Class 11, Chapter- 9: Hydrogen

Hydrogen: It was discovered by Henry Cavendish in 1766 by the action of dilute H2O4 on iron. It was named „inflammable air‟, Lavoisier gave it the name hydrogen (Creek: Hydra = water, gennas = producer]. It occurs in free state as well as in combined state.

Position of Hydrogen in the Periodic Table: Hydrogen resembles with alkali metals (group I) as well as halogens (group 17), At the same time, it differs from both in certain characteristics. That is why hydrogen if; called "rogue element". it has been placed in group 1 on the basis of its configuration 1s1.

Isotopes of Hydrogen: Hydrogen exists in the form of three isotopes :

Property	Protium	Deuterium	Tritium
Symbol	$^1H_1$	D or $^2H_1$	T or $^3H_1$
Particle present	$1p^+ + 1e^-$	$1p^+ + 1n^+ + 1e^-$	$1p^+ + 2n^+ + 1e^-$
Mass number	1	2	3
Atomic mass	1.008	2.0142	3.0170
Molecular formula	H_2	D_2	T_2
Melting point	13.96	18.73	20.62
Bond dissociation energy	435.90	443.40	446.90
Nuclear spin	1/2	1	1
Radioactivity	Non-radioactive	Non-radioactive	Radioactive

Dihydrogen [H2]

Methods of Preparation:

Lab Methods:

(i) Metals which have reduction potential lesser than H, can liberate H_2 from acids.

$$Zn + H_2SO_4 \text{ (dilute)} \rightarrow ZnSO_4 + H_2$$

Pure zinc is not used because it reacts slowly. The presence of some impurities increases the rate of reaction due to the formation of electrochemical couple's. Concentrated sulphuric acid is also not used because it oxidises, formed H_2 into H_2O.

$$Zn + 2H_2SO_4 \text{ (conc.)} \rightarrow ZnSO_4 + SO_2 + 2H_2O$$

(ii) It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

b) Commercial production of dihydrogen:

(i) By the electrolysis of acidified water

ii) From water gas (Bosch process): Carbon dioxide is removed by dissolving it in water under pressure (20-25 atm) and hydrogen left behind is collected.

$$\underbrace{CO + H_2}_{\text{water gas}} + \underset{\text{steam}}{H_2O} \xrightarrow[773K]{Fe_2O_3 + Cr_2O_3} CO_2 \uparrow + 2H_2$$

(iii) From steam (Lane‟s process) Super heated steam is passed over iron filings heated to about 1023-1073 K when hydrogen is formed.

$$3Fe + 4H_2O\text{ (steam)} \xrightarrow{1023-1073\text{ K}} Fe_3O_4 + 4H_2$$

(iv) Highly pure (> 99.95%) dihydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.

(v) From hydrocarbons by partial oxidation

$$\underset{\text{natural gas}}{CH_4} + \underset{\text{steam}}{H_2O} \xrightarrow[1270\text{ K}]{\text{Ni-Cr catalyst}} CO + 3H_2$$

vi) It is also obtained as a by-product in the manufacture of NaOH and chlorine hy the electrolysis of brine solution. During electrolysis, the reactions that take place are

At anode, $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

At cathode, $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

The overall reactions by adding spectator Na^+ ions,

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \longrightarrow$$

$$Cl_2(g) + H_2(g) + 2Na^+ + 2OH^-(aq)$$

Physical Properties of Dihydrogen: Dihydrogen is a colorless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. It is neutral to litmus.

Chemical Properties of Dihydrogen:

(i) Reactivity The relative inertness of dihydrogen at room temperature is because of Its high enthalpy of H-H bond i.e. high bond dissociation energy. So its reactions take place under specific conditions only (at high temperature).

(ii) Action with non-metals

$$2H_2 + O_2 \xrightarrow[\text{or Electric discharge}]{970\text{ K}} 2H_2O(l);\ \Delta H^\circ = -285.9\text{ kJ mol}^{-1}$$

$$N_2 + 3H_2 \xrightarrow[\text{Fe (Mo)}]{673\text{ K}/200\text{ atm}} 2NH_3(g);\ \Delta H^\circ = -92.6\text{ kJ mol}^{-1}$$

$$H_2 + X_2 \xrightarrow{\text{Dark}} 2HX \text{ (where, } X \text{ represents halogens)}$$

Order of reactivity of halogens:

$$F_2 > Cl_2 > Br_2 > I_2$$

(iii) Reaction with metals Here H_2 acts as oxidising agent.

$$2Na + H_2 \xrightarrow{\Delta} 2NaH$$

$$Ca + H_2 \xrightarrow{\Delta} CaH_2 \text{ (Hydrolith)}$$

(iv) Reducing action of dihydrogen

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O$$

(v) Reactions with metal ions and metal oxides

$$H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$$

$$yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(l)$$

(vi) Reaction with organic compounds

$$\text{Veg. oil} + H_2 \xrightarrow{\text{Ni/400K}} \text{Veg. ghee}$$

$$R\text{—}CH{=}CH_2 + H_2 + CO \xrightarrow{[Co(CO)_4]_2} RCH_2CH_2CHO$$

$$RCH_2CH_2CHO + H_2 \xrightarrow[\Delta]{\text{Ni}} RCH_2CH_2CH_2OH$$

Uses of Dihydrogen:

(i) It is used in the manufacture of CH_3OH.

$$CO(g) + 2H_2(g) \xrightarrow{\text{Co}} CH_3OH(l)$$

(ii) It produces temperature of 2850°C and oxy-atomic hydrogen flame produces a temperature of 4000°C, so it is used in oxy-hydrogen flame.

(iii) The largest single use of H2 is in the synthesis of NH3 which is used in the manufacture Of HNO_3 and fertilizers.

(iv) Liquid hydrogen (LH_2) is used as rocket fuel.

(v) H_2 is used as a reducing agent in extraction of metals.

(vi) H_2 is used in fuel cell for generating electrical energy.

(vii) Hydrogen is used in the manufacture of synthetic petrol (By heating H_2 with coal and heavy oils under very high pressure in the presence of catalyst.)

Hydrides: The compounds of hydrogen with metals and non-metals are called hydrides. There are three types

a) Ionic Hydrides: These are formed by elements of group I, II, (except Be and Mg) by heating them in hydrogen. These are white colorless solids (crystalline) having high m.p. and b.p. easily decomposed by water, CO_2 or SO_2.

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$
$$CaH_2 + 2CO_2 \rightarrow (HCOO)_2Ca$$

They are strong reducing agents. Alkali metal hydrides are used for making LiAlH4, NaBH4 etc and for removing last traces of water from organic compounds.

b) Molecular or Covalent Hydrides: These are formed by elements of p-block having higher electro negativity than hydrogen.

1. **Electron deficient hydrides:** These are the hydrides which do not have sufficient number of electrons needed to form normal covalent bonds, e.g., BH_3, AlH_3, etc.

2. **Electron precise hydrides:** These are the hydrides which have exact number of electrons needed to form normal covalent bonds. e.g. hydrides of group 14 (CH_4, SiH_4, etc.)

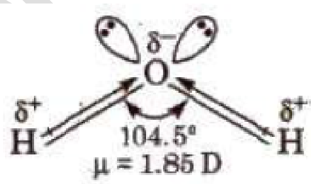
3. **Electron rich hydrides:** These are the hydrides which have greater number of electrons than required to form normal covalent bonds. e.g., hydrides of group 15, 16, 17, (NH_3, PH_3 ,H_2S, HF, HCl, etc). The excess electrons in these hydrides are present as lone pairs of electrons.

c) Metallic or Interstitial or Non – stoichiometric Hydrides: The transition metals and rare earth metals combine with hydrogen to from interstitial hydrides.

They exhibit metallic properties and are powerful reducing agents. They are non-stoichiometric hydrides and their composition varies with temperature and pressure for e.g., LaH 2.76, TiH1.73. Metals of group 7, 8 and 9 do not form hydrides and this region of the Periodic Table is called hydride gap.

Water

Water is the most abundant and widely distributed on the earth. It occurs in all the three physical states. H_2O is a covalent molecule in which oxygen is sp^3 hybridized. It has bent structure.



Structure of Ice:

Physical Properties of Water

1. Water is a colorless, odourless, tasteless liquid. It has abnormally high b.p., f.p., heat of vaporization due to hydrogen bonding.

2. Pure water is not a good conductor so it is made conductor by adding small amount of acid or alkali.

3. Density of ice (which is mass per unit volume) is lesser than that of water and it floats over water.

4. Water has maximum density at 4°0.

5. Water is a highly polar solvent with high dielectric constant 78.39. It interacts with polar or ionic substances effectively with the release of considerable amount of energy due to ion dipole

interaction. The dissolution of covalent compounds like urea, glucose and C_2H_5OH, etc is due to the tendency of these molecules to form hydrogen bond with water.

Chemical Properties of Water:

1. Water is amphoteric in nature. It has the ability to act as an acid as well as a base

$$\underset{\text{base}}{H_2O(l)} + \underset{\text{acid}}{HCl(aq)} \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{Cl^-(aq)}$$

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

2. In redox reactions, water reacts with metals and non- metals both.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

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

3. **In hydrated salts**, water may remain in five types such as coordinated water, hydrogen bonded water, lattice water, clathrate water and zeolite water.

4. A number of compounds such as calcium hydride, calcium phosphide. etc., undergo hydrolysis with water.

Purification of Water

It involves two processes

1. Removal of suspended impurities
2. Destroying the bacteria.

Suspended particles are removed by coagulation with alum followed by filtration.

Exposure to sunlight, boiling, chlorination (treatment with liquid Cl2 or bleaching powder), ozonisation and addition of CuSO5 are some processes which are employed to destroy bacteria.

Heavy Water [D2O]

It was discovered by Urey in 1932. It can be prepared by exhaustive electrolysis of ordinary water using nickel electrodes. It is colourless, odourless, tasteless liquid.

Chemical Reactions of Heavy Water

Uses of Heavy Water

It is used

1. in nuclear reactors to slow down the speed of neutrons and called moderator.
2. as a tracer compound to study the mechanisms of many reactions.

Soft and Hard Water

The water which produces large amount of lather with soap is known as soft water and which forms a scum with soap is known as hard water.

Types of Hardness of Water

 Temporary hardness It is due to the presence of bicarbonates of calcium and magnesium.

 Permanent hardness: It is due to the presence of chlorides and sulphates of calcium and magnesium.

Removal of Temporary Hardness

It can be achieved:

(a) By boiling The soluble bicarbonates are converted into insoluble carbonates.
(b) By Clark's process By adding lime water or milk of lime.

Removal of Permanent Hardness

(i) By adding washing soda The calcium or magnesium salts are precipitated as carbonates.
(ii) By adding caustic soda The temporary and permanent hardness can be removed by adding caustic soda.
(iii) By adding sodium phosphate (Na_3PO_4) The phosphates of calcium and magnesium are precipitated.
Similarly, magnesium also precipitate out in the form of magnesium phosphate, $Mg_3(PO_4)_2$.
(iv) Calgon's process Calgon is sodium hexa metaphosphate ($Na_6P_6O_{18}$). This calgon when added to hard water form soluble complex.
Similarly. Mg^{2+} can also precipitate as $Na_2[Mg_2(PO_3)_6]$ and water becomes free from Ca^{2+} and
Mg^{2+} Ions.
(v) Permutit process Permutit is hydrated sodium aluminium silicate $Na_2Al_2Si_2O_8.xH_2O$. It exchanges its sodium ions for divalent ions Ca^{2+} and Mg^{2+}..
Permutit when fully exhausted can be regenerated by treating with 10% solution of sodium chloride. It is most efficient method to gel water with zero degree of hardness.
(vi) By synthetic resins
These are of two types:
(a) Cation exchange resins are big molecules containing sulphonic acid group ($-SO_3H$). It is first changed into sodium salt with the general formula RNa. The hard water is passed through it so Ca^{2+} and M^{2+} are exchanged and removed.
The resins like permutit can be regenerated with a solution of NaCl.
(b) Anion exchange resins are also big molecules and can exchange anions. They contain an amino group.
The water is first passed through cation resins and then through anion tesin and pure distilled water is obtained.

Measurement of Degree of Hardness

Degree of hardness is defined as the number of parts of calcium carbonate or equivalent to various calcium and magnesium salts present in one million parts of water by mass. It is expressed in ppm.
Degree of hardness (in ppm) = (wt. of $CaCO_3$ (g)/ wt. of hard water (g)) x 106
The molecular wt. of $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$ and $MgSO_4$ is 162, 146, 111, 95, 136 and 120 respectively. The mol. wt. of $CaCO_3$ is 100.
Thus, 162 g $Ca(HCO_3)_2$, 146 g $Mg(HCO_3)_2$, 111 g$CaCl_2$, 95 g $MgCl_2$ 136 g $CaSO_4$ and 120 g $MgSO_4$are equivalent to 100 g $CaCO_3$.
Hydrogen Peroxide [H_2O_2]
H_2O_2 was discovered by J.L. Thenard in 1818. It is an important compound used in pollution control treatment of domestic and industrial effluents.

Methods of Preparation

Strength of Hydrogen Peroxide

The most common method to express the strength of H_2O_2 is in terms of the volume (in mL) of oxygen liberated at NTP by decomposition or 1 mL of that sample of H Z 0 2. A solution of H_2O_2 labelled as "10 volume" actually means "1 mL of such a solution of H_2O_2 on decomposition by heat produces 10 mL of oxygen at NTP".

(i) Strength of H_2O_2 in terms of normality

$(68 \times X/22.4) = 17 \times N \Rightarrow X = 5.6 \times N$

where, X is volume strength of H_2O_2.

(ii) % strength = (17/56) x volume strength

(iii) X = 11.2 x molarity.

Storage of Hydrogen Peroxide (H_2O_2)

It is stored in the presence of traces of alcohol, acetanilide or sodium pyrophosphate which slow down the rate of decomposition of hydrogen peroxide.

Chemical Properties of H_2O_2

1. **Acidic nature** It is weakly acidic in nature and pure hydrogen peroxide turns blue litmus red.

2. **Oxidising agent** It acts as a strong oxidising agent in acidic as well as in basic medium. e.g., oxidising action of HzOz is

(iii) Reducing agent

(a) In acidic medium

(b) In basic medium

(iv) Bleaching properties Its bleaching action is due to oxidation by atomic oxygen and permanent.

H_2O_2 rarr; H_2O + [O]

dye + [O] → dye is oxidised and bleached