Hydrogen

HYDROGEN Section - 1

Position of Hydrogen in the Periodic Table

Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration (ns^1) of alkali metals, which belong to the first group of the periodic table. On the other hand, like halogens (with $ns^2\ np^5$ configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, Helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form uni-positive ions, as well as with halogens, which gain one electron to form uni-negative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy hydrogen resembles more with halogens, $\Delta_i H$ of Li is 520 kJ mol^{-1}, $\Delta_i H$ of F is 1680 kJ mol^{-1} and $\Delta_i H$ of H is 1312 kJ mol^{-1}. Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens. It is always a matter of debate in which group hydrogen should be placed. It is best placed separately in the periodic table.

Isotopes of Hydrogen

Hydrogen has three isotopes : Protium $({}^1_1H)$, Deuterium $({}^2_1H)$ or D and Tritium $({}^3_1H)$ or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, Protium, has no neutrons, Deuterium (also known as Heavy Hydrogen) has one and Tritium has two neutrons in the nucleus.

The predominant form is Protium. Terrestrial hydrogen contains 0.0156% of Deuterium mostly in the form of HD. The Tritium concentration is about one atom per 10^{18} atoms of Protium. Of these isotopes, only Tritium is radioactive and emits low energy β^- particles ($t_{1/2}$ = 12.33 years).

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation.

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-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 (g L^{-1})	0.09	0.18	0.27

Preparation of Dihydrogen, H_2

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

Laboratory Preparation of Dihydrogen

1. It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

2. It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

Commercial Production of Dihydrogen :

1. Electrolysis of acidified water using platinum electrodes gives hydrogen. This method gives very pure H_2 but it is very expensive

$$2H_2O\ (l) \xrightarrow[\text{Traces of acid / base}]{\text{Electrolysis}} 2H_2\,(g) + O_2\,(g)$$

2. It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by 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 reaction is

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \longrightarrow Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

3. Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270K} nCO + (2n+1)H_2$$

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270\,K} CO(g) + 3H_2(g)$$

The mixture of CO and H_2 is called *Water gas*. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or '*Syngas*'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called 'Coal gasification'.

$$C(s) + H_2O(g) \xrightarrow{1270\,K} CO(g) + H_2(g)$$

It is difficult to obtain pure H_2 from water gas, since CO is difficult to remove. Still CO may be liquified at a low temperature under pressure. Thus seperating it from H_2. One more thing that can be done is the gas mixture can be mixed with steam, cooled to 400°C and passed over iron oxide to give H_2 and CO_2.

$$CO + H_2O \xrightarrow{Fe} CO_2 + H_2$$

This is called Water - gas shift reaction. This reaction increases the amount of H_2 and gives a method to extract H_2 easily. CO_2 in mixture of CO_2 and H_2 can be removed by dissolving mixture in water under pressure, or reacting mixture with K_2CO_3 solution giving $KHCO_3$, or by scrubbing mixture with sodium arsenite solution.

Physical Properties :

- Dihydrogen is a colorless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water.

Chemical Properties :

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H-H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. It is because of this factor that the dissociation of dihydrogen into its atoms is only ~ 0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H-H bond enthalpy.

1. **Reaction with halogens :** It reacts with halogens, X_2 to give hydrogen halides, HX.

$$H_2(g) + X_2(g) \longrightarrow 2HX(g) \qquad (X = F, Cl, Br, I)$$

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

2. **Reaction with dioxygen :** It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst and heating}} 2H_2O(l)\ ; \quad \Delta H = -285.9\ \text{kJ mol}^{-1}$$

3. **Reaction with dinitrogen :** It reacts with dinitrogen to form ammonia.

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

This is the method for the manufacture of ammonia by Haber's process.

4. **Reaction with metals :** With many metals it combines at a high temperature to yield the corresponding hydrides.

$$H_2(g) + 2M(g) \longrightarrow 2MH(s)\ ; \qquad \text{where M is an alkali metal}$$

5. **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.

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

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

6. **Reactions with organic compounds :** It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee).

Uses of Dihydrogen

- The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.
- It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(l)$$

- It is widely used for the manufacture of metal hydrides.
- It is used as rocket fuel in space research.
- Dihydrogen is used in fuel cells for generating electrical energy. If has many advantages over the conventional fossil fuels and electric power. It does not produce any pollutions and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

HYDRIDES — Section - 2

Binary compounds of the elements with hydrogen are called hydrides. The type of hydride which an element forms depends upon its electronegativity and hence on the type of bond formed. Hydrides are conveniently studied under three classes.

(i) Ionic or salt like hydrides

(ii) Covalent or molecular hydrides

(iii) Metallic or interstitial hydrides

- **Ionic or salt like hydrides :** These are formed by metals of low electronegativity, i.e. alkali and alkaline earth metals by direct reaction with H_2 and some highly positive members of lanthanide series with the exception of Be and Mg whose hydrides show significant covalent character.

  The stability of the hydrides decreases as the size of the cation increases.

  $$LiH > NaH > KH > RbH > CsH$$

  $$CaH_2 > SrH_2 > BaH_2$$

  CaH_2 is called *Hydrolith*.

- **Covalent or Molecular hydrides :** These hydrides are formed by all the true non-metals (except zero group elements) and the elements like Al, Ga, Sn, Pb, Sb, Bi. Po, etc., which are normally metallic in nature. The simple hydride of B and Ga are dimeric materials, B_2H_6 (diborane) and Ga_2H_6 respectively and the hydride of aluminium is polymeric in nature, $(AlH_3)_n$.

- **Metallic or interstitial hydrides :** Many transition and inner-transition elements at elevated temperatures absorb hydrogen into the interstices of their lattices to yield metal-like hydrides, often called the interstitial hydrides. These hydrides are often non-stoichiometric and their composition vary with temperature and pressure. Formulae of some of the hydrides of this class are :

  $$TiH_{1.73}, CeH_{2.7}, LaH_{2.8}, PdH_{0.60}, ZrH_{1.92}$$

  The interstitial hydrides have metallic appearance and their properties are closely related to those of the parent metal. They possess strong reducing properties probably due to the presence of free hydrogen atoms in the metal lattice.