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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 electropositive, 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.

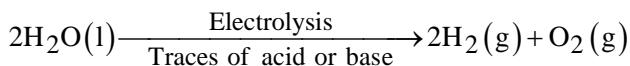
3. Isotopes of Hydrogen :

There are three isotopes of hydrogen :

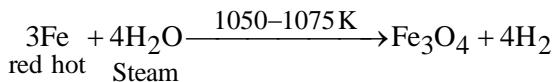
- Protium (commonly called as hydrogen, H) - A sample of hydrogen contains about 99.8% protium. Its nucleus constitutes one proton and no neutron. It contains only one electron in its K shell.
- Deuterium (${}_1^2H$ or D) - Its existence was first of all proposed by H. Urey (1931). The nucleus of deuterium 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.
- Tritium (${}_1^3H$ 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 β – rays. It has a half life period of 12.4 years.

4. Methods of preparation of hydrogen :

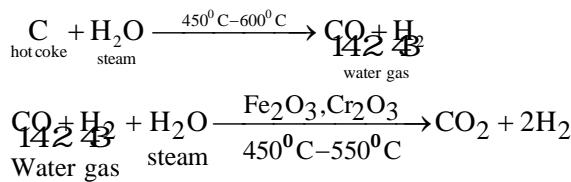
- By the electrolysis of water



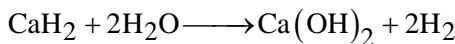
- From steam (Lane's process)



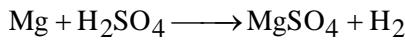
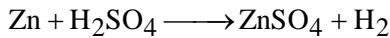
- From water gas (Bosch process)



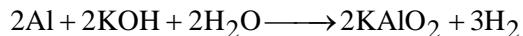
- From hydrolith, CaH_2



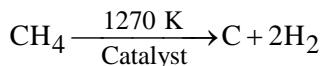
- From acids



(vi) From alkalies (Uyeno's method)



(vii) By thermal cracking of natural gas

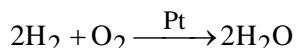


5. Physical properties of Hydrogen :

Hydrogen is a colourless, odourless, tasteless gas (b.p. 20.4 K and m.p. 13.8 K). It is the lightest gas (density 0.0899 g cm⁻³).

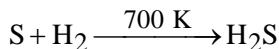
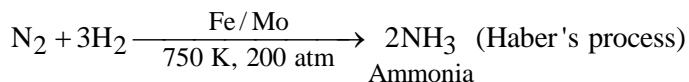
6. Chemical Properties of Hydrogen :

(i) On Combustion

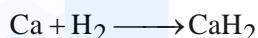
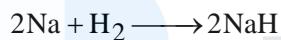


Note : Hydrogen does not support combustion but itself burns with pale blue flame.

(ii) With non-metals



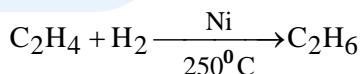
(iii) With metals : Forms ionic hydrides



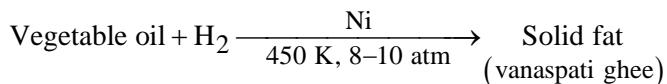
(iv) As a reducing agent



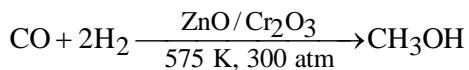
(v) Hydrogenation



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



Catalytic hydrogenation of CO gives methanol.



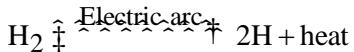
7. Uses of Hydrogen :

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).



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 occluded 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.

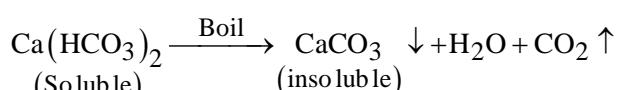
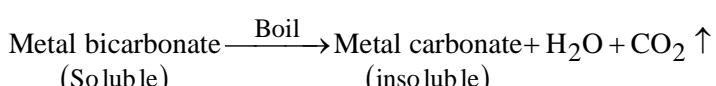
10. Types of Hardness of Water :

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

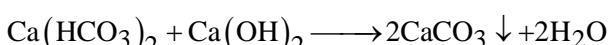
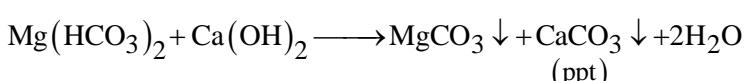
- (i) Temporary Hardness : It is caused due to the presence of soluble bicarbonates of calcium and magnesium.

Removal of temporary hardness :

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

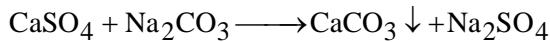


- (b) By treating with lime in calculated amount (Clark's process)

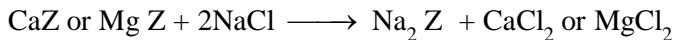
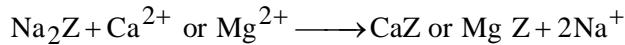


- (ii) Permanent Hardness : It is due to the presence of soluble chlorides and sulphates of calcium and magnesium.
Removal of Permanent hardness :
(a) Washing soda process - Washing soda, Na_2CO_3 can remove both temporary and permanent hardness.
Examples are :

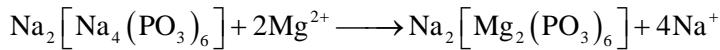
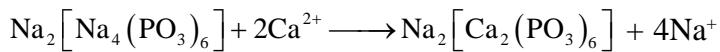




- (b) Permutit process (ion-exchange method) - Permutit (an artificial zeolite) is the trade name of hydrated sodium aluminium orthosilicate, $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$. The sodium ions of permutit are capable of exchanging the Ca^{2+} and Mg^{2+} ions present in hard water.



- (c) Calgon process - In this method hard water is percolated over calgon (sodium hexametaphosphate $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$).



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 $\text{MgSO}_4 \equiv 1$ mole CaCO_3 ; 120 ppm $\text{MgSO}_4 = 100$ ppm CaCO_3
 $\therefore 30$ ppm $\text{MgSO}_4 = 25$ ppm CaCO_3

Ex.2 Certain sample of 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 $\text{CaSO}_4 \equiv 1$ mole CaCO_3 ; 136 ppm $\text{CaSO}_4 \equiv 100$ ppm CaCO_3
 $\therefore 68$ ppm $\text{CaSO}_4 \equiv 50$ ppm CaCO_3
Similarly, 1 $\text{MgCl}_2 \equiv 1$ CaCO_3 ; 95 ppm $\text{MgCl}_2 \equiv 100$ ppm CaCO_3
 $\therefore 19$ ppm $\text{MgCl}_2 \equiv 20$ ppm CaCO_3

$$\begin{aligned} \text{Total hardness in water} &= \text{Hardness due to } \text{CaSO}_4 + \text{Hardness due to } \text{MgCl}_2 \\ &= 50 \text{ ppm} + 20 \text{ ppm} = 70 \text{ ppm} \end{aligned}$$

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 $\text{MgSO}_4 = 6 \times 10^{-3}$ g of $\text{MgSO}_4 = \frac{6 \times 10^{-3}}{120}$ mole of $\text{MgSO}_4 = 5 \times 10^{-5}$ mole of MgSO_4
1 mole of $\text{MgSO}_4 \equiv 1$ mole of $\text{CaCO}_3 = 100$ g of CaCO_3
 $\therefore 5 \times 10^{-5}$ mole of $\text{MgSO}_4 = 5 \times 10^{-5} \times 100$ g of $\text{CaCO}_3 = 5 \times 10^{-3}$ 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 contains $= \frac{5 \times 10^{-3}}{1000} \times 10^6 = 5$ 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.

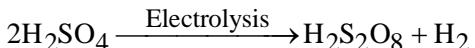
HYDROGEN PEROXIDE, H₂O₂ :

- #### (1) Method of preparation :

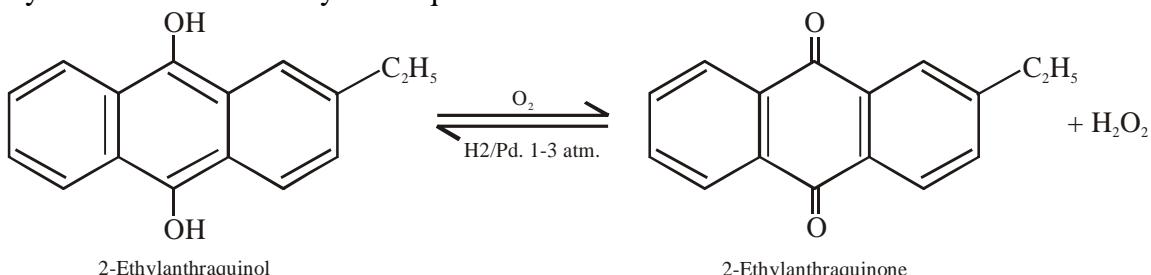
- (i) By the action of cold dil. H_2SO_4 on sodium or barium peroxide (Merck's process) :-



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



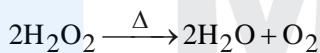
- (iii) By auto-oxidation of 2-ethyl anthraquinol



- (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 :

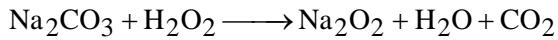
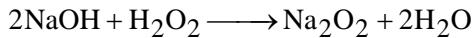
- (i) Decomposition : Hydrogen peroxide is unstable and decomposes on standing or on heating.



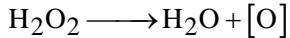
Note : The decomposition of H_2O_2 is catalysed by Pt, Ag, Co, Fe, MnO_2 etc.

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

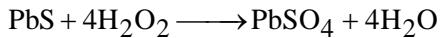
(ii) Acidic nature : Hydrogen peroxide is slightly acidic in character and forms peroxides with certain hydroxides and carbonates.



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



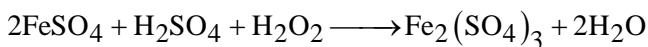
- (a) It oxidises black PbS to PbSO_4



- (b) It oxidises KI to iodine



- (c) It oxidises acidified FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$



- (d) It oxidises H_2S to sulphur



(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 :

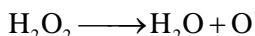
- (a) It reduces ozone to oxygen



- (b) It reduces Cl_2 to HCl

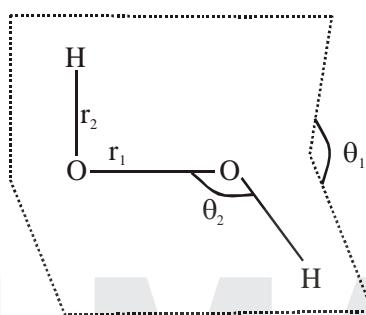


(4) As a bleaching agent : H_2O_2 acts as a mild bleaching agent. Its bleaching action is due to oxidation.

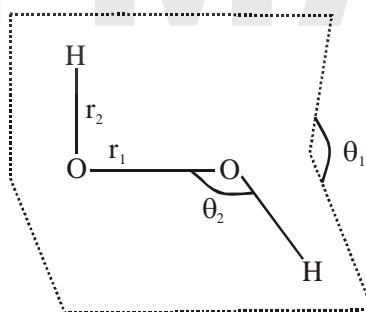


(5) Structure of H_2O_2 : Structure of H_2O_2 is slightly different in gas phase and crystalline phase.

$$r_1 = 147.5 \text{ pm}, r_2 = 95 \text{ pm}, \theta_1 = 111.5^\circ, \theta_2 = 94.8^\circ \text{ (Gas phase structure)}$$



$$r_1 = 98.5 \text{ pm}, r_2 = 145.8 \text{ pm}, \theta_1 = 90.2^\circ, \theta_2 = 101.9^\circ \text{ (Crystalline phase)}$$



(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 solution means 30 gm of H_2O_2 is present in 100 ml of solution

Note : (a) 10 V $\text{H}_2\text{O}_2 \equiv 3.035\%$ of $\text{H}_2\text{O}_2 \equiv 30.35 \text{ g/litre of } \text{H}_2\text{O}_2 \equiv 1.785 \text{ N}$

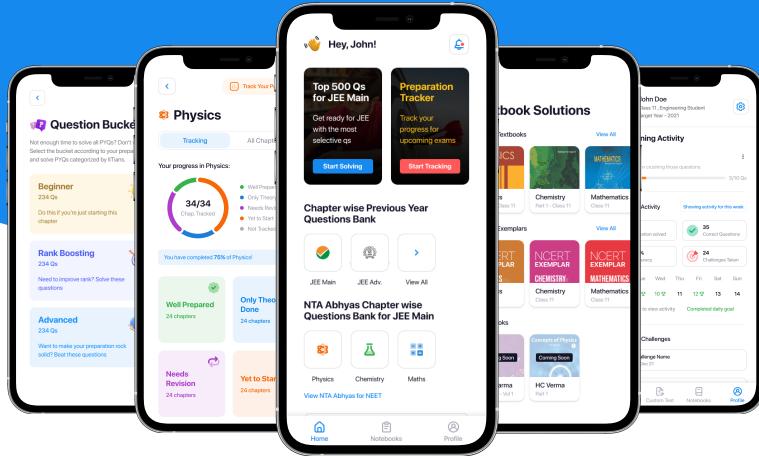
(b) Volume strength of $\text{H}_2\text{O}_2 = \text{Normality} \times 5.6 = \text{Molarity} \times 11.2$

(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.



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