B.Sc Part I (Hons.), Paper-IB (Inorganic chemistry)

Group-B, Unit-1 : Hydrogen & Hydrides

→ **Position of Hydrogen in PT:** Electronic Configuration of H_1 : $1s^1$. It has valency electron 1. No. of orbit in H atom is 1. Last electron (only electron of H occupies in s-orbital. So, for H, Group = 1, Period = 1, Block - S. Hence, hydrogen (H) is placed in 1st period & 1st group under s-block in the modern periodic table (PT) along with Li, Na, K, Rb, Cs & Fr due to following similarities: (i) H & other group-1 elements have similar outer electronic conf. ns^1 (n = 1 to 7) (ii) Both show constant oxidation state +1 (iii) Both are electropositive elements. (iv) Both react with oxygen to form M_2O type oxides. $2H_2 + O_2 \rightarrow 2H_2O$; $4M + O_2 \rightarrow 2M_2O$ (M = Li, Na, K...) (v) Both react with halogen to form MX type halides. $H_2 + X_2 \rightarrow 2HX$; $2M + X_2 \rightarrow 2MX$ (X = F, Cl, Br, I)

→ **Isotopes of Hydrogen:** There are three isotopes of hydrogen. They are:

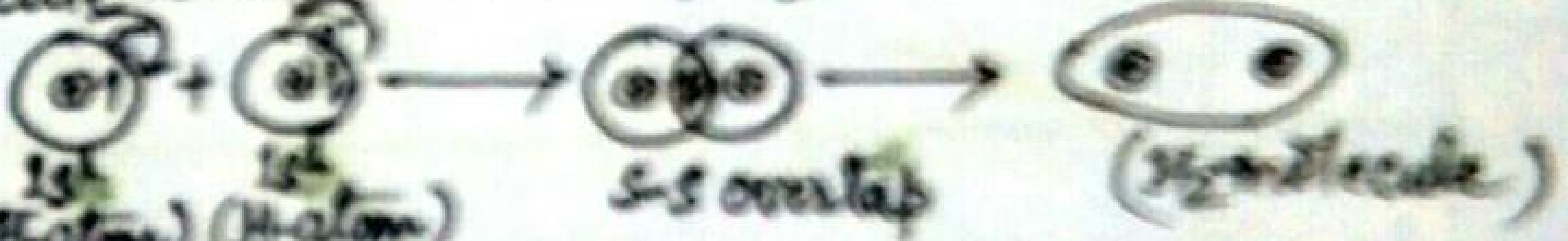
(i) Protium or Hydrogen (ordinary): This is most common isotope of hydrogen (abundance 99.984%), having atomic mass 1.008123. It consists of one proton in the nucleus and an electron revolving around it (1st orbit). It is represented as ^1_1H.

(ii) Deuterium or Heavy hydrogen: It is heavier isotope of hydrogen, having atomic mass 2.0142. It consists of one proton and one neutron in the nucleus and an electron revolving around it. It's abundance is only 0.016% of the total hydrogen. It is represented as ^2_1H or D.

(iii) Tritium or Radio hydrogen: It is unstable isotope of hydrogen and radioactive in nature. It's atomic mass is 3.017 and abundance is 10^{-15}% of total natural hydrogen. It consists of one proton and two neutrons in the nucleus and an electron revolving around it. It is represented as ^3_1H or T.

The three isotopes of H are chemically identical but physically distinct.

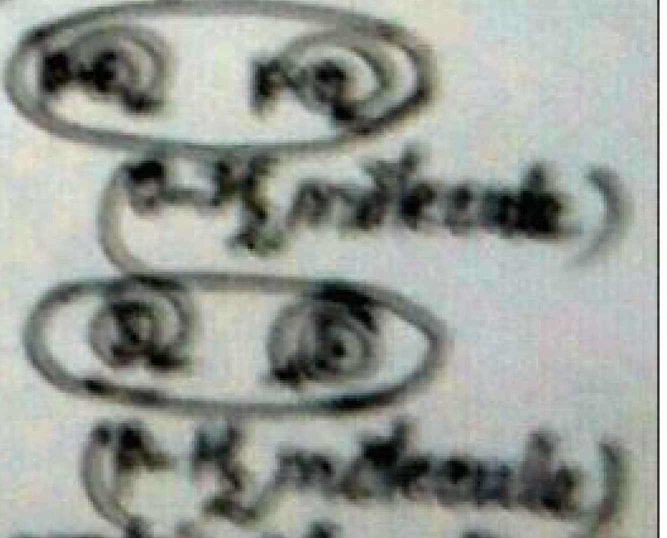
→ **Ortho & Para Hydrogen:** Hydrogen molecule is diatomic, i.e., H_2 molecule formed by overlap of 1s orbital (unpaired electron) of H atoms.



H atom consists of one proton & one electron. Like electrons, proton is also spinning about an axis. The two protons in the hydrogen molecule may be either same (or parallel) spins or opposite spins. Thus, molecular hydrogen (H_2) exists in two forms: (i) Ortho hydrogen (ii) Para hydrogen

(i) Ortho hydrogen (o-H_2): When the nuclei (p) of two bonded hydrogen atoms spin in the same direction or parallel spins, the molecular hydrogen is called ortho hydrogen (o-H_2)

(ii) Para hydrogen (p-H_2): When the nuclei (p) of two bonded hydrogen atoms spin in the opposite directions or opposite spins, the molecular hydrogen is called para hydrogen (p-H_2).



Ordinary hydrogen is a mixture of ortho & para hydrogens.

The two forms are in equilibrium at ordinary temperature, the ratio of ortho to para being 3:1. The equilibrium (o-$H_2 \rightleftharpoons p$-H_2) shifts to the left as the temperature is decreased. The two forms differ in their physical properties like specific heat, thermal conductivity, boiling point etc., but show similar chemical properties. Ortho hydrogen is more stable than para hydrogen. Pure para hydrogen can be obtained at low temperature (20 K).

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Hydrides:

Binary compounds of the elements with hydrogen are called hydrides. The hydrides may be divided into four fairly distinct classes. The type of hydride which an element forms depend on its electronegativity. Different types of hydrides are discussed below:

1. Ionic hydrides or Salt like hydrides: Elements of very high electropositive/low electronegativity can transfer to the H-atom and form ionic/salt like hydrides. These compounds are solids with ionic lattices and therefore called salt like or saline hydrides. Alkali metals (Group-1), Ca, Sr & Ba (Group-2) and some of the more electropositive lanthanides & actinides form ionic hydrides. They have general formula MH_x (where x = Valency of the metal).

Prepn → Ionic hydrides are ordinarily prepared by direct reaction between the pure metals and hydrogen at temperature ranging 150 to 700°C.

e.g. $Ca + H_2 \xrightarrow{150^\circ C} CaH_2$ (Calcium hydride) ; $2Li + H_2 \xrightarrow{600^\circ C} 2LiH$ (Lithium hydride)

Properties: (i) They are crystalline compounds with ionic lattice.
(ii) They have high melting points and their density is greater than that of the metal.
(iii) They conduct electricity when fused and librate hydride (H^-) ion.
(iv) Groups-1 & 2 metals hydrides have stoichiometric composition but with the lanthanides compositions such as $LaH_{2.7}$ & $CeH_{2.69}$ are characteristic of alloy.
(v) Li, Ca & Sr metal hydrides are comparatively stable in dry air. Others may ignite spontaneously.
(vi) All ionic hydrides react with water vigorously and liberate H_2 gas.

$LiH + H_2O \longrightarrow LiOH + H_2\uparrow$ (Lithium hydroxide)

(vii) They are powerful reducing agents especially at high temperature. They easily reduce some oxides to metals, CO_2 to formate and metal sulphates into metal sulphides.

$CO_2 + NaH \longrightarrow HCOONa$ (Sod. formate) ; $PbSO_4 + CaH_2 \longrightarrow PbS + Ca(OH)_2$; $ZnO + LiH \rightarrow Zn + LiOH$.

Uses: Li, Na & Ca-hydrides are most commonly used in preparing free metals and a variety of organic compounds. They are also good desiccants.

2. Covalent or molecular hydrides: Elements of Group 13 to 17 of periodic table form covalent hydrides of general formula XH_{8-n} (where n = group no. of the element). Since difference of electronegativity between Gr. 13-17 element & hydrogen is small, sharing of electrons favoured and hence covalent bond/compound formed. The covalent hydrides have a molecular lattice made up of individual saturated covalent molecules. These saturated covalent molecules are held together with only weak vander waal forces and in some cases hydrogen bonds. The group-13 hydrides are rather unusual. They are polymeric and also electron deficient.

Prepn → (i) Covalent hydrides are prepared by direct combination of H_2 with the free element. e.g., $H_2 + F_2 \longrightarrow 2HF$; $3H_2 + N_2 \longrightarrow 2NH_3$; $2H_2 + O_2 \longrightarrow 2H_2O$.
(ii) By hydrolyses of a metal boride, silicide, carbide etc. with water or dil. acid
e.g. $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2\uparrow$; $Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6\uparrow$.

(iii) By reduction of the appropriate halide (Si, Sn, Ge) in ether solution by $LiAlH_4$.

e.g. $GeCl_4 + 8H \xrightarrow{(LiAlH_4)} GeH_4\uparrow + 4HCl$
(Germanium hydride)

(iv) Electrolytic reduction of the solution of a compound. e.g. SnH_4 is pre[pared] by electrolysis of tin sulphate in H_2SO_4 solution. $SnSO_4 \xrightarrow[(Electrolysis)]{H_2SO_4(aq)} SnH_4$

Properties: (i) Solid covalent hydrides are generally soft, lower melting p[oints]. The liquid covalent hydrides have low boiling points.

(ii) All covalent hydrides are volatile although volatility is some what re[duced] in polynuclear hydrides of high molecular weights.

(iii) They are non-conductors in the liquid state.

(iv) They undergo thermal decomposition.

(v) Hydrides of heavier elements are less stable than those of lighter ele[ments].

3. Metallic or Interstitial hydrides: Elements of Group-3 to 8 form metallic hydrides [with] hydrogen. They exhibit wide difference in properties. The capacity to the metals to form their respective hydrides decreases progressively from G[roup-3] to 8. However, the elements of Group-3 (e.g.; Sc, Y, lanthanides, actinides) Group-4 (e.g. Ti, Zr, Hf) rank highest in their ability to absorb hydroge[n] the reactions are exothermic. Most of the metals, for example Group-8 ar[e pract]ically inert to hydrogen, although Pd is a notable exception. The met[allic] hydrides are non-stoichiometric and their chemical composition is va[riable]. The quantity of hydrogen present ordinarily bears no stoichiometric re[lation] to the metal; for example $ZrH_{1.92}$ & $TaH_{0.76}$

The metallic hydrides are less dense than the parent metal. They [have] strong reducing properties which suggest that hydrogen present in them [is in] atomic state and the molecular hydrogen undergoes dissociation on e[ntering] the metallic lattice. Interstitial hydrides find applications in m[...] manufacture of vaccum tube.

4. Intermediate hydrides: Elements of Groups. 11, 12 & also In, Tl of Grou[p ... form] intermediate hydrides with hydrogen. They yield unstable diatomic hydri[des of] the type MH (where M = Cu, Ag, Zn, Cd, In, Tl etc.) - e.g; CuH, InH etc.