UNIT 3   HYDROGEN

Structure

3.1 INTRODUCTION

In Units 1 and 2, you studied the periodic table and periodicity in the properties of elements. You must have noticed that the very first element in the periodic table is hydrogen. Hydrogen atom consists of only one proton and one electron. Hydrogen forms more compounds than any other element. Besides this, you should know that hydrogen is the most abundant of all the elements in the universe (73.9% by weight) and is the principal element in the solar atmosphere. However, it is much less abundant (0.14% by weight) on earth, where it exists only in the combined state. Keeping in view the importance of hydrogen, we will discuss some important aspects of the chemistry of hydrogen in this unit. Here, we will discuss its position in the periodic table, isotopes, manufacture, uses and hydrides in general. The specific hydrides, e.g., boranes, ammonia will be dealt with in their corresponding groups in the following units.

Objectives

After studying this unit you should be able to:

- justify the position of hydrogen in the periodic table,
- describe isotopes of hydrogen,
- differentiate between *ortho* and *para* forms of hydrogen molecule,
- describe the various methods for the manufacture of hydrogen,
- discuss the importance of hydrogen as a fuel,
- classify the binary hydrides according to their structure, and
- describe the conditions that are necessary for hydrogen bonding to occur and the characteristic properties of hydrogen bonded systems.

3.2 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Position of hydrogen in the periodic table is of particular interest. Hydrogen is the first element of the periodic table having electronic configuration $1s^1$. On one hand this configuration is similar to the outer electronic configuration (ns^1) of the alkali metals. On the other hand, like halogens, it is one electron short of the corresponding inert gas helium. Hydrogen, therefore, shows some properties similar to alkali metals, while some others are similar to those of the halogens.

Like alkali metals, hydrogen forms halides, oxides and sulphides. You know, the alkali metals have a high tendency of losing their outermost electron to form M^+ ions. Hydrogen also forms H^+ ion, but it does not do so, under normal conditions, because the ionisation energy of hydrogen (1312 kJ mol^{-1}) is much higher than that of the alkali metals, e.g., Li, 520; Na, 495; K, 418 kJ mol^{-1}.

In its high ionisation energy, hydrogen resembles more with halogens. The first ionisation energies of fluorine, chlorine, bromine and iodine are 1618, 1255, 1142 and 1007 kJ mol^{-1}. respectively. Due to its high ionisation energy, hydrogen forms a large number of covalent compounds by sharing a pair of electrons. Hydrogen like halogens forms a diatomic molecule by sharing a pair of electrons between the two atoms. By picking up an electron, hydrogen forms the hydride ion (H^-), just like the halogens form the halide ion (X^-).

From the above discussion, it is clear that hydrogen resembles both the alkali metals as well as the halogens. So, hydrogen can be placed with either of them in the periodic table. However, conventionally, it is kept along with the alkali metals in group 1 in the periodic table.

SAQ 1

a) Why does hydrogen resemble the alkali metals?

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b) Explain the formation of hydride ion.

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3.3 ISOTOPES OF HYDROGEN

You have studied that atoms of an element which have the same atomic number but different mass numbers are called **isotopes**. Hydrogen has three different isotopes having mass numbers, 1, 2 and 3, called ordinary hydrogen or protium ^1H, **deuterium** (D) or ^2H and **tritium** (T) or ^3H respectively. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen has no neutrons, deuterium has one and tritium has two neutrons in the nucleus (Fig. 3.1).

Deuterium is also called heavy hydrogen. These isotopes have same electronic configuration and therefore their chemical properties are almost the same. The only difference is in the rate of reactions. For example, hydrogen has a lower energy of activation than deuterium in its reaction with halogens and therefore, reacts faster.

However, the physical properties of hydrogen, deuterium and tritium differ considerably due to their large mass differences. Some of the important physical properties of hydrogen, deuterium and tritium are tabulated in Table 3.1.
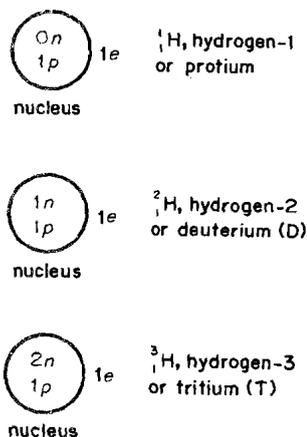

On 1p nucleus — 1e — ^1_1H, hydrogen-1 or protium

1n 1p nucleus — 1e — ^2_1H, hydrogen-2 or deuterium (D)

2n 1p nucleus — 1e — ^3_1H, hydrogen-3 or tritium (T)

Fig. 3.1: Isotopes of hydrogen.

3.3.1 Deuterium Compounds

Naturally occurring hydrogen contains 0.0156% deuterium. Like water, H_2O, which is the oxide of hydrogen, deuterium also forms an oxide, D_2O, which is known as **heavy water**. It can be obtained from ordinary water which contains 0.016% of deuterium oxide, either by fractional distillation or by electrolysis. Hydrogen is liberated more quickly than deuterium at the cathode and the residual liquid continuously gets richer in deuterium content on prolonged electrolysis. We can obtain virtually pure deuterium oxide. D_2O. by continuous electrolysis of water. Deuterium oxide is used as a moderator in nuclear reactors since it slows down neutrons quickly. Physical properties of H_2O and D_2O also differ from each other as in the case of H_2 and D_2. These are given in Table 3.2.

**Table 3.1: Properties of atomic and molecular hydrogen**

Properties	Hydrogen	Deuterium	Tritium
Natural abundance (%)	99.985	0.0156	10^{-15}
Atomic weight (C = 12)	1.008	2.014	3.016
Boiling point (K)	20.4	23.6	25.0
Melting point (K)	13.8	18.5	20.62
Density of liquid at b.p., H_2 ($10^3 \times$ kg m^{-3})	0.071		
*Ionisation energy, (kJ mol^{-1})	1312		
*Electron affinity, (kJ mol^{-1})	−73		
*Electronegativity (Pauling Scale)	2.1		
*Bond length, H_2(g) (pm)	74.9		
*Bond energy (ΔH_{atom}), H_2 (kJ mol^{-1})	436		
*Ionic radius, H$^-$ (pm)	208		
*Covalent radius (pm)	37		
*van der Waals radius (pm)	120		

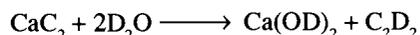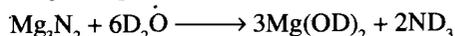* As expected hydrogen, deuterium and tritium will have similar values.

Table 3.2: Properties of water and heavy water

	H_2O	D_2O
Density at 293K (10^3 x kg m^{-3})	0.9982	1.1059
Melting point (K)	273.16	276.97
Boiling point (K)	373.16	374.58
Temperature of maximum density (K)	277.04	284.39
Dielectric constant at 298 K	78.39	78.06

Hydrogen and deuterium are obtained by similar methods.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2Na + 2D_2O \longrightarrow 2NaOD + D_2$$
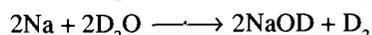
Many deuterium compounds, similar to those of hydrogen, are obtained from D_2O.

$$PCl_3 + 3D_2O \longrightarrow D_3PO_3 + 3DCl$$

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

We can also employ exchange reactions like those given below for the preparation of deuterium compounds:

$$NaOH + D_2O \longrightarrow NaOD + HDO$$

$$NH_4Cl + D_2O \longrightarrow HDO + NH_3DCl$$
$$\downarrow D_2O$$
$$NH_2D_2Cl$$
$$\downarrow D_2O$$
$$ND_4Cl \xleftarrow{\quad D_2O \quad} NHD_3Cl$$
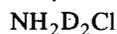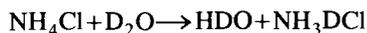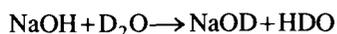
## 3.3.2 Tritium

Tritium differs from the other two isotopes of hydrogen in being radioactive. Naturally occurring hydrogen contains nearly 10^{-15} % tritium.The concentration of tritium increased by over a hundredfold when thermonuclear weapon testing began in 1954 but is now subsiding again as a result of the ban on atmospheric weapon testing.
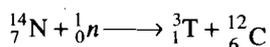
Tritium was first obtained synthetically by the bombardment of deuterium compounds such as $(ND_4)SO_4$ with fast deuterons.
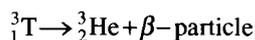
$$^2_1D + ^2_1D \longrightarrow ^3_1T + ^1_1H$$

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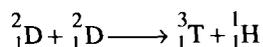
It is now prepared on a large scale by irradiation of lithium-6 in the form of Li/Mg alloy of LiF with slow neutrons in a reactor.

$$^6_3Li + ^1_0n \longrightarrow ^3_1T + ^4_2He$$
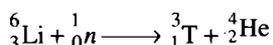
The following reaction occurs in nature:

$$^{14}_7N + ^1_0n \longrightarrow ^3_1T + ^{12}_6C$$

Tritium is radioactive and decays by emission of a beta-particle. Its half life period is 12.3 years.

$$^3_1T \longrightarrow ^3_2He + \beta-\text{particle}$$

Tritium can be easily incorporated into biological molecules because it behaves chemically, just like ordinary hydrogen. The radiation that tritium gives off within an organism, as a result of its decay, can cause many diseases, including cancer.

SAQ 2
Explain why chemical properties of isotopes of hydrogen are similar.

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3.4 *ORTHO* AND *PARA* HYDROGEN

Ortho and *para* are the two **different forms of hydrogen molecule**. We can explain this on the basis of the direction of the nuclear spin. When two hydrogen atoms combine to form a molecule, there are two possibilities. The two nuclei will either spin in the same direction (parallel spins) to give the form called *ortho* **hydrogen**, or they would spin in the opposite directions to give *para* **hydrogen** (Fig. 3.2). This phenomenon is known as **spin isomerism**.

Parallel spin
(*ortho* hydrogen)

Opposite spin
(*para* hydrogen)

Fig. 3.2: *Ortho* and *para* forms of hydrogen.

Due to spin isomerism, difference in their internal energy arises causing differences in physical properties like boiling point, specific heat and thermal conductivity of the *ortho* and *para* forms of hydrogen. *Para* hydrogen has a lower **internal energy** than that of *ortho* hydrogen. Hydrogen gas is an equilibrium mixture of *ortho* and *para* hydrogen. The ratio of *ortho* to *para* hydrogen varies with temperature as shown in Fig.3.3.

Internal energy is the sum total of translational, rotational, vibrational, and electronic energy of the molecule.

Evidently, this ratio increases with the rise in temperature upto a temperature of about 300 K (27°C) and remains constant thereafter. The percentage of *ortho* hydrogen at 300 K and above is 75%. This means that it is not possible to get 100% *ortho* hydrogen at any
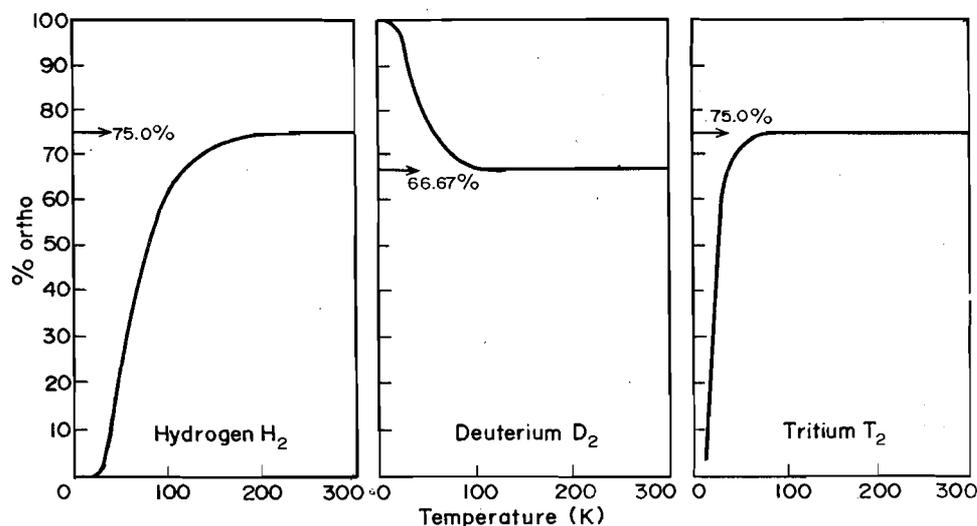
Fig. 3.3: *Ortho-para* equilibria for H_2, D_2 and T_2.

temperature. The equilibrium mixture of *para* and *ortho* hydrogen changes to almost 100% *para* hydrogen when cooled nearly to absolute zero. *Para* hydrogen is stable for weeks in the absence of catalysts like activated charcoal, Fe, Ni, Pt, O_2, NO_2, etc., which catalyse the conversion of *para* to *ortho* hydrogen. Similarly, deuterium and tritium also exhibit spin isomerism and exist in *ortho* and *para* forms. However, the ratio of *ortho* and *para* forms in deuterium and tritium is different from that in hydrogen. The variation of *ortho/para* ratio at different temperatures is also different. If you look carefully in Fig. 3.3, you will see that tritium resembles hydrogen more closely than deuterium in this respect.

SAQ 3
Write 'T' for true and 'F' for false in the given boxes for the following statements about *ortho* and *para* forms of hydrogen:

i) *Ortho* and *para* hydrogen are different due to difference in their nuclear spins. ☐

ii) *Ortho* and *para* hydrogen are different due to difference in their electron spins. ☐

iii) Physical properties of *ortho* and *para* hydrogen are similar. ☐

iv) *Para* hydrogen is more stable at lower temperatures. ☐

v) At 100 K percentage of *ortho* hydrogen in the mixture is 70%.! ☐

3.5 MANUFACTURE OF HYDROGEN

So far we studied the various isotopes of hydrogen and also the two forms of the hydrogen molecule. Hydrogen is an important industrial chemical about which you will study more in the following section. Let us start with its manufacture.

Water is the natural abundant source for the manufacture of hydrogen. Reduction of water to hydrogen can be carried out chemically as well as electrolytically. The common reducing agents are coke, carbon monoxide or hydrocarbons which reduce water to hydrogen at high temperatures.

Residue left from distillation of coal in the absence of air is known as coke.

Hydrogen is manufactured by allowing steam to react with red hot coke at about 1250K.

$$C + H_2O \xrightarrow{\sim 1250K} CO + H_2$$
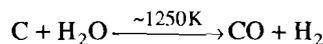
This mixture of CO and H_2 is also known as **water gas** and the reaction is referred to as water gas reaction. As this mixture ($CO + H_2$) is used for the synthesis of methanol and a number of hydrocarbons, this is also called **synthesis gas**.

Hydrogen is now produced by the reaction of natural gas (chiefly methane) with steam in presence of a nickel catalyst.

$$CH_4 + H_2O \xrightarrow[920-1170K]{Ni\ catalyst} CO + 3H_2$$
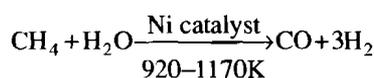
Similar reaction can occur with other hydrocarbons also. In both the above processes CO is converted to CO_2 and more hydrogen generated by passing the gases ($CO + H_2$) and steam over iron oxide or cobalt oxide catalyst.

$$CO + H_2O \xrightarrow[450-650K]{catalyst} CO_2 + H_2$$
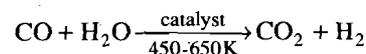
Hydrogen and carbon dioxide can be easily separated from each other by bubbling the gas mixture through water in which CO_2 is fairly soluble and H_2 virtually insoluble.

At higher temperatures, in the presence of catalysts (silica, alumina) hydrocarbons decompose and rearrange in what are called cracking reactions. These reactions, which are used in refining of petroleum, produce hydrogen as a by-product. One example of simple cracking reaction is the cracking of propane:

$$2CH_3 - CH_2 - CH_3 \xrightarrow[catalyst]{875K} CH_4 + CH_2 = CH_2 + CH_3 - CH = CH_2 + H_2 \uparrow$$
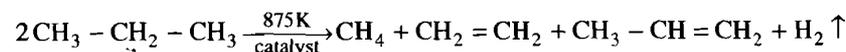
Electrolysis of acidified water using platinum electrodes is a convenient source of hydrogen (and oxygen). On a large scale, very pure hydrogen (>99.95%) can be obtained from the electrolysis of aqueous solutions of barium hydroxide between nickel electrodes.

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But hydrogen obtained by electrolysis of water is relatively expensive because of the cost of the electrical energy. However, hydrogen is economically obtained as a by-product in the electrolysis of brine solution in the manufacture of sodium hydroxide.

During electrolysis there is a competition at the anode between the oxidation of chloride ion and the oxidation of water.

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e$$
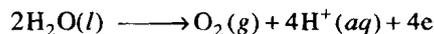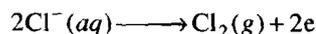
When a concentrated salt solution (brine) is used, the first reaction is the one that is observed. At the cathode, the reaction is the reduction of water because it is more easily reduced than Na^+.

$$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-(aq)$$
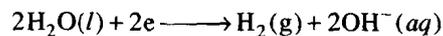
When we combine the anode and cathode reactions and include the Na^+ ion (which is actually a spectator ion), the overall reaction becomes
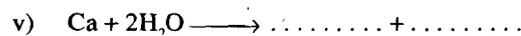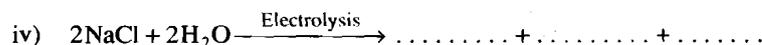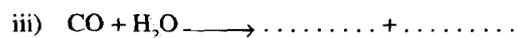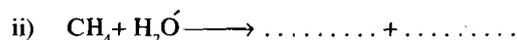
$$2Na^+ + 2Cl^- + 2H_2O \longrightarrow Cl_2(g) + H_2(g) + 2Na^+ + 2OH^-$$

In the laboratory hydrogen can be prepared by the reaction of water or dilute acids on electropositive metals such as alkali metals, alkaline earth metals, the metals of Group 12 (e.g., Zn) and the lanthanides. The reaction can be explosively violent with alkali metals (e.g., K, Rb). Convenient laboratory methods employ sodium amalgam or calcium with water, or zinc and tin with hydrochloric acid.

SAQ 4

Complete the following chemical reactions which take place during the formation of hydrogen:

i) $C + H_2O \longrightarrow$ .... + ...

ii) $CH_4 + H_2O \longrightarrow$ .... + ...

iii) $CO + H_2O \longrightarrow$ .... + ...

iv) $2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}}$ .... + ... + ...

v) $Ca + 2H_2O \longrightarrow$ .... + ...

3.6 PROPERTIES OF HYDROGEN

Hydrogen is the lightest element known. It is a colourless, odourless and tasteless gas. Hydrogen molecule is thermally stable and has little tendency to dissociate at normal temperatures, since the reaction

$$H_2(g) \longrightarrow 2H(g), \quad \Delta H = 436 \text{ kJ mol}^{-1}$$
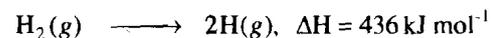
is highly endothermic. However, at high temperatures in an electric arc or under ultraviolet light, it does dissociate. The **atomic hydrogen** produced, exists for less than half a second after which it recombines to give molecular hydrogen and liberates a large amount of energy (436 kJ mol^{-1}) in the form of heat. Most of the transition metals catalyse the recombination reaction of atomic hydrogen.

Atomic hydrogen is a powerful reducing agent and reduces copper, silver and mercury salts to the metallic state. It combines with alkali metals to form hydrides, which we shall discuss in Section 3.8, reduces sulphur to hydrogen sulphide and carbon monoxide to formaldehyde. It also reacts with oxygen at room temperature to form hydrogen peroxide. The reactions can be written as:

$$AgNO_3 + H \longrightarrow Ag + HNO_3$$

$$Na + H \longrightarrow NaH$$

$$CO + 2H \longrightarrow HCHO$$

$$O_2 + 2H \longrightarrow H_2O_2$$
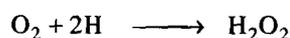
Atomic hydrogen is generally produced by passing ordinary hydrogen through an electric arc maintained between two tungsten electrodes. The atoms set free are carried away by a

stream of incoming hydrogen gas. These free atoms recombine at once on coming in contact with a metallic surface liberating a large amount of heat and thus raising the temperature of the metal very high, say to 4000-5000K. This principle is utilised in making of the 'atomic hydrogen welding torch' (Fig. 3.4). It provides an opportunity of welding at a very high temperature but in a reducing atmosphere.

Despite fairly high bond dissociation energy of hydrogen molecule, it is moderately reactive because hydrogen forms strong bonds with many other elements. It reacts with almost all elements except the noble gases. Hydrogen reacts with alkali and alkaline earth metals by accepting an electron to form ionic hydrides, e.g., KH and CaH_2. With non-metals, it forms covalent hydrides, e.g., NH_3, H_2O and HF. In Section 3.8, you will study more about the hydrides.
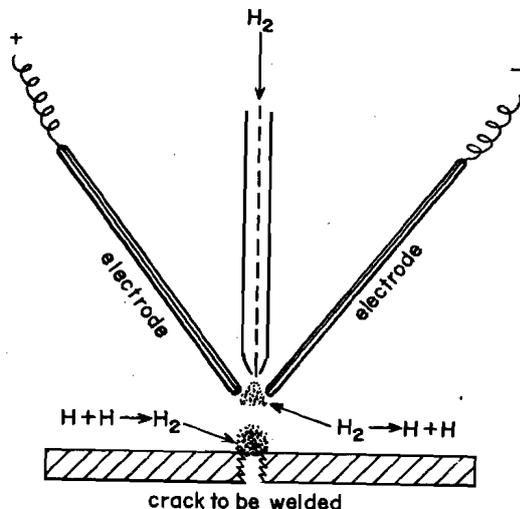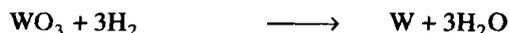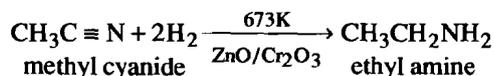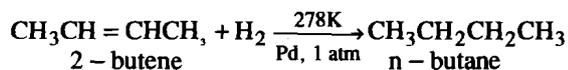

Fig.3.4: Atomic hydrogen welding torch.

Hydrogen is easily oxidised to water and; therefore, it acts as a very good reducing agent in a variety of situations. Hydrogen is used in metallurgy to reduce metal oxides to metals in cases where carbon cannot be used because the metal, e.g., Mo and W can form a carbide:

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

$$(NH_4)_2 MoO_4 + 3H_2 \longrightarrow Mo + 2NH_3 + 4H_2O$$

Hydrogen adds on the multiple bonds in organic compounds. In the presence of catalysts such as finely divided nickel, palladium or mixtures of metal oxides, unsaturated organic compounds are thus reduced to saturated compounds. For example,

$$CH_3CH = CHCH_3 + H_2 \xrightarrow[\text{Pd, 1 atm}]{278K} CH_3CH_2CH_2CH_3$$
$$\qquad 2-\text{butene} \qquad\qquad n-\text{butane}$$

$$CH_3C \equiv N + 2H_2 \xrightarrow[\text{ZnO/Cr}_2O_3]{673K} CH_3CH_2NH_2$$
$$\text{methyl cyanide} \qquad\qquad \text{ethyl amine}$$

Catalytic hydrogenation of unsaturated liquid vegetable oils to solid edible fats illustrates the industrial application of the reduction reaction; as the reduction of an oleate (ester of oleic acid) to the corresponding stearate (ester of stearic acid) would show:

$$CH_3(CH_2)_7 CH = CH(CH_2)_7 COOR + H_2 \longrightarrow CH_3(CH_2)_{16} COOR$$
$$\qquad\qquad \text{Oleate} \qquad\qquad\qquad\qquad \text{Stearate}$$

Hydrogen reacts with carbon monoxide in the presence of catalysts to form methanol:

$$CO + 2H_2 \xrightarrow{\text{cobalt}} CH_3OH$$
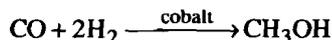
This reaction is known as hydroformylation reaction and is used in industrial preparation of methanol.

SAQ 5

Write chemical equations for the following reactions:

i)   Formation of methanol from coal

. . . .

. . . .

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ii)   Reduction of methyl cyanide

....

iii) Conversion of oleic acid into stearic acid

....

iv)   Reduction of ammonium molybdate to molybdenum

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3.7 USES OF HYDROGEN

Hydrogen is a very important industrial chemical. The largest single use of hydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers. As described in Section 3.6, hydrogen is used in the hydrogenation of vegetable oils, and manufacture of methanol. It is also used in metallurgy to reduce metal oxides to metals in special cases, e.g., Mo and W.

In spacecrafts, hydrogen gas is used in fuel cells (Fig. 3.5) for generating electrical energy and for providing clean drinking water to the astronauts. In a fuel cell, electrical energy is generated by the reaction of hydrogen and oxygen without evolution of any heat. This is sometimes called "**cold combustion**". A hydrogen-oxygen fuel cell may have an alkaline or acidic electrolyte. Figure 3.5 shows a hydrogen-oxygen fuel cell with porous carbon electrodes and KOH as electrolyte.
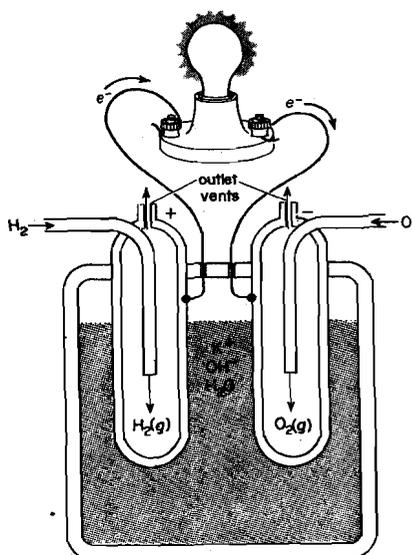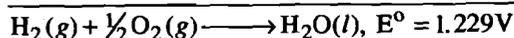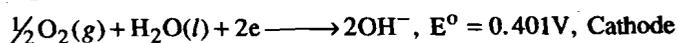

Fig. 3.5: A hydrogen-oxygen fuel cell with KOH electrolyte and porous carbon electrodes.

The half cell reactions are as given below:

$H_2(g) + 2OH^- \longrightarrow 2H_2O(l) + 2e$, $E^o = -0.828V$, Anode

$\frac{1}{2}O_2(g) + H_2O(l) + 2e \longrightarrow 2OH^-$, $E^o = 0.401V$, Cathode

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $E^o = 1.229V$
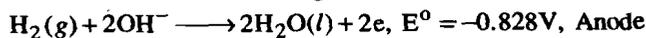
With acidic electrolyte, the half-cell reactions are as under:

$H_2(g) \longrightarrow 2H^+ + 2e$, $E^o = 0$, Anode

$\frac{1}{2}O_2(g) + 2H^+ + 2e \longrightarrow H_2O(l)$, $E^o = 1.229V$, Cathode

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $E^o = 1.229V$
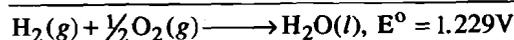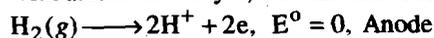
Thus, you can see from the above, that the electromotive force (e.m.f.) of the cell remains the same whether we use alkaline or acidic electrolyte. This is because we are using the same reactants at the electrodes in both the cases. Fuel cells have several advantages over other sources of energy. Firstly, in a fuel cell unlike in the dry cell or storage battery (which requires recharging also), the cathode and anode reactants are continuously supplied so that energy can be indefinitely withdrawn from it. Secondly, in a fuel cell energy is extracted from the reactants under more nearly ideal conditions. Therefore, the thermodynamic

efficiency of the fuel cells is higher than that of the most of the ordinary combustion processes. Fuel cells have efficiencies approaching 75%, whereas power plants that burn fuels have efficiencies of only about 40%.

Combustion of hydrogen is a highly exothermic reaction and produces no pollutants:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l), \quad \Delta H = -572 \text{ kJ}$$
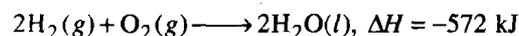
Liquid hydrogen is, therefore, used as a rocket fuel.

It has been recognised during the past two decades that the world reserves of fossil fuels like coal, oil and gas are finite, so they cannot last for ever. Similarly, the nuclear and hydroelectric power also cannot meet all our energy requirements. Moreover, these 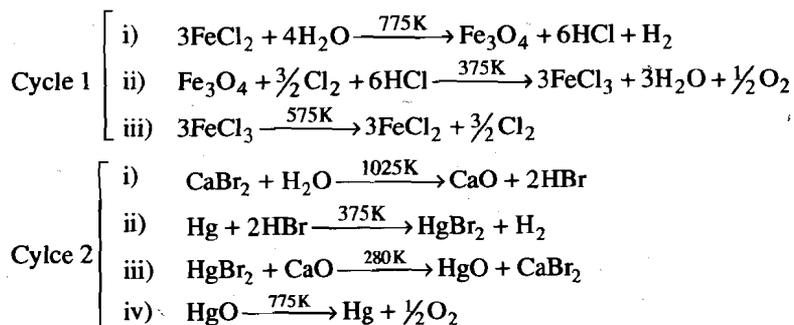sources pose a danger of environmental degradation. This has prompted an active search for alternative sources of energy. In addition to solar power, hydrogen is being considered a potential fuel for the future.

Hydrogen as a fuel has many advantages over the conventional fossil fuels and electric power. It is available in unlimited quantities in sea water. It is pollution free because the major product of its combustion is water with only traces of nitrogen oxides. It releases greater energy per unit weight of fuel in comparison to gasoline and other fuels. Hydrogen can be transported as a gas in high pressure pipelines, as a liquid in tankers and even as a solid in the form of metal hydrides. Unlike electricity, hydrogen can be stored and used when needed. You may then naturally think, why hydrogen has not replaced other fuels. There is a reason for this of course. At present, its manufacture from water is expensive. But that may change in future.

Hydrogen like electricity is a secondary source of energy because it is produced using energy from a primary source such as coal, nuclear fission or the sun. Water is very stable to thermal decomposition, it does not decompose to hydrogen and oxygen to any appreciable extent at practically viable temperatures. However, hydrogen can be conveniently prepared by electrolysis of water. But this method is not economical at present. In fact more energy has to be spent in electrolysis of water than that can be liberated by burning hydrogen as a fuel. Great efforts are being made to make electrolysis of water more energy-efficient so that the use of hydrogen as a fuel can become economically viable.

Non-electrolytic methods of preparation of hydrogen, e.g., thermochemical and photochemical hydrogen generation are also being studied. In thermochemical hydrogen generation, water is heated with certain chemicals to liberate hydrogen at much lower temperatures. In the past few years, several water splitting cycles have been identified, out of which two potentially useful cycles are given below:

Cycle 1
i) $3FeCl_2 + 4H_2O \xrightarrow{775K} Fe_3O_4 + 6HCl + H_2$
ii) $Fe_3O_4 + \frac{3}{2}Cl_2 + 6HCl \xrightarrow{375K} 3FeCl_3 + 3H_2O + \frac{1}{2}O_2$
iii) $3FeCl_3 \xrightarrow{575K} 3FeCl_2 + \frac{3}{2}Cl_2$

Cylce 2
i) $CaBr_2 + H_2O \xrightarrow{1025K} CaO + 2HBr$
ii) $Hg + 2HBr \xrightarrow{375K} HgBr_2 + H_2$
iii) $HgBr_2 + CaO \xrightarrow{280K} HgO + CaBr_2$
iv) $HgO \xrightarrow{775K} Hg + \frac{1}{2}O_2$

Thus by repeating reactions (i) — (iii) in Cycle 1 or reactions (i) — (iv) in Cycle 2, water can be splitted to H_2 and O_2.

Decomposition of water by solar energy in presence of catalysts is known as photochemical decomposition of water. Using special catalysts, scientists in France have been able to achieve the efficient decomposition of water under visible and ultraviolet light. If this process can be made industrial, a convenient method of converting solar energy directly to a useful form of stored chemical energy will be available.

SAQ 6
Write five important industrial uses of hydrogen.

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3.8 HYDRIDES

Hydrogen combines with a number of elements to form compounds called hydrides. As electronegativity of the element increases, the stability of hydrides also increases. Three types of hydride compounds are formed depending upon the electronegativity of the elements. These are classified into:

i) Ionic or saltlike or saline hydrides.

ii) Covalent or molecular hydrides.
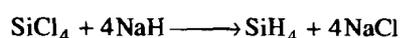
iii) Metallic or non-stoichiometric hydrides.

Now we shall discuss each type of hydrides in detail.
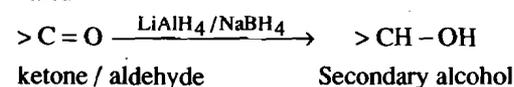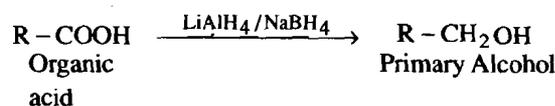
3.8.1 Ionic or Saltlike Hydrides

These are formed by metals which have low electronegativity values and are more electropositive with respect to hydrogen. These hydrides are formed by transfer of an electron from the metal to the hydrogen atom. Hydride ion is a peculiar chemical species and in contrast to proton which has vanishingly small size, it is unusually large. It is larger than any of the halide ions except iodide. The source of this apparent paradox lies in the lack of control by a single nuclear proton over two mutually repelling electrons.

Alkali and alkaline earth metals of groups 1 and 2 are sufficiently electropositive and force the hydrogen atom to accept an electron to form the hydride ion, H^-, e.g., lithium hydride Li^+H^- and calcium hydride $Ca^{2+}(H^-)_2$. When the metals are heated in hydrogen at 973 K, ionic hydrides are obtained. Ionic hydrides are white crystalline solids. They have high melting points and conduct electricity in fused state liberating hydrogen at the anode. Their density is higher than that of the metal.

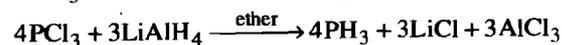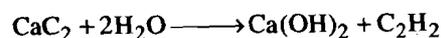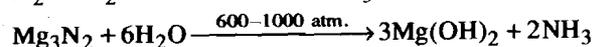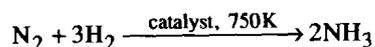They are powerful reducing agents specially at higher temperature, e.g.,

$$2CO + NaH \longrightarrow HCOONa + C$$

$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$$

$$PbSO_4 + 2CaH_2 \longrightarrow PbS + 2Ca(OH)_2$$

Li^+H^- and Na^+H^- are used in making valuable reducing agents like lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). These complex hydrides are frequentl; used in the reduction of aldehydes, ketones, acids and their derivatives to give alcohols.

$$\underset{\substack{\text{Organic} \\ \text{acid}}}{R-COOH} \xrightarrow{\text{LiAlH}_4/\text{NaBH}_4} \underset{\text{Primary Alcohol}}{R-CH_2OH}$$

$$\underset{\text{ketone / aldehyde}}{>C=O} \xrightarrow{\text{LiAlH}_4/\text{NaBH}_4} \underset{\text{Secondary alcohol}}{>CH-OH}$$

3.8.2 Covalent Hydrides

These hydrides are formed by elements of comparatively higher electronegativity, generally *p*-block elements and Be and Mg. The bonds formed in this class of hydrides are mostly covalent in character but in some cases, for example, in HF, the bond may be partially ionic.

The covalent hydrides can be prepared either by direct reaction of non-metals with hydrogen under suitable conditions or by the reaction of H_2O or acids on nitrides, carbides, borides, silicides, stannides of alkali and alkaline earth metals or by the reduction of halides. These are illustrated by the following reactions:

$$N_2 + 3H_2 \xrightarrow{\text{catalyst, 750K}} 2NH_3$$

$$Mg_3N_2 + 6H_2O \xrightarrow{600-1000 \text{ atm.}} 3Mg(OH)_2 + 2NH_3$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$AsCl_3 + 6H \xrightarrow{Zn+HCl} 4AsH_3 + 3HCl$$

$$4PCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 4PH_3 + 3LiCl + 3AlCl_3$$

These hydrides have a molecular lattice made up of individual saturated covalent molecules, with only weak van der Waals forces and in some cases hydrogen bonds holding the molecules together. This accounts for their softness, low melting and boiling points, their

volatility and lack of conductivity. Some covalent hydrides are unstable in the presence of air, e.g., stannane, SnH_4.

Some covalent hydrides of Groups 2 and 13 are electron deficient. These have structures between ionic and covalent hydrides. These are either dimeric, e.g., boron hydride (B_2H_6), or polymeric, e.g., beryllium hydride $(BeH_2)_n$, magnesium hydride $(MgH_2)_n$ and aluminium hydride $(AlH_3)_n$. You will study the detailed structure of these hydrides in Units 5 and 6 of this course.

3.8.3 Metallic Hydrides

On heating, hydrogen reacts with many transition metals, lanthanides and actinides to form metallic hydrides. Most of these have metallic appearance and are less dense than the parent metal. They all conduct heat and electricity though not as well as the parent metal (cf. ionic hydrides). Unlike the saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example, $TiH_{1.5-1.8}$, $VH_{0.56}$, $CrH_{1.7}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$, $TaH_{2.76}$, $LaH_{2.87}$, $YbH_{2.55}$, etc., approach the stoichiometric formulae given in Table 3.3. Most of these hydrides are stable to water upto 375 K but are quantitatively decomposed by acids and show reducing properties.

Table 3.3: Stoichiometric formulae of some metallic hydrides.

MH	(M = V, Cr, Ni, Cu, Ta, Pd)
MH_2	(M = Ti, Zr, Hf, V, Nb, Cr, Zn, Y; La-Lu except Pm; Th, Np, Pu, Am, Cm)
MH_3	(M = Y, La-Lu except Pm and Eu; Pa, U, Np, Pu, Am)

Formerly, these hydrides were termed as interstitial compounds in which hydrogen was thought to be accommodated in the interstices in the metal lattice producing distortion but no change in its type. But recent studies have shown that except for the hydrides of nickel, palladium, cerium and actinium, other hydrides of this class have lattice of a type different from that of the parent metal. For example, the hexagonal close packed lattice of some lanthanides is transformed to a face-centred cubic lattice in their dihydrides. As pointed out earlier, these interstitial hydrides are poorer conductors of electricity, exhibit less paramagnetism and are more brittle than the parent metal. These characteristics suggest that hydrogen is present in the metal lattice as hydrogen atoms rather than as hydrogen molecules. The single electron of hydrogen is paired with an electron of the metal, thereby reducing the extent of metallic bonding. Breaking of the H-H bond is in agreement with the fact that these metals catalyse reactions of hydrogen.

SAQ 7
What types of bonding do you expect in sodium hydride, methane and ammonia?

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3.9 HYDROGEN BONDING

One very important aspect of the chemistry of hydrogen is **hydrogen bonding**. When hydrogen is covalently bonded to a highly electronegative element like F, O, N, the electronegative element attracts the electron pair towards itself giving rise to an induced positive charge (δ^+) on the hydrogen atom and negative charge (δ^-) on the electronegative atom. For example,

$H^{\delta+} X^{\delta-}$, where X = electronegative atom.
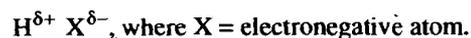
Due to this positive character, hydrogen attracts another electronegative atom of the neighbouring molecule forming a bond. This bond is known as the hydrogen bond. This is illustrated below:

$-------H^{\delta+}---X^{\delta-}---------H^{\delta+}---X^{\delta-}---------H^{\delta+}---X^{\delta-}---------$

'———' denotes covalent bond.
'-------' denotes hydrogen bond.

Thus hydrogen bond can be defined as "the attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same compound."

The hydrogen bond energy is only about 7-59 kJ mol^{-1} compared to the normal covalent bond energy of 389-665 kJ mol^{-1} for H-N, H-O and H-F bonds. Thus, hydrogen bond is much weaker than a covalent bond. Obviously, its length is also much longer than the covalent bond.

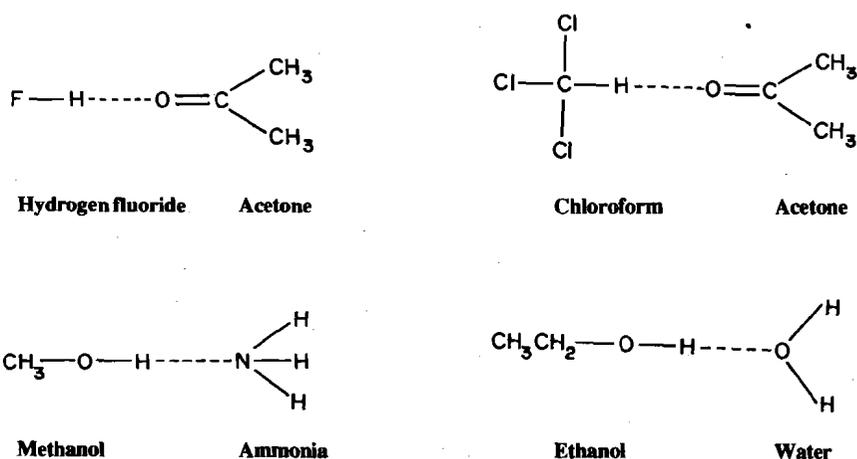There are two types of hydrogen bonding:

i) Intermolecular hydrogen bonding

ii) Intramolecular hydrogen bonding

3.9.1 Intermolecular Hydrogen Bonding

In this case, two or more molecules of the same compound or of different compounds are involved in hydrogen bonding. Some common examples of the intermolecular hydrogen bonding occurring between the molecules of same compound are HF, H_2O, alcohols, etc.

Hydrogen fluoride, (HF)$_n$

Cluster of water molecules, (H$_2$O)$_n$
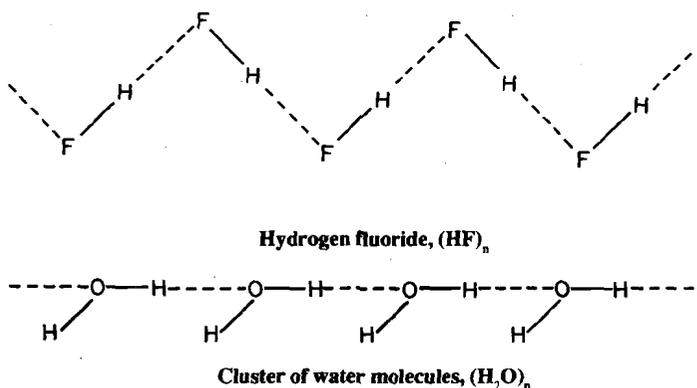
Examples of the intermolecular hydrogen bonding occurring between two different kinds of molecules are as following:

Hydrogen fluoride   **Acetone**   **Chloroform**   **Acetone**

Methanol   **Ammonia**   **Ethanol**   **Water**
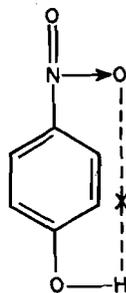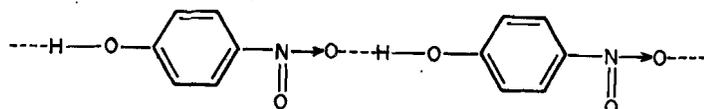
3.9.2 Intramolecular Hydrogen Bonding

Intramolecular hydrogen bond is formed between two atoms of the same molecule. As a consequence of this, generally a five or six membered ring called chelate ring is formed, e.g.,

o-Nitrophenol   **Salicylaldehyde**

You have seen above, that intramolecular hydrogen bonding takes place in molecules like o-nitrophenol and salicylaldehyde. Now, you may ask why intramolecular hydrogen bonding does not take place in p-nitrophenol? This is due to the large distance between the two groups (NO_2 and OH) in p-nitrophenol.

This type of hydrogen bonding is not possible.
However, it does show the usual intermolecular hydrogen bonding.

p-Nitrophenol

It is significant to note that the vast majority of intramolecular hydrogen bonding occurs where a five or six membered ring can be formed because of the stability associated with such rings.

3.9.3 Effect of Hydrogen Bonding

Hydrogen bonding plays a very significant role in determining the properties of compounds. It is also very important in most of the biological processes about which you may study in the Biochemistry course. We shall confine our discussion to a few important physical properties only, e.g., boiling point, melting point and solubility in water.

Boiling Point and Melting Point

If you look at the melting and boiling points of the hydrides of Group 14 elements, i.e., CH_4, SiH_4, GeH_4 and SnH_4 in Fig. 3.6, you will observe that melting and boiling points of the hydrides generally increase with the increase in molecular weight of the hydrides. But NH_3 in Group 15, H_2O in Group 16 and HF in Group 17 have abnormally high melting and boiling points as compared to other hydrides in their respective groups in the periodic table. This anomaly is explained on the basis of hydrogen bond formation.

In compounds where the molecules are linked by hydrogen bonds, some extra energy is required to break the intermolecular hydrogen bond and this is responsible for their higher boiling and melting points.

However, intramolecular hydrogen bonding has the opposite effect. For example, in ortho nitrophenol the groups present in ortho position are involved in intramolecular hydrogen bonding thus preventing the intermolecular hydrogen bond formation, i.e. association of the molecule. Due to the intramolecular chelated structure, o-nitrophenol is steam-volatile, whereas p-nitrophenol is not.

Water Solubility

Solubility of a substance increases markedly when hydrogen bonding is possible between the solvent and the solute molecules. For example, lower alcohols like methanol, ethanol etc., are highly miscible with water due to the hydrogen bonding with water molecules.
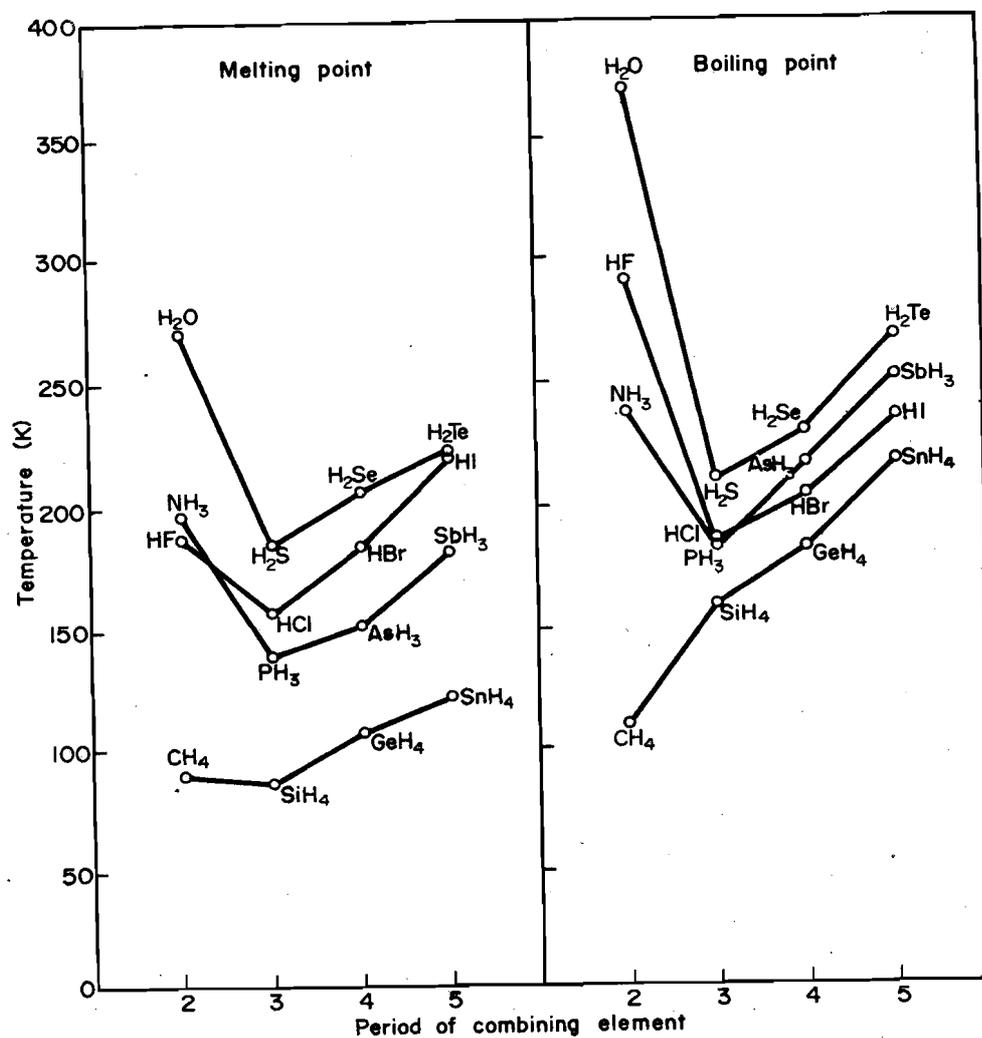
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Fig.3.6: (a) Melting point curves and (b) Boiling point curves of the molecular hydrides.

SAQ 8

a) What is the effect of hydrogen bonding on the properties of H_2O, HF and NH_3?

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b) Why is H_2O a liquid and H_2S a gas at room temperature?

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3.10 POLARISING POWER OF H⁺

You know that the polarising power of a cation, i.e., its ability to distort or polarise an anion is directly proportional to its positive charge and inversely proportional to its size. You can also say that the polarising power of a cation is proportional to the ratio of its charge to its size. This ratio is called the ionic potential of the cation. As the hydrogen cation, i.e., proton, is vanishingly small, it has a very high ionic potential and a vast polarising power. Due to this, free protons exist only in discharge tubes. Generally, these are found associated with other molecules. For example, with ammonia and water, these form

species like NH_4^+ and H_3O^+, H_5O^+, $H_9O_4^+$,etc. The aquated proton species are represented as $H^+(aq)$. Enthalpy of formation of these aquated proton species is very large (-1075 kJ mol^{-1}). It is mainly because of this reason that many covalent hydrides (H-X) are acidic in aqueous solution, i.e., they release $H^+(aq)$ ions even though the H-X bonds are often very strong, e.g.,

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
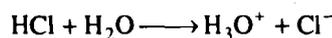
3.11 SUMMARY

Let us now summarise what we discussed in this unit:
● Hydrogen is the most abundant element in the universe.
● Hydrogen atom has only one electron and the cation is an elementary particle, the proton.
● It is difficult to assign one particular position to hydrogen in the periodic table due to its resemblance to alkali metals as well as to halogens.
● Hydrogen has three isotopes namely hydrogen (^1H), deuterium (D or ^2H) and tritium (T or ^3H).
● Hydrogen molecule exists in two forms, *ortho* and *para*.
● Hydrogen reacts with other elements to form three types of hydrides, i.e., ionic, covalent and metallic hydrides.
● Hydrogen can bridge electronegative elements (hydrogen bonding) and electropositive elements (hydride bridging).
● The largest single use of hydrogen is in the manufacture of ammonia. Its other uses are in the hydrogenation of vegetable oils, manufacture of methanol from coal, extraction of metals and in fuel cells.

3.12 TERMINAL QUESTIONS

1   Which of the following is correct? Tick ($\sqrt{}$) the correct one.

   i)   Hydrogen acts as
       (a) reducing agent
       (b) oxidising agent
       (c) both oxidising and reducing agent
       (d) None of the above

   ii) The electronic configuration of deuterium atom is
       (a) $1s^1$ (b) $2s^1$ (c) $1s^2$ (d) $2s^2$

   iii) Hydrogen molecule ion, H_2^+ contains
       (a) 1 electron   (b) 2 electrons
       (c) 3 electrons   (d) No electrons

   iv) SiH_4 is an example of which of the following type of hydrides:
       (a) ionic   (b) interstitial
       (c) metallic (d) covalent

   v)   Heavy water is
       (a) DOD   (b) HDO   (c) H_2O_2 (d) DTO

   vi) Polarising power of an ion increases
       (a) when charge of cation increases
       (b) when size of cation increases
       (c) when size of anion decreases
       (d) none of the above

2   Do *ortho* and *para* forms of hydrogen exist in deuterium and tritium?

3   Which hydrogen bond do you expect to be stronger and why?
   (a) S – H -----O   or   (b) O–H ----- S

4   Explain why the boiling points of hydrogen halides follow the trend

HF(293K) > HCl(188K) < HBr(206K) < HI(237K)
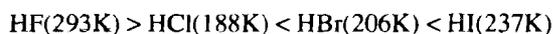
5 When a hydrogen bond is symbolized by X–H - - - - Y, what do the solid and the dotted lines represent? Which distance is shorter?

3.13 ANSWERS

Self Assessment Questions

1. a) Hydrogen resembles alkali metals because like alkali metals it also has one electron in 's' orbital, i.e., $1s^1$ configuration (see the similar properties from the text).

   b) Hydrogen needs one electron to reach the noble gas configuration, therefore, it has a tendency to take one electron and form hydride ion, H^-.

2. Most of the chemical properties are governed by the electronic configuration of the element. As the isotopes of hydrogen have the same electronic configuration, their chemical properties are closely similar.

3. i) T   ii) F   iii) F   iv) T   v) F

4. i) $C + H_2O \longrightarrow CO + H_2$

   ii) $CH_4 + H_2O \longrightarrow CO + 3H_2$

   iii) $CO + H_2O \longrightarrow CO_2 + H_2$

   iv) $2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} 2NaOH + H_2 + Cl_2$

   v) $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

5. i) $C + H_2O \longrightarrow CO + H_2$

   $CO + 2H_2 \longrightarrow CH_3OH$

   ii) $CH_3CN + 2H_2 \longrightarrow CH_3CH_2NH_2$

   iii) $CH_3(CH_2)_7 CH=CH(CH_2)_7COOH + H_2 \longrightarrow CH_3(CH_2)_{16}COOH$

   iv) $(NH_4)_2 MoO_4 + 3H_2 \longrightarrow Mo + 2NH_3 + 4H_2O$

6. i) manufacture of ammonia

   ii) manufacture of methanol

   iii) hydrogenation of vegetable oils

   iv) extraction of molybdenum and tungsten

   v) in fuel cells

7. Sodium hydride — ionic

   Methane   — covalent

   Ammonia   — covalent

8. a) Because of strong intermolecular hydrogen bonding, H_2O, HF and NH_3 exist as associated molecules. Therefore, their melting and boiling points are much higher than those of the corresponding hydrides in their respective groups.

   b) Water is a liquid because of hydrogen bonding, whereas in H_2S even if hydrogen bonding is present it is very weak.

Terminal Questions

1. i) a   ii) a   iii) a   iv) d   v) a   vi) a

2. Yes, but the percentage ratio of *ortho/para* in D_2 and T_2 is different from the ratio in H_2.

3. Hydrogen bond in, S–H -----O is stronger than O–H ----- S as O is more electronegative than S.

4. As we move down the group the boiling point of HCl, HBr, HI increases due to increased van der Waals forces. However, in HF the boiling point is anomalously high due to the hydrogen bonding.

5. Solid line represents the covalent bond and the dotted line represents the hydrogen bond. As hydrogen bond is much weaker than the covalent bond, the bond length of the former is more than that of the latter.