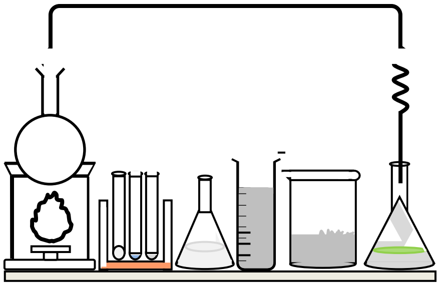

Chapter – 7

HYDROGEN

1 BASIC CONCEPT

Hydrogen is the simplest among the known elements. The word ‘Hydrogen’ means water producer. When burnt in oxygen, it produces water and hence Lavoisier suggested the name ‘Hydrogen’ for it. Hydrogen atom contains one proton and one electron. Normally hydrogen exists as diatomic molecule, H_2 which is known as dihydrogen. The existence of atomic hydrogen is only possible at high temperatures.

ATOMIC AND MOLECULAR PROPERTIES OF HYDROGEN

Atomic Properties		**Molecular Properties**	
Ionisation enthalpy, (kJ mol^{-1})	1312	Melting point, (K)	13.96
Electron gain enthalpy (earlier electron affinity), (kJ mol^{-1})	–73	Boiling point, (K)	20.4
Electronegativity	2.1	Density, (gl^{-1})	0.0899
Atomic radius, (pm)	37	Bond length, (pm)	74.4
Ionic radius (H^-), (pm)	208	Bond enthalpy, (kJ mol^{-1})	435.9

2 POSITION OF HYDROPGEN IN PERIODIC TABLE

The atomic number of hydrogen is one and it has an electronic configuration of $1s^1$. Since its electronic configuration resembles those of alkali metals as well as halogens, it shows resemblance with them in most of the properties. Therefore it is very difficult to place it either with elements of group 1 or those of group 17. Because of this reason hydrogen is even called ‘rogue element’.

2.1 RESEMBLANCE WITH ALKALI METALS

Hydrogen resembles alkali metals in the following respects:

(i) Electronic configuration:

The hydrogen atom has one electron in the outermost shell like the alkali metals.

Element	H	Li	Na
Atomic number	1	3	11
Electronic configuration	$1s^1$	$1s^2, 2s^1$	$1s^2, 2s^2, 2p^6, 3s^1$

(ii) Cation formation:

Hydrogen like alkali metals forms singly charged cation by losing the outermost electron. Since the ionization energy of H is very high so the compounds containing H^+ will only be formed if the ionization energy can be provided by some other process e.g. hydration.

$$H(1s^1) \longrightarrow H^+ + e^-$$

$$Na(1s^2, 2s^2, 2p^6, 3s^1) \longrightarrow Na^+(1s^2, 2s^2, 2p^6) + e^-$$

(iii) Affinity for non–metals:

Both hydrogen and alkali metals combine with halogens to form halides, with oxygen to give oxides and with sulphur to give sulphides. For example,

HCl	H_2O	H_2S
NaCl	Na_2O	Na_2S

(iv) Electropositive nature:

When an aqueous solution of hydrogen chloride or a molten alkali metal halide is electrolysed, both hydrogen and an alkali metal is liberated at the cathode.

Compound	$HCl \longrightarrow H^+ + Cl^-$	$NaCl \longrightarrow Na^+ + Cl^-$
At cathode:	$H^+ + e^- \longrightarrow \frac{1}{2} H_2(g)$	$Na^+ + e^- \longrightarrow Na$

(v) Reducing character:

$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$B_2O_3 + \underset{\text{(an alkali metal)}}{\underset{\text{potassium}}{6K}} \longrightarrow 2B + 3K_2O$$

2.2 RESEMBLANCE WITH HALOGENS

Hydrogen resembles halogens in the following respects:

(i) Electronic configuration:

Both hydrogen and halogens are one electron short of saturation in their outermost shell. After gaining one electron, they acquire stable configuration of the nearest noble gas. Thus, both behave as univalent non–metals as shown below.

$\underset{1s^1}{H} + e^- \longrightarrow \underset{1s^2}{H^-}$ (This corresponds to He)

$\underset{1s^2,\ 2s^22p^6,\ 3s^23p^5}{Cl} + e^- \longrightarrow \underset{1s^2,\ 2s^22p^6,\ 3s^23p^6}{Cl^-}$ (This corresponds to Ar)

$\underset{2,\ 8,\ 18,\ 7}{Br} + e^- \longrightarrow \underset{2,\ 8,\ 18,\ 8}{Br^-}$ (This corresponds to Kr)

(ii) Hydrides and halides:

Hydrogen combines with alkali and alkaline earth metals to form hydrides similar to halides.

$H_2 + 2Na \longrightarrow 2NaH$; $Cl_2 + 2Na \longrightarrow 2NaCl$

$H_2 + Ca \longrightarrow CaH_2$; $Cl_2 + Ca \longrightarrow CaCl_2$

The fused hydrides on electrolysis produce hydrogen at anode, like chlorine from fused chlorides.

$H^- \xrightarrow{\text{at anode}} \frac{1}{2} H_2(g) + e^-$; $Cl^- \xrightarrow{\text{at anode}} \frac{1}{2} Cl_2(g) + e^-$

(iii) Ionisation enthalpy:

The ionisation enthalpy of hydrogen is closer to halogens and much different from alkali metals.

	Hydrogen	Alkali metals					Halogens			
Element	H	Li	Na	K	Rb	Cs	F	Cl	Br	I
Ionisation enthalpy / kJ mol^{-1}	1312	520	496	419	403	376	1680	1256	1142	1008

(iv) Formation of covalent compounds:

Like halogens, hydrogen readily combines with non–metals such as carbon, silicon, and nitrogen etc. to form covalent compounds.

With hydrogen:	CH_4 Methane	SiH_4 Silane	NH_3 Ammonia
With halogens:	CCl_4 Carbon tetrachloride	$SiCl_4$ Silicon tetrachloride	NCl_3 Nitrogen trichloride

2.3 PROPERTIES OF HYDROGEN IN WHICH IT DIFFERS FROM BOTH THE ALKALI METALS AS WELL AS HALOGENS

Hydrogen has some properties which neither resemble alkali metals nor halogens.

For example,

(i) The oxide of hydrogen, H_2O is neutral, while the oxides of halogens, e.g., Cl_2O, ClO_2, Cl_2O_7 etc. are acidic and the oxides of alkali metals, e.g. Na_2O, K_2O etc are basic.

(ii) Hydrogen atom has no inner electrons and no unshared electrons.

Key points

1. Hydrogen shows resemblance in most of the properties with alkali metals and also with halogens.

3 ISOTOPES OF HYDROGEN

ISOTOPES OF HYDROGEN

Hydrogen has three isotopes. The most abundant and stable isotope is that of protium $({}_1^1\text{H})$.

The stable isotope deuterium $({}_1^2\text{H or D})$ is also called heavy hydrogen. The third isotope called tritium $({}_1^3\text{H or T})$ is radioactive ($t_{1/2}$ = 12.33 year). It emits low energy β–particles but no γ–radiations.

$${}_1^3\text{H} \longrightarrow {}_2^3\text{He} + {}_{-1}^{0}\text{e}$$

It is prepared artificially by the bombardment of nitrogen or an isotope of lithium with neutron.

$${}_7^{14}\text{N} + {}_0^1\text{n} \longrightarrow {}_6^{12}\text{C} + {}_1^3\text{H}$$

$${}_3^{6}\text{Li} + {}_0^1\text{n} \longrightarrow {}_2^{4}\text{He} + {}_1^3\text{H}$$

The relative abundances of these three isotopes in nature are:

$$1 : 1.56 \times 10^{-4} : 1 \times 10^{-17}$$

Deuterium is usually prepared from heavy water (D_2O). Heavy water (D_2O) is obtained by electrolytic enrichment of ordinary water. Heavy water is used as a coolant and moderator in nuclear reactors. It is also used for the preparation of deuterated compounds.

$$\underset{\text{aluminium carbide}}{Al_4C_3} + 12D_2O \longrightarrow \underset{\text{deuterated methane}}{3CD_4} + 4Al(OD)_3$$

All the three isotopes of hydrogen have the same electronic configuration. So, all the three isotopes give similar chemical reactions. However, due to the mass difference, there is significant difference in their physical properties and also in the rates of their reactions. Ordinary hydrogen undergoes reactions more rapidly than deuterium. This is referred to as the isotope effect.

Key points

1. Hydrogen has three isotopes namely protium, deuterium and tritium.
2. Nucleus of protium has only one proton and **no neutron**.
3. Isotope tritium is **radioactive** in nature and emits low energy β-particles.

PRACTICE PROBLEMS

PP1. Which isotope of hydrogen is radioactive?

PP2. What is the name of the isotope of hydrogen which contains 1 proton and 1 neutron?

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4 DIHYDROGEN ; H_2 MOLECULE

As we discussed earlier, hydrogen exists as diatomic molecule, H_2. To distinguish H_2 from H, the atomic form; H_2 is known as dihydrogen.

4.1 OCCURRENCE

Hydrogen is the most abundant element in the universe. About half the mass of the sun and some other stars is made up of hydrogen. Similarly, Saturn and Jupiter mostly consist of hydrogen. In the combined form it constitutes 15.4% of the earth's crust and oceans.

4.2 PREPARATION OF HYDROGEN OR DIHYDROGEN

Hydrogen can be prepared by various methods. Some of them are described below:

(i) By the action of metals on water:

Metals occurring above hydrogen in the electrochemical series displace hydrogen from water under the conditions depending upon their reactivity.

(a) Action of metals on cold water:

Elements like sodium, potassium, calcium etc., displace hydrogen from water at room temperature. With alkali metals the reaction is explosive.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2(g)$$
$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2(g)$$

(b) Action of metals on boiling water:

Metals like magnesium and aluminium in powder form decompose boiling water, giving hydrogen gas.

$$Mg + H_2O(\text{boiling}) \longrightarrow MgO + H_2$$
$$2Al + 3H_2O(\text{boiling}) \longrightarrow Al_2O_3 + 3H_2$$

(c) By passing steam over heated metals:

When steam is passed over some heated metals, such as, zinc, magnesium and iron, hydrogen gas is obtained.

The apparatus consists of a long silica tube containing iron filings heated to redness. Steam is passed over heated iron, hydrogen so evolved is collected over water.

$$\underset{\text{(red hot)}}{3Fe} + 4H_2O(\text{steam}) \rightleftharpoons \underset{\text{(ferroso–ferric oxide)}}{Fe_3O_4} + 4H_2(g)$$

(ii) By the action of water on metal hydrides:

Hydrides of alkali and alkaline earth metals react readily with water producing hydrogen.

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

(iii) From acids:

Acid contains replaceable hydrogen. Electropositive metals, such as, zinc, iron, aluminium, magnesium etc., which appear above hydrogen in electrochemical series displace hydrogen from acids. For example,

$$Zn + \text{dil. } H_2SO_4 \longrightarrow ZnSO_4(aq) + H_2(g) \quad \text{(Laboratory method)}$$
$$Mg + \text{dil. } H_2SO_4 \longrightarrow MgSO_4(aq) + H_2(g)$$

(iv) From Alkalies:

Hydrogen can be prepared by the action of boiling caustic soda or caustic potash solutions on metals like zinc, aluminium, tin etc., or on a non–metal like silicon.

$$Zn + 2NaOH \xrightarrow{\Delta} \underset{\text{(sodium zincate)}}{Na_2ZnO_2} + H_2$$

$$2Al + 2NaOH + 2H_2O \xrightarrow{\Delta} \underset{\text{(sodium meta aluminate)}}{2NaAlO_2} + 3H_2$$

$$Sn + 2NaOH + H_2O \xrightarrow{\Delta} \underset{\text{(sodium stannate)}}{Na_2SnO_3} + 2H_2$$

$$Si + 2NaOH + H_2O \xrightarrow{\Delta} \underset{\text{(sodium silicate)}}{Na_2SiO_3} + 2H_2$$

$$2Al + 2KOH + 2H_2O \xrightarrow{\Delta} 2KAlO_2 + 3H_2 \quad \text{(Uyeno's method)}$$

4.3 COMMERCIAL PRODUCTION OF HYDROGEN

Water is one of the most abundant and cheaper source of hydrogen (or dihydrogen). Hydrogen is commercially obtained from water using different methods.

(i) Bosch process:

Water gas is mixed with excess of steam and passed over a heated catalyst, ferric oxide and little chromium oxide at 450°C. Carbon monoxide is oxidised to CO_2. This is called water gas.

Note: As the CO and H_2 mixture is also used for the synthesis of methanol and a numbr of hydrocarbons, it is also called synthetic gas or 'syngas'.

$$CO + H_2O \xrightarrow{Fe_2O_3 + Cr_2O_3} CO_2 + H_2$$

(ii) Lane's process:

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

(iii) By electrolysis of water:

This process is suitable for places where cheap electric supply is available. Since water is a bad conductor of electricity, it is made conducting by the addition of small quantity of sulphuric acid or sodium hydroxide. Hydrogen so obtained is 99.9% pure.

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

The SO_4^{2-} does not get involved in the electrode reaction. The ion, which gets oxidised at the anode in preference to SO_4^{2-} is OH^- (coming from the ionisation of water).

$$\begin{array}{llllll}
\text{At cathode:} & H^+ + e^- & \longrightarrow & H & & \\
 & H + H & \longrightarrow & H_2(g) & & \\
\text{At anode:} & H_2O & \longrightarrow & OH^- & + & H^+] \times 4 \\
 & OH^- & \longrightarrow & OH & + & e^-] \times 4 \\
 & 2OH & \longrightarrow & H_2O & + & O] \times 2 \\
 & O + O & \longrightarrow & O_2(g) & & \\
\hline
\text{Net reaction:} & 2H_2O & \longrightarrow & 4H^+ & + & O_2(g) + 4e^- \\
\hline
\end{array}$$

4.4 PROPERTIES OF DIHYDROGEN

4.4.1 Physical Properties

(i) Hydrogen (dihydrogen) is a colourless, odourless, tasteless and combustible gas. It is the lightest element known.

(ii) Hydrogen (dihydrogen) is slightly soluble in water, 21.5 mL/L at NTP. Many metals like platinum black or palladium adsorb considerable quantities of hydrogen.

4.4.2 Chemical Properties

Hydrogen is quite reactive and can form compounds by gaining, losing, or by sharing the single electron in its outermost shell. It also reacts by gaining a single electron to achieve the helium (noble gas) configuration in hydride formation. It is highly combustible gas and burns in air or dioxygen with a pale blue flame to form water. However, it is not a supporter of combustion.

Because of its high bond dissociation enthalpy (436 kJ mol^{-1}), dihydrogen is not particularly reactive. At elevated temperatures or in the presence of catalysts, it combines with many non–metals to form covalent hydrides. With reactive metals (e.g., alkali metals) it forms salt–like hydrides, in which its oxidation state is –1.

In addition to covalent and salt like hydrides, hydrogen (dihydrogen) forms interstitial hydrides with metals such as platinum, palladium and nickel. In the interstitial hydrides, hydrogen atoms because of their small size occupy the interstitial sites in the metallic crystal. Some typical chemical reactions of hydrogen (dihydrogen) are described below.

(i) With di nitrogen:

Hydrogen reacts with nitrogen at about 450 – 500°C and under high pressure (200 – 900 atm) in the presence of a catalyst to give ammonia.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{200 atm, 450°C}]{\text{Fe/Mo}} 2NH_3(g) + \text{Heat}$$

This reaction forms the basis of Haber's process for the manufacture of ammonia from nitrogen and hydrogen.

(ii) Reaction with halogens:

It reacts with halogens, X_2 to give hydrogen halides, HX.

$$H_2(g) + X_2(g) \rightarrow 2HX(g) \quad (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

(iii) Reaction with dioxygen:

It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(l) \qquad \Delta H^o = -285.9 \text{ kJ mol}^{-1}.$$

(iv) With Metals:

Highly electropositive metals such as sodium, lithium and calcium react at high temperatures with hydrogen to form hydrides. In such compounds each hydrogen atoms accepts one electron to become a negative hydride ion, H^-. These hydrides are ionic compounds and very unstable to water. These react with water giving hydroxide of the metal and hydrogen gas.

$$NaH + H_2O \xrightarrow{\Delta} NaOH + H_2(g)$$

$$Ca + H_2 \xrightarrow{\Delta} Ca^{2+}(H^-)_2$$

$$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + H_2(g)$$

Metals like iron, nickel, palladium etc., take up hydrogen and form interstitial or metallic hydrides.

(v) Hydrogenation of unsaturated hydrocarbons:

Unsaturated hydrocarbons such as alkenes and alkynes add dihydrogen in the presence of a catalyst to form saturated hydrocarbons.

$$CH_2=CH_2 + H_2 \xrightarrow[473\ K]{Ni\ or\ Pt\ or\ Pd} CH_3-CH_3$$

$$HC\equiv CH + 2H_2 \xrightarrow[473\ K]{Ni\ or\ Pt\ or\ Pd} H_3C-CH_3$$

Hydrogenation of unsaturated organic compounds in the presence of heterogeneous and homogenous catalyst is used in many industrial processes.

(vi) Hydroformylation of olefins:

Olefins react with carbon monoxide and dihydrogen in presence of octacarbonyl dicobalt as catalyst under high temperature and pressure to form aldehydes.

$$RHC=CH_2 + H_2 + CO \xrightarrow[\text{High temperature, pressure}]{[Co(CO)_4]_2} RCH_2CH_2CHO$$

This reaction is called hydroformylation or the oxo process. The aldehydes thus obtained on subsequent catalytic reduction give alcohols.

$$\underset{\text{Aldehyde}}{RCH_2CH_2CHO} + H_2 \xrightarrow{\text{catalyst}} \underset{\text{Alcohol}}{RCH_2CH_2CH_2OH}$$

(vii) Hydrogenation of oils:

The vegetable oils such as soyabean oil, cotton seed oil, ground nut oil are called polyunsaturated oils since they contain many C=C bonds. When these oils are exposed to air for prolonged periods, the double bonds present in them undergo oxidation and the oil becomes rancid i.e. develop unpleasant taste. To avoid this, double bonds are reduced.

For this purpose, dihydrogen is bubbled through edible oil in the presence of finely divided nickel at 473 K when the oils are converted into solid fats.

$$\underset{\text{(Liquid)}}{\text{Edible oil}} + H_2 \xrightarrow{Ni,\ 473K} \underset{\text{(Solid)}}{\text{Edible fat}}$$

This process is called hydrogenation or hardening of oils and is used in the manufacture of vegetable ghee like Dalda, Gagan, Rath etc. from vegetable oils.

(viii) Reduction of metal oxides and ions:

Dihydrogen acts as a reducing agent and hence reduces oxides of certain less electropositive metals such as those of Cu, Pb, Fe etc. to the corresponding metals.

For example,

$$CuO + H_2 \xrightarrow{heat} Cu + H_2O$$

$$PbO + H_2 \xrightarrow{heat} Pb + H_2O$$

$$Fe_3O_4 + 4H_2 \xrightarrow{heat} 3Fe + 4H_2O$$

The oxides of strongly electropositive metals such as those of alkali and alkaline earth metals are not reduced by this method.

Dihydrogen also reduces some metal ions in aqueous solution. For example,

$$Pb^{2+}(aq) + H_2(g) \longrightarrow Pb(s) + 2H^+(aq)$$

4.5 USES OF DIHYDROGEN

1. Liquid hydrogen mixed with liquid oxygen is used as rocket fuel in space research programmes.
2. It is used in the atomic hydrogen and oxy-hydrogen torches for cutting and welding.
3. In the process of metallurgy it is used to reduce heavy metal oxides to metals.
4. One of the most important use of hydrogen is in the manufacturing of ammonia, which is a starting material for the manufacturing of various fertilizers.
5. It is used to hydrogenate the vegetable oils.

Key points

1. Hydrogen is the most abundant element in the universe. In the combined form it constitutes 15.4% of the earth's crust and oceans.
2. Hydrogen is quite reactive and can form compounds by losing, or by gaining, or by sharing the single electron in its outermost shell.

5 HYDRIDES

Hydrogen forms binary compounds with other elements. These compounds are known as **hydrides.** Hydrogen can combine with large number of the elements, like metals and non-metals to form the hydrides. Hydrides are classified into three different categories depending upon their nature of bonding and behaviour.

1. Ionic or Saline Hydrides
2. Covalent or Molecular Hydrides
3. Metallic or Interstitial Hydrides

5.1 IONIC HYDRIDES

They are also called **Salt–like** or **Saline** hydrides. These are binary compounds of hydrogen and electropositive elements like alkali metals and alkaline earth metals. LiH, NaH, CaH_2 etc. are some common examples of ionic hydrides. Some characteristic properties of these hydrides are as follows:

5.5.1 Physical properties of ionic hydrides

(i) All salt–like (or saline) hydrides are crystalline solids with high melting and boiling points

(ii) These hydrides are denser than the corresponding metals.

(iii) In molten state, these hydrides are electrically conducting.

(iv) Thermal stability

Except LiH (m.p 691°C), all other ionic hydrides decompose before melting. The thermal stability of hydrides follows the order,

$LiH > NaH > KH > RbH > CsH$

$CaH_2 > SrH_2 > BaH_2$

5.5.2 Chemical properties of ionic hydrides

(i) Reducing action:

All hydrides of group 1 and 2 elements are strong reducing agents particularly at higher temperatures.

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

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

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

$$CO_2 + CaH_2 \longrightarrow (HCOO)_2Ca$$

(calcium formate)

(ii) Reaction with nitrogen:

Alkaline earth metal hydrides react with nitrogen to form nitrides

$$3CaH_2 + N_2 \longrightarrow Ca_3N_2 + 3H_2$$

LiH forms nitride through many steps

$$LiH \xrightarrow{+N_2} LiNH_2 \xrightarrow{+N_2} Li_2NH \xrightarrow{+N_2} Li_3N$$

(lithium amide) (lithium imide) (lithium nitride)

(iii) Reaction with $AlCl_3$ and $B(OCH_3)_3$:

LiH reacts with $AlCl_3$ (anhydrous) to form lithium aluminium hydride.

$$\underset{\text{(etheral)}}{4LiH} + \underset{\text{(anhydrous)}}{AlCl_3} \longrightarrow Li[AlH_4] + 3LiCl$$

$$4NaH + B(OCH_3)_3 \longrightarrow Na[BH_4] + 3NaOCH_3$$

Both $Li[AlH_4]$ and $Na[BH_4]$ are used as reducing agent in organic and inorganic synthesis.

5.2 COVALENT HYDRIDES OR MOLECULAR HYDRIDES

Covalent (or molecular) hydrides are given by p–block elements (except Tl) and s–block elements (Be and Mg). This is because the difference between the electronegativity of these elements and hydrogen is very small. Being covalent, they are volatile compounds.

- The elements Sn, Pb, Sb, Bi, Te, Po and halogens give only mononuclear hydrides.

- The elements B, Al, Ga, In, C, Si, N, O and S give both mononuclear as well as polynuclear (or polymeric) hydrides.

Molecular hydrides are further classified according to the relative number of electrons and bonds in their Lewis structure in following kinds of covalent hydrides:

(i) electron-deficient hydrides
(ii) electron-precise hydrides
(iii) electron-rich hydrides.

Electron-deficient hydrides, as the name suggests, have too few electrons for writing its conventional Lewis structure and hence act as Lewis acids. Example: B_2H_6

Electron-precise compounds, have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds. Example: CH_4

Electron-rich hydrides, have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. Examples: NH_3 has one lone pair, H_2O has two lone pairs and HF has three lone pairs.

Note: They all behave as Lewis bases.

5.3 METALLIC OR NON-STOICHIOMETRIC OR INTERSTITIAL HYDRIDES

d–block elements of groups 3, 4, 5 (Sc, Ti, V, Y, Zr etc.), 10, 11, 12 (Pd, Cu, Zn etc.) and f–block elements on heating with H_2 under pressure form hydrides. In group 6, Cr alone forms the hydride, CrH. The metals of group 7, 8 and 9 do not form any hydride. In fact, the region of the periodic table from group 7 to 9 which do not form hydrides, is referred to as the **hydride gap**. These hydrides have properties similar to those of the parent metals and hence are called metallic hydrides. In these hydrides, hydrogen atoms being small in size, occupy space in the metallic lattice that is why these hydrides are also called interstitial hydrides. However, it is not certain whether the hydrogen is present in the interstitial sites as hydrogen atoms or H^+ ions with delocalized electrons.

5.3.1 Properties of metallic hydrides

(i) They are hard, have a metallic cluster, conduct electricity and have magnetic properties.
(ii) The density of these hydrides is lower than those of metals from which they are formed. Since the crystal lattice expands due to inclusion of H_2.
(iii) These hydrides are often non–stoichiometric (Z_rH_x where $x = 1.30 – 1.75$, T_iH_x where $x = 1.8 – 2.0$ etc). Further the ratio of H–atoms to the metal atoms is not fixed but varies with temperature and pressure. In fact in such hydrides, the law of constant composition does not hold good.

Key points

1. At the elevated temperature or in the presence of catalysts, hydrogen combines with many non-metals to form covalent hydrides.
2. With reactive metals i.e. alkali metals, it forms salt–like hydride and shows **–1** oxidation state.

6 WATER

Water is an important hydride of oxygen. It is most common, abundant and easily obtainable of all chemical compounds. As like oxygen, water is also important for our existence. It can be easily transformed from the liquid to the solid and to the gaseous states. It is also used as solvent and is known as universal solvent.

6.1 STRUCTURE OF WATER

6.1.1 Polar Nature of H_2O

Oxygen is more electronegative than hydrogen. Because of its high electronegativity, oxygen atom in a water molecule pulls the shared pairs of electrons more towards itself. As a result, the O–H bond acquires polarity. Since the two O–H bonds in water are inclined at an angle, hence the net dipole moment of water molecule is not zero. The actual dipole moment of water molecule is 1.84 Debye.

6.1.2 Structure of Water Molecule in the Liquid State

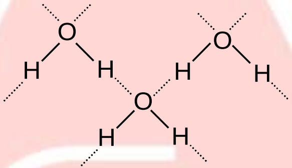
In liquid water, water molecules are held together by intermolecular hydrogen bonds.

Each oxygen can form two hydrogen bonds utilising both the lone pairs on it. Experimental studies suggest that liquid water consists of aggregates of varying number of water molecules held together by hydrogen bonds and 'free' water molecules in a dynamic equilibrium. The aggregates continuously forming, collapsing and reforming. Thus, in liquid water, the equilibrium $nH_2O \rightleftharpoons (H_2O)_n$ exists. Hydrogen bonding has a very profound effect on the properties of water.

6.1.3 Structure of Water Molecule in the Solid State

Ice, the solid form of water can exist in different crystalline forms depending on the conditions for freezing the water. In the 'normal' hexagonal ice, each oxygen atom is tetrahedrally surrounded by four other oxygen atoms. One hydrogen atom lies in between each pair of oxygen as shown in the figure. Thus, each hydrogen is covalently bonded to one oxygen atom and linked to another oxygen atom by a hydrogen bond. Such

an arrangement leads to a packing with large open spaces. The density of ice is, therefore, less than that of liquid water. When ice melts some of the hydrogen bonds are broken and the water molecules become more closely packed. As a result, there is an increase in the density of water above its melting points (273 K). The density of water attains a maximum value of 1 g/mL at 277 K (4°C). Above 277 K, the density decreases due to the normal temperature effects.



6.2 PHYSICAL PROPERTIES OF WATER

Water is a colourless and volatile liquid. It has various unusual properties in the condensed phase which arises due to intermolecular H-bonding. On comparing with the hydrides of the other elements of the same group, water shows abnormally high boiling point, freezing point, heat of vapourisation and heat of fusion. The high heat of vapourisation and high heat capacity are responsible for moderation of the climate and body temperature of the living organisms. Due to high dielectric constant, water behaves as a great solvent and some covalent organic compounds show greater solubility in it. Water is an excellent solvent for transportation of ions and molecules needed for the plant and animal metabolism.

6.3 CHEMICAL PROPERTIES OF WATER

Water shows a versatile chemical behaviour. It acts as an acid, a base, an oxidising agent, a reducing agent and as a ligand to metal ions. Some typical chemical properties of water are described below:

(i) Self–ionisation of water:

A water molecule can act as an acid and a base. So, water shows self–ionisation in accordance with the equilibrium.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This reaction is also called autoprotolysis of water.

This reaction is characterised by an equilibrium constant called ionic product constant (K_w) defined as,

$$K_w = [H_3O^+]\,[OH^-]$$

At 298 K, $K_w = 1.0 \times 10^{-14}\ mol^2L^{-2}$

The autoprotolysis of water is thus of great importance in acid–base chemistry.

(ii) Oxidising and reducing nature of water:

Water can act both as an oxidising as well as a reducing agent. With active (more electropositive) elements, water acts as an oxidising agent and in turn gets reduced to give H_2 gas. The reduction potential for the reduction of water at $[OH^-] = 10^{-7}$ mol/L is –0.41 V, viz,

$2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$ $\quad E = -0.41\ V$ for $[OH^-] = 10^{-7}\ mol\ L^{-1}$

The potential for the reaction,

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$

$E = +0.82V$ for $[H^+] = 10^{-7}\ mol\ L^{-1}$.

Oxidation of water by fluorine is represented by the equation:

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

(iii) Hydrolysis reactions

Water can hydrolyse salts of weak acids with strong bases or salts of weak bases with strong acids or salts of weak acids and weak bases. In this H^+ and OH^- of water interact with anions and cations of the compound respectively, leading to the formation of an acid or base or both. For example,

(a) Hydrolysis of Na_2CO_3:

$$Na_2CO_3(s) + H_2O(excess) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + 2H_2O \longrightarrow H_2CO_3 + 2OH^-$$

The resulting solution is basic due to the presence of OH^- ions.

(b) Hydrolysis of $FeCl_3$:

$$FeCl_3(s) + H_2O(excess) \longrightarrow Fe^{3+}(aq) + 3Cl^-(aq)$$

$$2Fe^{3+}(aq) + 6H_2O \longrightarrow 2Fe(OH)_3(s) + 6H^+(aq)$$

The resulting solution is acidic due to the presence of H^+ ions.

(c) Hydrolysis of $BiCl_3$ and $SbCl_3$:

$$BiCl_3 + H_2O \longrightarrow BiOCl\downarrow + 2HCl$$

$$SbCl_3 + H_2O \longrightarrow SbOCl\downarrow + 2HCl$$

(d) Hydrolysis of non–metals halides:

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

(e) In some cases, hydrolysis of a salt may lead to the formation of a compound, which precipitates out of the solution. For example, silicon tetrachloride on hydrolysis gives SiO_2.

$$SiCl_4(l) + 4H_2O(l) \longrightarrow SiO_2.2H_2O(s) + 4HCl$$

(iv) Hydrate Formation:

Water reacts with certain metal salts to form hydrates. These are of three types.

(i) Water molecules form complex ions by combining with metal ions through coordinate bond for example in $[Ni(H_2O)_6]^{2+}$. H_2O forms coordinate bonds with Ni^{+2}.

(ii) Water molecules are coordinated by hydrogen bonding to oxoanions. For example $CuSO_4.5H_2O$ where four water molecules are coordinated to the central Cu^{2+} ion while the fifth water molecule is hydrogen bonded to sulphate.

(iii) Water is present as lattice. For example, in some alkali metal fluorides and chlorides ($KF.2H_2O$, $NaCl.2H_2O$), water molecules occupy interstitial sites in the crystal lattice.

(v) Reaction with hydrides, nitrides, carbides, phosphides and arsenides:

Water reacts with hydrides, nitrides, carbides, phosphides and arsenides at ordinary temperature liberating hydrogen, ammonia, ethyne, phosphine and arsine respectively.

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

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

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{(ethyne)}}{C_2H_2}$$

$$Al_4C_3 + 12\,H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{\text{(phosphine)}}{2PH_3}$$

$$Na_3As + 3H_2O \longrightarrow 3NaOH + \underset{\text{(arsine)}}{AsH_3}$$

Key points

1. Water has high dielectric constant and due to which it behaves as an universal solvent.
2. Water shows amphoteric nature and it is neutral towards litmus paper.
3. In liquid water, water molecules are held together by intermolecular hydrogen bonds. Because of it water shows various unusual properties.
4. In ice, one water molecule makes four hydrogen bonds which results in a cage–like structure with less density than water.

PRACTICE PROBLEMS

PP5. Which type of bonds are broken when water evaporates?

PP6. Give the products of electrolysis of H_2O and D_2O.

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7 HARD AND SOFT WATER

Water is classified into two categories depending upon its behaviour towards soap solution.

(a) Soft water: Water is described as being soft if it lathers readily with soap solution. Distilled water and rain water are examples of it.

(b) Hard water: Water is described as being hard if it does not lather readily with soap solution. Sea water and river water are examples of it.

7.1 CAUSE OF HARDNESS OF WATER

Hardness of water is due to the dissolved impurities of salts like the bicarbonates, chlorides and sulphates of calcium and magnesium. Hard water does not produce lather with soap solution readily because the cationic impurities present in hard water react with soap to form a precipitate of calcium and magnesium salts of fatty acids.

7.1.1 Behaviour of Hard Water Towards Soap

Soap is the sodium salt of long chain fatty acid ($C_{17}H_{35}COO^-Na^+$, sodium stearate). When soap is added to hard water, it reacts with the calcium and magnesium ions present in hard water to form insoluble calcium or magnesium stearate (white and curdy precipitate).

$$\underset{\text{in hard water}}{Ca^{2+}} + \underset{\text{from soap}}{2C_{17}H_{35}COO^-} \longrightarrow \underset{\text{precipitate (calcium stearate), insoluble}}{(C_{17}H_{35}COO)_2Ca\downarrow}$$

or $$CaCl_2 + 2C_{17}H_{35}COONa \longrightarrow 2NaCl + (C_{17}H_{35}COO)_2Ca\downarrow$$

$$\underset{\text{in hard water}}{Mg^{2+}} + \underset{\text{from soap}}{2C_{17}H_{35}COO^-} \longrightarrow \underset{\text{precipitate (magnesium stearate), insoluble}}{(C_{17}H_{35}COO)_2Mg\downarrow}$$

or $$MgCl_2 + 2C_{17}H_{35}COONa \longrightarrow 2NaCl + (C_{17}H_{35}COO)_2Mg\downarrow$$

As a result, soap will not produce lather with water until all the calcium and magnesium ions have been precipitated. Thus, a part of the soap is wasted and washing becomes wasteful. This is also the reason why hard water is not fit for washing (laundry) purposes.

7.1.2 Behaviour of Soft Water Towards Soap

Soap is the sodium salt of long chain fatty acid, e.g., sodium stearate ($C_{17}H_{35}COONa$). Sodium salt of stearic acid is soluble in water, whereas the calcium and magnesium salts are insoluble. So, when soap (sodium salt) is added to soft water (in the absence of Ca^{2+} and Mg^{2+} ions), it dissolves and forms lather readily. No soap, therefore, is wasted while using soft water.

7.1.3 Hard Water is not fit for Industrial Use

In industry, if hard water is used in boilers (for steam generation), calcium bicarbonate present in it decomposes to form insoluble calcium carbonate.

$$\underset{\text{in hard water}}{Ca(HCO_3)_2} \xrightarrow{\text{boiling}} \underset{\substack{\text{insoluble}\\ \text{calcium carbonate}}}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

Calcium carbonate precipitates in the boiler tubes as a very hard (stone–like) layer. If the hard water contains calcium sulphate, it leaves a deposit of calcium sulphate on the walls of the boiler tubes. These deposits of calcium carbonate or calcium sulphate in the boiler tubes are bad conductors of heat. Therefore, a lot of fuel is wasted during steam generation.

Moreover, when such solid layers (deposits) crack, the hot water comes in contact with red hot boiler surface and gets vapourised. This generates a large amount of steam and the pressure inside the boiler increases suddenly. This may sometimes lead to the bursting of the boiler.

7.2 TYPES OF HARDNESS

The hardness of water is of two types:

(a) Temporary hardness : It is due to the presence of soluble bicarbonates of calcium and magnesium. The term ‘temporary’ indicates that, mostly such type of hardness is removed by just boiling the water.

(b) Permanent hardness : It is due to the presence of chlorides and sulphates of calcium and magnesium. The term ‘permanent’ indicates that such type of hardness cannot be removed by just boiling the water.

7.3 SOFTENING OF HARD WATER

The process of removal of metallic ion impurities responsible for hardness of water is known as **softening of water.**

7.3.1 METHODS TO REMOVE TEMPORARY HARDNESS

(i) By boiling the hard water

Temporary hardness in water can be easily removed by boiling. On boiling, calcium/magnesium bicarbonate decomposes to give calcium/magnesium carbonate, which is insoluble in water. Therefore, it precipitates out.

$$Ca(HCO_3)_2 \xrightarrow{\text{boiling}} \underset{\text{insoluble calcium carbonate}}{CaCO_3\downarrow} + H_2O + CO_2$$

(ii) By the addition of slaked lime (Clark's process).

In Clark's process, slaked lime, $Ca(OH_2)$ is added to the temporary hard water. Insoluble calcium carbonate precipitates out and no longer produce hardness.

$$\underset{\text{slaked lime}}{Ca(HCO_3)_2} + Ca(OH)_2 \longrightarrow \underset{\text{insoluble calcium carbonate}}{2CaCO_3\downarrow} + 2H_2O$$

7.3.2 METHODS TO REMOVE PERMANENT HARDNESS

(i) By the addition of washing soda (sodium carbonate):

Calcium and magnesium ions present in hard water react with sodium carbonate to produce insoluble carbonates. The water now contains soluble and harmless sodium salts.

$$\underset{\text{cause of permanent hardness}}{CaSO_4} + Na_2CO_3 \longrightarrow \underset{\text{insoluble}}{CaCO_3\downarrow} + Na_2SO_4$$

$$\underset{\text{cause of permanent hardness}}{MgCl_2} + Na_2CO_3 \longrightarrow \underset{\text{insoluble}}{MgCO_3\downarrow} + 2NaCl$$

(ii) Calgon process:

Calgon is a trade name of a complex salt, sodium hexametaphosphate $(NaPO_3)_6$. It is used for softening hard water. Calgon ionises to give a complex anion, $Na_4P_6O_{18}^{2-}$.

$$\underset{\text{calgon}}{(NaPO_3)_6 \text{ or } Na_2(Na_4P_6O_{18})} \longrightarrow 2Na^+ + \underset{\text{complex anion}}{Na_4P_6O_{18}^{2-}}$$

When Calgon is added to hard water, calcium and magnesium ions from hard water displace sodium ions from the anion of the calgon.

$$\underset{\text{from hard water}}{Ca^{2+}} + \underset{\text{anion of calgon}}{Na_4P_6O_{18}^{2-}} \longrightarrow \underset{\text{goes into solution}}{2Na^+} + (CaNa_2P_6O_{18})^{2-}$$

As a result, calcium and magnesium ions from hard water are removed in the form of a complex with calgon, thus softening the water. The released sodium ions go into the water.

(iii) By the ion–exchange process:

(a) Inorganic exchangers using zeolite (Permutit process):

Permutit is a complex chemical compound called sodium aluminium silicate, which is insoluble in water. Zeolites are naturally–occurring minerals containing sodium aluminium silicates. Permutit or zeolites are packed in a suitable container and a slow stream of hard water is passed through this material. As a result, calcium and magnesium ions present in hard water are exchanged with sodium ions in the permutit (Na^+ Al–Silicate$^-$).

$$\underset{\text{in hard water}}{CaCl_2} + \underset{\text{permutit}}{Na_2Al_2Si_2O_8} \longrightarrow CaAl_2Si_2O_8 + 2NaCl$$

$$\underset{\text{in hard water}}{MgSO_4} + \underset{\text{permutit}}{Na_2Al_2Si_2O_8} \longrightarrow MgAl_2Si_2O_8 + Na_2SO_4$$

The outgoing water contains sodium salts, which do not cause hardness.

(b) Organic exchangers:

Ion exchange resins are giant organic molecules with high molecular masses and are essentially of two types:

1. Cation exchange resins:

These resins consist of giant hydrocarbon frame work attached to acidic groups such

as –COOH (Carboxyl) or $-SO_2OH$ (sulphonic acid) groups. They may be represented by the general formula R–COOH or $R-SO_2OH$ where R represents the giant hydrocarbon frame work.
Since these resins can exchange H^+ ions with cations such as Ca^{2+} and Mg^{2+} ions present in hard water, they are called cation exchange resins or simply cation exchangers.

2. **Anion exchange resins:**

These resins consists of giant hydrocarbon frame work attached to basic groups such as OH^- (hydroxide) ions usually in this form or substituted ammonium hydroxides and may be represented by the general formula, $R-\overset{+}{N}H_3OH^-$ where R denotes the giant hydrocarbon frame work. Since these resins can exchange OH^- ions with anions such as Cl^- and SO_4^{2-} ions present in hard water, they are called anion exchange resin or simply anion exchangers.

The entire process of softening the hard water takes place in two steps:

Step 1. By passing the hard water through cationic exchanger:

Hard water is passed through a tank packed with cation exchange resin supported over gravel. All the cations present in hard water are exchanged with H^+ ions furnished by the resins.

$2R-COO^-H^+ + CaCl_2 \longrightarrow (RCOO)_2Ca + 2H^+ + 2Cl^-$
(cation exchange resin) (From hard water)

$2R-COO^-H^+ + MgSO_4 \longrightarrow (RCOO)_2Mg + 2H^+ + SO_4^{2-}$
(cation exchange resin) (From hard water) (Exhausted resin)

Step 2. By passing the hard water through anionic exchanger:

The water, which comes out from the bottom of the first tank is richer in H^+ ions. This water is then passed through a second tank packed with the anion exchange resin. Here the Cl^- and SO_4^{2-} ions present in hard water are exchanged with OH^- ions of the resin.

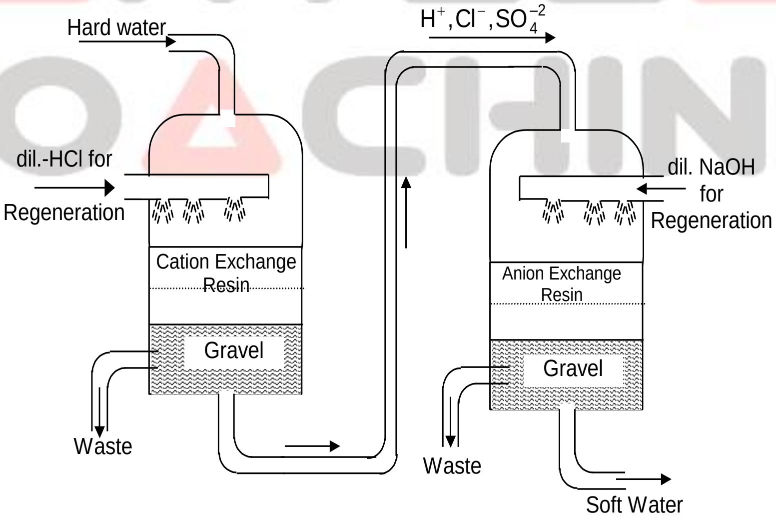
$R-\overset{+}{N}H_3OH^- + Cl^- \longrightarrow R-\overset{+}{N}H_3Cl^- + OH^-$
(Anion exchange resin) (in water)

$2R-\overset{+}{N}H_3OH^- + SO_4^{2-} \longrightarrow (R-\overset{+}{N}H_3)_2SO_4^{2-} + 2OH^-$

Simultaneously, the H^+ ions coming from the first tank combine with the OH^- ions liberated in the second tank to form water.

$H^+ + OH^- \longrightarrow H_2O$

Thus, the water obtained by this method is free from all types of cations as well as anions.



REMOVAL OF HARDNESS BY THE ORGANIC ION EXCHANGER

Key points

1. Hard water does not produce lather with soap solution readily.
2. Dissolved impurities of salts like bicarbonates, chlorides and sulphates of calcium and magnesium cause hardness.

PRACTICE PROBLEMS

PP7. Hard water sample is allowed to pass through cation exchange resin. Will it produce lather with soap readily?

PP8. When zeolite is treated with hard water which ions are exchanged with sodium ions?

8 HYDROGEN PEROXIDE

Traces of hydrogen peroxide are found in the atmosphere and water. It is also present in the juice of certain plants.

8.1 PREPARATION OF H_2O_2

Preparation: In laboratory, hydrogen peroxide may be prepared from sodium peroxide or barium peroxide.

(i) From sodium peroxide (Merck's method):

In this method, sodium peroxide is added in small amounts at a time to an ice cold dilute solution (20 percent) of sulphuric acid.

$$Na_2O_2 + \underset{\text{ice cold}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O_2$$

Sodium sulphate is removed by crystallisation and a dilute solution of H_2O_2 is obtained.

(ii) From barium peroxide (BaO_2) :

In this case, a paste of $BaO_2.8H_2O$ is prepared and added gradually to an ice–cold dilute sulphuric acid. The solution is kept well–stirred throughout.

$$BaO_2 + \underset{\text{ice cold}}{H_2SO_4} \longrightarrow BaSO_4\downarrow + H_2O_2$$

Barium sulphate precipitates out, leaving behind a dilute solution of hydrogen peroxide. Phosphoric acid can also be used in place of sulphuric acid.

Alternatively, a current of carbon dioxide is passed through a suspension of barium peroxide in cold water.

$$BaO_2 + H_2O + CO_2(g) \longrightarrow BaCO_3\downarrow + H_2O_2$$

The precipitated barium carbonate is removed by filtration.

8.2 PRODUCTION OF H_2O_2

(i) By the electrolysis of ammonium hydrogen sulphate:

Hydrogen peroxide can be prepared on a large scale by the electrolysis of ammonium hydrogen sulphate dissolved in excess of sulphuric acid using platinum electrodes and a high current density. In this process, ammonium persulphate is produced by oxidation at the anode while hydrogen is liberated at the cathode.

$$NH_4HSO_4 \longrightarrow H^+ + NH_4SO_4^- \text{ (dissociation)}$$

At anode: $$2NH_4SO_4^- \longrightarrow \underset{\text{ammonium persulphate}}{(NH_4)_2S_2O_8} + 2e^-$$

At cathode: $$2H^+ + 2e^- \longrightarrow H_2(g)$$

The solution containing ammonium persulphate is heated at 43 mm Hg pressure when it hydrolyses yielding hydrogen peroxide.

$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$$

Hydrogen peroxide along with water distils over. The aqueous solution (30–40% H_2O_2) is concentrated to 85–90 percent by fractional distillation under reduced pressure. Water, being more volatile, passes over first.

Ammonium bisulphate recovered as above is used again.

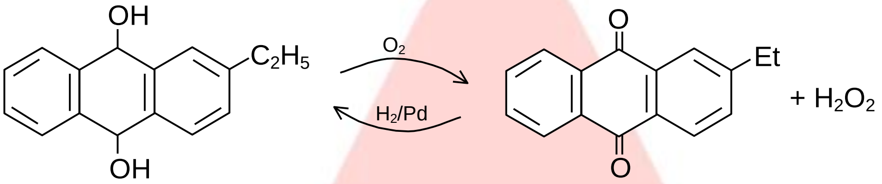
In order to have high current density; (i.e. current strength per unit area of the electrode) at the anode, the area of the anode is kept small.

(ii) By autoxidation of 2–ethylanthraquinol:

The modern process for the manufacture of H_2O_2 is based on the autoxidation of 2–ethylanthraquinol. In this process, air is passed through 10 percent solution of this compound in a mixture of benzene and an alcohol containing 7–11 carbon atoms.

The resulting 2–ethylanthraquinone is then reduced by passing hydrogen under a pressure of 1 to 3 atmospheres at 4°C. This gives back 2–ethylanthraquinol. This method, thus involves alternate oxidation and reduction steps.

Hydrogen peroxide formed in this reaction is extracted with water and the dilute solution of H_2O_2 is concentrated to obtain H_2O_2 of the required strength.

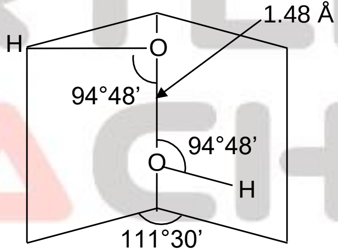


8.3 PHYSICAL PROPERTIES OF H_2O_2

(i) Pure hydrogen peroxide is a pale–blue syrupy liquid with a bitter taste.
(ii) It is soluble both in water and alcohol.
(iii) Pure H_2O_2 is weakly acidic and exists as associated liquid due to hydrogen bonding.
(iv) Its density is 1.469 g/mL. High specific gravity of H_2O_2 as compared to water is due to strong association of molecules due to hydrogen bonding.
(iv) It melts at 272.4 K (–0.7°C) and boils under 1 atm pressure at 423.2 K (150°C) with violent decomposition. However, it can be distilled under reduced pressure (≈ 26 torr) at 69.2°C.
(v) It is diamagnetic.
(vi) Due to its high dielectric constant, (93.7 for pure H_2O_2) it behaves as an excellent solvent for electrolytes.

8.4 STRUCTURE OF H_2O_2

Hydrogen peroxide molecule in the gas phase has a non–planar structure. The bond lengths are, O–O bond length 147.5 pm, O–H bond length 95 pm. Each H–O–O bond angle is about 94.8°, while the angle between the planes containing the hydrogen atoms is 111.5°.



Structure of H_2O_2 in the gas phase

In the crystal, the angle between the planes containing hydrogen atoms gets reduced from 111.5 to 90.2° on account of hydrogen bonding. The two oxygen atoms are joined by a single electron–pair bond.

8.5 CHEMICAL PROPERTIES OF H_2O_2

Hydrogen peroxide has an interesting chemistry because of its ability to function as an oxidant as well as a reductant in both acid and alkaline solutions. The oxidation state of oxygen in hydrogen peroxide is –1. It can, therefore, be oxidised to O_2 (zero oxidation state) or reduced to H_2O or OH^- (–2 oxidation state for oxygen). On the whole, hydrogen peroxide is a very powerful oxidising agent and a poor reducing agent.

(i) Stability

Thermodynamically, hydrogen peroxide is unstable as shown by the following equation

$$H_2O_2(l) \longrightarrow H_2O(l) + \tfrac{1}{2} O_2(g) \qquad \Delta_rG^\circ = -122.6 \text{ kJ mol}^{-1}$$

As the reaction from left to right is accompanied by a decrease of free energy, it is a spontaneous process. However, its decomposition at 25°C in the absence of catalysts is slow. The catalyst which accelerates the decomposition are platinum, silver, cobalt, iron, copper, manganese dioxide, etc. and light. Concentrated H_2O_2 solution can result into uncontrolled decompositions leading to explosion. H_2O_2 is thus, stored in coloured wax–lined bottles (as rough glass surfaces also causes its decomposition). A few stabilizers such as acids, acetanilide, pyrophosphates and stannates are added to slow down the decomposition of H_2O_2.

(ii) Acidic nature

Hydrogen peroxide is a weak acid. Its dissociation constant for the equilibrium,

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

is 1.5×10^{-12} at 20°C.

With alkalies, it gives corresponding peroxides.

$$H_2O_2 + 2NaOH \longrightarrow \underset{\text{sodium peroxide}}{Na_2O_2} + 2H_2O$$

(iii) Oxidising properties

Hydrogen peroxide provides an atom of oxygen (nascent oxygen) readily. Therefore, it acts as a strong oxidising agent in acidic as well as alkaline solutions. Some typical oxidation reactions given by H_2O_2 are:

(a) It oxidises lead sulphide to lead sulphate (in acidic medium)

$$\begin{array}{l} [H_2O_2 \longrightarrow H_2O + O] \times 4 \\ PbS + 4O \longrightarrow PbSO_4 \\ \hline 4H_2O_2 + PbS \longrightarrow 4H_2O + PbSO_4 \\ \hline \end{array}$$

(b) It oxidises acidified ferrous sulphate to ferric sulphate (in acidic medium)

$$\begin{array}{l} H_2O_2 \longrightarrow H_2O + O \\ 2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O \\ \hline H_2O_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_2O \\ \hline \end{array}$$

(c) It oxidises potassium iodide to iodine (in neutral solution)

$$\begin{array}{l} H_2O_2 \longrightarrow H_2O + O \\ 2KI + H_2O + O \longrightarrow 2KOH + I_2 \\ \hline H_2O_2 + 2KI \longrightarrow 2KOH + I_2 \\ \hline \end{array}$$

(d) It oxidises sodium arsenite to sodium arsenate.

$$\begin{array}{l} H_2O_2 \longrightarrow H_2O + O \\ Na_3AsO_3 + O \longrightarrow Na_3AsO_4 \\ \hline H_2O_2 + Na_3AsO_3 \longrightarrow H_2O + Na_3AsO_4 \\ \hline \end{array}$$

(e) With acidified potassium dichromate, it gives a deep blue solution containing CrO_5, which is fairly stable in ethereal solution. $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

(iv) Reducing properties

Hydrogen peroxide acts as a reducing agent in the presence of other oxidising agents. This is because it can take up an atom of oxygen to give water and oxygen gas. Some typical reactions showing the reducing property of hydrogen peroxide are given below.

(a) It reduces silver oxide to silver

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

(b) It reduces chlorine to hydrochloric acid

$$\begin{array}{l} Cl_2 + H_2O \longrightarrow 2HCl + O \\ H_2O_2 + O \longrightarrow H_2O + O_2 \\ \hline Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2 \\ \hline \end{array}$$

(c) It decolourises pink colour of acidified solution of potassium permanganate.

$$\begin{array}{l}
2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\
H_2O_2 + O \longrightarrow H_2O + O_2\ ] \times 5 \\
\hline
2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \\
\hline
\end{array}$$

(d) It gives a green colour with acidified potassium dichromate solution.

$$\begin{array}{l}
K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O \\
H_2O_2 + O \longrightarrow H_2O + O_2\ ] \times 3 \\
\hline
K_2Cr_2O_7 + 4H_2SO_4 + 3H_2O_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2 \\
\hline
\end{array}$$

(e) It reduces alkaline solution of potassium ferricyanide to potassium ferrocyanide.

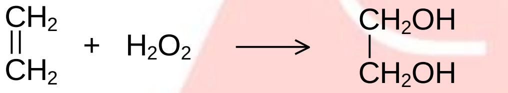
$$\begin{array}{l}
2K_3[Fe(CN)_6] + 2KOH \longrightarrow 2K_4[Fe(CN)_6] + H_2O + O \\
H_2O_2 + O \longrightarrow H_2O + O_2 \\
\hline
2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2 \\
\hline
\end{array}$$

(f) It reduces ozone to oxygen

$$\begin{array}{l}
O_3 \longrightarrow O_2 + O \\
H_2O_2 + O \longrightarrow H_2O + O_2 \\
\hline
O_3 + H_2O_2 \longrightarrow H_2O + 2O_2 \\
\hline
\end{array}$$

(v) Addition reaction

Hydrogen peroxide is capable of adding itself to double bond.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O_2 \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

ethane–1, 2–diol

(vi) As a bleaching agent

It acts as a bleaching agent for delicate materials like wool, silk, ivory. It bleaches hair to golden yellow colour. The bleaching action of H_2O_2 is due to its oxidising character.

$$H_2O_2 \longrightarrow H_2O + [O]$$

8.6 USES OF H_2O_2

(i) It is used as a mild bleaching agent for bleaching delicate articles such as hair, silk, wool, etc.

(ii) It restores the colour of the old lead paints blackened by the action of H_2S. The lead sulphide (black) gets oxidised to lead sulphate (white).

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

Key points

1. H_2O_2 has an ability to function as an oxidant as well as a reductant in both acidic and alkaline solution.
2. The oxidation state of oxygen in H_2O_2 is **–1**.

PRACTICE PROBLEMS

PP9. What is the role of H_2O_2 in the given reaction?

$$H_2O_2 + Cl_2 \longrightarrow 2HCl + O_2$$

10 HYDROGEN ECONOMY

In our present day life, the production of energy depends on the traditional energy sources. Natural fossil fuels like coal, LPG, natural gas etc. are limited and the use of nuclear power has its own limitations.

In this regard, a prospective alternative is **Hydrogen Economy.** The transportation and storage of energy in the form of liquid or gaseous hydrogen is the basic principle of hydrogen economy. As electricity cannot be stored and its transmission has various problems, hydrogen economy permits transmission of energy, not as electric power but in the form of hydrogen. So hydrogen economy suggests that hydrogen can be used as an alternative energy source. Use of hydrogen as a fuel has some advantages, which are as follows:

1. Hydrogen is abundantly available in the universe.
2. Use of hydrogen as fuel provides pollution free atmosphere because its combustion product is water.
3. Heat of combustion per gram of hydrogen is more than twice that of a jet fuel.
4. Hydrogen-oxygen fuel cell provides other possibilities of powering motor vehicles.
5. Hydrogen is an excellent reducing agent and can replace coal in many industrial processes involving reduction because it produces less atmospheric pollution than carbon.