Hydrogen and Its Compounds.

(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) It 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…

(ii) Hydrogen also resembles halogens (Group VIII 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 $F, Cl, \ldots$ 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 behavior 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 9th most abundant element in the earth's crust.

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

(i) **Laboratory method:** Inthe laboratory, dihydrogen can be prepared by the action of dil. H_2SO_4 on granulated Zinc, $Zn + H_2SO_4(\text{dil.}) \rightarrow ZnSO_4 + H_2$

(ii) **Industrial method**

(a) By the electrolysis of water**:** The hydrogen prepared by this method is highly pure. Dihydrogen is collected at cathode. $2H_2O(\text{l}) \xrightarrow{\text{Electrolysis}} 2H_{2(\text{g})} + O_{2(\text{g})}$

(b) Hydrocarbon steam process: H_2 is prepared by the action of steam on hydrocarbon. e.g.

$$\underset{}{CH_4} + \underset{\text{(Steam)}}{H_2O} \xrightarrow{1170\,K} CO + 3H_2$$

(c) Bosch process: $\underset{\text{water gas}}{H_2 + CO} + \underset{\text{steam}}{H_2O} \xrightarrow[Fe_2O_3,\, Cr_2O_3]{773\,K} CO_2 + 2H_2$

(d) Lane's process: H_2 is prepared by passing alternate currents of steam and water gas over red hot iron. The method consists of two stages,

Oxidation stage: $\underset{\textit{Iron filings}}{3Fe} + \underset{(\textit{Steam})}{4H_2O} \xrightarrow{1025-1075\,K} \underset{\text{Magnetic oxide of iron}}{Fe_3O_4} + 4H_2 + 161\,KJ$

Reduction stage: $2Fe_3O_4 + \underset{\text{water gas}}{4CO + 4H_2} \rightarrow 6Fe + 4CO_2 + 4H_2O$

(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 $(kJ\,mol^{-1})$ – 1312; Electron affinity $(kJ\,mol^{-1})$ –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, $H_2 \xrightarrow{2000\,K} H + H$. Its bond dissociation energy is very high, $H_2 \rightarrow H + H$; $\Delta H = 435.9\,kJ\,mol^{-1}$. 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. $2Na + H_2 \xrightarrow{Heat} 2NaH$;
$Ca + H_2 \xrightarrow{Heat} CaH_2$.

With transition metals (elements of d – block) such as Pd, Ni, 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:** $2H_2 + O_2 \xrightarrow{970\ K} 2H_2O$; $N_2 + 3H_2 \xrightarrow[750\ K,\ \text{Pressure}]{Fe,\ Mo} 2NH_3$

$H_2 + F_2 \xrightarrow{Dark} 2HF$; $H_2 + Cl_2 \xrightarrow[673\ K,\ \text{Pressure}]{Sunlight} 2HCl$

$H_2 + Br_2 \rightarrow 2HBr$; $H_2 + I_2 \xrightarrow[Pt]{673\ K} 2HI$

The reactivity of halogen towards dihydrogen decreases as, $F_2 > Cl_2 > Br_2 > I_2$

As a result, F_2 reacts in dark, Cl_2 in the presence of sunlight, Br_2 reacts only upon heating while the reaction with I_2 occurs in the presence of a catalyst.

(iii) **Reaction with unsaturated hydrocarbons:** H_2 reacts with unsaturated hydrocarbons such as ethylene and acetylene to give saturated hydrocarbons.

$\underset{Ethylene}{H_2C = CH_2} + H_2 \xrightarrow[473\ K]{Ni\ or\ Pt\ or\ Pd} \underset{Ethane}{CH_3 - CH_3}$; $\underset{Acetylene}{HC \equiv CH} + 2H_2 \xrightarrow[473\ K]{Ni\ or\ Pt\ or\ Pd} \underset{Ethane}{CH_3 - CH_3}$

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.

$\underset{(liquid)}{\text{Vegetable oil}} + H_2 \xrightarrow[473\ K]{Ni} \underset{(solid)}{Fat}$

(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 H_2 (iv) In the manufacture of synthetic petrol, (v) In the preparation of many compounds such as NH_3, CH_3OH, Urea etc, (vi) It is used in the oxy-hydrogen torch for welding if temperature around 2500°C is required. It is also used in atomic hydrogen torch for welding purposes in which temperature of the order of 4000°C is required.

Different forms of hydrogen

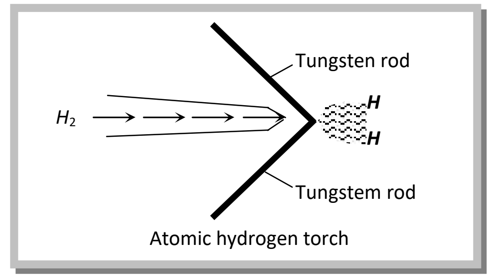
(1) **Atomic hydrogen:** It is obtained by the dissociation of hydrogen molecules. The atomic hydrogen is stable only for a fraction of a second and is extremely reactive. It is obtained by

passing dihydrogen gas at atmospheric pressure through an electric arc struck between two tungsten rods.

The electric arc maintains a temperature around 4000 – 4500°C. As the molecules of dihydrogen gas pass through the electric arc, these absorb energy and get dissociated into atoms as

$$H_2(g) \xrightarrow[arc]{Electric} 2H(g) : \Delta H = 435.90\, KJ\, mol^{-1}$$

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 $KMnO_4$ (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 $KMnO_4$ by nascent hydrogen.

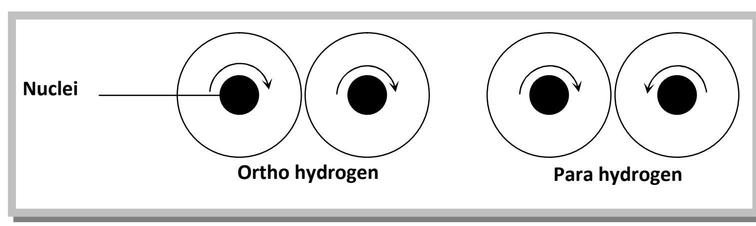
$$KMnO_4 + \underset{Molecular}{H_2} + H_2SO_4 \rightarrow No\ Reaction\ ; \quad Zn + H_2SO_4 \rightarrow ZnSO_4 + \underset{Nascent\ hydrogen}{2[H] \times 5}$$

$$2KMnO_4 + 3H_2SO_4 + 10H \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

(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 ⇌ Para hydrogen. The amount of ortho and para hydrogen varies with temperature as,

(a) At 0°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.

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

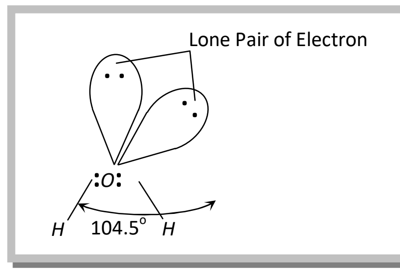
Name	Symbol	Atomic number	Mass number	Relative abundance	Nature radioactive or non-radioactive
Protium or Hydrogen	${}_{1}^{1}H$ or H	1	1	99.985%	Non-radioactive
Deuterium	${}_{1}^{2}H$ or D	1	2	0.015%	Non-radioactive
Tritium	${}_{1}^{3}H$ or T	1	3	10^{-15} %	Radioactive

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 $(kJ\ mol^{-1})$	0.117	0.197	0.250
Heat of vaporisation $(kJ\ mol^{-1})$	0.994	1.126	1.393
Bond energy $(kJ\ mol^{-1})$	435.9	443.4	446.9

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°, which is less than the normal tetrahedral angle (109.5°) . 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 $(1 g\, cm^{-3})$ at 4°C.

(2) **Heavy water:** Chemically heavy water is deuterium oxide (D_2O). It was discovered by **Urey**. It has been finding use in nuclear reactors as a moderator because it slows down the fast moving neutrons and therefore, helps in controlling the nuclear fission process.

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

Some physical constants of H_2O and D_2O at 298 K

Constant	**Ordinary water H_2O**	**Heavy water D_2O**

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

$$H_2O + H_2O \rightleftharpoons \underset{Hydronium\ ion}{H_3O^+} + OH^-;\ K_W = 1.0 \times 10^{-14}\ mol^2 L^2 \text{ at 298K}$$

(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 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. $2Na + \underset{Oxidising\ agent}{2H_2O} \rightarrow 2NaOH + H_2$; $2F_2 + \underset{Reducing\ agent}{2H_2O} \rightarrow 4HF + O_2$

(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 $(Ca^{+2} \text{ and } Mg^{+2})$ present in hard water react with soap to form insoluble precipitates,

$\underset{\text{From hard water}}{M^{+2}} + \underset{\text{Sodium stearate(soap)}}{2C_{17}H_{35}COONa} \rightarrow \underset{\text{Metal stearate(PPt.)}}{(C_{17}H_{35}COO)_2M} + 2Na^+$,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.

$$\underset{\text{Cal.bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{PPt.}}{CaCO_3} + CO_2 + H_2O;\ \underset{\text{Mag.bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{PPt.}}{MgCO_3} + CO_2 + H_2O$$

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

$$\underset{\text{Soluble}}{Ca(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{Insoluble}}{2CaCO_3} \downarrow + 2H_2O$$

$$\underset{\text{Soluble}}{Mg(HCO_3)_2} + \underset{\text{Lime}}{Ca(OH_2)} \longrightarrow \underset{\text{(Insoluble)}}{MgCO_3 \downarrow + CaCO_3} \downarrow + 2H_2O$$

(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.

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{ppt.}{CaCO_3} + 2NaCl \;;\; MgSO_4 + Na_2CO_3 \longrightarrow \underset{ppt.}{MgCO_3} + Na_2SO_4$$

Permutit method: This is a modern method employed for the softening of hard water. Hydrated sodium aluminium silicate $(Na_2Al_2Si_2O_8.xH_2O)$ 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.

$$\underset{\text{Sodium zeolite}}{Na_2Z} + \underset{\text{(From hard water)}}{Ca^{+2}} \longrightarrow \underset{\text{Cal zeolite}}{CaZ} + 2Na^+ \;;\; Na_2Z + \underset{\text{(From hard water)}}{Mg^{+2}} \longrightarrow \underset{\text{Magnesium zeolite}}{MgZ} + 2Na^+$$, where

$$Z = Al_2Si_2O_8.\; xH_2O$$

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.

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

(ii) **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.

$$2H_2SO_4 \xrightarrow[\text{Elecrolysis}]{} \underset{\text{Peroxy disulphuric acid}}{H_2S_2O_8(aq.)} + H_2(g)$$

This is drawn off from the cell and hydrolyzed 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.

(2) **Physical properties:** Pure H_2O_2 is a thick syrupy liquid with pale blue color. It is more viscous and dense than water. It is completely miscible with water, alcohol and ether in all proportions.

(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, $2H_2O_2 \longrightarrow 2H_2O + O_2$; $\Delta H = -196.0\,kJ$

(ii) **Oxidising nature:** It is a powerful oxidizing agent. It acts as an oxidizing 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 oxidizing agents and thus, acts as a reducing agent, $H_2O_2 + \underset{\substack{\text{From oxidising} \\ \text{agent}}}{O} \longrightarrow H_2O + O_2$. 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, $H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$

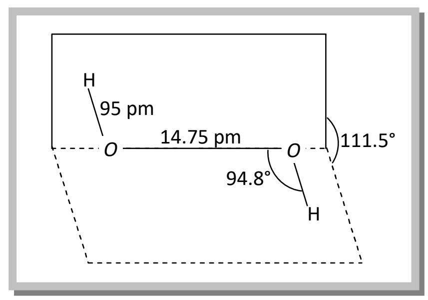
(iv) **Bleachingaction:** H_2O_2 acts as a bleaching agent due to the release of nascent oxygen.

$H_2O_2 \longrightarrow H_2O + O$

Thus, the bleaching action of H_2O_2 is due to oxidation. It oxidizes the coloring matter to a colorless product, Coloring matter +O →Color less matter

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

(4) **Structure of H_2O_2:** H_2O_2 has non-planar structure in which two H-atoms are arranged in two directions almost perpendicular to each other and to the axis joining the two oxygen atoms. The O – O linkage is called peroxide linkage.



(5)**Strength of H_2O_2:** The strength of H_2O_2 is expressed in terms of weight or volume,

(i) **As weight percentage:** The weight percentage of H_2O_2 gives the weight of H_2O_2 in 100 g of solution. For example, a 40% solution by wt. means 40 g of H_2O_2 are present in 100 g of solution.

(ii) **As volume:** The strength of H_2O_2 is commonly expressed as volume. This refers to the volume of oxygen which a solution of H_2O_2 will give. For example, a "20 volume" of H_2O_2 means that 1 litre of this solution will give 20 liters of oxygen at NTP.

(6) **Uses of H_2O_2**

(i) It is used as an antichlor in bleaching because it can reduce chlorine.

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

(ii) It is used for restoring the color of lead paintings.

(iii) It is used as an antiseptic for washing wounds, teeth and ears under the name perhydrol.