HYDROGEN

1. Unique Position of Hydrogen in Periodic Table :
   Its position in the periodic table is anomalous because it resembles both with alkali metals and halogens. Not only this, some properties of hydrogen are different from both families. Electronic configuration of hydrogen atom is $1s^1$. Thus hydrogen atom have dual tendency i.e. either to lose one electron like alkali metals (but this tendency is lesser than alkali metals because its ionisation energy is higher) or to gain one electron like halogens. In brief, hydrogen behaves as an electropositve, electronegative and amphoteric element and so it neither belongs to alkali metals nor to halogens.
2. Occurrence of Hydrogen :
   It is the most abundant and lightest element in the universe. About half of the mass of the sun, stars and planets is of hydrogen. The source of the sun's energy which is necessary for life on earth is due to the fusion of hydrogen nuclei to form helium. It constitutes about 0.9% by weight of earth crust and is the ninth element in order of abundance on the earth.
3. Isotopes of Hydrogen :
   There are three isotopes of hydrogen :
   (i) Protium (commonly called as hydrogen, H) - A sample of hydrogen contains about 99.8% protium. Its nucleus constitutes one proton and no neutron. It contains only one electron in its K shell.
   (ii) Deuterium (^2_1H or D) - Its existence was first of all proposed by H. Urey (1931). The nucleus of deuterium contains one proton and one neutron. its density is twice that of hydrogen and rate of diffusion is slower than hydrogen. It is produced by electrolysis of heavy water, D_2O.
   Note : Protium and deuterium are naturally occurring stable isotopes of hydrogen.
   (iii) Tritium (^3_1H or T) - Tritium is the heaviest isotope of hydrogen and its nucleus contains one proton and two neutrons. It is radioactive in nature and emits $\beta -$rays. It has a half life period of 12.4 years.
4. Methods of preparation of hydrogen :
   (i) By the electrolysis of water

$$2H_2O(l) \xrightarrow[\text{Traces of acid or base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

   (ii) From steam (Lane's process)

$$\underset{\text{red hot}}{3Fe} + \underset{\text{Steam}}{4H_2O} \xrightarrow{1050-1075K} Fe_3O_4 + 4H_2$$

   (iii) From water gas (Bosch process)

$$\underset{\text{hot coke}}{C} + \underset{\text{steam}}{H_2O} \xrightarrow{450^0C-600^0C} \underbrace{CO + H_2}_{\text{water gas}}$$

$$\underbrace{CO + H_2}_{\text{Water gas}} + \underset{\text{steam}}{H_2O} \xrightarrow[450^\circ C-550^\circ C]{Fe_2O_3, Cr_2O_3} CO_2 + 2H_2$$

   (iv) From hydrolith, CaH_2

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

   (v) From acids

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

(vi) From alkalies (Uyeno's method)

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$$

(vii) By thermal cracking of natural gas

$$CH_4 \xrightarrow[\text{Catalyst}]{1270\text{ K}} C + 2H_2$$

5. Physical properties of Hydrogen :

Hydrogenis a colourless, odourless, tastless gas (b.p. 20.4 K and m.p. 13.8 K). It is the lightest gas (density 0.0899 gcm^{-3}).

6. Chemical Properties of Hydrogen :

(i) On Combustion

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Note : Hydrogen does not support combustion but itself burns with pale blue flame.

(ii) With non-metals

$$N_2 + 3H_2 \xrightarrow[750\text{ K, }200\text{ atm}]{Fe/Mo} \underset{\text{Ammonia}}{2NH_3} \quad \text{(Haber's process)}$$

$$S + H_2 \xrightarrow{700\text{ K}} H_2S$$

(iii) With metals : Forms ionic hydrides

$$2Na + H_2 \longrightarrow 2NaH$$

$$Ca + H_2 \longrightarrow CaH_2$$

(iv) As a reducing agent

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

(v) Hydrogenation

$$C_2H_4 + H_2 \xrightarrow[250^\circ C]{Ni} C_2H_6$$

Note : This process is widely used in the manufacture of vanaspati ghee from unsaturated vegetable oils.

$$\text{Vegetable oil} + H_2 \xrightarrow[450\text{ K, }8\text{–}10\text{ atm}]{Ni} \underset{\text{(vanaspati ghee)}}{\text{Solid fat}}$$

Catalytic hydrogenation of CO gives methanol.

$$CO + 2H_2 \xrightarrow[575\text{ K, }300\text{ atm}]{ZnO/Cr_2O_3} CH_3OH$$

7. Uses of Hydrogen :

In the manufacture of ammonia, methanol, synthetic petrol and vanaspati ghee. It is used in oxy-hydrogen flame (oxy-hydrogen torch) for welding.

8. Different forms of Hydrogen :

(i) Ortho and Para Hydrogen - The spins of two electrons in hydrogen molecule (H_2) are always in opposite directions (Pauli's exclusion principle). However, the spins of two nuclei (protons) may be either in the same direction or in opposite direction. When the spins of two nuclei are in the same direction, the molecule of hydrogen is known as ortho hydrogen, but when the spins of two nuclei are in opposite direction, the hydrogen molecule is known as para hydrogen. At room temperature ordinary hydrogen is a mixture of 75% ortho hydrogen and 25% para hydrogen, but on cooling the percentage of para form increases. These two forms are identical in chemical properties but differ in thermal conductivity and specific heat.

(ii) Nascent Hydrogen (New Born hydrogen) - Freshly generated hydrogen known as nascent hydrogen. It is much more reactive and is more powerful reducing agent than ordinary hydrogen because it exists in atomic state.

(iii) Atomic Hydrogen - When molecular hydrogen is passed through an electric arc, it decomposes into atomic hydrogens (used as atomic hydrogentorch and in welding).

$$H_2 \xrightarrow{\text{Electric arc}} 2H + \text{heat}$$

Atomic hydrogen is used in atomic hydrogen torch.

Note :

(i) Nascent hydrogen can be produced even at room temperature but atomic hydrogen is produced at elevated temperatures.

(ii) Nascent hydrogen can never be isolated but atomic hydrogen can be isolated

(iii) Reducing power of atomic hydrogen is much greater than that of nascent hydrogen.

(iv) Occluded Hydrogen - Some metals (e.g. Pt, Pd, Ni, etc) absorb large amount of H_2 under certain conditions. This absorbed H_2 gas is known as occuluded hydrogen. It is given off when the metal is heated.

9. Hard and Soft Water :

Water which does not form lather with soap easily and hence is unfit for washing is called hard water. Water which forms lather with soap easily is called soft water.

Causes of hardness - Hardness of water is due to the presence of bicarbonates (HCO_3^-), sulphates (SO_4^{2-}) and chlorides (Cl^-) of calcium and magnesium.

10. Types of Hardness of Water :

Hardness of water is of two types (i) Temporary hardness; (ii) Permanent hardness.

(i) Temporary Hardness : It is caused due to the presence of soluble bicarbonates of calcium and magnesium.

Removal of temporary hardness :

(a) By boiling - On boiling the water, the soluble bicarbonates decompose into insoluble carbonates. The insoluble material is removed out

$$\underset{\text{(Soluble)}}{\text{Metal bicarbonate}} \xrightarrow{\text{Boil}} \underset{\text{(insoluble)}}{\text{Metal carbonate}} + H_2O + CO_2 \uparrow$$

$$\underset{\text{(Soluble)}}{Ca(HCO_3)_2} \xrightarrow{\text{Boil}} \underset{\text{(insoluble)}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

(b) By treating with lime in calculated amount (Clark's process)

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3 \downarrow + \underset{\text{(ppt)}}{CaCO_3} \downarrow + 2H_2O$$

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

(ii) Permanent Hardness : It is due to the presence of soluble chlorides and sulphates of calcium and magnesium.

Removal of Permanent hardness :

(a) Washing soda process - Washing soda, Na_2CO_3 can remove both temporary and permanent hardness. Examples are :

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$

$$Mg(HCO_3)_2 + Na_2CO_3 \longrightarrow MgCO_3 \downarrow + 2NaHCO_3$$

(b) Permutit process (ion-exchange method) - Permutit (an artificial zeolite) is the trade name of hydrated sodium aluminium orthosilicate, $Na_2Al_2Si_2O_8.xH_2O$. The sodium ions of permutit are capable of exchanging the Ca^{2+} and Mg^{2+} ions present in hard water.

$$Na_2Z + Ca^{2+} \text{ or } Mg^{2+} \longrightarrow CaZ \text{ or } Mg\ Z + 2Na^+$$

$$CaZ \text{ or } Mg\ Z + 2NaCl \longrightarrow Na_2\ Z + CaCl_2 \text{ or } MgCl_2$$

(c) Calgon process - In this method hard water is percolated over calgon (sodium hexametaphosphate $Na_2[Na_4(PO_3)_6]$.

$$Na_2\left[Na_4(PO_3)_6\right] + 2Ca^{2+} \longrightarrow Na_2\left[Ca_2(PO_3)_6\right] + 4Na^+$$

$$Na_2\left[Na_4(PO_3)_6\right] + 2Mg^{2+} \longrightarrow Na_2\left[Mg_2(PO_3)_6\right] + 4Na^+$$

Ex.1 Determine the degree of hardness of a sample of water in terms of ppm of $CaCO_3$ containing 30 ppm of $MgSO_4$.

Sol 1 mole $MgSO_4 \equiv$ 1 mole $CaCO_3$; 120 ppm $MgSO_4$ = 100 ppm $CaCO_3$

$\therefore$ 30 ppm $MgSO_4$ = 25 ppm $CaCO_3$

Ex.2 Certain sample fo water was found to contain 68 ppm of $CaSO_4$ and 19 ppm of $MgCl_2$. What will be the total hardness of water in terms of ppm of $CaCO_3$

Sol 1 mole $CaSO_4 \equiv$ 1 mole $CaCO_3$; 136 ppm $CaSO_4 \equiv$ 100 pm $CaCO_3$

$\therefore$ 68 ppm $CaCO_4 \equiv$ 50 ppm $CaCO_3$

Similarly, 1 $MgCl_2 \equiv$ 1 $CaCO_3$; 95 ppm $MgCl_2 \equiv$ 100 ppm $CaCO_3$

$\therefore$ 19 ppm $MgCl_2 \equiv$ 20 ppm $CaCO_3$

Total hardness in water = Hardness due to $CaSO_4$ + Hardness due to $MgCl_2$

= 50 ppm + 20 ppm = 70 ppm

Ex.3 Calculate the degree of hardness in terms of ppm of $CaCO_3$ of a sample of water containing 6 mg of magnesium sulphate per kg of water.

Sol. 6 mg of $MgSO_4 = 6 \times 10^{-3}$ g of $MgSO_4 = \dfrac{6\times10^{-3}}{120}$ mole of $MgSO_4 = 5 \times 10^{-5}$ mole of $MgSO_4$

1 mole of $MgSO_4 \equiv$ 1 mole of $CaCO_3$ = 100 g of $CaCO_3$

$\therefore$ 5×10^{-5} mole of $MgSO_4 = 5 \times 10^{-5} \times 100$ g of $CaCO_3 = 5 \times 10^{-3}$ g of $CaCO_3$

Thus, 1000 g of water contains $MgSO_4$ equivalent to 5×10^{-3} g of $CaCO_3$

10^6 g (one million) of water contans = $\dfrac{5\times10^{-3}}{1000}\times10^6 = 5\text{g of } CaCO_3$

$\therefore$ Hardness of the given water = 5 ppm

HEAVY WATER, D_2O :

It was discovered by Urey in 1932. Ordinary water contains traces of heavy water (about 1 part of D_2O is present in 600 parts of water). It can be obtained by repeated electrolysis of ordinary water in alkali medium. Heavy water is a colourless, odourless and tasteless liquid. The chemical properties of D_2O are almost similar to the ordinary water. However, its physical properties are slightly different from water It is used as a moderator in nuclear reactor.

HYDROGEN PEROXIDE, H_2O_2 :

(1) Method of preparation :

(i) By the action of cold dil. H_2SO_4 on sodium or barium peroxide (Merck's process) :-

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

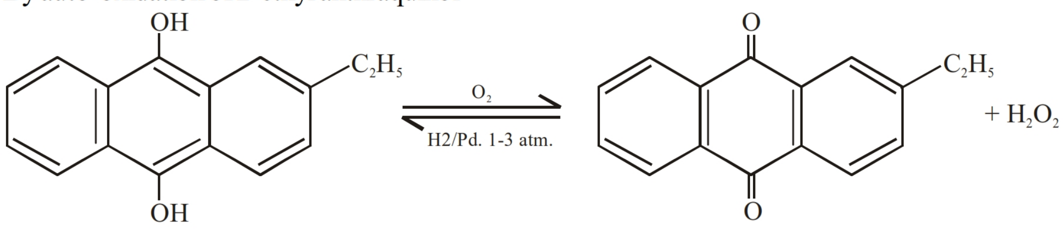
$$BaO_2 + H_2SO_4 \longrightarrow H_2O_2 + BaSO_4$$

(ii) By hydrolysis of peroxydisulphuric acid, $H_2S_2O_8$ (obtained by the electrolytic oxidation of H_2SO_4) :-

$$2H_2SO_4 \xrightarrow{\text{Electrolysis}} H_2S_2O_8 + H_2$$

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

(iii) By auto-oxidation of 2-ethyl anthraquinol



2-Ethylanthraquinol 2-Ethylanthraquinone

(2) Physical properties of H_2O_2 : It is pale blue syrupy liquid with bitter taste (b.p. 423.2 K, m.p. 272.4 K, density 1.44 gcm^{-3}). It decomposes on heating. It is completely miscible in water, ether and alcohol.

(3) Chemical properties of H_2O_2 :

(i) Decomposition : Hydrogen peroxide is unstable and decomposes on standing or on heating.

$$2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$$

Note : The decomposition of H_2O_2 is catalysed by Pt, Ag, Co, Fe, MnO_2 etc.

- The decomposition can be suppressed by the addition of glycerol, phosphoric acid and acetanilide.

(ii) Acidic nature : Hydrogen peroxide is slightly acidic in character and forms peroxides with certain hydroxides and carbonates.

$$2NaOH + H_2O_2 \longrightarrow Na_2O_2 + 2H_2O$$

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2$$

(iii) Oxidising nature : It is a powerful oxidising agent because it readily produces nascent oxygen (O).

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

(a) It oxidises black PbS to $PbSO_4$

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

(b) It oxidises KI to iodine

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

(c) It oxidises acidified $FeSO_4$ to $Fe_2(SO_4)_3$

$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

(d) It oxidises H_2S to sulphur

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

(iv) Reducing nature : It can also take up nascent oxygen (O) to form molecular oxygen and so it acts as a reducing agent. Important examples are :

(a) It reduces ozone to oxygen

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

(b) It reduces Cl_2 to HCl

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

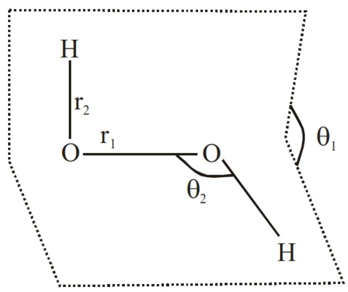
(4) As a bleaing agent : H_2O_2 acts as a mild bleaching agent. Its bleaching action is due to oxidation.

$$H_2O_2 \longrightarrow H_2O + O$$

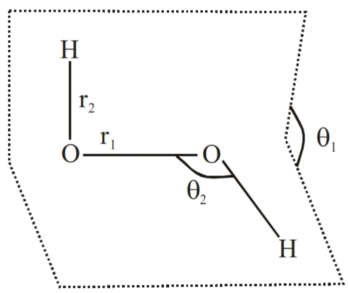
Coloured substance + O $\longrightarrow$ Colourless substance

(5) Structure of H_2O_2 : Structure of H_2O_2 is slightly different in gas phase and crystalline phase.

r_1 = 147.5 pm, r_2 = 95 pm, $\theta_1 = 111.5^0$, $\theta_2 = 94.8^0$ (Gas phase structure)



r_1 = 98.5 pm, r_2 = 145.8 pm, $\theta_1 = 90.2^0$, $\theta_2 = 101.9^0$ (Crystalline phase)



(6) Strength of H_2O_2 : Concentration of H_2O_2 is expressed in terms of volume strength. Volume strength represents the volume of O_2 obtained at N.T.P. by the decomposition of one volume of H_2O_2 solution e.g. 20 V H_2O_2 means 1 ml of H_2O_2 provides 20 ml of O_2 at N.T.P. However sometimes the concentration of H_2O_2 in a solution is expressed as percentage of H_2O_2 (in solution (w/v)) e.g. 30% H_2O_2 soluton means 30 gm of H_2O_2 is present in 100 ml of solution

Note : (a) 10 V H_2O_2 $\equiv$ 3.035% of H_2O_2 $\equiv$ 30.35 g/litre of H_2O_2 $\equiv$ 1.785 N

(b) Volume strength of H_2O_2 = Normality × 5.6 = Molarity × 11.2

(7) Uses of H_2O_2 : Hydrogen peroxide is used -

(i) As an antiseptic and germicide for washing wounds, teeth and ears under the name Perhydrol.

(ii) As an oxidant for rocket fuels

(iii) For bleaching delicate things like hair, wool, feathers, ivory etc.

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

(v) For restoring the original white colour of tarnish old lead painting.