9. HYDROGEN

Position in the Periodic Table

Hydrogen shows resemblance with both Alkali metals of the first group and halogens of the 17th group. Like alkali metals it has one electron in the outer most shell and forms unipositive ions. Hydrogen forms oxides, halides and sulphides similar to alkali metals.

Like halogens, it requires only one electron to complete the valence shell configuration. So it gains one electron to form uninegative ion. It exists as diatomic molecule, combines with metals to form hydrides and form a large number of covalent compounds with non-metals.

At the same time it shows some differences from alkali metals and halogens. Unlike alkali metals it has very high ionisation enthalpy, exists as diatomic molecule and is a typical non-metal. Unlike halogens, it has very low reactivity and readily forms positive ions.

So eventhough Hydrogen resemblance with both alkali metals and halogens, it differs from them as well. So it is placed separately in the periodic table.

Isotopes of Hydrogen

Hydrogen has three isotopes – Protium (${}_1H^1$), Deuterium (${}_1H^2$) and Tritium (${}_1H^3$). These isotopes differ from one another in number of neutrons only. Ordinary Hydrogen (protium) has no neutrons, Deuterium has one neutron and Tritium has two neutrons in the nucleus.

The major form is Protium. The abundance of Deuterium is 0.0156% and that of Tritium is about 1 atom per 10^{18} atoms of protium. Only Tritium is radioactive. Since these isotopes have same electronic configuration, they have almost the same chemical properties.

Preparation of Dihydrogen or Hydrogen (H_2)

In the laboratory, H_2 is prepared by the following methods:

1. The reaction between granulated zinc and dilute HCl.

   $Zn + HCl \rightarrow ZnCl_2 + H_2$
2. The reaction of Zn with aqueous alkali

   $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

   (Sodium zincate)

Commercially Hydrogen is prepared by the following methods:

1. Electrolysis of acidified water with platinum electrodes

   $2H_2O(l) \xrightarrow{electrolysis} 2H_2(g) + O_2(g)$
2. It is obtained as a byproduct in the manufacture of NaOH and Chlorine by the electrolysis of brine solution (NaCl solution).

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

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

   The overall reaction is

   $2Na^+\,(aq) + 2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2Na^+\,(aq) + 2OH^-(aq)$
3. By the reaction of steam on hydrocarbons or coke at high temperature in the presence of catalyst.

   $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

The mixture of CO and H_2 is called water gas. Since it is used for the synthesis of methanol and large number hydrocarbons, it is also called ***synthesis gas or syn gas***.

Now syngas is also produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called ***'coal gasification'***.

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

The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst. This is called ***water-gas shift reaction***.

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

Properties of dihydrogen

Chemical Properties

1. **Reaction with halogens**

   Dihydrogen reacts with halides to form hydrogen halides (HX). $H_2(g) + X_2(g) \rightarrow 2HX(g)$

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2. **Reaction with O_2:** $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

3. **Reaction with N_2**

$$N_2(g) + 3H_2(g) \xrightarrow[\text{Fe/Mo}]{\text{773K, 200 atm}} 2NH_3(g)$$

4. **Reaction with metals**

Dihydrogen combines with metals at higher temperature to form metal hydrides.

$2M + H_2 \rightarrow 2MH$; where M is an alkali metal.

5. **Reaction with organic compounds**

It reacts with many organic compounds in presence of catalyst to form hydrogenated compounds.

e.g. $H_2 + CO + R\text{-}CH = CH_2 \rightarrow \underset{\text{(aldehyde)}}{R\text{-}CH_2\text{-}CH_2\text{-}CHO}$

$H_2 + R\text{-}CH_2\text{-}CH_2\text{-}CHO \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$

Uses of Dihydrogen

1. Dihydrogen is mainly used for the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
2. It is used in the manufacture of vanaspathi fat by the hydrogenation of vegetable oils.
3. It is widely used for the manufacture of metal hydrides
4. It is used for the preparation of hydrogen chloride, methanol etc.
5. In metallurgical processes, it is used to reduce heavy metal oxides to metals.
6. Atomic hydrogen and oxy-hydrogen torches are used for cutting and welding purposes.
7. It is used as a rocket fuel in space research.
8. It is used in fuel cells for generating electrical energy.

HYDRIDES

The binary compounds of hydrogen with other elements are called Hydrides. They are classified into three:

1. **Ionic or saline or salt-like hydrides**:

These are stoichiometric compounds of H_2 with s-block elements. They are crystalline, non-volatile solids. They are non-conductors in the solid state but conduct electricity in the molten state or in aqueous solution state. LiH, BeH_2 and MgH_2 are significantly covalent in nature.

e.g. NaH, KH, CaH_2, BaH_2 etc.

2. **Covalent or Molecular Hydrides**:

These are the hydrides of p-block elements. Examples are CH_4, NH_3, H_2O and HF. Being covalent, they are volatile compounds. Molecular hydrides are further classified into 3 according to the relative numbers of electrons and bonds in their Lewis structure - (i) *electron-deficient* (ii) *electron-precise* and (iii) *electron-rich hydrides*.

An electron-deficient hydride has very few electrons for writing its Lewis structure. E.g. Diborane (B_2H_6). All elements of group 13 will form electron-deficient compounds. They act as Lewis acids (i.e. they accept electron pairs).

Electron-precise compounds have the required number of electrons to write their Lewis structures. All elements of group 14 form such compounds (e.g., CH_4, SiH_4 etc.)

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15 to 17 form such compounds. They behave as Lewis bases (i.e., electron donors).

3. **Metallic Hydrides**:

These are formed by many d-block and f-block elements. However, the metals of group 7, 8 and 9 do not form this hydride. They are almost always nonstoichiometric, being deficient in hydrogen. They conduct heat and electricity. e.g. $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$ etc.

In these hydrides the hydrogen atom is occupied in the metal lattice. So they are also called ***interstitial hydrides***. Due to the property of absorption of hydrogen on interstitial sites, they are widely used as hydrogenation catalysts.

WATER

Water is a liquid with high boiling point. This is due to extensive hydrogen bonding in water. On comparison to other liquid water has a higher specific heat capacity, thermal conductivity, surface tension, dipole moment, dielectric constant etc.

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Ice is the crystalline form of water. It has a highly ordered three dimensional hydrogen bonded structure. Hydrogen bonding gives its an open type structure with wide holes. So it has low density and floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life.

Hard and soft water

Water which does not easily form lather with soap is called hard water. It is due to the presence of calcium and magnesium salts in the form chlorides, sulphates and bicarbonates. Water free from soluble salts of calcium and magnesium is called soft water. It easily forms lather with soap.

Soaps are sodium or potassium salts of fatty acids like palmitic acid, stearic acid oleic acid etc. They react with calcium or magnesium salts presenting in hard water and form precipitates.

Types of hardness of water

There are two types of hardness of water – temporary hardness and permanent hardness.

I. Temporary Hardness

Hardness which can be removed by simple boiling is called temporary hardness. It is due to the presence of bicarbonate of calcium and magnesium. The following methods are used to remove temporary hardness.

1. ***Boiling***: During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$, which can be removed by filtration.
   $Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$
   $Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$
2. ***Clark's method***: In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.
   $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$
   $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$

II. Permanent Hardness

Hardness which cannot be removed by boiling is called Permanent hardness. It is due to the presence of soluble chlorides and sulphates of calcium and magnesium in water. It can be removed by the following methods:

1. **Treatment with washing soda** (Sodium carbonate): Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

$CaCl_2 + 2Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$
$MgCl_2 + 2Na_2CO_3 \rightarrow MgCO_3 \downarrow + 2NaCl$
$CaSO_4 + 2Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$

2. **Calgon's method**: Sodium hexametaphosphate ($Na_6P_6O_{18}$) is commercially called 'calgon'. When it is added to hard water, the Ca and Mg ions in hard water are replaced by Na^+ ions

$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$
$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

3. **Ion-exchange method**: This method is also called zeolite/permutit process. Zeolite /permutit is hydrated sodium aluminium silicate which can be written as NaZ. When this is added to hard water, exchange reactions take place.

$2NaZ + M^{2+} \rightarrow MZ_2 + 2Na^+$ (where M = Mg or Ca)

Permutit/zeolite is regenerated for further use by treating with an aqueous sodium chloride solution.

$MZ_2 + 2NaCl \rightarrow 2NaZ + MCl_2$

4. **Synthetic resins method**: This method is more efficient than zeolite process. Pure demineralised water can be obtained by this method. Here the hard water is first passed through a cation exchange (acidic) resin which contains H^+ ions (H^+ Resin) and then through anion exchange (basic) resin which contains OH^- ions (OH^-Resin). The cations (Ca^{2+} and Mg^{2+} ions) present in hard water is exchanged with H^+ ion and the anions (Cl^- and SO_4^{2-}) are exchanged with OH^- ions.

$H^+ \text{ Resin} + Ca^{2+} \longrightarrow Ca^{2+} \text{ Resin} + H^+$
$OH^- \text{Resin} + Cl^- \longrightarrow Cl^- \text{ Resin} + OH^-$
$H^+ + OH^- \longrightarrow H_2O$

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HYDROGEN PEROXIDE (H_2O_2)

Preparation

It can be prepared by the following methods:

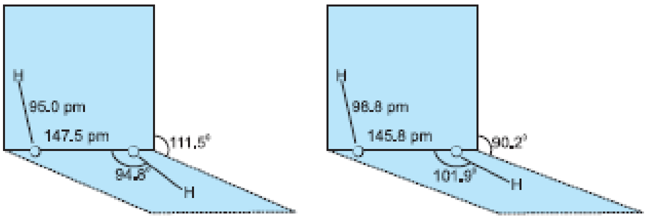
i. It is prepared by acidifying barium peroxide and removing excess water by evaporation under reduced pressure. $BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$

ii. Industrially it is prepared by the auto-oxidation of 2-alklylanthraquinols.

2 ethylanthraquinol $\rightleftharpoons$ H_2O_2 + oxidised product

Structure

Hydrogen peroxide has a non-planar structure as follows:



(a) Gas phase (b) Solid phase

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Chemical properties

H_2O_2 acts as an oxidising as well as reducing agent in both acidic and alkaline media.

1. Oxidising action in acidic medium
   $2Fe^{2+} + 2H^+ + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$
   $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
2. Reducing action in acidic medium
   $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$
   $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$
3. Oxidising action in basic medium
   $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$
   $Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$
4. Reducing action in basic medium
   $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$
   $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

Storage

H_2O_2 decomposes slowly on exposure to light.

$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

Bleaching action of H_2O_2

H_2O_2 is used as a good bleaching agent. This is because H_2O_2 decomposes to form nascent hydrogen which is responsible for its bleaching action.

$H_2O_2 \longrightarrow H_2O + [O]$

Uses

1. In daily life it is used as hair bleach and as a mild disinfectant. As an antiseptic it is sold in the market as perhydrol.
2. It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.
3. It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals.
4. It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats etc.
5. It is also used in Environmental (Green) Chemistry.

HEAVY WATER (D_2O)

D_2O is called heavy water. It is used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. It is used for the preparation of other deuterium compounds.

e.g. $CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$

HYDROGEN ECONOMY

The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. Dihydrogen is also used in fuel cells for generation of electric power.

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