Chapter 1

Hydrogen and s block

Day - 1

HYDROGEN

- Hydrogen is the lightest element known since it has an atomic mass of 1.0079
- Hydrogen resembles Group 1 elements
- Hydrogen also resembles elements of group 17 (Halogens)
- (H^+) is of size ~10^{-5} A^o. This is extremely small as compared to normal atomic and ionic sizes of ~1 A^o. As a consequence, H^+ does not exist freely and is always associated with other atoms or molecules.
- Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table

OCCURRENCE

It is the most abundant element in the universe (70% of the total mass of the universe). It is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans

Isotope	proton	electron	neutron	At. Mass
protium, $^1H_1$	1	1	0	1
Deuterium, $^2H_1$ or D	1	1	1	2
tritium, $^3H_{1or}$ T	1	1	2	3

H is the predominant form 99.98%

D is (0.0156% of total)

T. (one atom per 10^{18} atoms)

Tritium is radioactive and emits low energy ß particles (t½, 12.33 years).

Preparation of Hydrogen Gas

Laboratory Preparation

(i) $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

(ii) $Zn + 2NaOH \rightarrow Na_2ZnO_2$(Sodium zincate) + H_2

Commercial Production

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

(ii) High purity (>99.95%) hydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes

(iii) By the electrolysis of brine solution.

anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

cathode: $2H_2O\ (l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

$2NaCl\ (aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$

Water gas: - is the mixture of CO and H_2

Water-gas shift reaction

$C(s) + H_2O \xrightarrow[Ni]{1000°C} CO + H_2$ $\quad$ $CO(g) + H_2O \xrightarrow[iron\ cromate]{400°C} CO_2 + H_2$

PROPERTIES OF HYDROGEN

Physical Properties

- Hydrogen gas is a colourless, odourless, tasteless, highly combustible gas.
- It is lighter than air and insoluble in water.

Chemical Properties

- The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. it is relatively inert at room temperature.
- Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by

(i) loss of the only electron to give H^+,

(ii) gain of an electron to form H^-, and

(iii) sharing electrons to form a single covalent bond

(i) Reaction with halogens

$H_2(g) + X_{2(}g) \rightarrow 2HX(g)$, While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

(ii)Reaction with oxygen

$2H_2(g) + O_2\ (g) \rightarrow 2H_2O(l)$; DH = –285.9 kJ mol^{-1}

(iii) Reaction with nitrogen

$3H_2(g) + N_2(g) \xrightarrow[iron]{400°C} 2NH_3(g)$

(iv) Reactions with metals:

it forms corresponding hydrides $H_2(g) + 2M(g) \rightarrow 2MH(s)$; where M is an alkali metal

(v) Reactions with metal ions and metal oxides:

It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

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

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

(vi) Reactions with organic compounds:

It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance

USES OF HYDROGEN GAS

1. The single largest use of hydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
2. Hydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soybean, cotton seeds etc.
3. It is used in the manufacture of bulk organic chemicals, particularly methanol.
4. It is widely used for the manufacture of metal hydrides.
5. It is used for the preparation of hydrogen chloride, a highly useful chemical.
6. In metallurgical processes, it is used to reduce heavy metal oxides to metals.
7. Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of hydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
8. It is used as a rocket fuel in space research.
9. Hydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

HYDRIDES

Hydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides. If 'E' is the symbol of an element then hydride can be expressed as EH_X (e.g., MgH_2) or E_XH_Y (e.g., B_2H_6)

The hydrides are classified into three categories:

(i) Ionic or saline or salt like hydrides	**(ii) Covalent or molecular hydrides**	**(iii) Metallic or non-stoichiometric hydrides**
These are stoichiometric compounds of hydrogen formed with most of the s-block elements However, significant covalent character is found in the lighter metal hydrides such as LiH, BeH_2 and MgH_2. In fact BeH_2 and MgH_2 are polymeric in structure. The ionic hydrides are crystalline, non-volatile and non-conducting in solid state	Hydrogen forms molecular compounds with most of the p-block elements. examples are CH_4, NH_3, H_2O and HF. For convenience hydrogen compounds of non-metals have also been considered as hydrides. Being covalent, they are volatile compounds. Molecular hydrides are further classified into three	These are formed by many d-block and f-block elements. However, the metals of group 7, 8 and 9 do not form hydride. These hydrides conduct heat and electricity; they are almost always non-stoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$ $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, etc
On electrolysis liberate hydrogen gas at anode, which confirms the existence of H^- ion.	(i) electron-deficient: they have too few electrons for writing its conventional Lewis structure. ex. Diborane (B_2H_6) all elements of group 13 will form these	

Saline hydrides react violently with water producing hydrogen gas	(ii) electron-precise: have the required number of electrons to write their Lewis structures. All elements of group 14 form such these (e.g., CH_4)
Lithium hydride is rather unreactive at moderate temperatures with O_2 or Cl_2. It is, therefore, used in the synthesis of other useful hydrides	(iii) electron- have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH3 has 1- lone pair, H_2O – 2 and HF –3 lone pairs)rich hydrides.