

# Hydrogen

## (1) Position of hydrogen in the periodic table

Hydrogen is the first element in the periodic table. Hydrogen is placed in no specific group due to its property of giving electron (When  $H^-$  is formed) and also losing electron (When  $H^+$  is formed).

(i) Hydrogen is placed in group I (Alkali metals) as,

(a) It has one electron in its (Outer) shell- $1s^1$  like other alkali metals which have (inert gas)  $ns^1$  configuration.

(b) It forms monovalent  $H^+$  ion like  $Li^+, Na^+ \dots$

(c) Its valency is also 1.

(d) Its oxide ( $H_2O$ ) is stable as  $Li_2O, Na_2O$ .

(e) It is a good reducing agent (In atomic as well as molecular state) like  $Na, Li \dots$

(ii) Hydrogen also resembles halogens (Group VII A) as,

(a) It is also diatomic ( $H_2$ ) like  $F_2, Cl_2 \dots$

(b) It also forms anion  $H^-$  like  $F^-, Cl^- \dots$  by gain of one electron.

(c)  $H^-$  has stable inert gas ( $He$ ) configuration as  $CH_4, C_2H_6$  like halogens  $CCl_4, SF_2Cl_2$  etc.

(d)  $H$  is one electron short of duplet (Stable configuration) like  $F, Cl, \dots$  which are also one electron deficient than octet,  $F-2s^2 2p^5$ ;  $Cl-3s^2 3p^5$ .

(e) (IE) of  $H(1312 kJ mol^{-1})$  is of the same order as that of halogens.

(iii) (IE) of  $H$  is very high in comparison with alkali metals. Also size of  $H^+$  is very small compared to that of alkali metal ion.  $H$  forms stable hydride only with strongly electropositive metals due to smaller value of its electron affinity ( $72.8 kJ mol^{-1}$ ).

(iv) In view of the anomalous behaviour of hydrogen, it is difficult to assign any definite position to it in the periodic table. Hence it is customary to place it in group I (Along with alkali metals) as well as in group VII (Along with halogens).

(2) **Discovery and occurrence** : It was discovered by **Henry Cavendish** in 1766. Its name hydrogen was proposed by **Lavoisier**. Hydrogen is the 9<sup>th</sup> most abundant element in the earth's crust.

Hydrogen exists in diatomic state but in triatomic state it is called as Hyzone. Systematic name of water is oxidane.

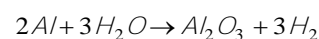
(3) **Preparation of Dihydrogen** : Dihydrogen can be prepared by the following methods,

(i) *By action of water with metals*

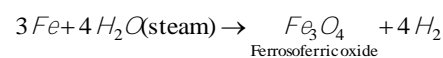
(a) Active metals like  $Na, K$  react at room temperature



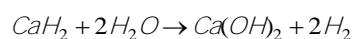
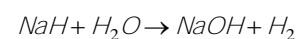
(b) Less active metals like  $Ca, Zn, Mg, Al$  liberate hydrogen only on heating.



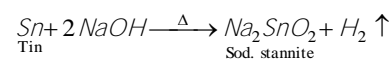
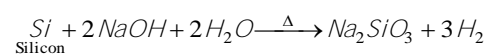
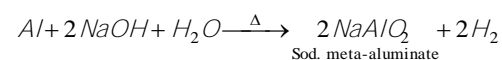
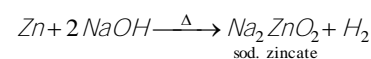
(c) Metals like  $Fe, Ni, Co, Sn$  can react only when steam is passed over red hot metals.



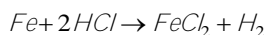
(ii) *By the action of water on alkali and alkaline earth metals hydrides*



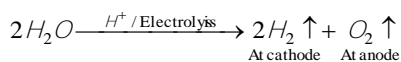
(iii) *By reaction of metals like  $Zn, Sn, Al$  with alkalies ( $NaOH$  or  $KOH$ )*



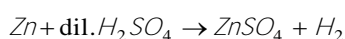
(iv) **By action of metal with acids** : All active metals which lie above hydrogen in electrochemical series, can displace hydrogen gas from dilute mineral acids like  $HCl$ ,  $H_2SO_4$ .



(v) **By the electrolysis of acidified water**



(vi) **Laboratory method** : In laboratory, it is obtained by action of granulated zinc with dilute  $H_2SO_4$ .



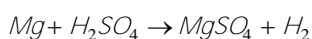
It must be noted that

(a) Pure zinc is not used for the preparation of  $H_2$  as rate of reaction of pure  $Zn$  with dil.  $H_2SO_4$  is quite slow.

(b) Conc.  $H_2SO_4$  is not used because then  $SO_2$  gas is evolved instead of  $H_2$ .

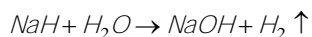
(vii) **Preparation of pure hydrogen**: It can be obtained by

(a) The action of pure dil.  $H_2SO_4$  on pure magnesium ribbon.

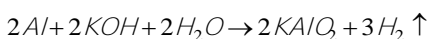


(b) Hydrogen of high purity (> 99.95%) is obtained by electrolysis of warm aqueous barium hydroxide between nickel electrodes.

(c) By the action of water on sodium hydride.



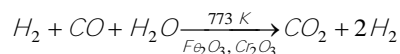
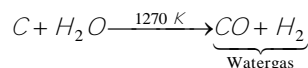
(d) By the action of  $KOH$  (aq.) on aluminium.



(viii) **Commercial production of dihydrogen**

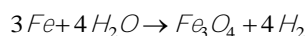
(a) **Bosch process** : In this method, water gas is mixed with twice its volume of steam and passed over heated catalyst  $Fe_2O_3$  in the presence of a promoter  $Cr_2O_3$  or  $ThO_2$  at 773 K when  $CO_2$  and  $H_2$  are obtained.  $CO_2$  is removed by dissolving it in

water under pressure (20-25 atm) and  $H_2$  left undissolved is collected.

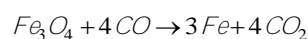
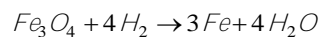


About 18% of the world's production of  $H_2$  is obtained from coal.

(b) **Lane's process** : By passing steam over spongy iron at 773-1050 K.

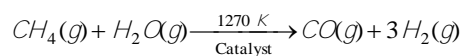


The ferrosferric oxide ( $Fe_3O_4$ ) so produced is reduced back to iron with water. this reaction is known as **Vivification reactions**



(c) **By electrolysis of water** : Electrolysis of acidified water using platinum electrodes is used for the bulk preparation of hydrogen.

(d) **From hydrocarbons** : Hydrocarbons (alkanes) react with steam at high temperature to produce carbon monoxide and hydrogen, e.g.,



The mixture of  $CO$  and  $H_2$  so obtained can be converted into hydrogen as in Bosch process. About 77% of the world's production of  $H_2$  is obtained from hydrocarbons.

(e) It is also produced as a by-product of the brine electrolysis process for the manufacture of  $Cl_2$  and  $NaOH$ .

(4) **Physical properties of dihydrogen** : It is a colourless, tasteless and odourless gas. It is slightly soluble in water. It is highly combustible. The Physical constants of atomic hydrogen are,

Atomic radius (pm) – 37

Ionic radius of  $H^-$  ion (pm) – 210

Ionisation energy ( $\text{kJ mol}^{-1}$ ) – 1312

Electron affinity ( $\text{kJ mol}^{-1}$ ) – 72.8

Electronegativity – 2.1

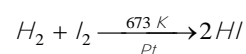
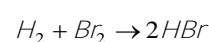
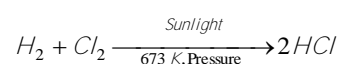
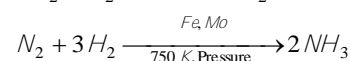
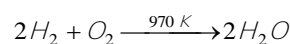
#### (5) Chemical properties of dihydrogen :

Dihydrogen is quite stable and dissociates into hydrogen atoms only when heated above 2000 K,  $\text{H}_2 \xrightarrow{2000 \text{ K}} \text{H} + \text{H}$ . Its bond dissociation energy is very high,  $\text{H}_2 \rightarrow \text{H} + \text{H}$ ;  $\Delta H = 435.9 \text{ kJ mol}^{-1}$ . Due to its high bond dissociation energy, it is not very reactive. However, it combines with many elements or compounds.

(i) **Action with metals** : To forms corresponding hydrides.  $2\text{Na} + \text{H}_2 \xrightarrow{\text{Heat}} 2\text{NaH}$ ;  
 $\text{Ca} + \text{H}_2 \xrightarrow{\text{Heat}} \text{CaH}_2$ .

With transition metals (elements of  $d$  – block) such as  $\text{Pd}$ ,  $\text{Ni}$ ,  $\text{Pt}$  etc. dihydrogen forms interstitial hydrides in which the small molecules of dihydrogen occupy the interstitial sites in the crystal lattices of these hydrides. As a result of formation of interstitial hydrides, these metals adsorb large volume of hydrogen on their surface. This property of adsorption of a gas by a metal is called **occlusion**. The occluded hydrogen can be liberated from the metals by strong heating.

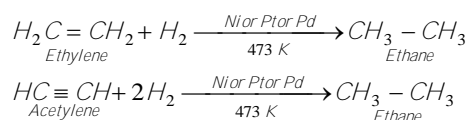
#### (ii) Reaction with Non-metals



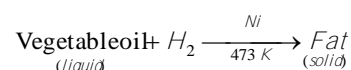
The reactivity of halogen towards dihydrogen decreases as,  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

As a result,  $\text{F}_2$  reacts in dark,  $\text{Cl}_2$  in the presence of sunlight,  $\text{Br}_2$  reacts only upon heating while the reaction with  $\text{I}_2$  occurs in the presence of a catalyst.

(iii) **Reaction with unsaturated hydrocarbons** :  $\text{H}_2$  reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.

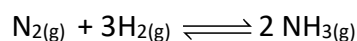


This reaction is used in the **hydrogenation or hardening of oils**. The vegetable oils such as groundnut oil or cotton-seed oil are unsaturated in nature because they contain at least one double bond in their molecules. Dihydrogen is passed through the oils at about 473 K in the presence of catalyst to form solid fats. The vegetable ghee such as Dalda, Rath, etc. are usually prepared by this process.

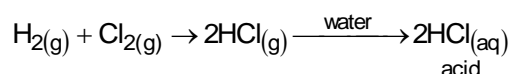


#### (6) Uses of Dihydrogen

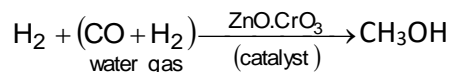
- (i) As a reducing agent
  - (ii) In the hydrogenation of vegetable oils
  - (iii) As a rocket fuel in the form of liquid  $\text{H}_2$
  - (iv) In the manufacture of synthetic petrol
  - (v) In the preparation of many compounds
- a) Synthesis of Ammonia by Haber's process.



b) Preparation of HCl



c) Synthesis of Methyl alcohol:



d) In the production of vanaspathi or Margarine:

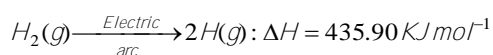
(vi) It is used in the oxy-hydrogen torch for welding if temperature around  $2500^{\circ}\text{C}$  is required. It is also used in atomic hydrogen torch for welding purposes in which temperature of the order of  $4000^{\circ}\text{C}$  is required.

vii) Synthetic petrol is prepared by Fischer-Tropsch process. Here Iron oxide is used to remove sulphur from a mixture of water gas and Hydrogen.

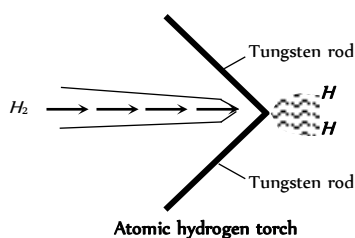
### Different forms of hydrogen

(1) **Atomic hydrogen** : It is obtained by the dissociation of hydrogen molecules. The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. It is obtained by passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.

The electric arc maintains a temperature around  $4000 - 4500^{\circ}\text{C}$ . As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as

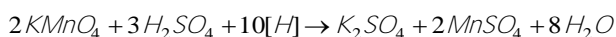
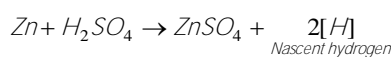
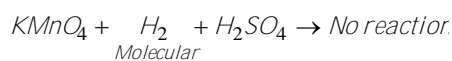


This arrangement is also called atomic hydrogen torch.

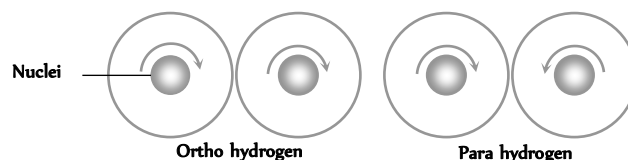


(2) **Nascent hydrogen** : The hydrogen gas prepared in the reaction mixture in contact with the substance with which it has to react, is called nascent hydrogen. It is also called newly born hydrogen. It is more reactive than ordinary

hydrogen. For example, if ordinary hydrogen is passed through acidified  $\text{KMnO}_4$  (pink in colour), its colour is not discharged. On the other hand, if zinc pieces are added to the same solution, bubbles of hydrogen rise through the solution and the colour is discharged due to the reduction on  $\text{KMnO}_4$  by nascent hydrogen.



(3) **Ortho and para hydrogen** : A molecule of dihydrogen contains two atoms. The nuclei of both the atoms in each molecule of dihydrogen are spinning. Depending upon the direction of the spin of the nuclei, the hydrogen is of two types,



(i) Molecules of hydrogen in which the spins of both the nuclei are in the same directions, called ortho hydrogen.

(ii) Molecules of hydrogen in which the spins of both the nuclei are in the opposite directions, called para hydrogen.

Ordinary dihydrogen is an equilibrium mixture of ortho and para hydrogen. Ortho hydrogen  $\rightleftharpoons$  Para hydrogen. The amount of ortho and para hydrogen varies with temperature as,

(a) At  $0^{\circ}\text{K}$ , hydrogen contains mainly para hydrogen which is more stable.

(b) At the temperature of liquefaction of air, the ratio of ortho and para hydrogen is 1:1.

(c) At the room temperature, the ratio of ortho to para hydrogen is 3:1.

(d) Even at very high temperatures, the ratio of ortho to para hydrogen can never be more than 3:1.

Thus, it has been possible to get pure para hydrogen by cooling ordinary hydrogen gas to a very low temperature (close to 20 K) but it is never possible to get a sample of hydrogen containing more than 75% of ortho hydrogen. i.e., Pure ortho hydrogen can not be obtained.

(4) **Hydrides** : Hydrogen forms binary hydrides of the type  $MH_x$  or  $M_mH_n$  with

(a) All main group elements except noble gases and probably indium and thallium.

(b) All lanthanoids and actinoids.

(c) Transition metals (*Sc, Y, La, Ac, Tc, Zr, Hf* and to a lesser extent *V, Nb, Ta, Cr, Cu* and *Zn*). In group 6 only *Cr* forms hydride (*CrH*).

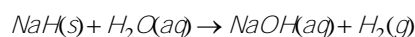
Hydrides are classified into three main categories.

(i) **Saline or ionic hydrides** : Most of the *s*-block metals form this type of hydrides. These are non-volatile, non-conducting crystalline solids. However, *BeH<sub>2</sub>* and *MgH<sub>2</sub>* have covalent polymeric structure. These ionic hydrides have rock-salt structure. Thermal stability of 1<sup>st</sup> and 2<sup>nd</sup> group hydrides are in the order;



*BeH<sub>2</sub>*, *MgH<sub>2</sub>* and *LiH* have significant covalent character.

Electrolysis of solution of saline hydride in molten alkali halide produces  $H_2$  at anode. Saline hydrides react explosively with water.

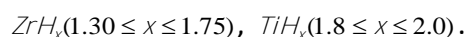


The fire so produced cannot be extinguished by  $CO_2$  as it gets reduced by the hot metal hydride. Only sand is useful, as it is a solid.

Alkali metal hydrides are used for making *LiAlH<sub>4</sub>*, *NaBH<sub>4</sub>* etc. Alkali metal hydrides are also used for the removal of last traces of water from organic compounds.

(ii) **Metallic or interstitial hydrides** : Elements of groups 3, 4, 5 (*d*-block) and *f*-block elements form metallic hydrides. In group 6, only *Cr* forms hydride (*CrH*). Metals of group 7, 8, 9 do not form hydrides. This region of periodic table from group 7 to group 9 is known as hydride gap. Examples of hydrides of group 3 to 5 are, *ScH<sub>2</sub>*, *YH<sub>2</sub>*, *YH<sub>3</sub>*, *LaH<sub>2</sub>*, *LaH<sub>3</sub>*, *TiH<sub>2</sub>*, *ZrH<sub>2</sub>*, *HfH<sub>2</sub>*, *VH*, *VH<sub>2</sub>*, *NbH*, *NbH<sub>2</sub>*, *TaH*

The *f*-block metals form hydrides of limiting compositions of  $MH_2$  and  $MH_3$ . All these hydrides are non-stoichiometric with variable composition e.g.,



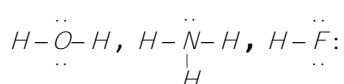
Most of these hydrides are good conductors of electricity in solid state.

Metallic hydrides can be used to store hydrogen especially in cars working on fuel cells.

(iii) **Molecular or covalent hydrides** : Hydrogen form molecular compounds with *p*-block elements (*B, C, N, O, F; Si, P, S, Cl; Ga, Ge, As, Sb, Br; In, Sn, Sb, Te, I; Tl, Pb, At*). common examples of such hydrides are *CH<sub>4</sub>*, *NH<sub>3</sub>*, *H<sub>2</sub>O*, *HF* etc. The stability of these

hydrides decreases down the group. For example,  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ . In a period the stability increases with increasing electronegativity. For example,  $CH_4 < NH_3 < H_2O < HF$ . Molecular hydrides are classified as electron rich, electron precise and electron deficient hydrides.

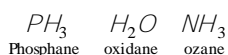
(a) *Electron rich molecular hydrides* : These hydrides have one or more lone pairs of electrons around the central more electronegative element. For example



(b) *Electron precise molecular hydrides* : Elements of group 14 form such hydrides. The bond length increases on going down the group. A common example of electron precise molecular hydrides is  $CH_4$ .

(c) *Electron deficient molecular hydrides* : These hydrides have lesser number of electrons than that required for writing the conventional Lewis structure. A common example of such molecular hydride is diborane,  $B_2H_6$ .

(d) *Systematic names of molecular hydrides* : The systematic names of these hydrides are obtained from the name of the element and the suffix -ane. For example,



## Isotopes of Hydrogen

Isotopes are the different forms of the same element, which have the same atomic number but different mass numbers.

### Isotopes of hydrogen

Name	Sym bol	Ato mic num	Mass num ber	Relativ e abunda	Nature radioacti ve or
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		ber		nce	non- radioacti ve
Protium	${}^1_1H$ or $H$	1	1	99.985 %	Non- radioacti ve
Deuterium	${}^2_1H$ or $rD$	1	2	0.015%	Non- radioacti ve
Tritium	${}^3_1H$ or $rT$	1	3	$10^{-15}$ %	Radioacti ve

### Physical constants of $H_2$ , $D_2$ and $T_2$

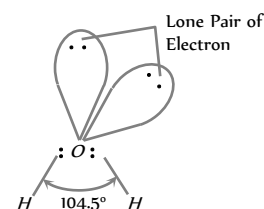
Property	$H_2$	$D_2$	$T_2$
Molecular mass	2.016	4.028	6.03
Melting point (K)	13.8	18.7	20.63
Boiling point (K)	20.4	23.9	25.0
Heat of fusion ( $\text{kJ mol}^{-1}$ )	0.117	0.197	0.250
Heat of vaporisation ( $\text{kJ mol}^{-1}$ )	0.994	1.126	1.393
Bond energy ( $\text{kJ mol}^{-1}$ )	435.9	443.4	446.9

**Isotopic effect** : In general chemical properties of isotopes are same but quantitative differences are noticed amongst them. For example, the reaction between  $H_2$  and  $Cl_2$  is 13.4 times faster between  $D_2$  and  $Cl_2$  under similar conditions. Such differences in chemical properties, which are due to difference in the mass numbers of isotopes is known as isotopic effect.

## Water

Water is the oxide of hydrogen. It is an important component of animal and vegetable matter. Water constitutes about 65% of our body. It is the principal constituent of earth's surface.

(1) **Structure** : Due to the presence of lone pairs, the geometry of water is



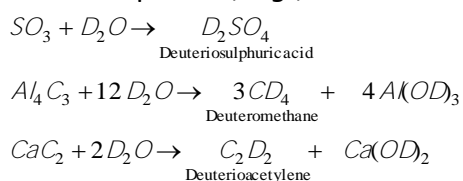
distorted and the  $H-O-H$  bond angle is  $104.5^\circ$ , which is less than the normal tetrahedral angle ( $109.5^\circ$ ). The geometry of the molecule is regarded as angular or bent. In water, each  $O-H$  bond is polar because of the high electronegativity of oxygen (3.5) in comparison to that of hydrogen (2.1). The resultant dipole moment of water molecule is 1.84D.

**In ice**, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms; **two by covalent bonds and two by hydrogen bonds**. The resulting structure of ice is open structure having a number of vacant spaces. Therefore, the density of ice is less than that of water and ice floats over water. It may be noted that water has maximum density ( $1\text{g cm}^{-3}$ ) at  $4^\circ\text{C}$  ( $277\text{K}$ ).

(2) **Heavy water** : Chemically heavy water is deuterium oxide ( $D_2O$ ). It was discovered by **Urey**.

It is obtained as a by-product in some industries where  $H_2$  is produced by the electrolysis of water.

Heavy water ( $D_2O$ ) is used (a) as a moderator and coolant in nuclear reactors (b) in the study of mechanism of chemical reactions (c) as a starting material for the preparation of a number of deuterium compounds, e.g.,



(3) **Physical properties** : Water is colourless, odourless and tasteless liquid at ordinary temperature.

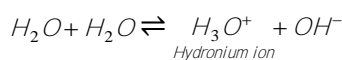
At  $273\text{K}$  water is in equilibrium with ice and vapour this point is known triple point.

**Some physical constants of  $H_2O$  and  $D_2O$  at  $298\text{K}$**

Constant	Ordinary water $H_2O$	Heavy water $D_2O$
Molecular mass	18.015	20.028
Maximum density ( $\text{g cm}^{-3}$ )	1.000	1.106
Melting point (K)	273.2	276.8
Boiling point (K)	373.2	374.4
Heat of fusion ( $\text{kJ mol}^{-1}$ ) at $273\text{K}$	6.01	6.28
Heat of vaporisation ( $\text{kJ mol}^{-1}$ ) at $373\text{K}$	40.66	41.61
Heat of formation ( $\text{kJ mol}^{-1}$ )	-285.9	-294.6
Ionisation constant	$1.008 \times 10^{-14}$	$1.95 \times 10^{-15}$

(4) **Chemical properties** : Water shows a versatile chemical behaviour. It behaves as an acid, a base, an oxidant, a reductant and as ligand to metals.

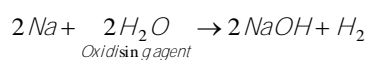
(i) **Dissociation of water** : Water is quite stable and does not dissociate into its elements even at high temperatures. Pure water has a small but measurable electrical conductivity and it dissociates as,



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

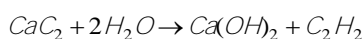
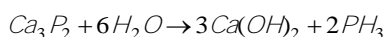
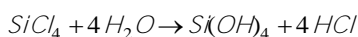
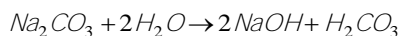
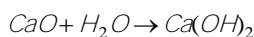
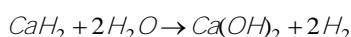
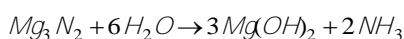
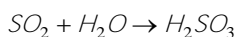
(ii) **Amphoteric nature** : Water can act both as an acid and a base and is said to be amphoteric. However, water is neutral towards litmus and its  $\text{pH}$  is 7.

(iii) **Oxidising and reducing nature** : Water can act both as an oxidising and a reducing agent in its chemical reactions. e.g.



(iv) **Hydrolytic reactions** : Water can hydrolyse many oxides, halides, hydrides, carbides, nitrides,

phosphides, carbonates etc. to give an acid or a base or both as shown below :



(v) **Water forms hydrates with metal salts** :

There are three main types of hydrates.

(a) Compounds in which water molecule are co-ordinated to the metal ion (complex compounds)  $[Ni(OH_2)](NO_3)_2$ ,  $[Al(OH_2)_6]Cl_3$  etc.

(b) Compound in which water molecule may be hydrogen bonded to oxygen to form oxo-anion. For example in  $CuSO_4 \cdot 5H_2O$ , 4 molecules of water are co-ordinated to  $Cu^{2+}$  while the fifth molecule is hydrogen bonded to  $SO_4^{2-}$  ion.

(c) In some compounds, water molecule occupies, interstitial sites in the crystal lattice e.g.,  $BaCl_2 \cdot 2H_2O$ .

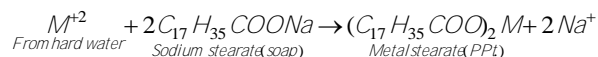
### (5) Hard and Soft water

Water which produces lather with soap solution readily is called **soft water**. e.g. distilled water, rain water and demineralised water.

Water which does not produce lather with soap solution readily is called **hard water**. e.g. sea water, river water, well water and tap water.

(i) **Cause of hardness of water** : The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium.

Hard water does not produce lather because the cations ( $Ca^{+2}$  and  $Mg^{+2}$ ) present in hard water react with soap to form insoluble precipitates,



Where  $M = Ca$  or  $Mg$

Therefore, no lather is produced until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap.

(ii) **Type of hardness of water** : The hardness of water is of two types,

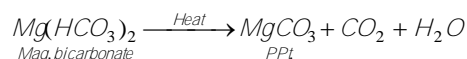
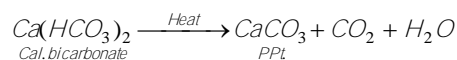
(a) **Temporary hardness** : This is due to the presence of bicarbonates of calcium and magnesium. It is also called carbonate hardness.

(b) **Permanent hardness** : This is due to the presence of chlorides and sulphates of calcium and magnesium. It is also called non-carbonate hardness.

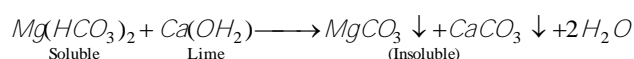
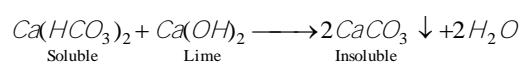
(iii) **Softening of water** : The process of the removal of hardness from water is called softening of water.

(a) **Removal of temporary hardness** : It can be removed by the following methods,

- **By boiling** : During boiling, the bicarbonates of  $Ca$  and  $Mg$  decompose into insoluble carbonates and give  $CO_2$ . The insoluble carbonates can be removed by filtration.



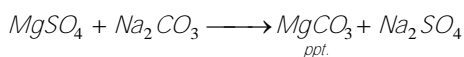
- **Clark's method** : This process is used on a commercial scale. In this process, calculated amount of lime  $[Ca(OH)_2]$  is added to temporary hard water.



(b) **Removal of permanent hardness** : Permanent hardness can be removed by the following methods,

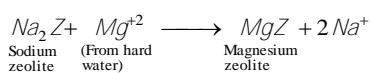
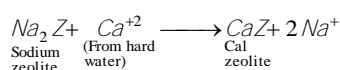


- By washing soda method : In this method, water is treated with a calculated amount of washing soda ( $Na_2CO_3$ ) which converts the chlorides and sulphates of *Ca* and *Mg* into their respective carbonates which get precipitated.



- Permutit method : This is a modern method employed for the softening of hard water. hydrated sodium aluminium silicate ( $Na_2Al_2Si_2O_8 \cdot xH_2O$ ) is called permutit. These complex salts are also known as zeolites.

The permutit as loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions. Therefore this method is also called ion exchange method.



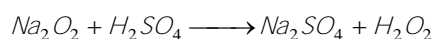
where  $Z = Al_2Si_2O_8 \cdot xH_2O$

## Hydrogen peroxide

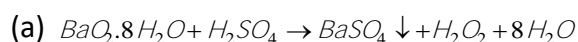
Hydrogen peroxide ( $H_2O_2$ ) was discovered by French chemist **Thenard**.

(1) **Preparation** : It is prepared by

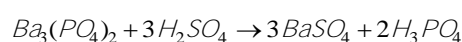
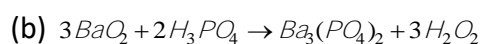
(i) **Laboratory method** : In laboratory,  $H_2O_2$  is prepared by Merck's process. It is prepared by adding calculated amounts of sodium peroxide to ice cold dilute (20%) solution of  $H_2SO_4$ .



(ii) By the action of sulphuric acid or phosphoric acid on hydrated barium peroxide  $BaO_2 \cdot 8H_2O$

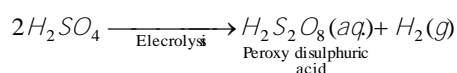


It must be noted that anhydrous barium peroxide does not react readily with sulphuric acid (because a coating of insoluble barium sulphate is formed on its surface which stops further action of the acid). Therefore, hydrated barium peroxide,  $BaO_2 \cdot 8H_2O$  must be used.



Phosphoric acid is preferred to  $H_2SO_4$  because soluble impurities like barium persulphate (from  $BaO_2 \cdot 8H_2O + H_2SO_4$ ) tends to decompose  $H_2O_2$  while  $H_3PO_4$  acts as preservative (negative catalyst) for  $H_2O_2$ .

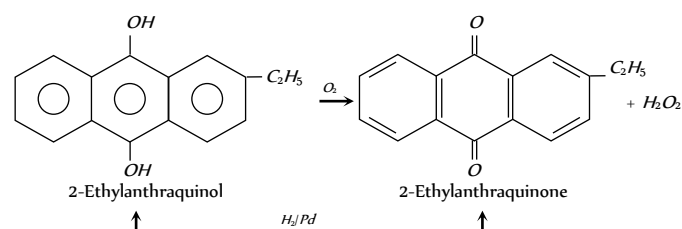
(iii) **Industrial method** : On a commercial scale,  $H_2O_2$  can be prepared by the electrolysis of 50%  $H_2SO_4$  solution. In a cell, peroxy disulphuric acid is formed at the anode.



This is drawn off from the cell and hydrolysed with water to give  $H_2O_2$ .

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$  The resulting solution is distilled under reduced pressure when  $H_2O_2$  gets distilled while  $H_2SO_4$  with high boiling point, remains undistilled.

(iv) **By redox process** : Industrially  $H_2O_2$  is prepared by the auto-oxidation of 2-alkylanthraquinols. The process involves a cycle of reactions. The net reaction is the catalytic union of  $H_2$  and  $O_2$  to give  $H_2O_2$ .



The  $H_2O_2$  formed (about 1%) is extracted with water and concentrated.

## (2) Physical properties

- (i) Pure hydrogen peroxide is a pale blue syrupy liquid.
- (ii) It freezes at  $-0.5^\circ\text{C}$  and has a density of 1.4 in pure state.
- (iii) Hydrogen peroxide is diamagnetic.
- (iv) It is more highly associated via hydrogen bonding than water.
- (v) Although it is a better polar solvent than  $H_2O$ . However, it can't be used as such because of strong autooxidation ability.
- (vi) Dipole moment of  $H_2O_2$  is 2.1 D.

## (3) Chemical properties

(i) **Decomposition** : Pure  $H_2O_2$  is an unstable liquid and decomposes into water and  $O_2$  either upon standing or upon heating,  
 $2H_2O_2 \longrightarrow 2H_2O + O_2; \Delta H = -196.0 \text{ kJ}$

(ii) **Oxidising nature** : It is a powerful oxidising agent. It acts as an oxidising agent in neutral, acidic or in alkaline medium. *e.g.*  $2KI + H_2O_2 \longrightarrow 2KOH + I_2$  [In neutral medium]

$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$  [In acidic medium]

$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$  [In alkaline medium]

(iii) **Reducing nature** :  $H_2O_2$  has tendency to take up oxygen from strong oxidising agents and thus, acts as a reducing agent,  
 $H_2O_2 + O \xrightarrow{\text{From oxidising agent}} H_2O + O_2$ . It can act as a reducing agent

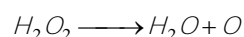
in acidic, basic or even neutral medium.

In acidic medium,  $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$

In alkaline medium,

$H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$

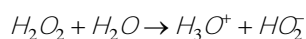
(iv) **Bleaching action** :  $H_2O_2$  acts as a bleaching agent due to the release of nascent oxygen.



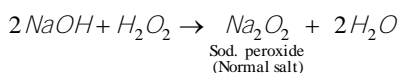
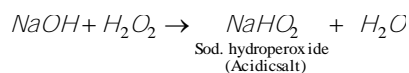
Thus, the bleaching action of  $H_2O_2$  is due to oxidation. It oxidises the colouring matter to a colourless product, Colouring matter + O  $\rightarrow$  Colourless matter.

$H_2O_2$  is used to bleach delicate materials like ivory, silk, wool, leather etc.

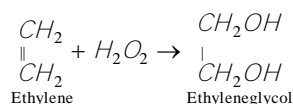
(v) **Acidic nature** : Anhydrous hydrogen peroxide is acidic in character ( $K_a = 1.55 \times 10^{-12}$  at 298 K). its dissociation in aqueous solution may be given as



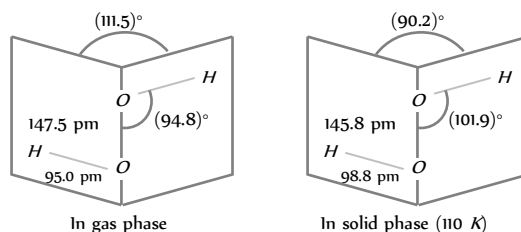
It forms two types of salts



(vi) **Addition reactions** : Hydrogen peroxide is capable of adding itself to ethylenic linkage.



(4) **Structure of  $H_2O_2$**  : Hydrogen peroxide is non-linear, non-planar molecule. It has an open book structure. The  $-O-O-$  linkage is called peroxy linkage. The structure is shown below.



(5) **Concentration of  $H_2O_2$**  : Dilute  $H_2O_2$  is concentrated to about 50% by slow evaporation on a water bath. It is further concentrated to 90% in a vacuum desiccator using conc.  $H_2SO_4$  as dehydrating agent. Further concentration to 99% is obtained by

distillation under reduced pressure. Last traces of moisture in 99% of  $H_2O_2$  are removed or anhydrous  $H_2O_2$  is obtained by cooling it to 263 K in a cold bath of ether and dry ice followed by seeding with a few crystals of solid  $H_2O_2$  when needle-shaped crystals of 100%  $H_2O_2$  separate out. These crystals are removed, dried and melted to get 100%  $H_2O_2$ .

(6) **Storage of  $H_2O_2$**  :  $H_2O_2$  is not stored in glass bottles since the alkali metal oxides present in glass catalyse its decomposition. It is, therefore, stored in paraffin wax coated glass, plastic or teflon bottles. Small amounts of acid, glycerol, alcohol, acetanilide and  $H_3PO_4$  are often used as stabilizers to check its decomposition.

#### Uses of hydrogen peroxide

(i) For bleaching delicate articles like wool, hair, feather, ivory, etc.

(ii) For restoring colour of old lead paintings whose white lead has blackened due to formation of  $PbS$  by  $H_2S$  of atmosphere. Hydrogen peroxide converts the black lead sulphide to white lead sulphate

(iii) As an aerating agent in production of sponge rubber.

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

(v) In the manufacture of sodium perborate, sodium percarbonate. These are used in high quality detergents.

(vi) As an antichlor.

(vii) As an oxidant for rocket fuel.

(viii) In the detection of  $Ti$ ,  $V$  and  $Cr$  ions with which it forms peroxides of characteristic colours.

(ix) In the production of epoxides, propylene oxide and polyurethanes.

(x) In the synthesis of hydroquinone, pharmaceuticals (cephalosporin) and food products like tartaric acid.

(xi) For pollution control of domestic effluents where it restores the aerobic conditions of sewage wastes. For pollution control of industrial effluents

containing  $CN^-$  ions.  $H_2O_2$  oxidises  $CN^-$  ions to harmless products.

✍ Hydrogen forms more compounds than even carbon.

✍ Metals like  $Pd$ ,  $Pt$ ,  $Au$  etc., have the property of absorbing large quantity of hydrogen at normal or higher temperature. Colloidal  $Pd$  can absorb 2950 times its own volume of hydrogen and  $Pd$  metal can absorb 900 times its own volume of hydrogen.

This phenomenon is known as occlusion of hydrogen. The occlusion property of these metals is in the order

Colloidal Palladium > Palladium > Platinum > Gold > Nickel.

✍ In solids, water molecules can also be present as zeolite water and clathrate water.

✍ Ice is a good thermal insulator.

✍ 30%  $H_2O_2$  is called perhydrol. Its volume strength is 100 and molarity is 8.8.