

## HYDROGEN & ITS COMPOUNDS

### OCCURRENCE, ISOTOPES, PREPARATION, PROPERTIES, USES OF HYDROGEN

- + The first element in the periodic table is Hydrogen.
- + The lightest of all the elements is Hydrogen.
- + The only atom without neutrons is Protium.
- + The element without suitable position in the periodic table is Hydrogen.
- + Hydrogen should belong to the s-block as its electron configuration is  $1s^1$ .
- + The properties in which Hydrogen resembles alkali metals are
  - a) Like alkali metals, "H" has one electron in the valence shell
  - b) Like Alkali metals, H forms  $H^+$  ion
  - c) Like Alkali metals, "H" forms monoxides and peroxides
  - d) Like Alkali metals, "H" acts as reductant
- + The properties in which Hydrogen resembles Halogens are
  - a) Like Halogens, it is diatomic molecule ( $H_2$ )
  - b) Like Halogens, it is short of one electron to attain inert gas configuration
  - c) The Ionisation potential value of "H" is much nearer to those Ionisation potential values of Halogens.
  - d) H can also form hydride ion  $H^-$
- + Hydrogen has 3 isotopes. They are
  - Protium
  - Deuterium
  - Tritium
- + Theoretically the number of possible Hydrogen molecules is 6. They are  $H_2$ ,  $D_2$ ,  $T_2$ , HD, HT and DT.
- + Ordinary Hydrogen is more reactive than Deuterium.
- + All the isotopes of Hydrogen have
  - a) The same position in the Long form of Periodic Table
  - b) Same electron configuration
  - c) Similar chemical properties
  - d) Same atomic radii
- + The isotopes of Hydrogen differ in their
  - a) Mass number
  - b) Number of neutrons
  - c) Chemical reactivity
  - d) Physical properties
  - e) Bond energy of molecules
- + The radioactive isotope of Hydrogen is Tritium.
- + Generally ordinary Hydrogen contains Tritium and Protium in the ratio 1:  $10^{17}$ .
- + Tritium can be obtained in the nuclear transformations such as
  - (Occurs in nature)
  - (Takes place in nuclear reactors)
- + The radioactive isotope of Hydrogen is **Tritium**. It exhibits radioactivity by Beta emission.

- + Tritium is harmless, since it emits only low energetic  $\alpha$ -radiation but not harmful  $\gamma$ -rays.
- + In the study of mechanism of various chemical reactions, Deuterium and Tritium are used as tracers.
- + As the mass number increases, the chemical reactivity decreases. So chemically least reactive isotope of Hydrogen is Tritium.
- + The physical properties of Hydrogen and Deuterium are.

| Property                     | Hydrogen H <sub>2</sub> | Deuterium D <sub>2</sub> |
|------------------------------|-------------------------|--------------------------|
| Bond length                  | 0.7414Å                 | 0.7414Å                  |
| Bond energy                  | 436 KJ/mole             | 443.4 KJ/mole            |
| Latent heat of fusion        | 0.117KJ/mole            | 0.197 KJ/mole            |
| Latent heat of vapourisation | 0.904 KJ/mole           | 1.226 KJ/mole            |
| B.P                          | -252.6°C                | -249.4°C                 |
| M.P                          | -259.2°C                | -254.4°C                 |
| Molecular mass               | 2.016                   | 4.03                     |

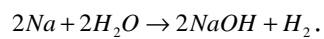
- + Hydrogen is the most abundant element in the universe.
- + H<sub>2</sub> is absorbed by metals like Pd. This is known as **Occlusion of Hydrogen**.
- + Hydrogen accounts for 15.4% of all atoms in earth's crust. On this count it is second largest available element on earth's crust.
- + a) Metals having lower SRP than hydrogen reacts with acids to liberate H<sub>2</sub>  
This method is used to prepare hydrogen in the laboratory.
- + b) Hydrogen is also prepared by the action of alkali on metals like, Zn, Al, Sn
- + H<sub>2</sub> is the byproduct in the electrolysis of brine. Pure H<sub>2</sub> is obtained in this process.
- + Large quantities of H<sub>2</sub> are prepared cheaply by the action of steam on red hot coke.  
Where this gas mixture is passed over a catalyst (Fe<sub>2</sub>O<sub>3</sub>/Cr), CO is oxidised to CO<sub>2</sub>
- + In petroleum industry cracking of naphtha and fuel oil produce H<sub>2</sub> as by product.
- + In an electric arc at the high temperature or under the influence of u.v. radiations atomic hydrogen is formed and it is extremely reactive and brings about many reductions at ordinary temperatures.
- + At high temperature (nearly about 2275 K), H<sub>2</sub> molecule decomposes to give atomic hydrogen.
- + H<sub>2</sub> burns in air or O<sub>2</sub> and forms water. This reaction takes place at ordinary temperature in presence of Pd or Pt black.
- + H<sub>2</sub> reduces metal oxides and their halides to the corresponding metals.
- + H<sub>2</sub> combines with many organic compounds in the presence of catalyst
  - i) Hydrogenation of oils to give fats
  - ii) Hydrogenation of olefins yields aldehydes.
- + Active metals like alkali metals and alkaline earth's to give hydrides at high temperatures.
  - i) By passing H<sub>2</sub> over fused Ca, Calcium hydride is formed
- + LiH is prepared by the union of Li and H<sub>2</sub>  
LiAlH<sub>4</sub> is prepared by adding LiH to anhydrous AlCl<sub>3</sub> in dry ether.

- + Ionic hydrides are formed by high electropositive elements. Eg: LiH, BeH<sub>2</sub>, MgH<sub>2</sub>.....  
On electrolysis of these molten hydrides, H<sub>2</sub> gas is liberated at anode
- + Most of the p-block elements form covalent or molecular hydrides  
Eg: CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF  
Molecular hydrides are of three types
  - a) electron deficient eg. B<sub>2</sub>H<sub>6</sub>, (AlH<sub>3</sub>)<sub>n</sub>
  - b) electron - Precise eg : CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> ....
  - c) electron rich eg : NH<sub>3</sub>, H<sub>2</sub>O.....
- + Many of the d-block elements form non-stoichiometric hydrides. These compounds may exist over a wide range of composition  
Eg: PdH<sub>0.7</sub> ; TiH<sub>1.8</sub> ;CrH, ZrH<sub>1.3-1.75</sub>  
These lattices of these hydrides except few are different from those of the parent metals.
- + Unsaturated hydrocarbons add on one or more moles of hydrogen to form saturated hydrocarbons

### Preparation Hydrogen:

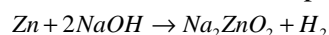
- + Action of water on active metals:

In cold :

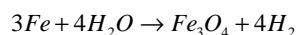


In hot

Action of alkalis on amphoteric metals : (Zn, Al, Pb, Sn, Sb)



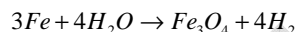
In steam :



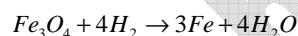
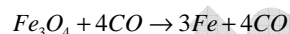
- + Action of water on metal hydride (hydrolith) CaH<sub>2</sub>

### Manufacture:

- + Lane process: super heated steam is passed over heated iron (1000°C)



Iron oxide is then reduced by water gas (CO + H<sub>2</sub>) to iron at 1000°C.



This is called water gas shift reaction

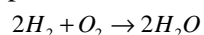
### Properties of Hydrogen:

#### Physical properties:

- + Sparingly soluble in H<sub>2</sub>O, inflammable, less reactive
- + Low M.P. (used as cryogenic fluid to lower temperature)

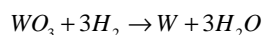
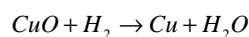
#### Chemical properties:

- + Reacts slowly at room temperature. It is neutral towards litmus. it is combustible and burns in air with a pale blue flame.



- + Reducing action:

H<sub>2</sub> + Heated metal oxides metal



## + Uses of Hydrogen

Hydrogen is used

i) in metallurgy

ii) as a fuel.

iii)  $H_2$  is used in the synthesis of Ammonia by Haber's process.

iv) When water gas mixed with  $H_2$  is passed over  $ZnO + CrO_3$  catalyst, then Methyl alcohol is obtained.

v) The unsaturated vegetable oils like cotton seed oil, ground nut oil on hydrogenation give saturated fats. Here the catalyst is Raney Nickel. This is called **hardening of oils**. (or) production of vanaspati (margarine).

## HYDRIDES, IONIC, COVALENT AND INTERSTITIAL COMPOUNDS:

- \* Hydride is used for binary compounds of hydrogen with other elements.
- \* On the basis of properties and type of bonding, hydrides may be of following four types.
  - 1) Ionic or salt like or saline hydrides.
  - 2) Covalent or molecular hydrides.
  - 3) Metallic or interstitial hydrides.
  - 4) Polymeric hydrides and complex hydrides.

### **Ionic or Saline Hydrides**

- \* These are hydrides of elements having low electro negativity.
- \* These are formed by alkali metals, alkaline earth metals (except Be and Mg).
- \* Saline hydrides are generally white or light grey, non-volatile solids.  
Ex:  $LiH$ ,  $NaH$ ,  $KH$ ,  $RbH$ ,  $CaH_2$ ,  $SrH_2$

### **Covalent or Molecular Hydrides**

- \* These hydrides are formed mainly by p-block elements. (Except noble gases)
- \* These hydrides usually consist of discrete covalent molecules held together by weak van der Waals' forces.
- \* These hydrides are usually volatile.
- \* The melting and boiling points of covalent hydrides are low.  
Ex:  $PH_3$ -phosphane,  $H_2O$ -Oxidane,  $NH_3$ -Azane

### **Metallic or Interstitial Hydrides**

- \* Hydrides are formed by d and f-block metals with electro negativity ranging from 1.2 to 1.4.
- \* These hydrides are usually non-stoichiometric.  
Ex:  $TiH_{1.73}$ ,  $LaH_{2.8}$
- \* The transition metals of groups 7,8 and 9 do not form hydrides and this region of periodic table is referred as hydride gap.

### **Polymeric Hydrides and Complex Hydrides**

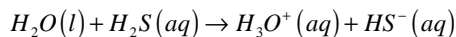
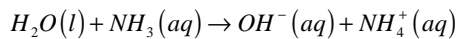
- \* Polymeric hydrides are formed by elements having electro negativity in the range 1.4 to 2.0.  
Eg:  $(BeH_2)_n$ ,  $(AlH_3)_n$ ,  $(InH_3)_n$ ,  $(SiH_4)_n$ .

- \* In the complex hydrides  $H^-$  ion acts as ligand and is attached to central metal atom.  
Eg:  $LiAlH_4, NaBH_4$

## PHYSICAL AND CHEMICAL PROPERTIES OF WATER:

### Chemical properties of water:

- \* It has the ability to act as an acid as well as a base.



The above two reactions indicates that water as amphoteric nature.

### Auto-protolysis:

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

acid-1      base-2      acid-2                      base-1  
(acid)      (base)      (conjugate acid)      (conjugate base)

- \*  $2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$

- \*  $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

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

### Hydrolysis Reaction:

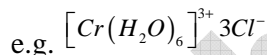
- \*  $P_4O_{10}(s) + 3H_2O(l) \rightarrow 4H_3PO_4(aq)$

- \*  $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

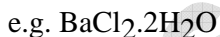
- \*  $N^{3-}(s) + 3H_2O(l) \rightarrow NH_3(g) + 3OH^-(aq)$

### Hydrates Formation:

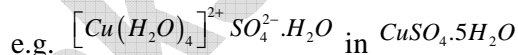
(i) Co-ordinated water



(ii) Interstitial water



(iii) Hydrogen-bonded water



### Hard and soft water:

- \* Chemically soap is sodium stearate.
- \* Water which gives good lather readily with soap is known as soft water.
- \* Water which does not give lather readily with soap but precipitates soap is known as hard water.
- \* Hardness of water is expressed in terms of ppm of  $CaCO_3$ . That means the number of grams of  $CaCO_3$  (or) its equivalent part present in 1 million grams of water is known as **hardness**.
- \* The disadvantages of using hard water are
  - a) It produces boiler scales

- b) It causes wastage of soap in laundries
- \* Chemically boiler scales are  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Boiler scales can be removed by using calgon
  - \* Hardness is of two types. They are
    - 1) Temporary hardness
    - 2) Permanent hardness
  - \* Temporary hardness of water arises due to the presence of the bicarbonates of Ca and Mg.
  - \* Permanent hardness of water arises due to the presence of the chlorides and sulphates of Ca and Mg (also salts of Fe).
  - \* Temporary hardness of water can be removed by
    - 1) Boiling
    - 2) Clark's Method
  - \* Boiling removes the temporary hardness due to the conversion of soluble bicarbonates into insoluble carbonates
 
$$\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{Mg}(\text{HCO}_3)_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O} + \text{CO}_2$$
  - \* In Clark's method, temporary hardness can be removed by adding a calculated quantity of milk of lime
 
$$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$$

In this method, addition of excess of lime is to be avoided since it will itself cause artificial permanent hardness.

    - a) Using  $\text{Na}_2\text{CO}_3$ , both temporary and permanent hardness can be removed.
  - \* The methods used for removing permanent hardness are
    - a) Permutit method/Ion exchange method
    - b) Synthetic resins method
    - c) Calgon method
  - \* a) Permutit is an artificial zeolite. Chemically permutit is hydrated sodium aluminosilicate. Its formula is  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ .
 

Gan's permutit process is also known as Base Exchange process. Here the reaction involved is

$$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O} + \text{Ca}^{2+} \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O} + 2\text{Na}^+$$

This method is also called ion exchange method or zeolite process.
  - \* The exhausted permutit is regenerated by soaking it with 10% NaCl solution [Brine solution]
    - b) Nowadays hard water is softened by using synthetic cation exchangers.
  - \* This method is more efficient than zeolite process.
  - \* Cation exchange resins contain large organic molecule with  $-\text{SO}_3\text{H}$  group and are water insoluble.
  - \* Ion exchange resin ( $\text{RSO}_3\text{H}$ ) is changed to  $\text{RNA}$  by treating it with NaCl.
  - \* The resin exchanges  $\text{Na}^+$  ions with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water to make the water soft.
 
$$2\text{RNA}(s) + \text{M}^{2+}(aq) \rightarrow \text{RM}_2(s) + 2\text{Na}^+(aq)$$
  - \* The resin can be regenerated by adding aqueous NaCl solution.
  - \* Pure de-mineralised water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the  $\text{H}^+$  form) and an anion-exchange (in the  $\text{OH}^-$  form) resins.
 
$$2\text{RH}(s) + \text{M}^{2+}(aq) \rightarrow \text{MR}_2(s) + 2\text{H}^+(aq)$$
  - \* In this cation exchange process,  $\text{H}^+$  exchanges for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and other cations present in water.
  - \* This process results in proton release and thus makes the water acidic. In the anion exchange process:
 
$$\text{RNH}_2(s) + \text{H}_2\text{O}(l) \rightarrow \text{RNH}_3^+ \cdot \text{OH}^-(s)$$

$$\text{RNH}_3^+ \cdot \text{OH}^-(s) + \text{X}^-(aq) \rightarrow \text{RNH}_3^+ \cdot \text{X}^-(s) + \text{OH}^-(aq)$$

- \*  $\text{OH}^-$  exchanges for anions like  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  etc. present in water.  $\text{OH}^-$  ions, thus, liberated neutralise the  $\text{H}^+$  ions set free in the cation exchange.  

$$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$$
- \* The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions respectively.  
 (c) Calgon is sodium hexameta phosphate. Its formula is  $\text{Na}_2 [\text{Na}_4 (\text{PO}_3)_6]$  or  $(\text{Na PO}_3)_6$
- \* Calgon forms water soluble complex compounds with Calcium and Magnesium salts and thus removes boiler scales.
- \* Calgon removes hardness by forming complex compounds with the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions of hard water.

#### Geometry of water:

- + In the gas phase water is a bent molecule with a bond angle  $104.5^\circ$  and O-H bond length of 95.7 pm.
- + In the liquid phase water molecules are associated together by hydrogen bonds.
- + The crystalline form of water is ice. At normal pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form.
- + Density of ice is less than that of water. Therefore, an ice cube floats on water.
- + In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

#### Geometry of ice:

- + Ice has a highly ordered three dimensional hydrogen bonded structure.
- + Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.
- + Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.
- + The Physical constants of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are

| S.No | Physical Property                                   | $\text{H}_2\text{O}$ | $\text{D}_2\text{O}$   |
|------|-----------------------------------------------------|----------------------|------------------------|
| 1.   | Molecular weight                                    | 18                   | 20                     |
| 2.   | Freezing point                                      | $0^\circ\text{C}$    | $3.82^\circ\text{C}$   |
| 3.   | Boiling point                                       | $100^\circ\text{C}$  | $101.42^\circ\text{C}$ |
| 4.   | Max. density                                        | 1g/cc                | 1.1g/c.c.              |
| 5.   | Temp. of max density                                | $4^\circ\text{C}$    | $11.6^\circ\text{C}$   |
| 6.   | Dielectric constant                                 | 82                   | 80.5                   |
| 7.   | Ionic product                                       | $1 \times 10^{-14}$  | $3 \times 10^{-15}$    |
| 8.   | Viscosity at $20^\circ\text{C}$ (millipoises)       | 10.09                | 12.6                   |
| 9.   | Specific heat at $20^\circ\text{C}$                 | 1                    | 1.018                  |
| 10.  | Latent heat of vaporisation (J/g)                   | 2253                 | 2329                   |
| 11.  | Solubility of NaCl/100g water at $25^\circ\text{C}$ | 35.9                 | 30.5                   |

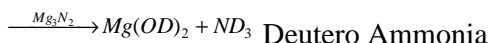
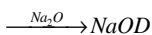
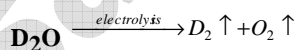
## HEAVY WATER, HYDROGEN PEROXIDE PREPARATIONS, REACTIONS, USES AND STRUCTURE

### Heavy water

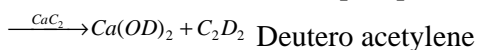
- \* Heavy water was prepared by Urey by the exhaustive electrolysis of alkaline water.
- \* Heavy water is Deuterium oxide.
- \* Natural water contains 1 part of heavy water in 6000 parts of ordinary water. 100% D<sub>2</sub>O can be obtained by 3 methods. They are
  - a) Exhaustive electrolysis of alkaline water
  - b) Fractional distillation
  - c) Exchange reactions
- \* Heavy water is prepared by the exhaustive electrolysis of water containing N/2 NaOH.
- \* In the preparation of heavy water by electrolytic method, the cathode is steel vessel and anode is a perforated cylindrical Nickel sheet.
- \* D<sub>2</sub>O can be prepared by exchange reactions. When H<sub>2</sub>S gas is passed through hot water, the hydrogen atoms in H<sub>2</sub>S exchange their places with deuterium from D<sub>2</sub>O present in water. Thus H<sub>2</sub>S becomes enriched with D<sub>2</sub>S. On passing the H<sub>2</sub>S gas enriched with D<sub>2</sub>S through cold water, the deuterium from D<sub>2</sub>S and Hydrogen from H<sub>2</sub>O exchange places and the cold water becomes richer in D<sub>2</sub>O. The process is repeated.
- \* The Physical constants of H<sub>2</sub>O and D<sub>2</sub>O are

| S.No | Physical Property                     | H <sub>2</sub> O    | D <sub>2</sub> O    |
|------|---------------------------------------|---------------------|---------------------|
| 1.   | Molecular weight                      | 18                  | 20                  |
| 2.   | Freezing point                        | 0°C                 | 3.82°C              |
| 3.   | Boiling point                         | 100°C               | 101.42°C            |
| 4.   | Max. density                          | 1g/cc               | 1.1g/c.c.           |
| 5.   | Temp. of max density                  | 4°C                 | 11.6°C              |
| 6.   | Dielectric constant                   | 82                  | 80.5                |
| 7.   | Ionic product                         | 1x10 <sup>-14</sup> | 3x10 <sup>-15</sup> |
| 8.   | Viscosity at 20°C(millipoises)        | 10.09               | 12.6                |
| 9.   | Specific heat at 20°C                 | 1                   | 1.018               |
| 10.  | Latent heat of vaporisation (J/g)     | 2253                | 2329                |
| 11.  | Solubility of NaCl/100g water at 25°C | 35.9                | 30.5                |

### \* Chemical Properties of D<sub>2</sub>O:







### Hydrogen peroxide :

- + The formula of Hydrogen peroxide is  $\text{H}_2\text{O}_2$ .
- +  $\text{H}_2\text{O}_2$  is also known as oxygenated water.
- + (-O-O-) bond is known as peroxy linkage.
- +  $\text{H}_2\text{O}_2$  is a dibasic acid. Its molecular weight is 34 and its equivalent weight is 17.
- + Perchloric acid,  $\text{MnO}_2$ ,  $\text{PbO}_2$ ,  $\text{TeO}_2$ ,  $\text{KMnO}_4$  etc. do not contain peroxy bond.
- + In the laboratory,  $\text{H}_2\text{O}_2$  is prepared by the action of ice cold dil.  $\text{H}_2\text{SO}_4$  on  $\text{Na}_2\text{O}_2$  (or) hydrated Barium Peroxide [ $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ ].
- +  $\text{H}_2\text{O}_2$  can also be obtained by passing  $\text{CO}_2$  gas through a suspension of Barium peroxide in water.
- + In the preparation of  $\text{H}_2\text{O}_2$  from  $\text{BaO}_2$ , Phosphoric acid is preferred to dil  $\text{H}_2\text{SO}_4$ . This is because  $\text{H}_3\text{PO}_4$  increases the stability of  $\text{H}_2\text{O}_2$ .
- + In auto oxidation method, the starting substance is 2-ethyl anthraquinone.
- + The reagent used for reducing 2-ethyl anthraquinone to 2-ethyl anthraquinol is  $\text{H}_2/\text{Pd}$ .
- + On aerial oxidation 2-ethylanthraquinol gives  $\text{H}_2\text{O}_2$ .
- + In electrolytic method,  $\text{H}_2\text{O}_2$  is manufactured by the electrolysis of 50%  $\text{H}_2\text{SO}_4$  (or) a mixture of  $(\text{NH}_4)_2\text{SO}_4$  + dil.  $\text{H}_2\text{SO}_4$  using platinum anode and lead cathode.
- + The product obtained at anode by the electrolysis of 50%  $\text{H}_2\text{SO}_4$  is  $\text{H}_2\text{S}_2\text{O}_8$ .
- + During the electrolysis of 50%  $\text{H}_2\text{SO}_4$ , the gas liberated at the cathode is  $\text{H}_2$ .
- + a)  $2\text{H}_2\text{SO}_4 \xrightarrow{\text{Ionisation}} 2\text{H}^+ + 2\text{HSO}_4^-$   
At cathode  
 $2\text{H}^+ + 2\text{e}^- \xrightarrow{\text{Reduction}} \text{H}_2$   
At anode  
 $2\text{HSO}_4^- \xrightarrow{\text{Oxidation}} \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$
- + b) Peroxy disulphuric acid solution on distillation under reduced pressure gives  $\text{H}_2\text{O}_2$ .  
 $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_5$  (Caro's acid)  
 $\text{H}_2\text{SO}_5 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$
- + The common name of  $\text{H}_2\text{S}_2\text{O}_8$  is Marshall's acid. Its chemical name is Perdisulphuric acid.
- + During distillation,  $\text{H}_2\text{O}_2$  undergoes decomposition below its boiling point. So it is purified by distillation under reduced pressure.
- + The strength of  $\text{H}_2\text{O}_2$  can be expressed in  
a. Volume strength b. Molarity  
c. Normality d. Weight-Volume Percentage
- + The volume of  $\text{O}_2$  gas at S.T.P. obtained by the decomposition of 1 c.c. of  $\text{H}_2\text{O}_2$  solution is known as its volume strength. It is denoted by V.
- + Perhydrol is 30% (w/v)  $\text{H}_2\text{O}_2$  solution. Its Molarity is 8.93M. Its Normality is 17.86 N and it contains 300g/Lit (or) 0.3g/ml.

- + On long standing or on heating,  $H_2O_2$  undergoes decomposition. The equation for the decomposition of  $H_2O_2$  is  $2H_2O_2 \rightarrow 2H_2O + O_2$
- + 90%  $H_2O_2$  is used as an oxidant for rocket fuel.
- + The boiling point of  $H_2O_2$  is  $152^{\circ}C$ .
- +  $H_2O_2$  exhibits
  - a) Oxidising properties b) Reducing properties
  - c) Bleaching property d) Acidic Property
 It cannot exhibit dehydrating property.
- +  $H_2O_2$  has greater reactivity in basic medium. It is because bases catalyse the decomposition of  $H_2O_2$ .
- +  $H_2O_2$  is a stronger oxidising agent and a weaker reducing agent.
- + The antiseptic action and the bleaching action of  $H_2O_2$  involve the oxidising properties.
- + During decomposition,  $H_2O_2$  undergoes disproportionation.
- + When  $H_2O_2$  acts as an oxidising agent, it undergoes reduction.  $H_2O_2$  is a powerful oxidant, but poor reductant
- + The reactions in which  $H_2O_2$  acts as a reducing agent, there will be the liberation of  $O_2$ .
- +  $H_2O_2 + 2H^+ + O_2 + 2e^-$ .  $E^0 = -0.67V$  represents the reducing property of  $H_2O_2$ .
- + The fundamental equation for oxidising property of  $H_2O_2$  is
 
$$H_2O_2 \rightarrow H_2O + (O)$$
- + The oxidising properties of  $H_2O_2$  in both acidic and basic media are due to
 
$$\xrightarrow{2H^+ + 2e^-} 2H_2O \quad (E^0 = +1.77V)$$

(Reduction)

$$H_2O_2$$

$$\xrightarrow{2e^-} 2OH^- \quad (E^0 = +0.87V)$$

(Reduction)
- + The SRP values indicate that  $H_2O_2$  is a strong oxidising agent in acidic medium and weak oxidising agent in basic medium.
- + **Oxidising properties of  $H_2O_2$** 

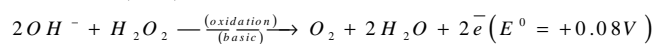
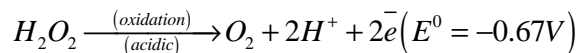
$$\xrightarrow{\text{black PbS}} H_2O + PbSO_4 \downarrow \text{White}$$

$$\xrightarrow{KI + H_2O} I_2 + KOH$$

$$\xrightarrow{\text{Sod. sulphite } Na_2SO_3} H_2O + Na_2SO_4$$

$$\xrightarrow{\text{pot. Ferrocyanide } K_4[Fe(CN)_6]} H_2O + K_3[Fe(CN)_6]$$

pot. Ferricyanide
- + The bleaching action of  $H_2O_2$  is due to its oxidising nature.
 
$$H_2O_2 \rightarrow H_2O + (O)$$
- +  $H_2O_2$  is used to bleach silk, wool, ivory and hair.
- +  $H_2O_2$  is used to bleach black hair to golden yellow colour under the common name Auricome.
- + The fundamental equation for reducing property of  $H_2O_2$  is
 
$$H_2O_2 + (O) \rightarrow H_2O + O_2$$
- + In both acidic and basic media,  $H_2O_2$  shows reducing properties as



+ **The reducing properties of H<sub>2</sub>O<sub>2</sub>** are

+ H<sub>2</sub>O<sub>2</sub> is used to clean wounds since it acts as disinfectant and germicide.

+ H<sub>2</sub>O<sub>2</sub> is used to restore the colour of old oil paintings.

These two are specific tests for H<sub>2</sub>O<sub>2</sub>.

+ H<sub>2</sub>O<sub>2</sub> turns starch - Iodide paper to blue colour. It is not a specific test for H<sub>2</sub>O<sub>2</sub>. Because it is a general test given by all oxidising agents

+ H<sub>2</sub>O<sub>2</sub> can be estimated by Iodometric method.

H<sub>2</sub>O<sub>2</sub> is treated with KI liberating I<sub>2</sub>. Then the liberated Iodine is titrated against standard Hypo solution.

+ The structure of H<sub>2</sub>O<sub>2</sub> in **gaseous state** can be shown as:

+ In H<sub>2</sub>O<sub>2</sub> molecule the HOO bond angle is 94° 48<sup>1</sup>

+ In H<sub>2</sub>O<sub>2</sub> molecule the dihedral angle is 111°30<sup>1</sup>

+ In H<sub>2</sub>O<sub>2</sub> molecule the O\_\_O bond length is 1.48Å° and the O – H is 0.97Å°

+ In crystalline H<sub>2</sub>O<sub>2</sub>, the dihedral angle 111°30<sup>1</sup> is reduced to 90°, due to Hydrogen bonding.

The values of bond length and bond angles in gaseous H<sub>2</sub>O<sub>2</sub> are different from that of solid and liquid states.

+ The difference in the bond lengths and bond angles from one state to another state of H<sub>2</sub>O<sub>2</sub> is due to difference in hydrogen bonding.