# *Chapter-1*

# HYDROGEN AND ITS COMPOUNDS

## Hydrogen

**Symbol : H** **At. No. : 1**

**Placed with alkali metals as well as Halogens** **At. wt. : 1.008**

**Electronic configuration – $1s^1$**

Hydrogen is the first element in the periodic table. Due to its unique electronic configuration and small size, it shows some special properties. It resembles alkali metals as it can form $H^+$ ion. It is the lightest element having maximum specific heat. It's inversion temperature is –80°C. It is the only element whose atom has no neutron.

### Resemblance of Hydrogen with alkali metals :

(i) Electronic configuration : All the alkali metals as well as Hydrogen contain only one electron in their valence shell.

$H_1 \rightarrow 1s^1$ $Na_{11} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^1$

(ii) Electropositive nature :

$H \rightarrow H^+ + e$ $Li \rightarrow Li^+ + e$ $Na \rightarrow Na^+ + e$

Like alkali metals Hydrogen can undergo oxidation to show electropositive nature.

(iii) Valency – Alkali metals and Hydrogen are monovalent.

HCl NaCl

(iv) Liberation at cathode : Hydrogen liberates at cathode like alkali metals during electrolysis.

(v) Reducing property : Hydrogen is a strong reducing agent like the alkali metals.

$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(g)$

$TiCl_4 + 4Na \xrightarrow{Ar} Ti + 4NaCl$

(vi) Affinity for electronegative element : Both Hydrogen and alkali metals have great affinities for electronegative elements like, halogens, Sulphur, Oxygen etc.

### Resemblance of Hydrogen with Halogens :

**(i)** ***Electronic configuration :*** Like halogens, Hydrogen is short of one electron for stability in the outermost orbit as explained above.

$H + e \rightarrow H^-$ $F + e \rightarrow F^-$

**(ii)** ***Atomicity :*** All halogens exist as diatomic covalent molecules $F_2$, $Cl_2$ etc. In a similar way, Hydrogen is a diatomic covalent molecule.

$H_2$ $Cl_2$ $Br_2$

**(iii)** ***Valency :*** Both alkali metals and Hydrogen are monovalent.

**(iv)** ***Oxidation state :*** Halogen shows –1 oxidation state in halides. Similarly in ionic hydrides, oxidation state of Hydrogen is –1.

$Li^+H^-$ $Na^+H^-$ $Na^+F^-$

**(v)** ***Physical state :*** Hydrogen is a gas like $F_2$ and $Cl_2$.

(vi) *Non-metallic nature :* Like halogens, Hydrogen is a non-metal.

**(vii)** ***Ionization potential :*** I.P. of Hydrogen is almost equal to that of halogens.

| | |
|---|---|
| H | 13.12 eV |
| F | 16.8 eV |
| Cl | 12.55 eV |
| Br | 11.43 eV |
| I | 10.09 eV |

**(viii)*Reaction with non-metals:*** Both the halogen and Hydrogen combine with other non-metals by forming single bonds to give compounds like $CCl_4$, $CH_4$, $SiCl_4$.

## Occurrence of Hydrogen

Nearly 1% Hydrogen (by weight) occurs in the earth's crust. In uncombined form, it is found in traces in atmosphere. Free Hydrogen is found in many volcanic and other natural gases, in the sun's atmosphere etc. Combined Hydrogen is very widely distributed in the nature in the form of water, organic substances, Ammonia, Hydrogen sulphide etc.

Sources of Hydrogen :

(1) Water (2) Acids (3) Alkali

## Forms of Hydrogen

### (i) Isotopes of Hydrogen

$^{1}_{1}H$ Protium $^{2}_{1}D$ Deuterium $^{3}_{1}T$ Tritium

### (ii) Atomic Hydrogen

$$H_2 \xrightarrow{\text{Electric Arc}} 2H;\ \Delta H = 104.5 \text{ kcal mol}^{-1}$$

$t_{1/2}$ for atomic Hydrogen is 0.3 seconds only.

### (iii) Nascent hydrogen

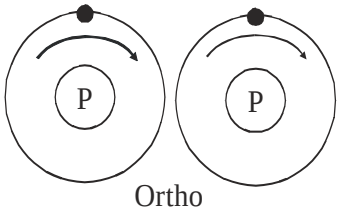
$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2[H]$

Since the magnitude of energy varies with the nature of the reaction, hence the reactivity of nascent Hydrogen is different from different sources. Nascent Hydrogen is molecular Hydrogen which is at higher pressure.

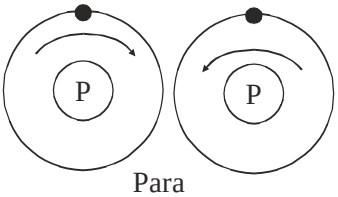
### (iv) Occluded Hydrogen

Some metals (transition metals) adsorb relatively large volume of $H_2$ gas under certain conditions. Pd absorbs 900 times its own volume. The Hydrogen is evolved when the metal is heated. Adsorbed or occluded Hydrogen is more reactive than molecular Hydrogen.

### (v) Ortho and para hydrogen



Ortho



Para

When the spins of both the protons (nucleus) in the **Hydrogen molecule** are in the same direction then this form is known as ortho Hydrogen. The molecule of Hydrogen in which both the protons are spinning in opposite direction known as para Hydrogen. These are **nuclear isomers**. At normal temperature the ratio of ortho and para Hydrogen is 3 : 1, but as the temperature is lowered, the proportion of para Hydrogen increases (at 20°C).

## Preparation of Hydrogen

(i) By the action of acids on metals

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

(ii) Action of alkali on amphoteric metals

$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

(iii) Action of water on active metals

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

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

(iv) From hot water

$Mg + H_2O \rightarrow MgO + H_2$

(v) From steam : Magnetite $Fe_3O_4$ (oxide with magnetic properties alongwith $H_2$ is produced).

$3Fe + 4H_2O \rightleftharpoons \underset{\text{Magnetite}}{Fe_3O_4} + 4H_2$

### Manufacturing

(i) Bosch process :

$C + H_2O \rightarrow CO + H_2$

$H_2 + CO + H_2O \xrightarrow[Cr_2O_3]{Fe_2O_3} 2H_2 + CO_2$

$CO_2 + H_2O \xrightarrow{25\ atm} H_2CO_3$

(ii) Lane process

$3Fe + 4H_2O \xrightarrow{1000\,^\circ C} Fe_3O_4 + 4H_2$

### Physical Properties

(i) Colourless, odourless, tasteless gas

(ii) Sparingly soluble in water due to non-polar nature

(iii) Density is 0.09 gm/lit

(iv) B.P. is 20.4 K

(v) Pd metal can adsorb $H_2$ gas

## Chemical Properties

(i) Hydrogen is not a reactive gas, because its bond energy is very high (104 Kcal $mol^{-1}$). It is inflammable gas and burns in air with a pale blue flame forming water.

$2H_2 + O_2 \rightarrow 2H_2O$

(ii) With non-metals

$N_2 + 3H_2 \xrightarrow[500°C]{Fe} 2NH_3 + 22.4$ kcals

$C + 2H_2 \rightarrow CH_4$

$H_2 + Cl_2 \rightarrow 2HCl$

(iii) With metals

$2Na + H_2 \rightarrow 2NaH$

$Ca + H_2 \rightarrow CaH_2$

(iv) Reducing nature

$ZnO + H_2 \rightarrow Zn + H_2O$

$CuO + H_2 \rightarrow Cu + H_2O$

(v) With unsaturated compounds

$R - CH = CH_2 + H_2 \xrightarrow[250°C]{Ni} R - CH_2 - CH_3$ (Sabatier & Sanderens reaction)

$R - C \equiv CH + H_2 \xrightarrow[250°C]{Ni} R - CH = CH_2$ (Sabatier & Sanderens reaction)

(vi) Hydrogenation – oils are the mixture of triglycerides of unsaturated fatty acids. When Hydrogen gas is passed through a vegetable oil at 180°C under pressure in the presence of Nickel as a catalyst. It is converted into a triglycerides having higher melting point. 'Vegetable ghee' is also known as hardening of oils.

### Uses :

(i) In the manufacture of $NH_3$ (Haber's process), synthetic petrol (Fischer-Tropsch process), methyl alcohol.

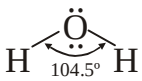
(ii) In filling balloons and airship.

(iii) As a reducing agent.

(iv) In the preparation of vegetable ghee from vegetable oil.

(v) As a fuel in rocket propellant.

## WATER

$H_2O$ 


Hybridization of Oxygen is $sp^3$ but due to presence of two lone-pair of electrons on the central Oxygen atom, its structure is bent and bond angle is less than tetrahedral angle.

Water molecules are associated with inter-molecular Hydrogen bond. It's density is maximum at 4°C.

## Hard and Soft Water

A sample of water which easily produces lather with soap is known as "Soft Water" while "hard water" doesn't give lather with soap easily.

The soluble $Ca^{+2}$ $Mg^{+2}$ ions react with soap to give Ca or Mg soap which being insoluble in water get precipitated.

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

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

## Hardness of Water and Removal

(i) Temporary hardness : It is due to the dissolution of bicarbonates of Ca and Mg in water. It can be removed by boiling.

$Ca(HCO_3)_2 \xrightarrow{\text{Boiling}} CaCO_3 + H_2O + CO_2$

$Mg(HCO_3)_2 \xrightarrow{\text{Boiling}} MgCO_3 + H_2O + CO_2$

It can also be done by adding lime

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$

$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + MgCO_3 + 2H_2O$

## Permanent Hardness and Removal

It is due to dissolution of chloride and sulphates of Ca and Mg. It cannot be removed by boiling water. It can be removed by :

### (a) Adding washing soda

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

### (b) Permutit Method

Permutit is an artificial zeolite. It is Sodium alumino orthosilicates i.e., $Na_2Al_2Si_2O_8 \cdot H_2O$ which is taken in the form of a bead and hard water containing $Ca^{++}$ and $Mg^{++}$ ions is percolated through the bead. The hardness causing ions are retained by the bead and $Na^+$ ions from bead, form soluble salt like $NaHCO_3$. To recharge the bead after complete exhaustion, it is treated with NaCl solution which regenerates the zeolite bead. This process removes both types of temporary and permanent hardness.

$Na_2Z + Ca(HCO_3)_2 \downarrow \rightarrow CaZ \downarrow + 2NaHCO_3$

$CaZ \text{ (or } MgZ) + 2NaCl \xrightarrow{\text{(or } MgHCO_3)} Na_2Z + CaCl_2 \text{ (or } MgCl_2)$

**(c) Calgon Process :** Calgon which is also known as Grahm's salt is the trade name of Sodium hexa meta phosphate $(NaPO_3)_6$. The $Ca^{+2}$ and $Mg^{+2}$ ions dissolved in hard water react with calgon to produce complex anions, which are very inactive and dont produce a ppt. with soap.

$Na_2[Na_4(PO_3)_6] + 2CaCl_2 \longrightarrow Na_2[Ca_2(PO_3)_6] + 4NaCl$

**(d) By Ion Exchange Resin :** Resins are giant organic molecules attached with acidic or basic groups. Cation exchange resin contain –COOH or $-SO_3H$ group. These removes cations like $Na^+$, $Ca^{+2}$, $Mg^{+2}$, $Fe^{+2}$ etc. by exchange with $H^+$.

Anion exchange resins contains $-NH_2$ group they are represented by $RN^+H_3OH^-$. These resins remove negative ions such as $Cl^-$, $SO_4^{-2}$, $NO_3^-$ etc.

## Degree of Hardness :

Degree of hardness is usually expressed in parts per million (ppm) and thus may be defined as the number of parts by weight of $CaCO_3$ (equivalent to Calcium and Magnesium salt) present in a million ($10^6$) parts by weight of water.

1 ppm = 1 part of $CaCO_3$ in $10^6$ parts of water.

**Ex. 1.** A sample of water contains (a) 10 ppm of $CaCO_3$ (b) 90 ppm of $MgSO_4$ and (c) 111 ppm of $CaCl_2$. Then calculate total hardness of this sample.

**Sol.** Water hardness is calculated in terms of $CaCO_3$ hardness only. Therefore,

$CaCO_3 \equiv MgSO_4 \equiv CaCl_2$.

Mol. mass 100 120 111

Therefore, hardness for (a) = 10 ppm, (b) = $\frac{90\times100}{120}$ = 75 ppm, (c) = $\frac{111\times100}{111}$ = 100 ppm.

Therefore total hardness = 10 + 75 + 100 = 185 ppm.

The formula for conversion of hardness in terms of $CaCO_3$ is

$$\text{Hardness in ppm of } CaCO_3 = \frac{\text{ppm of other species}}{\text{Molecular mass of other species}} \times 100$$

## Hydrides :

Hydrogen combines with a number of metals which have low electronegative values and are electropositive with respect to Hydrogen i.e., alkali and alkaline earth metals (except Be and Mg). These are formed by the transference of electrons from metals to the Hydrogen atom, and convert Hydrogen into hydrides $H^-$.

Such Hydrides have high melting point and boiling point and conduct electricity in fused state liberating Hydrogen at the anode. Their density is higher than that of the metal.

Thermal stability decreases with increasing size of cations

$LiH > NaH > KH > RbH > CsH > CaH_2 > SrH_2$

## Molecular or Covalent Hydrides

These are formed by elements of highly electronegative elements (viz. non metals) which share electrons with Hydrogen. In most of the cases, bonds are covalent in character, although in some cases (e.g. HF) the bond is partly ionic in nature. Such hydrides are soft, have low melting point and boiling point. They have low electrical conductivity so, stability decreases down the group.

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

But along a period, the stability increases with increasing electronegativity of the element, forming the hydride;

$CH_4 < NH_3 < H_2O < HF$

They become increasingly acidic in character on moving along a period from left to right. So, $NH_3$ is a weak base, $H_2O$ is neutral, while HF is acidic.

### Metallic or Interstitial Hydrides

Such hydrids are formed by Be, Mg (s-Block) and Transition elements. These are interstitial compounds as the Hydrogen atoms occupy interstitial places in the metal lattices. These are non-stoichiometric compounds and give out Hydrogen easily, and are used as strong reducing agents. This suggest that Hydrogen is in atomic state have zero O.No.

### Hydrogen Peroxide, $H_2O_2$

**Preparation :**

(i) (a) By the reaction of $H_2SO_4$ or $H_3PO_4$ on hydrated $BaO_2$

$$BaO_2 \cdot 8H_2O + H_2SO_4 \longrightarrow BaSO_4 \downarrow + H_2O_2 + 8H_2O$$

It is important to note that anhydrous $BaO_2$ does not react readily with $H_2SO_4$ as a coating of insoluble $BaSO_4$ is formed on its surface which stops further action of the acid.

(b) $$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

$$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$$

Treatment of $H_3PO_4$ is preferred to $H_2SO_4$ as soluble impurities like Barium persulphate (from $BaO_2 \cdot 8H_2O_2$) tends to decompose $H_2O_2$ while $H_3PO_4$ acts as a negative catalyst.

$$BaO_2 + H_2O_2 \longrightarrow BaO + H_2O + O_2$$

(ii) By adding calculated quantity of $Na_2O_2$ to a 20% ice cold $H_2SO_4$ solution (Merck's process)

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

### Manufacture of $H_2O_2$

(i) By the electrolysis of 50% $H_2SO_4$ to give perdisulphuric acid $H_2S_2O_8$, which on distillation gives 30% solution of $H_2O_2$.

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$$

At cathode, $2H^+ + 2e \longrightarrow 2H \longrightarrow H_2$

At anode, $2HSO_4^- \longrightarrow 2HSO_4 + 2e$

$$2HSO_4 \longrightarrow H_2S_2O_8$$

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

(ii) By the auto-oxidation of 2-Ethyl anthraquinol. It is the most modern method.

2-Ethyl anthraquinol $\xrightarrow{air}$ 2-Ethyl anthraquinone + $H_2O_2$

So, obtained 2-Ethylanthraquinone is reduced by Hydrogen in presence of Pd as a catalyst.

## Concentration of $H_2O_2$

Concentration of $H_2O_2$ solution is a dangerous operation, because impurities (particularly organic matter or metallic ion) present in the solution helps in decomposition. However, it can be performed continuously in the following ways :

(a) By freezing $H_2O_2$ solution when some water separates out as ice.

(b) By careful evaporation of the solution when water being more volatile than $H_2O_2$ will be removed till 30% solution is obtained.

(c) Concentration upto 90% $H_2O_2$ can be obtained by distillation under reduced pressure at a temperature below 60°C.

(d) Further concentration can be achieved by cooling 90% solution till crystallisation.

## Strength of $H_2O_2$

Concentration of $H_2O_2$ is expressed in terms of volume strength i.e., 10 volume, 15 volume, 20 volume etc. $H_2O_2$ solution. In fact, it represents the volume of $O_2$ obtained at NTP by the decomposition of 1 ml of $H_2O_2$ solution. e.g., 20 ml $H_2O_2$ means 1 ml of this solution on decomposition evolves 20 ml of $O_2$ at NTP.

Sometimes the concentration of $H_2O_2$ is expressed as percentage of $H_2O_2$ in solution (W/v). Thus 30% solution of $H_2O_2$ means 30 gm $H_2O_2$ are present in 100 ml of solution of $H_2O_2$ (sol. $H_2O_2$ is known as perhydrol). **Formula for Conversion : 1 volume = 3.03 gm/lit of $H_2O_2$ = 0.089 M or 0.178 N.**

## Properties of $H_2O_2$

### (1) Physical :

(i) Pure $H_2O_2$ is a pale-blue syrupy liquid.

(ii) It decomposes rapidly at its normal boiling point of 151°C at 76 cm pressure.

(iii) It is an unstable liquid and decomposes into water and Oxygen either on standing or on heating. In order to check its decomposition, it is kept in a wax lined coloured bottles with a few drops of $H_3PO_4$, glycerol, or acetanilide to prevent its decomposition.

(iv) It is diamagnetic.

(v) In pure state, its di-electric constant is 93.7.

(vi) pure $H_2O_2$ is weakly acidic in nature, while its aqueous solution is neutral.

(i) Decomposition

$$2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2 \quad \Delta H = -196 \text{ kJ}$$

(ii) Oxidising and reducing nature :

$H_2O_2$ acts as a strong oxidising agent under acidic and alkaline conditions. Oxidation in acidic medium is slow while rapid in alkaline solution as $H_2O_2$ itself is a weak acids.

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$$

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

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

$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$

$$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + 2H_2O + I_2$$

$$H_2O_2 + H_2S \longrightarrow 2H_2O + S$$

$$2K_4[Fe(CN)_6] + H_2O_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KOH$$

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow K_2SO_4 + 2CrO_5 + 5H_2O$$

(Blue)

$$4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$$

$$H_2O_2 + 2OH^- + 2e \longrightarrow 2H_2O + 2O^{-2}$$

$$2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2$$

**Reducing nature**

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2O_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2$$

$$O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$$

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

$$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$

### (iii) Bleaching action

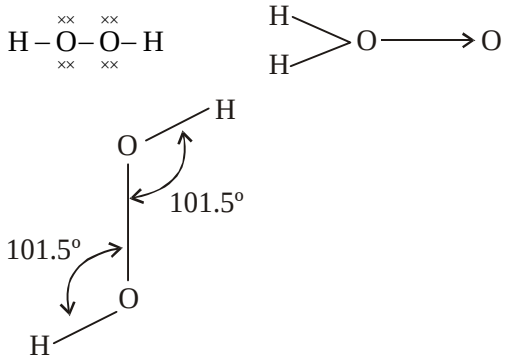
$H_2O_2$ acts as a bleaching agent due to oxidising nature e.g., bleached human hair (black to golden brown), ivory, silk, wool, feather etc.

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

### (iv) Addition properties

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

## Structure




## Uses

(i) As a bleaching agent.

(ii) In the restoration of colour of old paintings.

(iii) As an oxidising agent in laboratory.

(iv) As an antiseptic or germicide for washing wounds, teeth and ears under the name of perhydrol.

(v) As a propellant.

(vi) As an oxidant (liquid $H_2O_2$ + hydrazine) for rocket fuel.