Unit 5

HYDROGEN

5.1 Introduction

The dihydrogen (H_2) (hydrogen molecule) available in most abundance in the world and having number three in the order on the surface of the earth is seen as the biggest source of energy in future. Amongst all the elements, hydrogen has the simplest atomic structure. It is composed of one proton and one electron, even then it exists as a diatomic molecule or dihydrogen (H_2). It forms many compounds as compared to other elements. Do you know that dihydrogen can be used as an energy related source so that the global problem can be solved ?

5.2 Position of Hydrogen (H) in ...

Alkali metals form positively charged ions (cations) (Li^+, Na^+, K^+) by losing one electron. Similarly hydrogen can lose one electron and form positively charged ion or cation (H^+). The valency of alkali metals is considered as 1+. Like alkali metals, 1+ forms stable oxide, peroxide, halide and sulphide ions e.g Na_2O_2, H_2O_2, NaCl, HCl, Na_2S, H_2S. Hydrogen, like alkali metals, is a strong reducing agent. Though alkali metals are obtained in solid form, hydrogen is a gaseous nonmetal. The ionization enthalpy of metals is very less while the ionization enthalpy of hydrogen is very high (Li$\Delta_i H$ = 520kJ mol^{-1} and H$\Delta_i H$ = 1312kJ mol^{-1}). With reference to ionization enthalpy hydrogen has more similarity with halogens. (F$\Delta_i H$ = 1680 kJ mol^{-1}).

Hydrogen can be placed with halogens in group 17 (old - VII) because hydrogen possesses similarity with halogen elements of group 17.

Hydrogen forms hydride ion by accepting one electron whereas halogens form halide ions by receiving one electron. As halogen elements form stable diatomic molecule (F_2,Cl_2,Br_2), hydrogen molecules form diatomic (H_2) molecule. It combines with strongly electropositive elements like metals and form hydride compounds but, with reference to reactivity, it possesses very less reactivity in comparison to halogens. Halogen elements are coloured and strong oxidizing agents whereas hydrogen is a strong reducing agent.

Though hydrogen resembles alkali metals in many definite aspects, it also resembles non-metallic halogen elements, in fact it differs from them. Hence, the position of hydrogen is still uncertain that whether it can be considered in first group or seventeenth group. Hence, nowadays, instead of showing in first group or group 17, it is shown in the middle of the first period.

Hydrogen loses one electron and forms proton H^+, ionic radius 1.5×10^{-3}pm (pm = picometer = 10^{-12} meter) ion which is very small in comparison to atomic and ionic size (ionic radius 50 to 200 pm). Hence H^+ can not have free existence and it combines with other atom or molecule.

e.g. $H^+_{(aq)} + H_2O_{(l)} \rightleftharpoons H^+_3O_{(aq)}$

Hence, hydrogen element is unique from behaviour point of view. Therefore, it is placed separately in the first period.

5.3 Isotopes of Hydrogen

There are three isotopes of hydrogen which are known as protium (^1_1H), Deuterium or heavy hydrogen ^2_1H or D) and tritium (^3_1H or T). These isotopes differ from the point of view of the presence of neutrons. American scientist Harold C. Urey received the Nobel Prize in 1934 for separation of isotopes of hydrogen by physical method.

The nucleus of protium possesses only one proton, deuterium possesses one proton and one neutron and tritium possesses one proton and two neutrons. Thus their mass numbers are one, two and three respectively. Protium is in the highest proportion in dihydrogen available in nature. Its atoms are about 5000 times more than that of deuterium. The proportion of tritium atoms is very less. The relative proportion of atoms of tritium and protium is $1:10^{17}$. The property responsible for very low proportion of tritium is its radioactivity and emission of low energy β particles. Its half life is ($t_{1/2}$ = 12.33) years.

As the electronic configuration of these three isotopes is same, their chemical properties are similar but because of the difference in their binding energy, the change in reaction rate is observed. The physical properties of these isotopes are quite different because of their abundant quantity. This is shown in table 5.1

Table 5.1

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass ($gmol^{-1}$)	1.008	2.014	3.016
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.39	23.67	25.0
Density(gl^{-1})	0.09	0.18	0.27
Enthalpy of fusion (kJ mol^{-1})	0.117	0.197	-
Enthalpy of vaporization (kJ mol^{-1})	0.904	1.226	-
Enthalpy of bond dissociation (kJ mol^{-1}) at 298 K	435.88	443.35	-
Internuclear distance (pm)	74.14	74.14	-
Ionization enthalpy (kJ mol^{-1})	1312	-	-
Electron gain enthalpy (kJ mol^{-1})	-73	-	-
Covalent radius (pm)	37	-	-
Ionic radius (H^-) (pm)	208	-	-

5.4 Preparation of Dihydrogen and Its Physical Properties

Hydrogen is available in abundance in the nature in the form of compound, the water. Generally dihydrogen can be obtained by reaction of zinc metal with dilute hydrochloric acid, dilute sulphuric acid or concentrated aqueous alkali.

$$Zn_{(s)} + 2\,HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$
$$Zn_{(s)} + 2\,H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$$
$$Zn_{(s)} + 2\,NaOH_{(aq)} \rightarrow \underset{\text{(Sodium zincate)}}{Na_2ZnO_{2(aq)}} + H_{2(g)}$$

In laboratory, generally dihydrogen gas is prepared by using zinc and dilute H_2SO_4.

Industrial preparation of dihydrogen :

(i) Dihydrogen can be obtained by electrolysis of water in which few drops of sulphuric acid are added, between platinum electrodes.

$$2H_2O_{(\ell)} \xrightarrow[\text{Traces of acid}]{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

(ii) To obtain pure dihydrogen (> 99.95 %) the hot aqueous solution of barium hydroxide is electrolysed between two nickel electrodes.

(iii) Dihydrogen is obtained as a component of water gas by heating hydrocarbons or coal at 1270 K temperature using iron (Fe), nickel (Ni) catalyst.

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow[\text{[Ni]}]{1270\text{ K}} CO_{(g)} + 3H_{2(g)}$$

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1270\text{ K}} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{(Water gas)}}$$

This water gas is used in synthesis of methanol and hydrocarbons so that it is called syngas. Dihydrogen can be obtained by heating water gas at 673 K in presence of iron chromate ($FeCrO_4$) catalyst. With water vapor, carbon dioxide is removed and dihydrogen can be obtained.

$$[CO_{(g)} + H_{2(g)}] + H_2O_{(g)} \xrightarrow[(FeCrO_4)]{673\text{ K}} CO_{2(g)} + 2H_{2(g)}$$

(iv) Dihydrogen can be obtained by heating methanol at 50 bar (SI Unit is bar instead of atmosphere) and 673K temperature in presence of cuprous oxide catalyst

$$CH_3OH_{(l)} \xrightarrow[(Cu_2O)]{50\text{ bar } 673\text{K}} CO_{(g)} + 2H_{2(g)}$$

In the present time it is obtained from synthetic gas, sewage, saw dust, newspaper etc.

77% of the industrial production of dihydrogen is from petrochemicals, 18% from coal, 4% by electrolysis and 1% from other sources.

Physical Properties of Dihydrogen :

Dihydrogen (H_2) is a colourless, odourless and tasteless gas. It is lighter than air and is insoluble in water. It is a combustible gas. Dihydrogen is diamagnetic. The value of its reduction potential is 0.0 volt (V). Other properties are shown in table 5.1

Chemical properties of dihydrogen :

(i) Reactivity (reaction) with halogen :

Dihydrogen (H_2) reacts with dihalogen (X_2) and gives hydrogen halide (HX)

$$H_{2(g)} + X_{2(g)} \rightarrow 2HX_{(g)} \quad (X = F, Cl, Br, I)$$

(ii) Reactivity with oxygen :

Dihydrogen (H_2) gives hydrogen oxide-water (H_2O) by reacting violently with dioxygen.

$$2H_{2(g)} + O_{2(g)} \xrightarrow[\text{OR } \Delta]{\text{Catalyst}} 2H_2O_{(l)} \Delta H = -285.9 \text{ kJ mol}^{-1}$$

(iii) Reactivity with nitrogen :

Dihydrogen (H_2) reacts with dinitrogen giving ammonia gas

$$N_{2(g)} + 3H_{2(g)} \xrightarrow[\text{[Fe]}]{\text{673K, 200 bar}} 2NH_{3(g)} \Delta H = -92.6 \text{ kJ mol}^{-1}$$

(iv) Reactivity with metal

Dihydrogen reacts with many metals at high temperature and gives corresponding hydrides

$$H_{2(g)} + 2M_{(s)} \longrightarrow 2MH_{(s)}$$

(M = Alkali metal)

(v) Reactivity of metal ion and metal oxides :

Many metal ions in aqueous solutions and metal oxides (less reactive than Fe) react with dihydrogen and gives metal.

$$Pd^{2+}_{(aq)} + H_{2(g)} \rightarrow Pd_{(s)} + 2H^{+}_{(aq)}$$

$$M_xO_{y(s)} + yH_{2(g)} \rightarrow xM_{(s)} + yH_2O_{(\ell)}$$

$$Fe_2O_{3(s)} + 3H_{2(g)} \rightarrow 2Fe_{(s)} + 3H_2O_{(\ell)}$$

(vi) Reactivity with organic compounds :

Dihydrogen (H_2) gives hydrogenated product which possesses industrial importance, by reacting as strong reducing agent with many organic compounds in presence of catalyst.

$$\underset{\text{ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[\text{390K}]{\text{[Ni]}} \underset{\text{ethane}}{CH_3 - CH_3}$$

$$\underset{\text{ethyne}}{CH \equiv CH} + 2H_{2(g)} \xrightarrow[\text{390K}]{\text{[Raney Ni]}} \underset{\text{ethane}}{CH_3 - CH_3}$$

Edible fat (vegetable ghee) is formed by the hydrogenation of oil in presence of nickel catalyst.

Uses of dihydrogen :

(i) Dihydrogen is an important raw material for the industrial production of ammonia by Haber process

$$N_{2(g)} + 3H_{2(g)} \underset{\substack{200 \text{ bar} \\ \text{[Fe]}}}{\overset{673K}{\rightleftharpoons}} 2NH_{3(g)}$$

(ii) Dihydrogen in synthetic gas is useful for industrial production of methanol.

$$\underbrace{CO_{(g)} + 2H_{2(g)}} \xrightarrow[\substack{50 \text{ bar} \\ [Cu_2O]}]{573K} CH_3OH_{(\ell)}$$

(iii) Dihydrogen is useful for industrial production of important chemical like hydrochloric acid

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\nu} 2HCl_{(g)}$$

It is also useful in production of halogen acid like HBr and HI.

(iv) It is useful for obtaining metal from oxides of heavy metal and preparation of metal hydrides.

(v) Dihydrogen is useful as fuel in rockets used for space research and in fuel cells.

(vi) It is used in cutting and in welding work of metals in the molecular hydrogen and oxy-hydrogen flame.

5.5 Hydrides

Dihydrogen forms hydrides of the type MH_x or M_mH_n by reaction with most of the metals. Certain elements like indium (In) and thallium (Tl) do not give hydrides. Hydride compounds can be divided in to three types :

(1) Saline or ionic hydries

(2) Metallic or interstitial hydrides

(3) Molecular or covalent hydrides

5.5.1 Saline or Ionic hydrides :

Metal elements of s-block (group-1 and group-2) possess more electropositive character so it forms light metallic hydride compounds e.g LiH, NaH, BeH_2, and MgH_2

Hydrides of beryllium and magnesium possess polymeric structure like $(BeH_2)_n$ and $(MgH_2)_n$. Ionic hydrides are crystalline solid, nonvolatile and nonconductor of electricity but in their molten states they ionise and H^- liberates dihydrogen at the anode by oxidation during electrolysis.

$$2H^- \text{ (Melt)} \xrightarrow{\text{Anode}} H_{2(g)} + 2e^-$$

Saline hydrides react violently with water and liberate dihydrogen (H_2)

$$NaH_{(s)} + H_2O_{(l)} \rightarrow NaOH_{(aq)} + H_{2(g)}$$

Lithium hydride does not react with O_2 and Cl_2 at normal temperature, so they are used in preparation of other hydrides.

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

5.5.2 Metallic or non-stoichiometric or Interstitial hydrides : Metallic elements of d-block as well as p-block combine with dihydrogen and give metallic hydrides which are non-stroichiometric,

e.g (VH, VH_2, NbH, NbH_2, TiH, TiH_3, LaH_2, LaH_3, HfH_2)

Metals of groups 7, 8, and 9 do not form hydrides. Cr of group VI forms CrH which is not good conductor for heat and electricity like original metal.

Metallic hydrides are mostly non-stochiometric compounds e.g $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$ etc. In these metallic hydrides, hydrogen is absorbed in the interstitial places of the metals. During this there is no change in types of bonds in them and so they are called interstitial hydrides. Hydrides of metals like Ni, Pd, Ce and Ac possess different structures than their original metal. So the hydrides of these metals are used in more proportion in catalytic reaction like hydrogenation.

5.5.3 Molecular or Covalent hydrides :

Metallic and nonmetallic elements of p-block combine with hydrogen and give molecular hydrides e.g CH_4, NH_3, PH_3, SbH_3, H_2O, H_2S, H_2Se H_2Te, HF etc. Molecular hydrides can be classified as following on the basis of their Lewis structure.

(i) Electron deficient hydrides e.g. B_2H_6

(ii) Electron precise hydrides e.g. CH_4

(iii) Electron rich hydrides e.g. H_2O, HF

5.6 Water (H_2O)

Water plays an important role for living entities. Water is about 65% in human body and as high as about 95% in some of the vegetation. It is an important compound for living beings and is essential for life. It is a universal solvent. Water is distributed unevenly on the earth which in percentage is as given in table 5.2

Table 5.2

Natural sources	Percentage
Oceans	97.33
Saline lakes and inland seas.	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes or Ponds	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

5.6.1 Physical properties : Water is a colourless, tasteless and odourless liquid. Its melting point is 273 K and boiling point is 373 K. Its density at 298 K temperature is 1.00 gram cm^{-3} (Density is expressed in kg/m^3 or kgm^{-3} units in SI). It possesses polar properties and its molecule possesses angular structure which has sp^3 hybridisation. The H-O-H bond angle is about 104.5^0 instead of $109^0 28'$. It possesses anomalous volume expansion between 273 K to

277 K. At higher than this temperature it shows normal expansion like other liquids.

Structure of water : The bonds, bond length and bond angles formed between two H and one O present in H_2O are shown in Fig 5.1

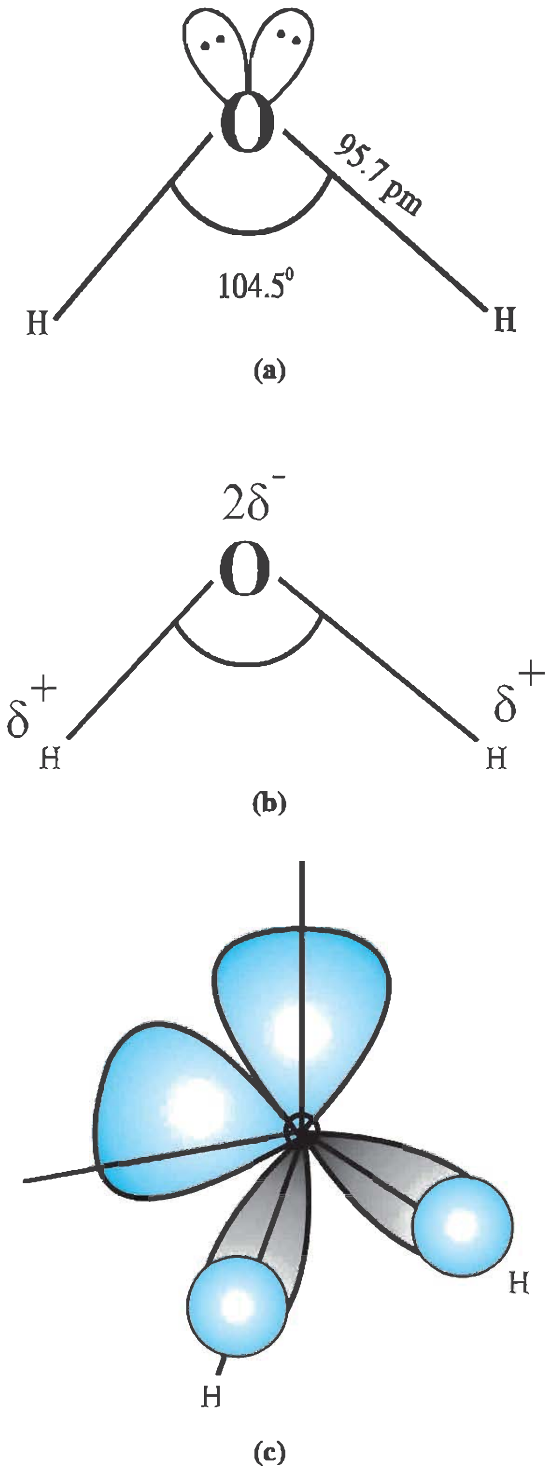


Figure 5.1

5.6.2 Structure of ice :

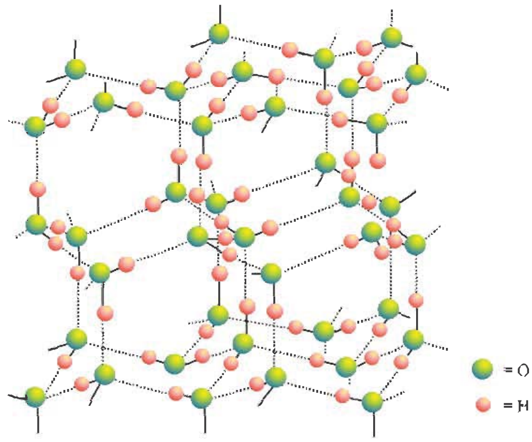


Figure 5.2

In ice, a definite three dimensional structure is formed by hydrogen bonds. This is shown in the figure 5.2. On examination of crystalline structure of ice with the help of X-rays, it is found that around each oxygen atom tetrahedral structure is formed and four oxygen atoms are arranged at 276 pm distance.

Because of hydrogen bond in ice, it forms big holes and forms spacious type structure. It maintains internally the definite volume of molecules.

5.6.3 Chemical properties :

(i) The concentration of water is 55.55 mollit^{-1} or M at 298 K. Because of its self ionization $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mollit^{-1} is obtained at equilibrium condition.

$$H_2O_{(l)} + H_2O_{(l)} = H_3O^+_{(aq)} + OH^-_{(aq)}$$

(ii) Its pH = pOH = 7.0. Hence it is a neutral solvent.

(iii) Water acts as amphoteric

Ammonium hydroxide is obtained by reaction of ammonia gas with water.

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightarrow \underset{\text{Acid}}{NH_4^+{}_{(aq)}} + \underset{\text{Base}}{OH^-{}_{(aq)}}$$

$$\underset{\text{Acid}}{H_2S_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightarrow \underset{\text{Base}}{HS^-{}_{(aq)}} + \underset{\text{Acid}}{H_3O^+{}_{(aq)}}$$

$$\underset{\text{Acid}}{HS^-{}_{(aq)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightarrow \underset{\text{Base}}{S^{2-}{}_{(aq)}} + \underset{\text{Acid}}{H_3O^+{}_{(aq)}}$$

(iv) Redox (oxidation and reduction) reaction with more electropositive metal it reduces hydrogen ion in water as an oxidizing agent.

$$2H_2O_{(l)} + 2Na_{(s)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

O_2 is liberated in the photochemical reaction.

$$6CO_{2(g)} + 6H_2O_{(l)} \xrightarrow[h\nu]{\text{Photo-synthesis}} C_6H_{12}O_{6(aq)} + 6O_{2(g)}$$

As a reducing agent it reduces fluorine to F^-

$$2F_{2(g)} + 2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + 4F^-_{(aq)} + O_{2(g)}$$

(v) Hydration reaction of water

$$P_4O_{10(s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4(aq)}$$

$$AlCl_{3(g)} + 6H_2O_{(l)} \rightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3Cl^-_{(aq)}$$

$$SiCl_{4(l)} + 2H_2O_{(l)} \rightarrow SiO_{2(g)} + 4HCl_{(aq)}$$

$$Ca_3N_{2(s)} + 6H_2O_{(l)} \rightarrow 3Ca(OH)_{2(aq)} + 2NH_{3(g)}$$

(vi) Some compounds are hydrous. The number of molecules of water associated with it is called water of crystallization

$CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $BaCl_2 \cdot 2H_2O$ (Metallic salt)

It also combines as ligand to form complex salt

$[Ni(H_2O)_6]^{2+}\, 2(NO_3)^-$, $[Cr(H_2O)_6]^{3+}\, 3Cl^-$ Complex salt

5.6.4 Hard water and Soft water : Rain water is mostly pure but some atmospheric gases mix with it. They are available as solid, liquid and gas on the surface of the earth. Thus, in any kind of water, some type of impurities are present and as it can easily flow it flows on the surface of earth. while flowing it passes through minerals like magnesite, dolomite etc. Magnesium hydrogen carbonate (Magnesium bicarbonate) enters into water as impurity over and above, sodium hydrogen carbonate (Sodium bicarbonate) sodium chloride, calcium sulphate, calcium chloride, magnesium sulphate, magnesium chloride and different minerals undergo chemical reactions and are added as impurities due to their solubility. In this way, salts of calcium and magnesium become soluble in water and the hardness enters into water. The definition of such a hard water can be given as follows :

The water which does not form lather easily with soap and wastes soap is called hard water.

When hard water comes in contact with soap, the cations from the sodium salts formed from fatty acids react with calcium and magnesium ion in water and insoluble calcium and magnesium salts are precipitated

$$2C_{17}H_{35}COONa + M^{2+}_{(aq)} \rightarrow (C_{17}H_{35}COO)_2M_{(s)} + Na^{2+}_{(aq)}$$

(Salt of Fatty acid) (M = Ca. Mg)

Thus, instead of removing dirt or cleansing reaction, majority of soap's amount is changed to calcium and magnesium salts. If hard water is used in boilers, salts deposit and hence, there are problems of bursting of boilers. Therefore, the water used in boilers must be soft, that is, the salt of Ca and Mg must be removed or minimized.

Hardness is of two types : (1) Temporary and (2) Permanent

Temporary hardness : In temporary hardness the salt of calcium and magnesium dissolved in water are calcium and magnesium hydrogen carbonates. This type of hardness can be removed by boiling the water. On boiling water, calcium and magnesium hydrogen carbonate soluble in water decompose by giving carbon dioxide and insoluble carbonates.

$$Mg(HCO_3)_{2(aq)} \xrightarrow{\Delta} MgCO_{3(s)} + 2CO_{2(g)} + H_2O_{(g)}$$

$$Ca(HCO_3)_{2(aq)} \xrightarrow{\Delta} CaCO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$$

Insoluble carbonates can be removed by filtration process. Temporary hardness can be removed by addition of lime water ($Ca(OH)_2$) to temporary hard water. In this reaction insoluble carbonate salts of calcium and magnesium are precipitated which can be removed by filtration process. This method is known as Clark's method.

$$Ca(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \rightarrow 2CaCO_{3(s)} + 2H_2O_{(l)}$$

$$Mg(HCO_3)_{2(aq)} + 2Ca(OH)_{2(aq)} \rightarrow 2CaCO_{3(s)} + Mg(OH)_{2(s)} + 2H_2O_{(l)}$$

Permanent hardness :

The permanent hardness enters into the water by bicarbonates dissolved in water and by chloride, and sulphate salts of calcium and magnesium. The permanent hardness can not be removed by boiling. The methods for removal of permanant hardness are as follows :

(i) Chemical methods : In this method amount of washing soda, determined by calculation is used. By this hardness (Ca^{2+} and Mg^{2+}, SO_4^{2-}, Cl^-) is removed. By addition of washing soda carbonates of calcium and magnesium are formed.

$$MCl_{2(aq)} + Na_2CO_{3(s)} \rightarrow MCO_{3(s)} + 2NaCl_{(aq)} \quad (M = Mg, Ca)$$

$$MSO_4 + Na_2CO_{3(s)} \rightarrow MCO_{3(s)} + Na_2SO_4$$

By use of sodium hexametaphosphate ($Na_6P_6O_{18}$), Ca^{2+}, and Mg^{2+} ions can be made ineffective. Sodium hexametaphosphate is known as 'Calgon' on commercial base.

$$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$$

$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow 2Na^+ + [Na_2MP_6O_{18}]^{2-}$$
(M=Mg,Ca)

Complex negative ion remains in solution.

(ii) Ion exchange method : The method of displacing or exchanging Ca^{2+} and Mg^{2+} present in soluble form in permanent hard water by the Na^+ ions is called ion exchange method. First of all, the mineral zeolite was used as positive ion exchanger. Zeolite is the calcium silicate having formula $Na_2Al_2Si_4O_{12}$. The complex structure is formed by aluminium (Al), silicon (Si) and oxygen (O) atoms in it. In this structure, there is a void like that in honey comb in which sodium ions are present. When the hard water passes over the particles of zeolite, some of the sodium ions come out from the zeolite and mix with the solution and Ca^{+2} and Mg^{+2} ions enter into their places; so they exchange their sites. So that they exchange there and Na^+ is released. This way hardness of water can be removed. The used zeolite can be again made efficient for reuse because Ca^{+2} and Mg^{+2} in them can also be exchanged.

If Z^- is considered as the small part of the structure of zeolite having one negative charge in water by Na^+, it can be shown by following reaction.

$$2Na^+Z^- + Ca^{2+} \rightarrow Ca^{2+}(Z^-)_2 + 2Na^+$$

(iii) Synthetic resin method : In the present times synthetic cation exchangers are used to soften the hard water. This method is more effective than the Zeolite method.

Cation exchange resin is a solid organic molecule having $-SO_3H$ group. The cation exchange resin (RSO_3H) reacts with NaCl and converted into RSO_3Na. When hard water passes through Ca^{2+}, Mg^{2+} ions present in water are exchanged by Na^+ ion that is Ca^{2+} and Mg^{2+} ions are removed from hard water and the water becomes soft.

$$2RSO_3Na_{(s)} + M^{2+}_{(aq)} \rightarrow (RSO_3)_2M_{(aq)} + 2Na^+_{(aq)}$$

where, $M^{2+} \equiv Ca^{2+}, Mg^{2+}$

To make this resin efficient again NaCl is passed through it.

In the same water, to remove anions from the water, anion exchange resins are used.

5.7 Hydrogen Peroxide : H_2O_2

In everyday life hydrogen peroxide is an important chemical to control pollutants formed industrially.

5.7.1 Preparation :

(1) In 1818, J. L. Thenard obtained hydrogen peroxide by the reaction of barium peroxide and sulphuric acid.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

(2) When bisulphate (HSO_4^-) ion containing solution is electrolytically oxidized at high current density, perdisulphuric acid is obtained which on hydrolysis gives hydrogen peroxide.

Anode :

$$2HSO^-_{4(aq)} \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H_{(aq)} + 2e^-$$
(perdisulphuric acid)

$$\xrightarrow[H_2O]{\text{hydrolysis}} 2HSO^-_{4(aq)} + 2H^+_{(aq)} + H_2O_{2(aq)}$$

(3) Industrially it can be prepared by self oxidation of 2-alkyl anthraquinol

$$\text{2-alkyl anthraquinol} \underset{H_2/Pd}{\overset{O_2\text{air}}{\rightleftarrows}} H_2O_2 + \text{oxidised product}$$

In hydrogen peroxide the amount of oxygen is two times more than the oxygen in water. The prefix 'per' means more. Hence the word peroxide is used. In hydrogen peroxide more oxygen is there as compared to that in hydrogen oxide (water) and it possesses peroxide bond structure.

5.7.2 Physical Properties : Hydrogen peroxide in the pure form is colourless but if it is in more proportion, it is a blue coloured dense liquid. Its density in solid form is 1.64 gcm^{-3} and in liquid form it is 1.44 gcm^{-3}. Its melting point is 272.4 K and boiling point is 423 K. It is a very strong oxidising agent. It carries out self oxidation of organic compounds. Its uses are due to its oxidising power. It completely mixes with water. H_2O_2 sold in the market has H_2O_2 30 % in 100 volume with water. At STP in one milliliter 30 % H_2O_2 gives 100 ml of oxygen. On commercial bases the sample from the market 3 % H_2O_2 is there in the sample of 10 volume. Let us study this matter by following example :

Example : Calculate the strength of 10 volume solution of H_2O_2.

Solution : 10 volume of H_2O_2 solution will give 10 litre O_2 at STP

$$2H_2O_{2(l)} \rightarrow O_{2(g)} + 2H_2O_{(l)}$$

$$2 \times 34 = 68g$$

The volume of 1 mole gas is 22.4 litre at STP

68 g H_2O_2 should be present in 22.4 litre O_2 gas

$\therefore$ How many gram of H_2O_2 will be in 10 litre O_2 gas

$$\therefore \frac{10 \times 68}{22.4} = 30.36 \text{ g}$$

5.7.3 Chemical properties : Hydrogen peroxide is an aqueous solution. By adding small amount of stabilizer like phosphoric acid, its oxidation and decomposition in water can be reduced.

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

Hydrogen peroxide can function as oxidising agent and reducing agent in both acidic and basic media. When hydrogen peroxide functions as an oxidising agent, the oxidation number of each atom of oxygen becomes –2 from –1. The examples are given below.

(a) $H_2SO_{3(aq)} + H_2O_{2(aq)} \rightarrow H_2SO_{4(aq)} + H_2O_{(l)}$

(b) $HNO_{2(aq)} + H_2O_{2(aq)} \rightarrow HNO_{3(aq)} + H_2O_{(l)}$

(c) $PbS_{(s)} + 4H_2O_{2(aq)} \rightarrow PbSO_{4(g)} + 4H_2O_{(l)}$

(d) $2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + H_2O_{2(aq)} \rightarrow 2Fe^{3+} + 2H_2O_{(l)}$

When hydrogen peroxide functions as a reducing agent, the oxidation number of each oxygen atom becomes O (zero) from –1. In acidic medium it decolourises potassium permanganate solution.

$$2KMnO_{4(aq)} + 3H_2O_{2(aq)} \rightarrow 2MnO_{2(s)} + 2KOH_{(aq)} + 2H_2O_{(l)} + 3O_{2(g)}$$

Some examples are given below :

(a) $HOCl_{(aq)} + H_2O_{2(aq)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} + O_{2(g)}$

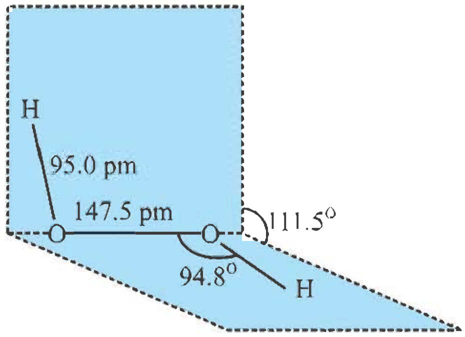
(b) $Cl_{2(g)} + H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$

(c) $I_{2(s)} + H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow 2I^-_{(aq)} + 2H_2O_{(g)} + O_{2(g)}$

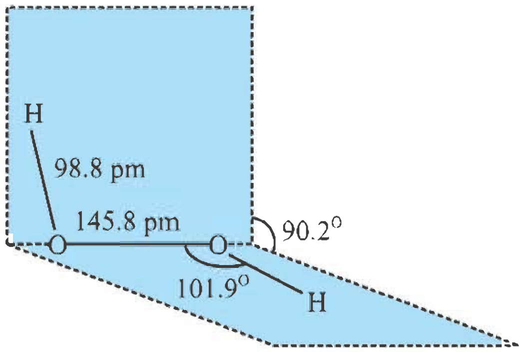
(d) $2Fe^{3+}_{(aq)} + H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow 2\ Fe^{2+}_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$

Structure :

There are two bonds O–O and H–O in hydrogen peroxide. In peroxide $(-O-O-)^{2-}$ ion is present. Its molecule is nonplanar. Its molecular structure is as follows :



Gaseous form



Solid form

Uses :

(1) Hydrogen peroxide is used as bleaching agent in industrial units like textile, paper, leather, oil, fat etc.

(2) In everyday life to bleach hair, and as mild disinfectant in dentistry which is sold in market as perhydral.

(3) Hydrogen peroxide is used in preparation of chemicals such as sodium percarbonate, sodium perborate etc. and used in preparation of good quality detergents.

(4) It is used as the controller of pollutants in industrial field. Especially it is used in oxidation of cyanide and oxidation of excreted materials. In present days it is used to decrease industrial pollution (Green chemistry) in maintenance of environment.

5.8 Heavy Water : D_2O

Heavy water is the oxide of deuterium the isotope of hydrogen. As deuterium oxide is considered as heavy water; it is largely used as moderator in nuclear reactors to obtain compounds of deuterium, to understand mechanism of a reaction exchange of ions etc. Heavy water (D_2O) is obtained as the by product during electrolysis of water used in production of fertilisers.

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

$$Al_4C_3 + 12D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$$

5.9 Economic Utility of Dihydrogen

Because of the decrease in quantity of crude oil available from the earth, not possible to store electrical energy and limitations of obtaining nuclear energy, the utility of dihyrogen can be the source of energy in its place.

The main aim and advantage of economic utility of dihydrogen is that the transfer of available energy is carried out in the form of hydrogen which solves the problems of storage and transmission of energy.

Use of liquid hydrogen as fuel :

By using liquid hydrogen as fuel the pollution of air can be decreased. It possesses very high efficiency in comparison to thermal power electric stations.

The scientists in America had used this type of fuel in the spaceshuttles in the Apollo programme. The use of this type of fuel in fuel cells, water vapours were obtained during cell reaction and it was cooled down whereby they got the drinking water.

It is a history for India that in October, 2005 only one pilot project was selected for use of dihydrogen as a fuel. Thereby new researches were taken up in the automobile age. Generally use of 5% dihydrogen in CNG is mixed for a vehicle like car, similarly simple and cheaper machines are manufactured for the use of dihydrogen as fuel. Scientists should give their contribution in solving the global problem of energy.

SUMMARY

Hydrogen atom is the lightest which possesses only one proton and one electron. It becomes positively charged by loss of the electron and is changed to proton. There are three isotopes of dihydrogen whose information we have studied in detail. In this unit preparation of hydrogen, its physical properties, chemical properties and its utility have been studied. Economic utility of dihydrogen, in fuel cell, rocket CNG etc. have been studied. Preparation of dihydrogen, its structure and properties have been discussed. We studied in this unit the methods of softening hard water. Heavy water and its uses as well as structure of ice, hydrogen economy etc. have also been discussed in this unit. Hydrogen peroxide is interesting non polar configuration possessing, compound used on a large scale in industrial field, for bleaching preparation of medicines in methods of control of pollutants and removal of industrial pollutants.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which of the following statements is true for dihydrogen ?

(A) It is a stable oxide and gives a peroxide

(B) It is an unstable oxide and gives a stable peroxide

(C) It violently reacts with dioxygen at normal temperature.

(D) It gives unstable peroxide.

(2) In which of the following dihydrogen is useful ?

(A) in fuel cell (B) in preparation of ammonia

(C) in preparation of vegetable ghee (D) in all the given

(3) Which method is useful to remove temporary hardness ?

(A) Heating the water and then cooling

(B) Resin method

(C) Ion exchange method

(D) None from the given

(4) Which scientist had obtained hydrogen peroxide from barium peroxide ?

(A) J. L Leonard (B) J.J. Thomson

(C) J.L Thenard (D) Goldstein

(5) What is correct about reactivity ?

(A) Protium = Tritium (B) Protium < Deuterium

(C) Protium > Deuterium (D) Protium = Deuterium

(6) $H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$ which reaction occurs in H_2O_2 in the given reaction ?

(A) Oxidation (B) Reduction

(C) Neutralisation (D) Redox

(7) Which substance is called "calgon" on commercial base ?

(A) Sodium pyrometaphosphate (B) Sodium metaphosphate

(C) Sodium hexametaphosphate (D) Sodium polyphosphate

(8) What is used as exchanger in ion exchange method ?

(A) alum (B) zeolite

(C) lime (D) all the given

(9) What is the correct formula of sodium hexametaphosphate ?

(A) $Na_4P_4O_{16}$ (B) $Na_6P_6O_{16}$

(C) $Na_6P_4O_{18}$ (D) $Na_6P_6O_{18}$

(10) What is the proportion of tritium relative to protium ?

(A) 10^{16} (B) 10^{17}

(C) 10^{-16} (D) 10^{-16}

2. Write answers of following questions in short :

(1) What is isotope ?

(2) Where in the modern periodic table hydrogen is placed ?

(3) Write names of isotopes of hydrogen.

(4) Mention the types of hydrides giving examples.

(5) Impurities of which metal ions are present in hard water ?

(6) Write molecular formula of heavy water.

(7) Write bond angle and type of hybridization in water.

(8) Write about Clark's method.

(9) Discuss structure of hydrogen peroxide.

(10) Hydrogen peroxide acts as oxidising agent. Write reaction equation for it.

(11) Write molecular formulas of two metallic hydrides.

3. Write answers of the following questions :

(1) Give explanation of isotopes of hydrogen in brief.

(2) Explain hard water and soft water.

(3) Write economic utility of dihydrogen.

(4) Explain the structure of H_2O.

(5) Write chemical methods for removal of permanent hardness.

(6) Write the ion exchange method for removal of permanent hardness.

(7) Write uses of hydrogen peroxide

4. Write answers of following questions in detail :

(1) Discuss the position of hydrogen in the modern periodic table.

(2) Write the preparation of dihydrogen and explain its physical and chemical properties.

(3) Write uses of dihydrogen.

(4) Write preparation of hydrogen peroxide and explain the physical and chemical properties.

(5) What are hydride compounds ? Explain them by giving types.

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