OH)_2 + 6Cl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$ Hot and Conc

However, when chlorine is passed over dry slaked lime, bleaching *powder* is obtained.

 $\begin{array}{c} \text{Ca(OH)}_2 + \text{Cl}_2 \longrightarrow \text{CaOCl}_2.\text{H}_2\text{O} \\ \text{Slaked lime} \end{array} \xrightarrow{\text{Bleaching powder}} \end{array}$ 

The actual composition of bleaching powder is Ca(OCl)<sub>2</sub> CaCl<sub>2</sub> Ca(OH)<sub>2</sub> 2H<sub>2</sub>O

8. Addition reactions. Chlorine forms addition compounds with  $SO_2$ , CO

> $SO_2 + Cl_2 SO_2Cl_2$ Sulphuryl Chloride

 $CO + Cl_2 COCl_2$ Carbonyl Chloride

(Phosgene)

(Phosgene is highly poisonous gas).

### **Uses of Chlorine**

It is used:

- (*i*) in the manufacture of bleaching powder, chlorates, hypochlorites, hydrochloric acid, chloroform, carbon tetrachloride and a number of synthetic organic compounds.
- (*ii*) in the purification of drinking water.
- (*iii*) as a bleaching agent for cotton fabrics, paper and rayon.
- (*iv*) in the extraction of gold and platinum.

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- (*v*) as an oxidising agent.
- (vi) as a germicide and disinfectant.
- (*vii*) for the manufacture of poisonous gases like phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub> . NO<sub>2</sub>) and mustard gas (Cl— $C_2H_4$ —S— $C_2H_4$ —Cl).

# 6.9 THE NOBLE GASES

The elements *helium* (He), *neon* (Ne), *argon* (Ar), *krypton* (Kr), *xenon* (Xe) and *radon* (Rn) are grouped together in *Group 18* of the Periodic Table. All of these are gaseous under ordinary conditions of temperature and pressure. The last number of the group *i.e.*, radon is obtained from radioactive disintegration of radium. All others are present in air in traces. They are also known as *rare gases* because they are found in very small quantities in nature. They are highly non-reactive and do not take part in chemical combinations to form compounds like other elements and are, therefore, also called *inert gases*.

## **General Trends in Physical Properties**

- 1. Physical State. All of them are mono atomic, colourless, odourless and tasteless gases.
- **2. Solubility.** They are sparingly soluble in water. The solubility generally increases with increase in atomic number.
- **3.** Boiling Point and Melting Point. Due to weak intermolecular van der Waal's forces between them they possess *very low b. p.* and *m. p.* in comparison to those of other substances of comparable atomic and molecular masses. However, the b.p. and m.p. increase with increase in atomic number because van der Waal's forces become stronger with increase in size of the atoms or molecules. Therefore, among noble gases radon has the highest m.p. and b.p. whereas He has the least m.p. and b.p.
- **4.** Atomic Radii. As we go down the group, the van der Waal's radius increases due to the addition of new electronic shells and increase in screening effect.
- **5. Ionisation Enthalpy.** The ionisation enthalpy of noble gases are very high. This is due to the stable configurations of noble gases.
- **6.** Enthalpy of Fusion and Enthalpy of Vaporization. In general, the enthalpies of fusion and the enthalpies of vaporization are low and increase down the group.

#### **Chemical Properties**

The noble gases are generally inert and do not participate in the reactions easily. The inertness of noble gases is due to the following reasons:

- (*i*) The atoms of noble gases have *stable closed shell electronic configurations*.
- (ii) The noble gases have exceptionally high ionisation energies.
- (iii) The noble gases have very low electron affinities.

#### **Uses of Noble Gases**

The important uses of noble gases are discussed below:

(*a*) **Helium**. (*i*) Because of its lightness and non-inflammability, helium is used to fill air ships and balloons for meteorological observations.

(*ii*) Because of its lightness it is used in inflating aeroplane tyres. (*iii*) For respiration by deep-sea divers. Helium oxygen mixture is used by deep-sea divers in preference to nitrogen oxygen mixtures. It is much less soluble in blood than nitrogen. This prevents 'bends' which is the pain caused by formation of nitrogen bubbles in blood veins when a diver comes to the surface.

(*iv*)*In treatment of asthma*. A mixture of oxygen and helium is used in the treatment of asthma.

(*v*)Helium is used to provide inert atmosphere in the melting and welding of easily oxidizable metals.

(*b*) **Neon.** (*i*) Mixed with helium it is used to protect electrical instruments from high voltages.

(*ii*)It is used for filling discharge tubes, which have characteristic colours and are widely used for advertising purposes.

(*iii*) Neon is also used in beacon lights for safety of air navigation as the light bossesses fog and storm-penetrating power.

(*iv*) Neon bulbs are used in botanical gardens and in green houses.

- (c) **Argon.** Along with nitrogen it is used in gas-filled *electric lamps* because argon is more inert than nitrogen.
- (*d*) **Radon.** (*i*) It is used for the treatment of cancer and other diseases.

(*ii*) It is used for radioactive studies.

# 6.10 WATER

Water (H<sub>2</sub>O) is an important hydride of oxygen, which is a principal (about 75%) constituent of earth's surface. It is most abundant, omnipresent and easily obtainable of all chemical compounds. It is a significant component of animal and vegetable matter and plays a vital role in their life processes. It ranks next to oxygen in importance for our existence. It constitutes about 65% of human body and about 95% by weight of some plants. It can be easily transformed from *liquid to solid* or from *liquid to gaseous* states and *vice versa*.

## **Aggregation of Water Molecules**

In gaseous state, the individual covalent molecules  $H_2O$  exist as such. However in liquid state, large aggregates of varying number of  $H_2O$ units are formed because of their association through intermolecular hydrogen bonds.



In fact, in liquid water, the free  $H_2O$  molecules and associated  $H_2O$  molecules exist in a state of dynamic equilibrium.

 $nH_2O \implies (H_2O)_n$ 

The extent of association, however, depends upon the conditions of temperature and pressure.

The intermolecular hydrogen bonding is responsible for the **abnormally high** *freezing point, boiling point, heat of fusion and heat of vapourisation* as compared to the hydrides of the other elements of oxygen family.

# **Physical Properties of Water**

Water has some unique features which arise due to intermolecular H-bonding.

Water has a higher values of specific heat, thermal conductivity and surface tension than most of the other liquids. These properties are responsible for water to play a vital role in the biosphere. The high heat of vaporisation and high specific heat of water are responsible for the moderating influence of water on the climate and body temperature of living organisms. Water is also excellent solvent for transporting ions and molecules needed by plant and animal metabolism.

### **Chemical Properties of Water**

1. Action towards litmus. Pure water is neutral to litmus.

**2. Decomposition.** Water is quite stable and does not dissociate even at high temperature. The dissociation into its elements is only 0.02% even at 1500 K

$$\mathrm{H}_{2}\mathrm{O}(\mathbf{I}) \longrightarrow \mathrm{H}_{2} + \frac{1}{2}\mathrm{O}_{2}$$

The small conductivity of pure water reveals its small dissociation into  $\rm H_3O^+$  and  $\rm OH^-$  ion

 $2H_2O \implies H_3O^+ + OH^-;$  (K<sub>w</sub> = 1 10<sup>-14</sup> at 298 K.)

**3. Acid-base reactions.** Water is *amphoteric* substance because it can act as acid as well as base as shown:

$$\begin{array}{c} H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^- \\ Acid & Base \end{array}$$

 $\underset{\text{Acid}}{\text{HCl}} + \underset{\text{Base}}{\text{H}_2\text{O}} \xrightarrow{} H_3\text{O}^+ + \text{Cl}^-$ 

Base

Acid

The self ionization of water can be represented as follows:

 $\begin{array}{ccccc} H_2O & + & H_2O & \Longrightarrow & H_3O^+ & + & OH\\ Acid_1 & Base_2 & Conjugate & Conjugate & Acid_2 \end{array}$ 

However, the pH of water at  $25^{\circ}$ C is 7 and it is neutral towards litmus.

**4. Oxidation-reduction reactiosn.** Water can undergo reduction as well as oxidation.

5. Hydration reactions. Water has the ability to combine with some metal salts to form compounds known as hydrates.

**6.** Water as a solvent. Water has a high dielectric constant (82) due to the polar character of its molecule. Water is an excellent solvent for

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many ionic as well as covalent compounds. *Dissolution of* ionic compounds *takes place because of* ion-dipole interactions. *Dissolution of* molecular compounds *such as alcohols, amides, urea, sugar, glucose, honey, etc., in water takes place because of the tendency of these substances to form* hydrogen bonds *with water molecules.* 

# 6.11 HARD AND SOFT WATER

Water is classified into two categories depending upon its behaviour towards soap solution. These are: *soft water* and *hard water*.

- (a) **Soft water.** *Water which produces lather with soap solution readily is called soft water.* Distilled water and rain water are common examples of soft water.
- (*b*) **Hard water**. *Water which does not produce lather with soap solution easily is called hard water*. River water, sea water, tap water are common examples of hard water.

## Cause of Hardness of Water

Hardness of water is due to the *dissolved impurities* of the *salts like bicarbonates, chlorides and sulphate of calcium and magnesium*. Water gets the contamination of these salts when it passes through the grounds and rocks. Hard water does not produce lather with soap solution readily because the cations ( $Ca^{2+}$  and  $Mg^{2+}$ ) present in hard water react with soap (which is a mixture of sodium salts of higher fatty acids like stearic acid, palmitic acid, oleic acid, etc.) to form a precipitate of calcium and magnesium salts of fatty acids.

$$M^{2+} + 2C_{17}H_{35}COONa \longrightarrow$$
Sodium stearate
$$(C_{17}H_{35}COO)_2M + 2Na^+$$
Metal stearate

(M = Ca or Mg)

Thus, no lather is produced until all the calcium and magnesium ions have been precipitated. This leads to the consumption and hence, wastage of lot of soap. Hard water is, therefore, not fit for washing purposes.

## **Types of Hardness**

The hardness of water is of two types: *temporary hardness* and *permanent hardness*.

- (*i*) **Temporary hardness.** It is due to the *presence of soluble bicarbonates of calcium and magnesium.* Such water is also said to possess **carbonate hardness.** The term temporary indicates that most of the hardness can be removed by simply boiling the water. The bicarbonates of calcium and magnesium are formed in water by dissolution of carbonates of calcium and magnesium in the presence of atmospheric carbon dioxide.
- (*ii*) **Permanent hardness.** It is due to the presence of *chlorides and sulphates of calcium and magnesium*. Such water is also said to possess **non-carbonate hardness**. The term permanent indicates that such type of hardness cannot be removed by simple boiling operation.

#### Softening of Hard Water

The process of removal of metallic ions ( $Ca^{2+}$  and  $Mg^{2+}$ ) responsible for hardness of water is known as **softening of water**. A number of methods are available to soften water depending upon the nature of dissolved mineral salts as described below:

#### Removal of Temporary Hardness

Temporary hardness can be removed by following methods:

**Boiling.** Temporary hard water is taken in large boilers and boiled for about fifteen minutes. Consequently, the bicarbonates of calcium and magnesium present in the water decompose into their insoluble carbonates which settle at the bottom of the tanks as precipitate. The insoluble precipitate are removed by filtration or decantation.

 $\begin{array}{c} M(HCO_3)_2 \xrightarrow{Heat} MCO_3 + H_2O + CO_2 \\ (Soluble) & (Insoluble) \end{array} \\ (M = Ca \text{ or } Mg) \end{array}$ 

**To Identify Hardness of Water** 

#### **Experiment:**

Take a sample of water in test-tube and add few drops of soap solution. Shake it well.

#### **Observation:**

Lather in formed. Lather is not formed.

#### Inference:

Soft water

Hard water

#### Result

When soap is added to hard water, these anions combine with  $Ca^{2+}$ and Mg<sup>2+</sup> ions to form calcium and magnesium salts which are in soluble in water.

 $M^{2+}$ +  $2C_{17}H_{35}COONa \longrightarrow (C_{17}H_{35}COO)_2M \downarrow + 2Na^+$ From Metal stearate Soap hard water (precipitate)

Where M = Ca or Mg.

## Exercise

## I. Multiple Choice Questions

- 1. Which oxide of carbon is useful in preparing metal carbonyls?
  - (a) Both  $CO_2$  and CO(b) CO
  - (c)  $CO_2$  only

- (d)  $CO_2$  and  $C_3O_2$ .
- 2. Which statement is not true about CO?
  - (a) It is a colourless gas
  - (b) It is odourless gas
  - (c) It is highly soluble in water
  - (d) It is poisonous gas.

## 3. Which allotropes of carbon is used as a moderator in reactor?

- (a) Graphite (b) Diamond
- (c) Both (a) & (b) (d) None of these
- 4. Which of the following is an amorphous allotropes of carbon?
  - (a) Graphite
  - (d) None of these (c) Coke

5. Which type of the coal has the highest heating value?

- (a) Anthracite
- (c) Sub-bituminous (d) Lignite
- 6. Syngas is a mixture of
  - (a) Hydrogen & Carbon monoxide
  - (b) Hydrogen & Carbon dioxide
  - (c) Helium & Carbon monoxide
  - (d) None of these

(b) Bituminous

(b) Diamond

- 7. Which of the following is true about ammonia?
  - (a) Ammonia is a colourless gas.
  - (b) Ammonia is lighter than air.
  - (c) Ammonia is insoluble in water.
  - (d) Ammonia liquefies on cooling under pressure.
- 8. Which of the following is an acidic oxide?
  - (a) CaO (b)  $K_2O$
  - (c)  $CO_2$  (d) BaO

#### II. Fill in the Blanks.

- 1. Liquid ammonia is used as a .....
- 2. ..... is a mixture of one part of conc. HNO<sub>3</sub> and three parts of conc. HCl.
- 3. ..... is called oil of vitriol.
- 4. ..... discovered chlorine.
- 5. ..... gas is used in electric lamps.

#### III. Answer the Following Questions

- 1. What are the isotopes of carbon?
- 2. List some uses of diamond.
- 3. What are the main uses of graphite?
- 4. What is dry ice? List its use.
- 5. What are the different types of coal?
- 6. What is destructive distillation of coal? What are the main products obtained by destructive distillation?
- 7. What are the differences between coal and coke?
- 8. How does ammonia react with solution of  $Cu^{2+}$  ions?
- 9. Write the laboratory preparation of dinitrogen.
- 10. Mention some uses of nitric acid.
- 11. Write the uses of sulphuric acid.