## 1. Details of Module and its structure

| Module Detail | |
|---|---|
| Subject Name | Chemistry |
| Course Name | Chemistry 02 (Class XI, Semester 02) |
| Module Name/Title | Hydrogen – Part 1 |
| Module Id | kech_20901 |
| Pre-requisites | Hydrogen, Periodic table, Isotopes |
| Objectives | After going through this module, the learner will be able to:<br>• Explain the position of hydrogen in the periodic table;<br>• Identify the modes of occurrence and preparation of dihydrogen on a small and commercial scale;describe isotopes of hydrogen;<br>• Explain how different elements combine with hydrogen to form ionic, molecular and nonstoichiometric compounds;<br>• Describe how an understanding of its properties can lead to the production of useful substances, and new technologies; |
| Keywords | Hydrogen, Isotopes of hydrogen, Hydride, Ionic/Saline hydride, Covalent/Molecular hydride, Matellic/non-stoichiometric hydride. |

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**Introduction**

Hydrogen has the simplest atomic structure among all the elements around us in Nature. In atomic form it consists of only one proton and one electron. However, in elemental form it exists as a diatomic ($H_2$) molecule and is called dihydrogen. It forms more compounds than any other element. Do you know that the global concern related to energy can be overcome to a great extent by the use of hydrogen as a source of energy? In fact, hydrogen is of great industrial importance as you will learn in this unit.

**Position of Hydrogen in the Periodic Table:** Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations. 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 $ns^2np^5$ 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 unipositive ions, as well as with halogens, which gain one electron to form uninegative 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 $mol^{-1}$, F is 1680 kJ $mol^{-1}$ and that 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.

Inspite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus ($H^+$) of ~$1.5\times10^{-3}$ pm size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200 pm. 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.

## Dihydrogen, $H_2$

### Occurrence:

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, 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. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

## Isotopes of Hydrogen:

Hydrogen has three isotopes: protium, $^{1}_{1}H$ , deuterium, $^{2}_{1}H$ or D and tritium, $^{3}_{1}H$ or T. Can you guess how these isotopes differ from each other ? 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. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical method.

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 (Table 1). However, in physical properties these isotopes differ considerably due to their large mass differences.

| 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 / $gL^{-1}$ | 0.09 | 0.18 | 0.27 |
| Enthalpy of fusion/kJ $mol^{-1}$ | 0.117 | 0.197 | - |
| Enthalpy of vaporization/kJ $mol^{-1}$ | 0.904 | 1.226 | - |
| Enthalpy of bond dissociation/kJ $mol^{-1}$ at 298.2K | 435.88 | 443.35 | - |
| Internuclear distance/pm | 74.14 | 74.14 | - |
| Ionization enthalpy/kJ $mol^{-1}$ | 1312 | - | - |
| Electron gain enthalpy/kJ $mol^{-1}$ | –73 | - | - |
| Covalent radius/pm | 37 | - | - |
| Ionic radius($H^-$ )/pm | 208 | | |

**Table 1.1.** Atomic and Physical properties of Hydrogen

(Source: NCERT Chemistry, Class XI, part 2, Chapter: Hydrogen, page no. 277)

**Preparation of Dihydrogen:**

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

*Laboratory Preparation of Dihydrogen:*

(i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.

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

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

$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

*Commercial Production of Dihydrogen:* The commonly used processes are outlined below:

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

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

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

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

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

The overall reaction is

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

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

$C_nH_{2n+2} + nH_2O \quad nCO + (2n+1)H_2$

e.g.,

$CH_4 (g) + H_2O (g) \; ¿ \xrightarrow{¿\; 1270 K, \ni \;¿} \; CO (g) + 3H_2 (g)$

The mixture of CO and H2 is called *water gas*. As this mixture of CO and H2 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'*.

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

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

$CO (g) + H_2O (g) \xrightarrow{673 K, Catalyst} CO_2 (g) + H_2 (g)$

This is called *water-gas shift reaction*. Carbon dioxide is removed by scrubbing with sodium arsenite solution.

Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

**Properties of Dihydrogen:**

***Physical Properties:***

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties alongwith those of deuterium are given in Table 1.

***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. What inferences would you draw from this fact? 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. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. 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.

The chemistry of dihydrogen can be illustrated by the following reactions:

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

$H_2$ (g) + $X_2$ (g) → 2HX (g) (X ⁘F,Cl, Br,I)

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

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

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

***Reaction with dinitrogen:*** With dinitrogen it forms ammonia.

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

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

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

$H_2$(g) + 2M (g) → 2MH (s);

where, M is an alkali metal

***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) → Pd (s) + $2H^+$ (aq)

$yH_2$ (g) + $M_xO_y$ (s) → xM (s) + $yH_2O$ (l)

***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:

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

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

$H_2 + CO + RCH{=}CH_2 \rightarrow RCH_2CH_2CHO$

$H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$

***Problem 1:*** Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide.

***Solution:*** (i) Dihydrogen reduces chlorine into chloride ($Cl^-$) ion and itself gets oxidized to $H^+$ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.

(ii) Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, $Na^+H^-$.

(iii) Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to $H_2O$, which is a covalent molecule.

**Uses of Dihydrogen**

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

   $$CO\,(g) + 2H_2\,(g) \xrightarrow{Cobalt\ catalyst} CH_3OH\,(l)$$

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 dihydrogen 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. Dihydrogen 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**

Dihydrogen, 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 $E_mH_n$ (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

**Ionic or Saline Hydrides:**

These are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character. 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. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of $H^-$ ion.

$$2H^- (melt) \xrightarrow{anode} H_2 (g) + 2e^-$$

Saline hydrides react violently with water producing dihydrogen gas.

$NaH (s) + H_2O (aq) \rightarrow NaOH (aq) + H_2 (g)$

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, e.g.,

$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$

$2LiH + B_2H_6 \rightarrow 2LiBH_4$

**Covalent or Molecular Hydride:**

Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar 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 according to the relative numbers of electrons and bonds in their Lewis structure into:

(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane ($B_2H_6$) is an example. In fact all elements of group 13 will form electron-deficient compounds. What do you expect from their behaviour? They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., $CH_4$) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. ($NH_3$ has 1 lone pair, $H_2O$ has 2 and HF has 3 lone pairs). What do you expect from the behaviour of such compounds? They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

***Problem 2:*** Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members? Give reasons.

***Solution:*** On the basis of molecular masses of $NH_3$, $H_2O$ and HF, their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points $NH_3$, $H_2O$ and HF will be higher than the hydrides of their subsequent group members.

**Metallic or Non-stoichiometric (or Interstitial) Hydrides**

These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH. These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example: $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5\text{-}1.8}$, $ZrH_{1.3\text{-}1.75}$, $VH_{0.56}$, $NiH_{0.6\text{-}0.7}$, $PdH_{0.6\text{-}0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for hydrogen storage and as a source of energy.

***Problem 3:*** Can phosphorus with outer electronic configuration $3s^2 3p^3$ form $PH_5$?

***Solution:*** Although phosphorus exhibits +3 and +5 oxidation states, it cannot form $PH_5$. Besides some other considerations, high $\Delta_a H$ value of dihydrogen and $\Delta_{eg} H$ value of hydrogen do not favour to exhibit the highest oxidation state of P, and consequently the formation of $PH_5$.

**Summary**

This module describes the Hydrogen, the lightest atom with only one electron and its three isotopes, namely: protium (H), deuterium (D) and tritium (T). Amongst these three, only tritium is radioactive. Inspite of its resemblance both with alkali metals and halogens, it occupies a separate position in the periodic table because of its unique properties. Hydrogen is the most abundant element in the universe. In the combined state, it is the third most abundant element on the earth’s surface.

Dihydrogen on the industrial scale is prepared by the water-gas shift reaction from petrochemicals. It is obtained as a byproduct by the electrolysis of brine. The H–H bond dissociation enthalpy of dihydrogen is the highest for a single bond between two atoms of any elements. This property is made use of in the atomic hydrogen torch which generates a temperature of ~4000K and is ideal for welding of high melting metals.

Dihydrogen possesses very high negative dissociation enthalpy, it combines with almost all the elements under appropriate conditions to form hydrides. All the type of hydrides can be classified into three categories: ionic or saline hydrides, covalent or molecular hydrides and metallic or non-stoichiometric hydrides. Alkali metal hydrides are good reagents for preparing other hydride compounds. Molecular hydrides (e.g., $B_2H_6$, $CH_4$, $NH_3$, $H_2O$) are of great importance in day-to-day life. Metallic hydrides are useful for ultra purification of dihydrogen and as dihydrogen storage media.

Among the other chemical reactions of dihydrogen, reducing reactions leading to the formation hydrogen halides, water, ammonia, methanol, vanaspati ghee, etc. are of great importance. In metallurgical process, it is used to reduce metal oxides. In space programmes, it is used as a rocket fuel. In fact, it has promising potential for use as a non-polluting fuel of the near future.