

## CHAPTER 10

# THE ATMOSPHERE AND THE INERT GASES

### The Composition of the Atmosphere

The atmosphere is the mixture of gases which surrounds the earth. A small portion of the atmosphere is called air although the distinction may not be well-marked. In ancient time air was considered to be an element. But in 1775, Lavoisier established that air is a mixture of nitrogen and oxygen together with other gases. Nitrogen, oxygen and a number of inert gases are present in the atmosphere besides carbondioxide, water vapour and dust. Traces of hydrogen, hydrogen sulphide, ammonia, oxides of nitrogen, sulphur dioxide and other gases are also present. The composition varies according to location on the earth's surface and altitude. The average composition of dry air at sea-level by volume is given in Table 10.1.

**Table 10.1. Composition of the atmosphere.**

<i>Component</i>	<i>Percent by volume</i>	<i>Remarks</i>
Nitrogen	77.16	
Oxygen	20.60	
Argon	0.94	
Carbondioxide	0.04	variable
Moisture	0.140	variable
Neon	0.0018	
Helium	0.0005	
Krypton	0.0001	
Xenon	0.000005	
Hydrogen	Traces	
Ozone	Traces	
Dust particles & other gases	Traces	variable

The percentage composition of dry and pure air does not vary much with location on the earth's surface or with altitude. However, density of air and pressure varies greatly with altitude. Thus, the average pressure of air at sea-level is 760 mm. Hg, but at 15000 feet it is about 400 mm. Hg, at 10 miles it is 40 mm. and at 30 miles altitude it is only 0.1 mm. Similarly, density of air decreases with altitude.

### Detection of the Presence of Main Constituents of Air

#### (a) Oxygen

Oxygen can be detected by a number of chemical methods :—

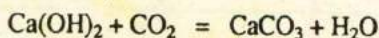
(i) By burning a number of metals and non-metals in air, it is found that the oxides of the elements are formed. Thus, phosphorus burns in air to form  $P_2O_5$ . Similarly, when air is passed over heated copper, formation of  $CuO$  takes place.

(ii) When a jar filled with  $NO$  gas is exposed to air, reddish brown fumes of  $NO_2$  is formed showing the presence of oxygen in air.

(iii) Oxygen is essential for life. Without oxygen no living being could exist on earth.

#### (b) Carbondioxide

(i) A vessel containing a sample of clear lime water, when exposed to air, becomes covered with a white crust. When air is passed through lime water, it turns milky. Lime water absorbs carbondioxide from air to form insoluble calcium carbonate by the reaction,



Carbondioxide may be released from this calcium carbonate by dilute acids.

(ii) Plants absorb  $CO_2$  from air in presence of moisture and sunlight with the help of chlorophyl in the green leaves. The process is known as photosynthesis.

#### (c) Moisture

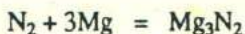
(i) A sample of caustic soda exposed in air turns into liquid after some time due to absorption of water vapour present in air.

(ii) Fused calcium chloride also absorbs water vapour when exposed to air and turns into liquid.

(iii) Water vapour is responsible for the formation of clouds which condenses into rain.

**(d) Nitrogen**

After the chemical removal of water vapour and carbondioxide from air by passing it through soda lime which absorbs both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and then burning the air with phosphorus or passing it through heated copper which takes up oxygen, the residual gas contains mostly nitrogen. The residual colourless gas is non-inflammable. Nitrogen combines with heated magnesium to form magnesium nitride:

**(e) Inert gases**

These are left as ultimate residue after removal of all other constituents.

**Liquid Air**

Before air is liquefied, it is freed from moisture and carbondioxide because these gases are solidified easily on cooling and may clog the pipes of the liquid air machine. Dust, water vapour and carbondioxide are removed from the air successively through a dust catcher, fused calcium chloride and slaked lime. The purified air is then subjected to a pressure of about 200 atmospheres and cooled to remove the heat produced by compression. The cooling is generally done by means of a mixture of salt and ice, or by cold water in the jacket containing the pipe (Fig. 10—1).

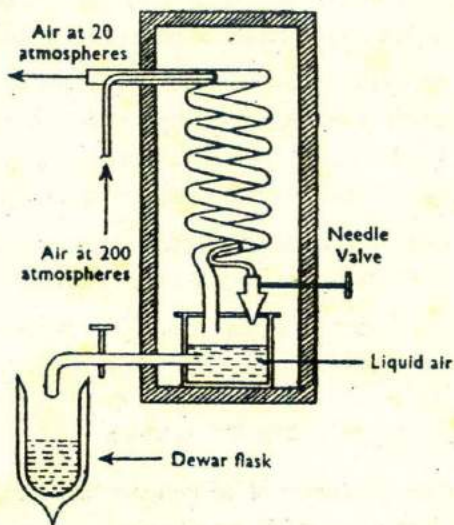


Fig. 10—1. A liquid air machine.

The cold compressed air is passed into the liquefying chamber through a needle valve where it expands suddenly to a pressure of about 20 atmospheres. This sudden expansion is accompanied by the absorption of heat and cools the air to a large extent due to Joule-Thomson effect. This cooled air is circulated round the spiral tube through the jacket, thereby further cooling the compressed air in the small inner coil of the liquefier. As the process continues, the air that escapes from the valve is colder than before, and finally the critical temperature is reached when the air becomes liquid.

### Properties of liquid air

- (i) Liquid air is a mobile liquid with a faint blue tinge.
- (ii) Evaporates rapidly in the open with the absorption of a large quantity of heat. It is stored in Dewar flasks.
- (iii) Liquid air is a mixture and, therefore, has no fixed boiling point. It boils at about  $-190^{\circ}\text{C}$  (b.p. of oxygen,  $-182.5^{\circ}\text{C}$  and nitrogen,  $-195.8^{\circ}\text{C}$ ).
- (iv) Physical properties of many substances are changed in liquid air.

### Applications of liquid air

- (i) Manufacture of commercial oxygen, nitrogen and inert gases. Liquid oxygen is a fuel for rockets and jet-propelled planes and missiles.
- (ii) Scientific researches at low temperatures. Thus, mercury freezes and becomes extremely hard in liquid air. Rubber, when immersed in liquid air, becomes hard and brittle. Fruits, flowers etc. become very hard. All metals become very good conductors of electricity when cooled in liquid air.
- (iii) Chemical reactions at the temperature of liquid air are being carried out. Synthetic procedures of new compounds make use of cooling by liquid air.
- (iv) Liquefaction of inert gases and subsequent separation by fractional distillation make use of liquid air.

## THE INERT GASES

The elements of the zero group of the Periodic Table starting from helium, the second element (atomic number 2), are all gases. These are Helium (2), Neon (10), Argon (18), Krypton (36), Xenon (54) and Radon (86). All these gaseous

elements are generally known as inert gases since normally they do not react with other substances and exist only in the free state. The atoms of these gases do not even form diatomic molecules, but remain as separate atoms in the gaseous state. These are also called *Noble gases* because of their property of remaining aloof from other elements. These are also known as *Rare gases* because of their presence in the atmosphere in extremely minute amounts (total of about 1% only).

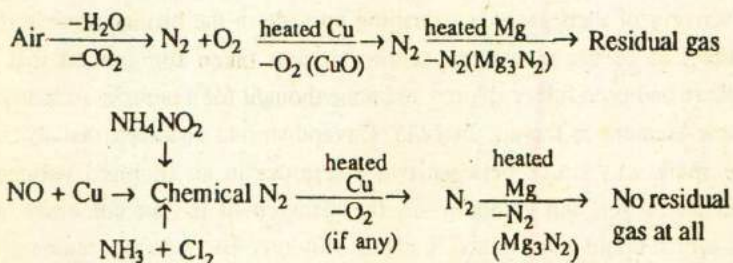
### The Discovery of the Inert Gases

The discovery of inert gases is a thrilling episode in the history of chemistry. Until the end of the nineteenth century it was taken for granted that the atmosphere had been fully explored and none thought for a moment of searching for a new element in the air. In 1785, Cavendish had observed that when an electric spark was struck between two electrodes in an enclosed volume of mixture of oxygen and common air, the nitrogen of the air combined with oxygen which could be absorbed in alkali solutions. But a small volume of the air, about  $\frac{1}{120}$ th part, could not be converted to nitrous acid and remained as residue. This important experiment of Cavendish had also passed into oblivion.

About a century later, Rayleigh in 1892, performed experiments for accurate determinations of the densities of gases, such as nitrogen, oxygen etc. Although the oxygen which he prepared by three different methods from chemical compounds or isolated from air had the same density, the results with nitrogen were puzzling. The atmospheric nitrogen was found to be heavier (to the extent of about 0.5%) than the nitrogen prepared by chemical methods, such as from ammonium nitrite, urea, oxides of nitrogen or nitric acid. The normal density of chemical nitrogen is 1.2505 g./l. whereas the atmospheric nitrogen has a density of 1.2572 g./l. Rayleigh repeated the experiment of Cavendish and confirmed the presence of unabsorbed residue.

It was known that each element gives its characteristic spectrum and from the spectral lines one can identify the elements. The spectrum analysis is a sort of finger print method for the identification of elements. Rayleigh was rather astonished to find that residual gas left after sparking nitrogen and oxygen did not give the spectrum of nitrogen but an unfamiliar type of spectrum.

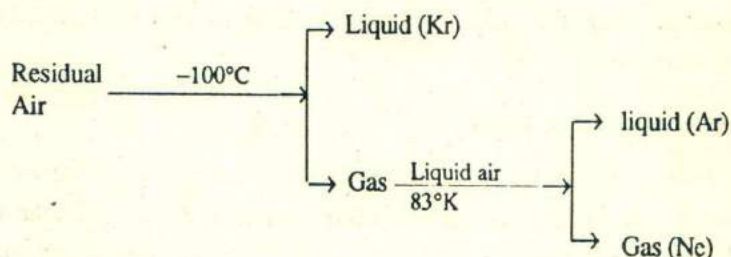
William Ramsay gained permission from Rayleigh to investigate into the chemistry of the atmospheric air. He passed air over red hot copper in order to remove oxygen and the residual nitrogen was passed over heated magnesium to find out whether it would be completely absorbed or not. After the gas was passed back and forth over heated magnesium taking all precautions to exclude dust, water vapour and carbon dioxide, everything was absorbed except about  $\frac{1}{80}$ th part of the original volume. The experiments of Ramsay on chemical nitrogen and atmospheric nitrogen are given schematically as follows :-



Rayleigh and Ramsay examined the spectrum of the residual gas and observed groups of green and red lines never observed before in the spectrum of any gas. A detailed study of this residual gas was made. The density of the purified residual gas was found to be 19.94 (H=1), its atomic weight was determined and chemical properties were investigated and was found to have no chemical activity. In 1894, Ramsay and Rayleigh announced the discovery of a new element, the first inert gas, and it was named Argon, "the lazy one", because of its chemical inactivity. Later on, it was proved that this residual gas was not pure argon but contained a number of other gases also.

In the year 1868, the French astronomer Janssen came to India to observe a total eclipse of the sun. He examined the chromosphere of the sun by means of a spectroscope and noticed a bright yellow line D<sub>3</sub>, which did not coincide with D<sub>1</sub> and D<sub>2</sub> lines of sodium. Lockyer concluded that the new line did not belong to any element then known to exist in terrestrial substances. He named it Helium (helios for the sun) and for about two decades helium was regarded as hypothetical element which might possibly exist only in the sun.

In 1888, Hillebrand noticed that when the mineral uraninite or *cleveite* is heated with acid, an inert gas is evolved which he believed to be nitrogen and thus missed a great discovery. Ramsay repeated the experiments and obtained a sample of the gas by heating cleveite with dilute sulphuric acid. Nitrogen present in the gas was removed by the sparking method over caustic alkali. Ramsay identified the spectrum of this gas and confirmed the presence of helium in the minerals. Thus the terrestrial helium was discovered.



Ramsay and Travers observed that helium obtained from different minerals differed in density and by diffusion method separated the gases into two fractions differing in densities to a great extent. The heavier fraction gave the spectrum similar to that of argon and the lighter fraction was helium. Thus argon was also discovered in minerals.

After the discovery of argon and helium their positions in the Periodic Table presented a problem. It was suggested that helium with atomic weight 4 might possibly belong to a new group of elements. The possibility of the existence of one element between helium and argon and at least two or more of higher atomic weights were suggested. Since argon was discovered in the residual gas obtained after removing the oxygen and nitrogen, Ramsay and Travers suspected the presence of other gases of similar nature in the residual gas. Starting with liquid air, by fractional evaporation and spectral analysis of the fractions, they first discovered a new inert gas in 1898 which was named Krypton (meaning hidden). After working on the density of this gas, it was found that the new element belonged between bromine and rubidium.

Continuing their search for the lighter gas, the residual air or mainly argon in the liquid state was subjected to fractional distillation under reduced pressure.

The more volatile fraction gave a complex spectrum with many brilliant red lines. The blaze of crimson light brought honour and fame to Ramsay and Travers. The new gas was named Neon (the new one) in 1898.

Ramsay and Soddy, in 1903, made the sensational discovery that helium was also produced by the atomic disintegration of radium. Later on, it was shown that many radio-elements on disintegration produce helium.

Dorn, in 1900, discovered radium emanation (Radon) as one of the disintegration products of radium. Radon resembled all other inert gases in the chemical inactivity.

### Sources of the Inert Gases

(1) *Inert gases in the air* : The inert gases are present in the air to a total of about 1%. Apart from argon, all other inert gases are present in the air in very minute amount and hence the name *rare gases*. The compositions of the inert gases in the air are :

Argon	0.932%
Neon	0.0015%
Helium	0.0005%
Krypton	0.0001%
Xenon	0.00001%

(2) *Other sources of inert gases* : Some minerals, such as uraninite, monazite, thorianite, cleveite etc. contain helium and also some argon which are evolved when the minerals are heated.

(3) The most important source of helium is the natural gas (mainly methane) from some petroleum springs.

(4) Inert gases are also present in some hot springs having their sources at great depths.

### Isolation of Inert Gases

**Helium:** 1. Helium may be isolated from various sources and purified. The most important source of helium is the natural gas from petroleum springs in the U.S.A. and Canada. Helium is obtained from the natural gas by cooling to a



very low temperature whereby all other gases present become solid or liquid and helium is left in the gaseous state.

2. Helium may be obtained from monazite by strong heating or by heating the mineral with dilute sulphuric acid. Helium thus obtained contains mainly other gases as impurity.

3. From hot springs helium may be collected by simple devices. This helium contains mainly argon as impurity.

Purification of helium is easily done by contact with coconut charcoal which, at the temperature of liquid air, absorbs all other gases except helium, hydrogen and neon. The coconut charcoal method is also applied to isolate the inert gases from one another and prepare samples of the gases.

#### Isolation of the Mixed Inert Gases

The mixed gases are allowed to come in contact with coconut charcoal in a bulk kept immersed in a cold bath in Dewar flask.

After about half an hour the unabsorbed gases are pumped off (Fig. 10—2).

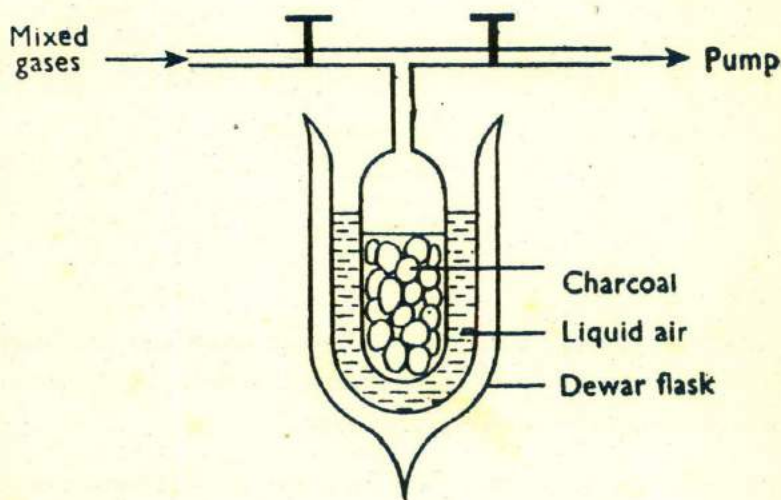
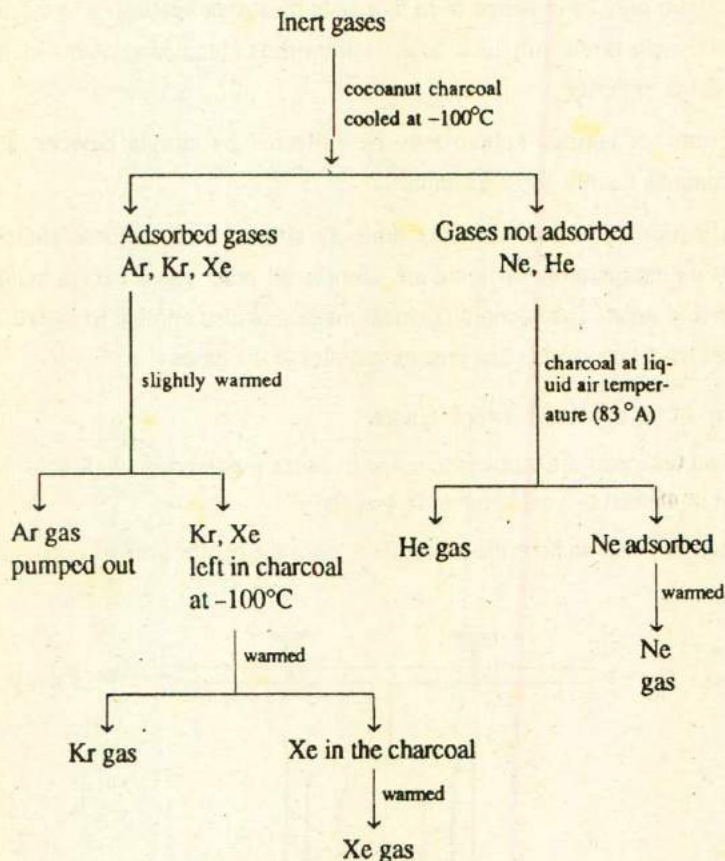


Fig. 10-2. Purification of inert gases (He) by coconut charcoal.

The plan of isolation of inert gases by this method is as follows :-



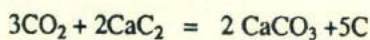
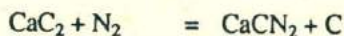
**Argon :** Argon is generally obtained from air which is the chief source. The isolation of the atmospheric argon is carried out in large scale. There are several procedures for the isolation of argon from air.

**1. Ramsay's original method :** Air freed from dust, carbondioxide and water vapour, is passed through a tube containing heated copper which removes oxygen (as  $\text{CuO}$ ) and the issuing gas is then passed through heated magnesium

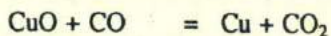
which removes nitrogen (as  $Mg_3N_2$ ). The residual gas contains mainly argon and other inert gases and is purified.

**2. Rayleigh's method :** A mixture of 11 volumes of oxygen and 9 volumes of air is subjected to electric discharge from a transformer of 6000-8000 volts, thereby nitrogen and oxygen of air combine to form nitric oxide. A fountain of caustic soda solution is discharged through a tube in the inside of the vessel to dissolve the nitric oxide formed. Impure argon was obtained by removing excess oxygen by means of alkaline pyrogallol solution.

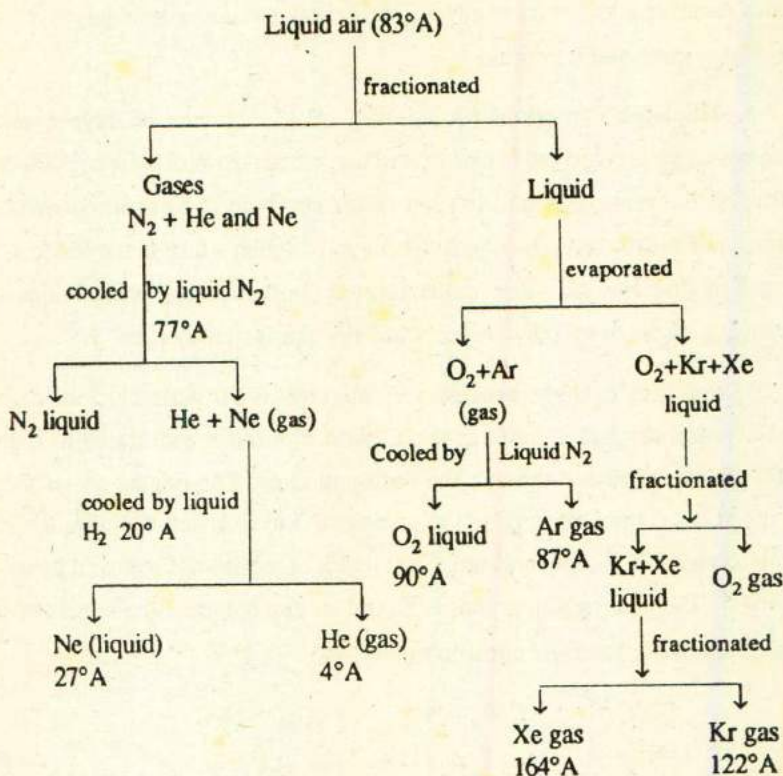
**3. Calcium carbide process :** A mixture of 90 parts calcium carbide and 10 parts calcium chloride is taken in an iron retort and heated to redness ( $800^\circ C$ ). Air is passed through the heated mixture. The issuing gas is passed over red hot copper oxide ( $CuO$ ) to convert  $CO$  to  $CO_2$  and then through solid  $KOH$  to absorb  $CO_2$  and moisture. Final traces of moisture is removed by means of  $P_2O_5$ . The gas, rich in argon, is stored in gas holders. The reactions that occur, remove oxygen and nitrogen as follows :



$CO$  formed during the reaction is removed by  $CuO$  :

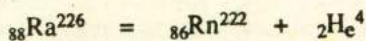


**Argon and other inert gases :** These are also obtained from liquid air by fractional liquefaction and evaporation at reduced pressure. There are quite a great deal of differences in the boiling points of the various constituents of liquid air. The plan of separation of all the inert gases may be outlined as follows and industrially used for the separation of all the inert gases.



**Radon :** Radon resembles in all other properties to the family of inert gases. It differs only in its radioactivity and undergoes spontaneous disintegration.

Radon is continually formed by the radioactive change of radium metal and its compounds under all conditions by the loss of He atoms or  $\alpha$ -particles. The equation for the change is,



Radon is best produced from an aqueous solution of a radium salt. Radium salt is dissolved in water and the solution is allowed to stand. On boiling the solution, radon is evolved along with some helium, oxygen and hydrogen.

### The Monoatomic Character of the Inert Gases

(1) The weights of 22.414 litres of the inert gases at N.T.P. have been found to be :

He	4.003 g.
Ne	20.183 g.
Ar	39.94 g.
Kr	83.80 g.
Xe	131.30 g.
Rn	222.00 g.

The above figures, therefore, give the molecular weights of the different inert gases. But these are also their respective atomic weights. It has already been stated that ordinarily the inert gases are devoid of chemical activity.

(2) The monoatomic nature was also proved by the measurement of specific heats of the gases. A gas molecule if it is diatomic or more complex molecule, by virtue of its three forms of motion, i.e., translational, vibrational and rotational, would require greater amount of energy to raise its temperature by 1°C than a molecule which is capable of only one kind of motion, e.g., translational motion. The inert gases have lower specific heats than hydrogen or oxygen and it is concluded that they occur as individual atoms. It has been shown that all the gases in which the ratio between the specific heat at constant pressure,  $C_p$ , and specific heat at constant volume,  $C_v$ , ( $C_p/C_v$ ) is equal to about 1.667, are monoatomic. The ratio for diatomic gases is about 1.4 and for triatomic gases 1.3. Experimental determinations of  $C_p/C_v$  of all the inert gases have given values ranging from 1.64 to 1.68. Hence the inert gases are monoatomic.

The electronic structures of the inert gases indicate that all the gases have electronic structures which are paired and have completely filled s or s and p orbitals as given in Table 10.2.

Table 10.2. Electronic structure of the inert gases.

At. No.	Elements	Electronic configurations
2	He	1s <sup>2</sup>
10	Ne	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>
18	Ar	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup>
36	Kr	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>
54	Xe	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>
86	Rn	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> 4d <sup>10</sup> 4f <sup>14</sup> 5s <sup>2</sup> 5p <sup>6</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>

Thus it may be concluded that an electronic structure represents an stable system in which all the electrons are paired and s and p orbitals in the outermost energy levels are completely filled. The elements possessing such electron arrangements must have a very stable atom and hence devoid of chemical activity. This fact is proved by the ionization potential of the inert gases as shown in Fig. 3—1.

## Properties of the Inert Gases

### 1. Physical Properties

All the inert gases are colourless, odourless and tasteless. They are somewhat soluble in water. Helium is the least soluble of all gases. All the gases can be liquefied and helium is the most difficult to liquefy. Liquid helium has been obtained first by Onnes in 1907 by the Joule-Thomson effect on the gas cooled previously to 15°A. The colourless liquid has very low density and has the lowest boiling point of all liquids, 4°A. Solid helium has been obtained by cooling liquid helium to 1°A under pressure. Liquid helium exists in two forms: He-I and He-II having a transition point but no triple point. Metals in liquid helium become superconductors of electricity. Liquid He-II has lowest viscosity and can flow upward along the surface of a glass container.

Radon gas glows strongly emitting heat and energy. Liquid and solid radon are colourless but glow with a bluish tinge in the dark.

The physical properties of the inert gases are summarized in Table 10.3.

Table 10.3. Physical properties of the inert gases.

Properties	He	Ne	Ar	Kr	Xe	Rn
1. Atomic Number	2	10	18	36	54	86
2. Electrons in the outermost levels	s <sup>2</sup>	s <sup>2</sup> p <sup>6</sup>	s <sup>2</sup> p <sup>6</sup>	s <sup>2</sup> p <sup>6</sup>	s <sup>2</sup> p <sup>6</sup>	s <sup>2</sup> p <sup>6</sup>
3. Atomic wt.	4.0	20.2	40	83.8	131	222
4. Atomic radius Å	0.93	1.60	1.91	2.0	2.2	—
5. Melting point °C	-272	-249	-187	-157	-112	-71
6. Boiling point °C	-269	-246	-186	-153	-107	-62
7. Critical temp. °C	-286	-220	-117	-63	-15	-104
8. Critical pressure (atmospheres)	2.26	26.9	48.0	54.3	58.2	62.4
9. C <sub>p</sub> /C <sub>v</sub>	1.65	1.64	1.65	1.69	1.67	—
10. Colour of spectra	Yellow	Red	Orange	Green	Blue	—

A comparison of the boiling points of the inert gases with other substances of comparable molecular weights is given in Table 10.4 to show the extremely low values for the inert gases.

**Table 10.4. Comparison of the boiling points (b.p.) and molecular weights (M.W.) of the inert gases with other comparable substances.**

<i>Substances</i>	<i>M. W.</i>	<i>b. p. (K)</i>
He	4	4.2
H <sub>2</sub>	2	20.3
Ne	20	27
CH <sub>4</sub>	16	92
Ar	40	87
HCl	37	189
Kr	84	121
CF <sub>4</sub>	88	135
Xe	131	164
n-C <sub>9</sub> H <sub>20</sub>	128	424
Rn	222	211
ICl <sub>3</sub>	233	350

## II. Chemical Properties

*The electronic configuration and the nature of the inert gases:* The chemical activity and the valence of an element depends upon the electronic configuration, particularly upon the type, the number and the arrangement of the electrons in the outermost energy level. The number of electrons in the outermost level of the inert gases is 8 derived from  $s^2p^6$  arrangement. In the case of helium it is 2 having  $1s^2$  electrons. Since these arrangements represent completed electronic level and account for chemical inactivity because of no tendency to alter the electronic arrangements by transfer or sharing of electrons, therefore, the inert gases do not even combine among themselves to form molecules but exist in monoatomic conditions.

The atoms of the inert gases have no electron affinity and do not gain electrons from reducing agents. They have higher ionization potential than those of any other elements and thus do not tend to lose electrons to oxidizing agents. On the other hand, many ions assume the stable electronic arrangement of the inert gases.

### Compound of the Inert Gases

In spite of the inert character of the inert gases, attempts have always been made to force them to enter into chemical combination by using unusual conditions with success. The tendency of compound formation by inert gases increases as the atomic number increases. Inert gas with higher atomic number have *d* orbitals available which participate in bond formation. He, Ne and Ar show less tendency to form compounds in view of low bond energies of their compounds. Xe, by far, gives large number of compounds while Rn chemistry is rather complicated because of its radioactive nature.

(1) Boothe and Wilson on the basis of thermal analysis showed the existence of a series of argon-boron trifluoride compounds at low temperatures :

Ar : BF<sub>3</sub>, Ar : 2BF<sub>3</sub>, Ar : 3BF<sub>3</sub> and so on.

These compounds have similar bonds as in the following molecules :

NH<sub>3</sub> : BF<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>O : BF<sub>3</sub>

(2) The dipole interaction of H<sub>2</sub>O molecule may polarize an inert gas and hydrate formation has been claimed having the following formula and exists at low temperatures and high pressures :

Ar : xH<sub>2</sub>O    Kr : xH<sub>2</sub>O    Xe : xH<sub>2</sub>O    where x is 1 to 6.

(3) Helides (from helium) of some metals have been made, such as HgHe, HgHe<sub>2</sub>, WHe<sub>2</sub>, FeHe etc. These "compounds" may be alloys in which small helium atoms occupy the interstitial positions in the crystal lattice and may not be true chemical compound.

(4) The inert gases become incorporated into the crystals of hydroquinone the molecule of which acts like a *cage*. These types of compounds are known as *clathrates* or cage compounds. They break up when the crystals are melted or dissolved in water; thereby the free gas is released.



(5) More recently xenon has been shown to form definite compounds particularly with the most electronegative element fluorine.  $\text{XeF}_4$  has been isolated in pure crystalline form. Other fluorides such as  $\text{XeF}_2$  and  $\text{XeF}_6$ , have also been made. Oxygen is also shown to form compounds with xenon.  $\text{XeO}_3$ ,  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$  have been isolated from the reaction products of xenon fluoride and water :  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$  and

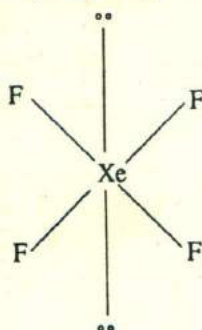
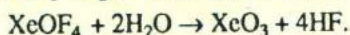
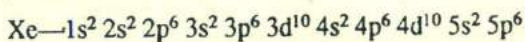


Fig. 10—3. Structure of  $\text{XeF}_4$ .

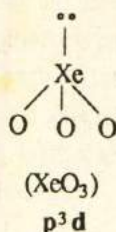
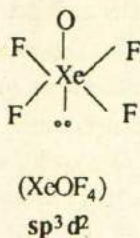
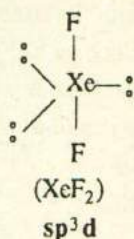
The structure of stable  $\text{XeF}_4$  molecule has been found to be square planar with  $\text{Xe—F}$  bond =  $1.93 \text{ \AA}$ . Since there are four pairs of electrons (8 electrons) in the outermost energy level of Xe, the formation of  $\text{XeF}_4$  crystals can be explained on the basis of octahedral arrangement using  $sp^3d^2$  hybridized orbitals of Xe having two axial positions occupied by two electron pairs as given in Fig. 10—3.

The formation of  $\text{Xe—F}$  bonds in  $\text{XeF}_4$  may be shown as follows on the basis of electron arrangements :—



	$5s^2$	$5p^6$		$5d^0$				
Xe (ground state)—	1l	1l	1l	1l	—	—	—	—
Xe (excited states)—	1l	1l	1	1	1	1	—	—
XeF <sub>4</sub> —	1l	1l	1l	1l	1l	1l	—	—
			F	F	F	F		
			<hr style="width: 100%; border: 0.5px solid black;"/> $sp^3d^2$ <hr style="width: 100%; border: 0.5px solid black;"/>					

Other compounds of Xe are formulated as follows :



## Uses of the Inert Gases

### 1. Uses of Helium :

(a) Because of its lightness and non-inflammability, helium is used for filling observation balloons.

(b) Helium is less soluble than nitrogen in the blood. Hence mixture of helium and oxygen are used by sea divers. This overcomes the disadvantage of using air at high pressure for respiration, because the nitrogen of air gets dissolved in the blood at high pressure and on surfacing the pressure is released but the dissolved nitrogen forms a pathological condition known as *bends* due to the formation of bubbles of nitrogen in the blood giving sudden pain.

(c) Mixtures of helium and oxygen are also used in the treatment of respiratory diseases such as asthma.

(d) Helium is used for inflating tyres of large aeroplanes.

(e) It is also used as an inert atmosphere for the melting and welding of easily oxidizable metals.

(j) Liquid helium produces lowest temperature and is used for scientific research.

(g) It is used in tube lights, vacuum drying etc.

### 2. Uses of Neon :

(a) Neon is used in neon lamps and signs. When an electric current is passed through neon under low pressure, it emits a brilliant orange-red glow which penetrates through mists and fogs. This is, therefore, used as beacon lights for air pilots.

(b) Neon is now-a-days extensively used in advertisement signs by coloured lights and in fluorescent tubes. The colour of neon in a lamp or tube may be changed by mixing with argon and mercury vapour and by using tubes made of glasses of special compositions. Lights of different shades can thus be obtained.

(c) Neon is used in television sets, radio-photography, sound movies etc. where ready responses to changes in electrical potential are required.

(d) Neon is also used for stimulation of growth of plants and flowers in the green houses.

### 3. Uses of Argon :

(a) Argon is used in gas-filled electric bulbs. It lowers the heat conductivity and complete chemical inertness makes it preferable to nitrogen. Thus the volatilization of tungsten filament is reduced and prolongs the life of the lamp. Ordinary tube lights contain a mixture of argon and mercury vapour

(b) With oxygen argon is used in welding to create an inert atmosphere. Argon is now widely used for welding of aluminium and stainless steel.

(c) Geiger-Counters are also filled with argon.

### 4. Uses of Krypton and Xenon :

(a) Krypton-xenon photographic flash tube has been developed for taking high speed photographic exposures. In cinematography, krypton flash is used to produce intense light.

(b) Krypton mixed with neon gives blue light in the electric tubes.

(c) Xenon imparts green colour to the electronic tube lights.

(d) Krypton is used in ionization chambers for cosmic ray measurements.

(e) Xenon has recently been used for making Bubble Chambers for detecting  $\gamma$ -rays, neutrons and other nuclear particles.

### 5. Uses of Radon :

Radon differs from other inert gases in its radioactive properties. Because of this property radon is used in the radiotherapy of malignant growth. It is particularly suitable in the non-surgical treatment of cancer. Radon is much more radioactive than radium and the therapeutic preparation of radon in small tubes is technically known as *seeds*.

## QUESTIONS AND PROBLEMS

1. How were helium, neon, and argon discovered? What are the properties and uses of these gases?
2. (a) Name the inert gases. Explain why they are inert and discuss their position in the Periodic Table of elements.  
(b) What are the important applications of the inert gases?
3. (a) Give a short account of the discovery of inert gases of the atmosphere. Why are these so called?  
(b) Discuss the important properties of the inert gases and mention some of their uses.
4. (a) What are inert gases? Show that the Bond Orders in  $\text{He}_2$  and  $\text{Ne}_2$  are zero.  
(b) Write a short account of the discovery of inert gases.  
(c) Explain why inert gases are chemically inactive.  
(d) Mention four uses of inert gases.
5. Give a short historical account of the discovery of Argon and Helium. How can they be separated and to what industrial use they have been put? Discuss the position of inert gases in the Periodic Table.
6. Describe the methods employed indicating the physico-chemical principle involved in the separation of rare gases of the atmosphere. Indicate their importance in chemistry.
7. What physical principles are employed in the liquefaction of air? What are the uses of liquid air?
8. Relate the chemical inactivity of the inert gases to their electronic structure.
9. How is argon obtained in a pure state? State its uses.
10. Give a brief account of the discovery of inert gases, their properties and uses.
11. Discuss the important properties of the inert gases and mention some of their uses.
12. Write notes on :- Discovery of inert gases and its impact on periodic classification.
13. Discuss "Elements of zero group are highly inert".
14. Why the tendency for compound formation of inert gases increases as the atomic number of elements increases?
15. Write equation for the reaction of  $\text{XeF}_4$  with  $\text{H}_2\text{O}$ .
16. Explain why  $\text{XeBr}_2$  has not been prepared.
17. Compare the structure of  $\text{ICl}_2^-$  and  $\text{XeCl}_2$ .
18.  $\text{O}_2^+\text{PtF}_6^-$  isolated by Bartlett gave rise to the preparation of  $\text{Xe}^+\text{PtF}_6^-$ . Compare the ionization energies of  $\text{O}_2$  (278.5 Kcal/mole) and of  $\text{Xe}$  (279.7 Kcal/mole) and the oxidation potential of  $\text{O}_2$  (g) and  $\text{Xe}$ (g) are 12.2 ev and 12.12 ev respectively to justify the reason of formation of the inert gas compounds.

## CHAPTER 11

# HYDROGEN, WATER & HYDROGEN PEROXIDE

### HYDROGEN

Hydrogen is the first element of the Periodic Table. By and large, hydrogen forms more compounds than any other element in the Periodic Table; much more than even carbon in organic chemistry.

#### Sources of Hydrogen

1. Hydrogen is the most abundant element in the universe. It is believed that 90% of the weight of the sun consists of hydrogen, so also other stars. This information is gathered by examining the solar spectra and spectra of stars.

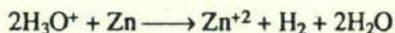
2. Water is the most abundant compound of hydrogen on the earth.

3. All organic compounds and natural organic substances contain hydrogen.

4. Hydrogen rarely occurs in the free state on the earth.

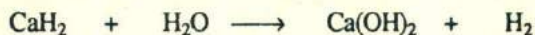
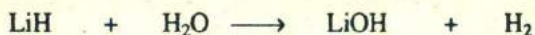
**Preparation :** Hydrogen is prepared both for experiment in the laboratory and on a large scale for industrial uses.

1. In the laboratory it is made by the action of an acid on zinc or other metals lying between magnesium and tin in the Activity Series of metals. The reaction takes place with the hydrogen ion  $\text{H}_3\text{O}^+$  :

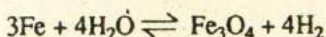


Notice that this is an oxidation-reduction reaction.

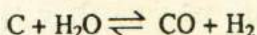
2. Metal hydrides react with water to produce hydrogen, Thus,



3. Commercially hydrogen is produced by passing steam over red-hot iron :

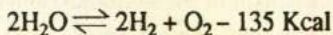


4. The least expensive method for producing commercial hydrogen is the water gas process in which steam is passed over hot carbon :



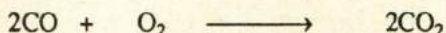
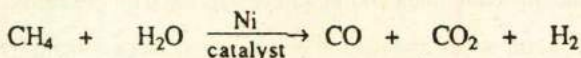
Notice that mixture of CO and H<sub>2</sub> are formed and generally the two gases are not separated. The mixture of CO and H<sub>2</sub> is known as water-gas and makes an excellent fuel. The mixture may be separated by fractional liquefaction.

5. The purest form of hydrogen is obtained by electrolysis of water :

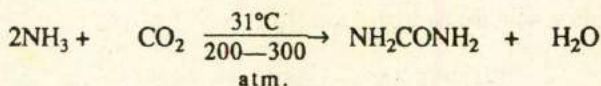
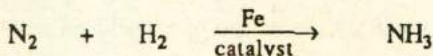


The oxygen is evolved at the anode and hydrogen at the cathode. The decomposition reaction is endothermic and requires supply of energy in the form of electric current. In practice alkaline solutions are electrolysed although acidulated water can also be used.

6. Mixture of CO + H<sub>2</sub> is also obtained when CH<sub>4</sub> from natural gas and steam is passed over heated catalyst (Cu or Ni) under pressure:



Hydrogen is combined with nitrogen to form ammonia which reacts with CO<sub>2</sub> to products urea.



### Properties of Hydrogen

*Physical Properties* : Hydrogen is the lightest of all known substances. It is a colourless, odourless gas slightly soluble in water. It is combustible. The following figures of the physical constants in Table 11.1 indicate some of the physical properties.

**Table 11.1. Properties of hydrogen.**

Atomic number	1
Atomic wt.	1.008
Bond energy in H <sub>2</sub>	103 Kcal/mol.
Bond length in H <sub>2</sub>	0.75 Å
Melting point	14° Absolute (K)
Boiling point	20° Absolute (K)
Critical temperature	33° Absolute (K)
Inversion temperature	195° Absolute (K)
Density at N. T. P.	0.09 g/l (STP)

Hydrogen has very low m. p. and b. p. indicating small intermolecular attraction in gaseous hydrogen molecule. Inversion temperature of 195°A indicates that when hydrogen gas is cooled to below 195°A, release of pressure produces cooling and liquefaction. Above 195°A, release of pressure produces warming. Hydrogen diffuses faster than any other gas because of the lowest molecular mass than all gases.

**Electronic Structure :** Hydrogen has only one electron,  $1s^1$ . All the alkali metals have also  $s^1$  electrons in the valence shell, but after the stable groupings of  $s^2p^6$  electrons. But the hydrogen electron is directly outside the nucleus which has no neutron but only proton. This difference in the electron position makes the chemistry of hydrogen different from that of alkali metals. The absence of inner completed electronic shell leads to certain differences in the properties of H and He with outer elements having similar configurations of the outer electrons.

Because the nucleus of the hydrogen atom consists of proton, a fundamental particle, it is of great importance in the field of nuclear chemistry and the cosmic chemistry of the universe.

Hydrogen molecule is diatomic, H<sub>2</sub>. During chemical reaction the molecule H<sub>2</sub> reacts by breaking the H—H bond for which quite high energy is required and H<sub>2</sub> reactions are generally slow.

**Chemical properties :** As mentioned, the chemical properties of hydrogen require the breaking up of the bond in H<sub>2</sub> molecule. This is quite readily achieved at elevated temperature. H<sub>2</sub> though relatively inactive at ordinary

temperature, enters into chemical combinations in a variety of ways mostly at elevated temperature :

(1) Hydrogen enters into chemical reaction by losing its electron, the compounds formed contain hydrogen in the +1 oxidation state.

(2) Hydrogen enters into chemical combination with other elements by gaining electron, the compounds formed have hydrogen in the -1 oxidation state.

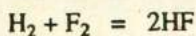
(3) Hydrogen also combines with some metals with 0 oxidation state.

### HYDRIDES

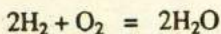
Binary compounds of hydrogen with another element is generally known as *hydrides*. Depending upon the mode of combination three types of hydrides are generally formed : (a) covalent or molecular hydrides (usually volatile). (b) ionic or salt-like hydrides, (c) metallic or interstitial hydrides.

1. *Compounds containing hydrogen in +1 oxidation state* : This is the most common combination of hydrogen and this happens when hydrogen combines with more electronegative elements than itself. Thus F, O, N, C etc. form HF, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> respectively containing hydrogen in the +1 oxidation states.

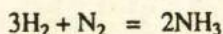
Thus hydrogen combines with non-metals directly under suitable conditions. With F<sub>2</sub> it combines at very low temperature to form HF :



Hydrogen combines with oxygen when ignited with release of energy.



With nitrogen it combines under pressure and in presence of a suitable catalyst to form NH<sub>3</sub> :

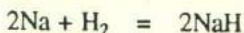


It may be noted that in all such compounds the hydrogen is not actually present as H<sup>+1</sup> but the bonding is mostly covalent with some degrees of ionic character depending upon the difference in electronegativity of the other elements and hydrogen. In acids and acid salts the +1 oxidation state of hydrogen is more pronounced as in NaHSO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub> etc.



2. *Compounds containing hydrogen in -1 oxidation state*: These are compounds in which hydrogen has gained an electron to form hydrogen  $H^-$  ion. When hydrogen combines with elements such as Li, Na, Ca etc. which are less electronegative than itself, the compound formed contains hydrogen in the -1 oxidation state. These compounds actually contain the true hydride ion ( $H^-$ ) and a positive metal ion and behave like ionic compounds or salts. Therefore, they are also called salt-like hydrides.

When the alkali metals are heated in hydrogen gas, alkali metal hydrides are formed. These are white crystalline solids:

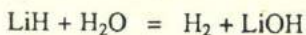


Similarly, alkaline earth metals form the hydrides such as  $CaH_2$ ,  $BaH_2$  etc.

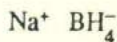
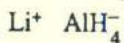
Some metal hydrides are regarded as salt-like, but are not ionic and are prepared by special methods rather than by direct union of the elements with hydrogen. Some of these are  $CuH_2$ ,  $MgH_2$ ,  $AlH_3$ ,  $HgH_2$  etc. although these appear to contain  $H^-$  ions but are less stable.

Salt-like hydrides of alkali metals conduct electricity in the molten condition and on electrolysis hydrogen gas is evolved at the anode proving H to be present as  $H^-$  state.

The hydride ions ( $H^-$ ) are unstable in water and are oxidized to  $H_2$ :



Complex hydrides are lithium aluminium hydride,  $LiAlH_4$ , sodium borohydride,  $NaBH_4$  etc. In these cationic and anionic species are:



These complex hydrides are solids and react with water to give  $H_2$ . They are conveniently used as reducing agents in organic chemistry.

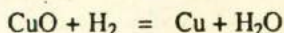
3. *Compounds containing hydrogen in the 0 oxidation state*: These compounds are generally known as metallic or interstitial hydrides. Thus uranium, palladium, zirconium etc. form hydrides by direct combination with hydrogen. These hydrides have metallic properties and do not form compounds of

fixed composition except in uranium hydride having the formula  $\text{UH}_3$ . The compound with palladium may be represented as  $\text{PdH}_n$ .

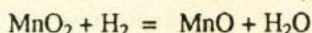
It is believed that these hydrides contain proton with a single electron (H atom) in the interstices of the metallic structure. Hydrogen is dissolved as elementary hydrogen in the metals and hence it is present in the 0 oxidation state.

### Reaction of hydrogen with compounds

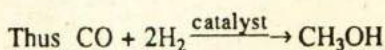
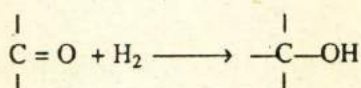
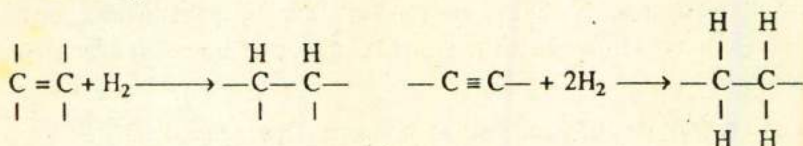
(1) Heated oxides of less electropositive and transition metals react with hydrogen with the formation of metal and water :



Sometimes a lower oxide of metal is also formed :



(2) In presence of catalysts and at elevated temperature the following reactions take place :



Such reactions are known as hydrogenation in which hydrogen is added to the molecule. These reactions are of great industrial importance.

**Uses of Hydrogen :** (1) Hydrogenation of materials such as of  $\text{N}_2$  (for  $\text{NH}_3$ ),  $\text{CO}$  (for  $\text{CH}_3\text{OH}$ ), coal, organic products and vegetable oils (for margarine) etc. are the most important fields of its application. (2) in oxyhydrogen and atomic hydrogen flames for welding. (3) As water gas in fuel. (4) Hydrogen bomb.

**Atomic Hydrogen :** When  $H_2$  gas is passed through an electric arc of tungsten wire at low pressure, it dissociates into atoms giving atomic hydrogen. The atomic hydrogen is very reactive and combines with non-metal such as S, P, As to form hydrides. With  $O_2$  it gives  $H_2O_2$ . When the atomic hydrogen is blown out of the tungsten arc by hydrogen gas, an intense heat is generated due to the combination of atomic H to form  $H_2$  (heat of formation of  $H_2$ ). The atomic hydrogen torch is used in welding.

**Nascent Hydrogen :** It has been presumed that at the instant when hydrogen is produced by means of chemical reactions, it is in the atomic state which ultimately combines in the molecular form and is evolved as  $H_2$ . Thus Sn and HCl or Zn and  $H_2SO_4$  produce nascent hydrogen at the instant when they react and have reducing properties and reduce  $Fe^{+3}$ ,  $Cr^{+6}$  to  $Fe^{+2}$  and  $Cr^{+2}$  state respectively.

**Hydrogen Bond :** One of the most important properties of hydrogen is its ability to form Hydrogen Bond. When hydrogen forms a bridge between two electronegative atoms of adjoining molecules, it is said to form a hydrogen bond. (see Chapter 2 page 100)

### Ortho and Para Hydrogen

As the electron is considered to be spinning on its own axis, similarly, the nucleus (protons and neutrons) have spins. Hydrogen molecule consists of two protons and these are spinning on their own axes. The conditions arise when two protons combine to form the hydrogen molecule. The two protons may be spinning in the same direction (parallel spins) or the two may be spinning in opposite directions (antiparallel). Hydrogen molecules containing parallel nuclear spins are known as ortho hydrogen and those having nuclear spins in opposite directions are called para hydrogen as shown in Fig. 11—1.

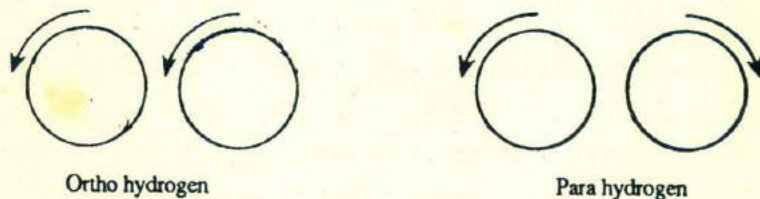


Fig. 11—1. Ortho and para hydrogen.

Ortho and para hydrogen have somewhat different physical properties and their stabilities differ at different temperatures. Information about such molecular rotation is often obtained by the study of molecular spectra. At room temperature 75% of ortho hydrogen is present in the ordinary hydrogen. At low temperature, proportion of para hydrogen increases.

### Isotopes of Hydrogen

Hydrogen occurs in nature in the form of three isotopes. They are,

- |                  |   |
|------------------|---|
| ${}_1\text{H}^1$ | Hydrogen, protium, p;                               |
| ${}_1\text{H}^2$ | Deuterium, heavy hydrogen, deuteron (Deuterium), D; |
| ${}_1\text{H}^3$ | Tritium, T.   |

There is only a very tiny amount of tritium in hydrogen. One atom of tritium is present for every  $10^7$  atoms of hydrogen; similarly, one atom of deuterium for  $5 \times 10^3$  atoms of hydrogen. There is quite considerable difference in the masses of the hydrogen atoms and this gives rise to quite appreciable difference in physical properties and also in chemical properties. The differences in properties arising out of the masses of isotopes are called *Isotopic Effect*. Thus the isotopic effect is maximum in the case of hydrogen isotopes than any other elements. Deuterium and tritium, because of their greater masses, have lower vapour pressures than ordinary hydrogen. These heavier isotopes become concentrated in the last portion of liquid hydrogen when it is allowed to evaporate.

Deuterium is of great importance in connection with heavy water and tritium in nuclear fusion reaction for creating hydrogen bomb.

### WATER

There is no other chemical substance which is so much familiar to us as water. Nearly three-fourths of the earth's surface is covered with water. The air and vegetable world contain high percentages of water. Water is a chemical of unique properties and hence its manifold applications.

### Physical Properties of Water

Water, when pure, has no colour, no taste and no odour. The pleasant taste of water is due to dissolved gases and salts. Some physical constants are given in Table 11.2.

Table 11.2 Physical properties of water.

Melting point	0.0°C
Boiling point at 760 mm.	100.0°C
Density at 4°C	1.0 g/ml.
Heat of fusion	79.7 cal/g.
Heat of vaporization	539.6 cal/g.

The amount of heat required to change the state of water or to raise its temperature is quite large as compared to other substances. Again, an interesting property is its highest density at 4°C. Similarly, the expansion in volume on freezing makes solid water (ice) float on the surface.

### Purification of Water

All natural waters are impure because of dissolved and suspended impurities. Sea water contains about 4% of dissolved solids. The following impurities may be present in water and their presence and quantities may vary according to the sources :—

1. *Suspended impurities* : Fine sand, clay, organic micro-organisms etc.

2. *Dissolved impurities* : Gases such as carbon dioxide, oxides of nitrogen, nitrogen, oxygen, argon, helium etc. Solids such as chlorides, sulphates and bicarbonates of Na, Mg, Ca, Al, Fe, potassium etc.

Purification of water is necessary both for human consumption and industrial applications. The great demand of pure water for city uses and for industries has created a world-wide problem.

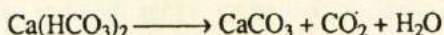
**Hard Water** : Water containing soluble calcium, magnesium salts are known as *hard water*. These are generally the sulphate, chloride and bicarbonate of calcium and magnesium. When only the bicarbonates of calcium and magnesium are present in water, the hardness is called *temporary*. But when the sulphate and chloride of calcium are present, the hardness is known as *permanent*. Hard water reacts with soap and gives rise to the precipitates of

insoluble calcium stearate. In boilers hard water forms insoluble crusts known as *boiler's scale* due to precipitation of insoluble carbonates etc. on the inside surface of the boilers and also tubes. This scale is a poor conductor of heat and causes waste of energy.

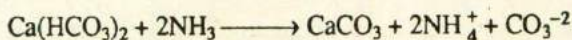
Hence removal of hardness of water is essential both for washing and industrial purposes.

**Softening of Water :** The process of removing hardness is called softening of water.

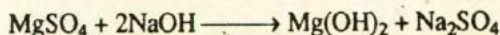
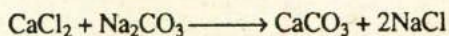
(1) **Boiling :** Temporary hardness can be removed by boiling, in which case the bicarbonates of calcium or magnesium are decomposed :



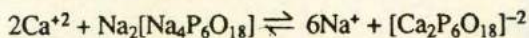
(2) **Liming :** Temporary hardness can also be removed by adding lime or an aqueous solution of ammonia :



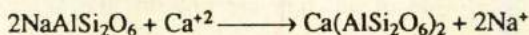
(3) **Caustic Process :** Non-carbonate hardness or permanent hardness is removed by adding  $\text{Na}_2\text{CO}_3$  or crude  $\text{NaOH}$  :



(4) **Calgon Process :** Sodium hexametaphosphate,  $(\text{NaPO}_3)_6$ , commercially known as *calgon*, is also used for softening. It reacts with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  to form a soluble complex ion :



(5) **Permutit Process :** Complex sodium-alumino-silicate, which is known as permutit or synthetic *zeolite*, is used for water softening by a process called *ion-exchange*. Water containing  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions are exchanged with harmless  $\text{Na}^+$  ion in the permutit bed. The permutit bed can be regenerated for use by means of strong  $\text{NaCl}$  solutions :



Regeneration :

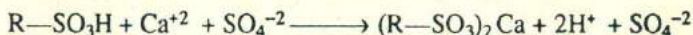


The above two reactions are actually reversible. The direction of the reaction can, therefore, be controlled by either excess of  $\text{Ca}^{+2}$  or  $\text{Na}^+$  :

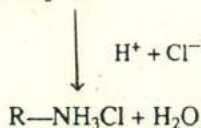
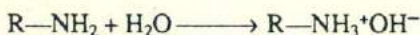
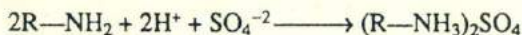


Zeolite removes both carbonate and non-carbonate hardness and can last for a long time.

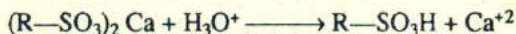
(6) *Synthetic Ion-exchangers* : Synthetic ion-exchangers of organic and inorganic origin have been developed which remove both cations and anions from hard water. The process of removing both the cations and anions from water by ion-exchangers is known as *demineralization*. Water is thus demineralized with the help of a combination of cation and anion exchangers. Thus, the cation exchanger containing  $-\text{SO}_3\text{H}$  groups in the giant molecule exchange with metal ions in water (R represents the resin matrix) :



To remove  $\text{H}^+$  ion it is passed through a resin bed which removes both  $\text{H}^+$  and  $\text{SO}_4^{-2}$  ions, e. g., polymers having basic amino group :

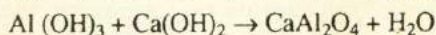
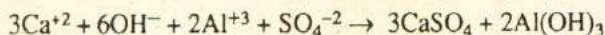
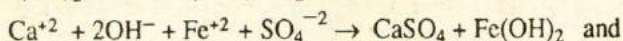


This process compares with that of distillation of water and this is now widely used for laboratory, domestic and industrial uses. Both the ion-exchangers can be regenerated by treatment with acid and basic solution respectively. Thus,



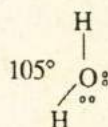
Thus the ions  $\text{Ca}^{+2}$  and  $\text{SO}_4^{-2}$  are swept away from the resins which is again ready for use.

Bacteria, viruses, small organisms and many organic matters are removed by chemical oxidation reactions using  $\text{CaCl}(\text{OCl})$ ,  $\text{NaOCl}$ ,  $\text{Cl}_2$  and  $\text{O}_3$ . Much of the suspended matter is removed by using gravel and sand. Very fine particles may be removed by formation of gelatinous or amorphous precipitate which coagulate the particles.  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_2$  are generally used in the forms of combination of  $\text{Ca}(\text{OH})_2$  and  $\text{FeSO}_4$ .  $\text{Ca}(\text{OH})_2$  however, may dissolve  $\text{Al}(\text{OH})_3$ .



### Structure of Water Molecule

The properties of water is closely connected with its structure. For example, pure water is a very poor conductor of electricity. This indicates that water molecule is composed of covalent bonds. Water has a high dipole moment. This indicates that bonds between H and O in  $\text{H}_2\text{O}$  are not linear like  $\text{H}-\text{O}-\text{H}$ . Because in this case the dipole moment would be negligible or zero. The two hydrogen atoms are actually bonded with oxygen at an angle of about  $105^\circ$  as shown below :—



It is obvious that the charges are unequally distributed in the molecule, oxygen containing more electrons forms the negative part and hydrogen the positive part of the molecule giving a dipole. This explains both dipole moment and dielectric properties of  $\text{H}_2\text{O}$ . The positive and negative parts are joined as part of one molecule and do not move in an electric field as in the case of ions.

X-ray studies indicate that the two hydrogen atoms are situated at the corner of a tetrahedron (distorted) with oxygen at the centre as shown in Fig. 11—?

The oxygen atom having lone pairs of electrons attract the hydrogen atoms of other  $\text{H}_2\text{O}$  molecules and hence the formation of hydrogen bond. Since this process is continued in all the molecules of water forming a giant molecule, water is called an *associated* liquid. This results in the formation of structure in



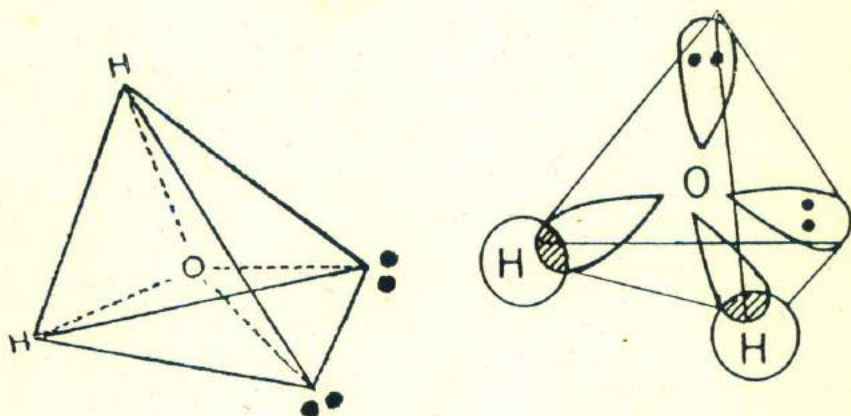
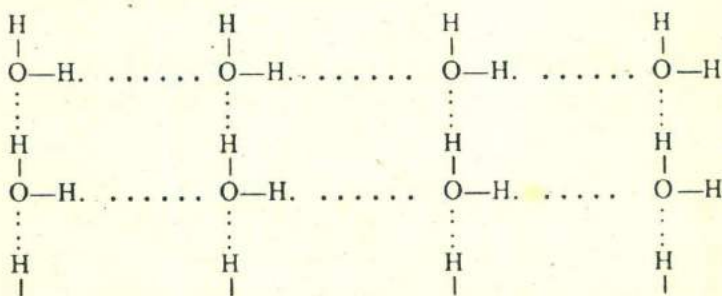


Fig. 11—2. (a) Tetrahedral structure of water molecule. (b) Overlap of hydrogen s orbitals with  $sp^3$  orbitals of oxygen in  $H_2O$ .

which each oxygen is surrounded by four hydrogen atoms in three dimensional pattern. A two-dimensional representation is given below. This tetrahedral structure is also shown by solid water (ice).



In ice, combination of the  $OH_4$  tetrahedra through the corners in three-dimensions gives rise to empty hexagonal spaces; because of this, ice has low density and floats on water.

Each oxygen atom in ice crystal is bonded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. The hexagonal empty space in ice is shown in two-dimensional pattern in Fig. 11—3.

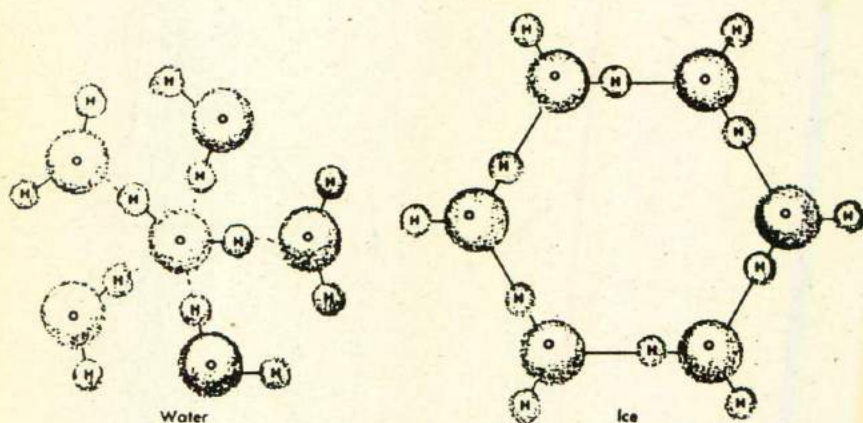
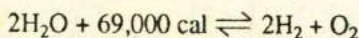


Fig. 11—3. Empty hexagonal space in two-dimensional pattern of ice. Compare with the plane geometry of liquid water.

### Chemical Properties of Water

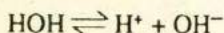
Water has a variety of chemical properties and, in fact, it is more active than what it actually appears.

1. **Thermal stability** : Water has great thermal stability and is not easily decomposed into its elements. The heat of decomposition of water is very high :



and at a temperature of  $272^\circ\text{C}$ , only 11.1% of water is decomposed. Compounds which are not easily decomposed into its elements are called thermally stable.

2. **Ionization** : Water is a poor conductor of electricity because it is only

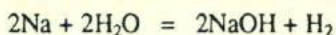


very slightly ionized in which hydrogen and hydroxyl ions have equal concentrations and it is, therefore, *neutral*. Any solution in water having hydrogen ion and hydroxide ion of equal concentrations is also called a *neutral solution*. Solution, in which hydrogen ion concentration is more than hydroxide

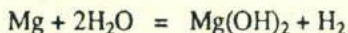
ion, is termed as *acidic*. A solution having hydrogen ion concentration less than hydroxide ion is called a *basic solution*.

### 3. Action of water with elements

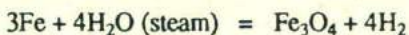
(a) *With metals* : Electropositive metals reacts with water violently. Thus Na, K, Ca etc. give vigorous reaction liberating hydrogen :



Magnesium reacts with hot water :



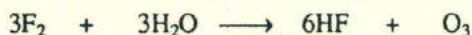
Heavy metals such as Fe, Zn, react with steam when hot :



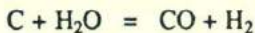
(b) *With non-metals* : Electronegative elements react with water at ordinary temperature. Thus  $\text{Cl}_2$ ,  $\text{Br}_2$  react with water to give—



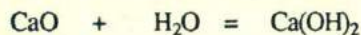
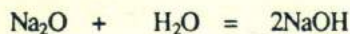
Fluorine reacts violently with water which actually burns in fluorine liberating  $\text{O}_2$  and  $\text{O}_3$  :



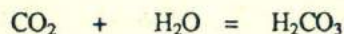
Nonmetals, such as carbon, react with steam at red hot condition :



4. *Action with oxides* : Basic oxides give metallic hydroxides which, when soluble, are strong bases :



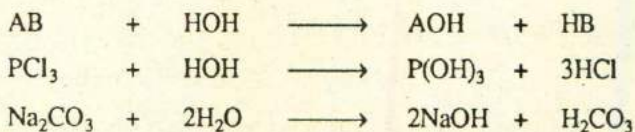
Acidic oxides react with water to form acids :



**5. Action with compounds :** On crystallisation from aqueous solutions a number of compounds, form hydrates. These are addition compounds with water which may be present in various modes of combination :



**6. Hydrolysis :** The double decomposition of a compound with water is called *hydrolysis*. Thus,



**7. Catalytic action of water :** Chemical reactions in nature involving decay, fermentation, digestion, growth etc. do not normally take place in absence of water. Intensive drying of some reactive gases makes them devoid of chemical activity. They react only in presence of small quantity of water. Thus intensively dried  $\text{H}_2$  and  $\text{Cl}_2$  do not react even in sunlight or ultra-violet light.  $\text{HCl}$  and  $\text{NH}_3$  do not react when dry But these gases react readily in presence of a slight amount of water. The exact mechanism of water behaving as a catalyst in chemical reactions has not yet been clearly explained.

**8. Water as a solvent :** Water is a very common solvent for universal use. But there are numerous compounds which are not soluble in water. The solvent property of water is limited by association due to hydrogen bonding and dissolution of a solute requires rupture of water molecules from this association in order to make room for a solute.

Molecular substances do not go into solution in water. Thus,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{C}_6\text{H}_6$  etc. are practically insoluble in water; the water structure remains intact in such cases. But solutions of compounds like  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_6\text{H}_{12}\text{O}_6$ ,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ,  $\text{NH}_3$  etc. in water are due to strong interactions because of the rearrangements of hydrogen bonds. Thus with  $\text{NH}_3$ , hydrogen bond is established between the N of  $\text{NH}_3$  and the O of  $\text{H}_2\text{O}$ . Similarly, the O of  $\text{CH}_3\text{OH}$  or  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  forms hydrogen bonds.

Most ionic compounds are soluble in water because of the dipole action of water molecule which enables the lattices of the ionic crystals to break apart into

ions, provided the lattice energies in the solids are overcome by the pull. Thus AgF is soluble in water whereas AgCl is not. NaCl is soluble in water whereas BaSO<sub>4</sub> is not.

The solubility of ionic solids in water depends mainly on the charges and the size of the ions in the ionic crystals. In fact, the explanation of solubility and insolubility of substances in water medium appears to pose complex questions and no simple satisfactory theory has yet been developed.

### HEAVY WATER

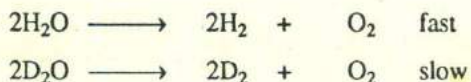
Water which is composed of deuterium oxide (D<sub>2</sub>O) molecules, is called heavy water.

In 1933, Urey showed that D<sub>2</sub>O is present in ordinary water to the extent of 1 part in 6,000 parts.

Water actually contains three types of molecules—HOH, HOD and DOD (ignoring tritium, T).

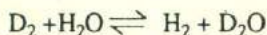
#### Preparation of Heavy Water

(1) Electrolysis of water containing N/2 alkali between nickel electrodes gives D<sub>2</sub>O. H<sub>2</sub>O molecules undergo electrolysis at a faster rate than D<sub>2</sub>O molecules :



After prolonged electrolysis the residual liquid remaining in the electrolytic cell on distillation becomes enriched in D<sub>2</sub>O. Pure D<sub>2</sub>O can be isolated in small amount on repeated processing.

(2) Exchange equilibrium process in which commercial hydrogen gas mixed with steam is passed over a catalyst to give D<sub>2</sub>O. The process is less costly and is applied in atomic energy work—D<sub>2</sub> in commercial hydrogen is exchanged with steam :



On condensing the steam to water it becomes enriched with  $D_2O$ . This water is then decomposed by the electrolytic process. The whole process is repeated until nearly pure  $D_2O$  (heavy water) is obtained.

**Properties :** Heavy water has the same appearance as the ordinary water. But there is marked difference between their physical properties.

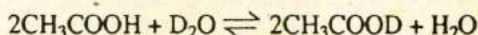
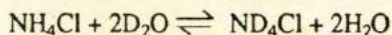
A comparison of certain physical constants of ordinary water and heavy water is shown in the Table 11.3

**Table 11.3. Physical properties of water and heavy water.**

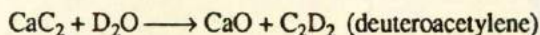
<i>Properties</i>	<i>Ordinary water</i>	<i>Heavy water</i>
1. Boiling point	100.0°C	101.4°C
2. Freezing point	0.0°C	3.8°C
3. Density g/cc. at 20°C	0.9982	1.05
4. Temperature of maximum density	4°C	11.6°C

### Exchange Reaction of Heavy Water

1. Hydrogen in any compound is exchanged with D :

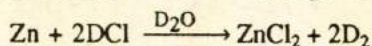
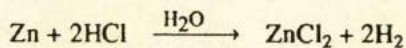


2. Pure compounds of D can be prepared by reactions similar to that of water. Thus,



3. **Tracer experiments :** Because heavy water,  $D_2O$ , is about 10% heavier than  $H_2O$  and can be readily distinguished from ordinary hydrogen by mass spectrograph or by weight, heavy water is useful as "tracer" in following the path of chemical reaction and also in physical changes such as digestion and metabolism in the body.

An example of a tracer experiment with  $D_2O$ , is the reaction between Zn and HCl solution in water :



Whether all the  $H_2$  comes from  $HCl$  or also from  $H_2O$  has been solved by tracing the reaction with  $D_2O$ . It has been found that  $H_2$  comes from both  $HCl$  and  $H_2O$ .

### Uses of Heavy Water

Heavy water is largely used to slow down fast neutrons in nuclear reactors and is one of the well-known *moderators* for atomic reactors. It is used for preparation of heavy hydrogen and for tracer studies,

### HYDROGEN PEROXIDE

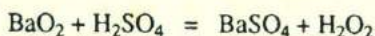
Hydrogen peroxide is one of the compounds containing oxygen-to-oxygen ( $-O-O-$ ) bonds. Very small amounts of hydrogen peroxide are found in dew, rain water and snow possibly due to cosmic radiation on oxygen.

### Preparation of Hydrogen Peroxide

Various methods of production of  $H_2O_2$  have been developed.

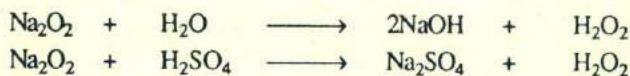
**1. From Barium Peroxide :** When  $BaO$  is heated in air, it is converted to  $BaO_2$  which in the hydrated condition forms  $BaO_2 \cdot 8H_2O$ .

$BaO_2$  is treated with dil.  $H_2SO_4$  solution by which  $H_2O_2$  is formed and remains in solution while insoluble  $BaSO_4$  is precipitated out :



$H_2O_2$  produced is dilute and unstable.

**2. From Sodium Peroxide :** Sodium peroxide,  $Na_2O_2$ , with cold water or dilute  $H_2SO_4$  gives  $H_2O_2$  :



$Na_2SO_4$  is removed by cooling the solution when the salt  $Na_2SO_4 \cdot 10H_2O$  is crystallised out.

**3. Electrolysis of  $H_2SO_4$  :** The modern process of producing  $H_2O_2$  is by electrolysis of solution of  $H_2SO_4$  or  $NH_4HSO_4$ . Electrolysis of  $H_2SO_4$  solution gives rise to the formation of perdisulphuric acid,  $H_2S_2O_8$ , at the anode





## Properties

Some of the physical properties of  $\text{H}_2\text{O}_2$  as compared with those of  $\text{H}_2\text{O}$  are given in Table 11.4.

**Table 11.4. Physical properties of  $\text{H}_2\text{O}_2$  compared to  $\text{H}_2\text{O}$**

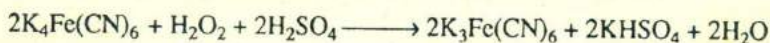
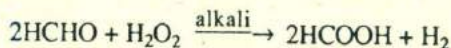
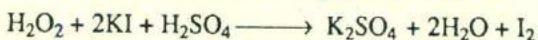
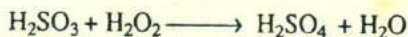
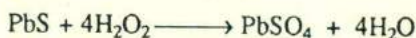
Properties	$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}$
Mol. wt.	34	18
m. p. ( $^{\circ}\text{C}$ )	0.9	0
b. p. ( $^{\circ}\text{C}$ )	151	100
Density g/cc.	1.46	1

Pure  $\text{H}_2\text{O}_2$  is thermally stable but in presence of impurities, even dust particles, it is dangerously explosive. It is stored with stabilizer (negative catalyst) such as a weak acid or an organic compound (acetanilide, glycerine). Heavy metal ions act as a positive catalyst and decompose  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O} + \text{O}_2$ .  $\text{H}_2\text{O}_2$  is miscible in water, alcohol and ether.

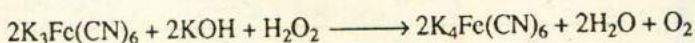
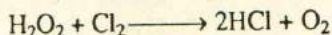
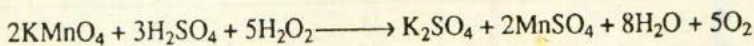
## Chemical properties of $\text{H}_2\text{O}_2$

The oxidation number of oxygen in  $\text{H}_2\text{O}_2$  is  $-1$  for each oxygen atom. This is not the normal oxidation number of oxygen in which it is not stable. The more stable oxidation number in which oxygen is stable is  $0$  or  $-2$ . Hence it is expected that  $\text{H}_2\text{O}_2$  will accept one electron to be present in  $-2$  oxidation state or will lose the one electron to have the  $0$  oxidation state. Hence  $\text{H}_2\text{O}_2$  acts both as an oxidizing agent (electron acceptor) and reducing agent (electron donor). The  $-\text{O}-\text{O}-$  linkage is one of the weakest covalent bonds and easily broken or converted to stable oxygen molecule.

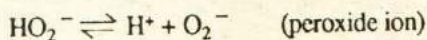
**$\text{H}_2\text{O}_2$  as an oxidizing agent:**  $\text{H}_2\text{O}_2$  acts as an oxidizing agent in all media, i.e., neutral or alkaline or acid solutions. A few examples are given below in the form of equations :



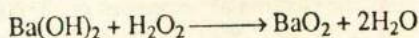
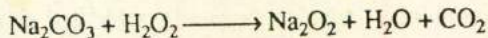
**H<sub>2</sub>O<sub>2</sub> as a reducing agent :** Reducing actions of hydrogen peroxide take place in acid, alkaline and neutral solutions, and gaseous oxygen is always evolved because H<sub>2</sub>O<sub>2</sub> is oxidized by loss of electron to form H<sup>+</sup> ion and O<sub>2</sub>. This happens in the case of reactions with powerful oxidizing agents. The following reactions are examples of H<sub>2</sub>O<sub>2</sub> as a reducing agent :



**H<sub>2</sub>O<sub>2</sub> as a weak acid :** Slight ionization of H<sub>2</sub>O<sub>2</sub> in water gives the following equilibrium equations :

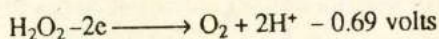
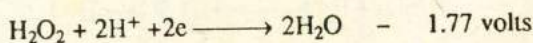


The acid character is shown in the evolution of CO<sub>2</sub> from Na<sub>2</sub>CO<sub>3</sub> and reaction with Ba(OH)<sub>2</sub>. It also gives acid salts such as NaHO<sub>2</sub>, NH<sub>4</sub>HO<sub>2</sub> etc. :



**Fenton's Reagent :** A solution of FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, is called Fenton's Reagent. It is used in organic chemistry for catalytic reactions such as polymerisation of acrylonitrile CH<sub>2</sub> = CH<sub>2</sub>—CN to its polymers. Neither FeSO<sub>4</sub>, nor H<sub>2</sub>O<sub>2</sub> alone has this property.

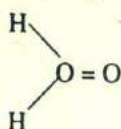
**Auto-oxidation or disproportionation of H<sub>2</sub>O<sub>2</sub> :** Hydrogen peroxide oxidizes Mn<sup>+2</sup> to MnO<sub>2</sub> and also reduces MnO<sub>2</sub> to Mn<sup>+2</sup> because of self-oxidation of H<sub>2</sub>O<sub>2</sub> :



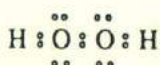
This property is due to the difference in the oxidation potential of the two processes.

**Structure of  $H_2O_2$** 

Formerly  $H_2O_2$  was regarded as having the formula, :



Although some of the properties such as reduction of  $H_2O_2$  are readily explained by the above structure, the experimental evidences show the presence of  $—O—O—$  chain. Thus  $H_2O_2$  is represented as  $H—O—O—H$ .  $H_2O_2$  is, therefore, known as dihydroxyl. The electronic structure of  $H_2O_2$  is given below :



But the two  $—OH$  groups in  $H_2O_2$  are not linear. The atoms actually lie in two planes as shown in Fig. 11—4.

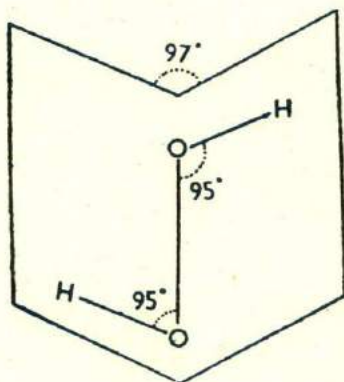
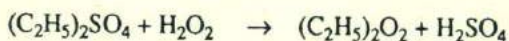


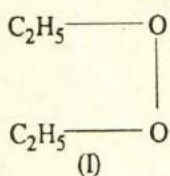
Fig. 11—4. Structure of  $H_2O_2$ .

The following reactions prove that  $H_2O_2$  has the structure containing peroxy  $—O—O—$  chain.

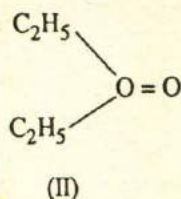
Diethyl sulphate reacts with  $H_2O_2$  to give diethyl peroxide :



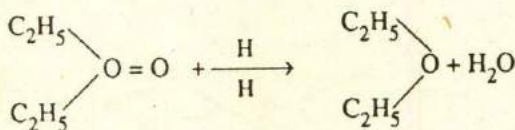
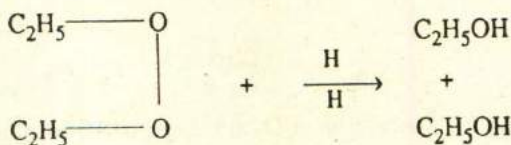
$(C_2H_5)_2O_2$  can have two structural formula as given by structures I and II.



or



If formula (I) is correct then on reduction with Zn and  $CH_3COOH$  it will form  $C_2H_5OH$  and if (II) is correct, the formation of ether,  $C_2H_5-O-C_2H_5$ , can be visualized.



In actual experiment only ethyl alcohol,  $C_2H_5OH$ , is formed. Hence  $H_2O_2$  has the formula  $H-O-O-H$ .

**Uses of  $H_2O_2$ :** (1) A 3% solution of  $H_2O_2$  is used as an antiseptic deodourizer, germicide and for bleaching.

(2) A 30% solution is used as a reagent in the laboratory as an oxidizing agent.

(3) Wool, hair, silk etc. are bleached by  $H_2O_2$ .

(4) 90%  $H_2O_2$  solution is used as high explosive and fuels in rockets and guided missiles.

(5) Polymerisation of organic substances containing  $C = C$  double bond is achieved by  $H_2O_2$ .

## QUESTIONS AND PROBLEMS

- Describe the methods of preparing Atomic Hydrogen and its properties, Explain Nascent Hydrogen, Atomic Hydrogen, Ortho and Para hydrogen.
- What are :
  - Deuterium,
  - Heavy water,
- Write a short note on heavy hydrogen.
- What is heavy water ? How does it differ from ordinary water ?
- Discuss the principles involved in the softening of hard water by various methods. Indicate the recent technique developed for this purpose.
- What are the special properties of  $H_2O_2$  ? How will you establish its structure ?
- What are the different oxidation states of hydrogen ? Give examples.
- Discuss some chemical properties of water. Why water is an associated liquid ?
- What are the different methods for the formation of  $H_2O_2$  ? How do you account for both the oxidizing and reducing properties of  $H_2O_2$  ? Illustrate with examples.
- Describe the production, reactions and uses of heavy water.
- Write a note on heavy hydrogen.
- Write short note on deuterium.
- Give short description of the preparation and uses of (a) hydrogen peroxide, (b) heavy water.
- Explain why  $H_2O$  is neutral.
- The molecular hydrides,  $H_2O$  and  $HCl$  react with each other in the following way:
$$HCl(g) + H_2O(l) \rightarrow H_3O^+ + Cl^-$$
Explain why the above reaction occurs.
- Write a chemical equation for the reaction of each of the following oxides with water and specify which are acidic and which are basic.
$$P_4O_{10} \quad CSO_2 \quad Li_2O \quad CO_2 \quad BaO$$
- Describe how would you convert polluted water into very pure water for use in refined chemical laboratories.

## CHAPTER 12

# THE PRINCIPLES OF METALLURGY

### Metals and Non-metals

The difference in properties between metals and non-metals lies in the fact that atoms of non-metals complete their valence level by sharing of electrons or by transfer of electrons from other atoms. For instance, halogens enter into chemical combination by taking up one electron from another atom or by sharing an electron pair. On the other hand, a metal normally enters into chemical combination by the loss of valence electrons. For instance, sodium loses one valence electron to form compounds. Metallic character decreases and non-metallic character increases with the increasing number of valence electrons. Also the metallic character increases with the increasing number of electron levels.

Looking into the Periodic Table there is no sharp dividing line between metals and non-metals as we progress across the periods of the Periodic Table and also down the groups. Many elements fall on the borderline and show both metallic and non-metallic characteristics. These are known as "metalloids". This class of elements include B, Si, Ge, As, Sb, Te etc. Of the 105 known elements only 17 shows primarily non-metallic character, 8 are metalloids and 70 are metals.

The main differences between the metals arise due to the differences in important physical and chemical properties. Metals are good conductors of heat and electricity and have familiar metallic lustre. Non-metals are poor conductor and have no lustre. Metallic crystals contain metallic bonds between atoms. Non-metals consists of covalent molecules or monoatomic gases. Metals are electropositive and their hydroxides are basic or amphoteric. Non-metals are

electronegative and their hydroxides are acidic. Metals have low ionization potentials and form cations. Non-metals have high electron affinity and form anions. Metals are good reducing agents and non-metals are good oxidising agents.

### Occurrence of the Metals

Metals occur in nature mainly in two states :—

(i) *Free state* : Less active metals below hydrogen in the activity series sometimes are found in the free state or *native state*. These are Cu, Ag, Au, Pt, etc.

(ii) *Combined state* : In most cases metals are found in the combined state with other substances which are called *minerals*.

The natural minerals in which metals or their compounds occur in the earth and from which the metals may be extracted economically are known as *Ores*.

Ores generally contain large percentages of rocky and earth materials which are called *gangue*.

### Metallurgy

The processes involved in the production of pure metals from their ores are known as Metallurgy. A general review of principles of metallurgy are given briefly as follows :—

The metallurgical operation will necessarily depend on the nature of the ore. The ores always require certain preliminary treatments known as ore dressing. These are :

(1) *Crushing, grinding and pulverizing of the ore* : This treatment is necessary for the reactivity and increasing the surface area of the ore for making it more reactive towards chemical attack.

(2) *Concentration of the ore* : This is done for removing more of the gangue. The concentration may be achieved by several techniques, such as,

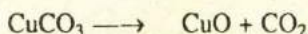
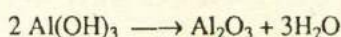
(a) *Washing* : Washing away the lighter particles of gangue with water on slightly inclined shaking table as in the case of gold and tin oxide.

(b) *Magnetic separation* : Metal-bearing ores which are attracted by a magnetic field are separated from non-magnetic impurities by passing the pulverized ore through a magnetic field. Magnetic iron ore may be concentrated in this manner.

(c) *Electrostatic separation* : The separation by means of electrostatic field may also be employed in some cases as in the case of magnetic separation. The charged particles are separated as in the case of selenium and arsenic.

(d) *Froth floatation process* : Finely ground ore is mixed with water in a tank to which some oil, such as pine oil, has been added. Air is blown to the mixture producing a great deal of froth. The metal-bearing ore particles adhere to the air bubbles in froth which floats on the surface. The gangues (impurities such as sand, clay, rock) which are wetted by water but not by the oil, sink to the bottom of the tank. The froth containing the ore is removed. This contains the metal in highly concentrated form. This method is particularly suitable for the sulphide ores of Zn, Pb, Cu and also used for carbonates and silicates.

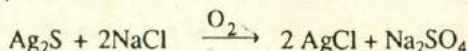
(3) *Calcination* : The process involves the preliminary heating of the ore in order to convert it to compounds which are more easily reduced to give the metals. Thus, ores containing moisture, hydroxides, carbonates are heated to expel the volatile matter and to decompose the compounds such as carbonate :



(4) *Roasting* : In this process the ore is heated to a high temperature in air either alone or with additional substances to effect chemical changes. This involves oxidizing, roasting, blast roasting, chloridising and sulphating roasting. The oxidizing and blast roasting are done to remove S, As, Sb from the ores in a blast of air and convert the ores to oxides :



Sometimes the ore is converted to chloride by heating with NaCl in presence of air. Thus,





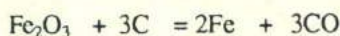
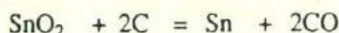
Sulphating is the roasting to convert a sulphide ore, such as  $\text{CuS}$ , to sulphate:



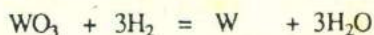
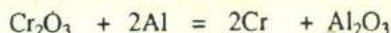
(5) **Smelting**: The process of extraction of the metal in the fused state from the roasted ore is known as smelting. This is based on the chemical reaction involving reduction of the metallic compound. Most metal ores even after roasting contain some gangues. This is removed by adding substances which combine with the impurities. These substances are known as *flux* which combine with the impurities and form fused mass known as *slag* which separates out. Thus,  $\text{Fe}_2\text{O}_3$  is used as flux in the smelting of  $\text{Cu}$ ,  $\text{Pb}$  ores.  $\text{Fe}_2\text{O}_3$  combines with  $\text{SiO}_2$  and form  $\text{FeSiO}_3$  as slag which is easily separated. Similarly,  $\text{CaF}_2$  is a good flux in smelting. Other oxides, such as  $\text{ZnO}$ ,  $\text{BaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  are also used as fluxes which combine with  $\text{SiO}_2$  to form silicates as slag. The slag is easily removed off from the molten metal because of the difference in the densities.

The methods generally employed for smelting of various ores are :

(a) Oxide ores are generally reduced with  $\text{C}$  :



(b) Other reducing agents such as  $\text{H}_2$ ,  $\text{Fe}$  and  $\text{Al}$  are also used;



(c) Electrochemical methods are used for the halides of  $\text{Na}$ ,  $\text{K}$ ,  $\text{Mg}$ ,  $\text{Al}$ ,  $\text{Ca}$  etc. Thus  $\text{Al}$  is produced from  $\text{Na}_3\text{AlF}_6$  or from  $\text{Al}_2\text{O}_3$  to which  $\text{NaF}$  and  $\text{AlF}_3$  have been added. The electrochemical process requires certain conditions to be followed rather rigidly. The selection of electrodes, the temperature of fusion, the voltage and current are some of the factors. To lower the fusion temperature and conduct electricity, proper fluxes are added.

(d) Metals occurring in the native state are separated by some convenient methods such as heating the ore and allowing the molten metal to drain away.

(6) *Hydrometallurgy* : In this process the metals present in the ore is made to go into aqueous solution due to some chemical changes. The metals is then separated by suitable means. Thus Ag is dissolved in dilute solutions of NaCN in presence of air forming  $\text{NaAg}(\text{CN})_2$  from which Ag is precipitated out by adding Zn.

(7) *Refining of metals* : Smelting process generally gives impure form of metals which require further purification. The contamination generally consists of small quantities of other metals and non-metals such as Si, P, S, C etc. The process of removing the last traces of impurities from the smelted metal is known as refining. Various methods of refining are employed for the purification.

(a) Volatile and low boiling metals such as Zn and Hg are purified by distillation.

(b) By simple oxidation the impurities oxidize away in the molten state when a blast of air is passed in a suitable furnace. Thus S, C, P etc. can be easily removed from metals.

(c) Liquation process is used when the impurities are not easily fusible than the metal. Thus Sn can be fused on an inclined table and thus flows away from higher melting impurities. Similarly, Zn is separated from Pb at the melting point of Zn. The heavier Pb which does not melt at that temperature settles down to the bottom whereas molten Zn floats on top and is separated.

(d) Electrolytic method is the most used method for the refining of many metals. The impure metal is made the anode and the pure metal the cathode of an electrolytic cell. Thus Cu, Au, Zn etc. are refined.

The different types of furnaces and extraction appliances which are used in smelting process have been described at the appropriate places in this book. Some of the well-known furnaces are : (i) kiln, (ii) blast furnace, (iii) reverberatory furnace, (iv) muffle furnace, (v) tube furnace, (vi) rotary kiln furnace, (vii) electric furnace of various designs, (viii) various types of electrolytic cells.

## QUESTIONS AND PROBLEMS

1. Describe with examples, the general principles underlying the extraction of metals from their ores.
2. What are the properties which distinguish metallic elements from non-metallic elements ?
3. Explain the concentration of sulphide ores by floatation process.
4. Write notes on the following :—
  - (a) Smelting,
  - (b) Hydrometallurgy,
  - (c) Roasting of ores,
5. What are the process for concentrating the ores from the natural minerals ?
6. Why is it necessary for the purification of the metals extracted from the ores? Discuss some of the methods of refining.
7. Describe the differences between metals and non-metals.