CHE-MM: XI

9. HYDROGEN

Hydrogen (*hydro*^{G}= water + *gene*^{G} =producing, because it produces water when burnt in air) is the lightest atom with only one e^-.

In the free-state, it is not found in the earth's atmosphere. However, in the combined state, it is the 3rd most abundant element on the earth's surface.

Position of Hydrogen in Periodic Table

Hydrogen is placed at the top of group 1 of periodic table. Its position, however, is not justified because of its **resemblance with alkali metals** and **halogens**.

Resemblance with alkali metals

- Both have **1 e^- in the valence** shell and forms **unipositive ions**.
- Forms oxides, halides and sulphides.

Resemblance with halogens

- It is a **non-metal**
- Both **require 1 e^- to complete the valence** shell configuration. So it gains 1 e^- to form **uninegative ion.**
- Exists as **diatomic molecule** (H_2)
- Combines with **metals to form hydrides** (H^-)
- Combines with non-metals to give **covalent compounds**.
- H has very **high ionisation enthalpy**

Isotopes

Hydrogen has 3 isotopes –

1) **Protium / Ordinary Hydrogen** ($_1H^1$) - Has no neutrons (99.98%)
2) **Deuterium / Heavy Hydrogen** ($_1H^2$) - Has 1 neutron (0.016%)
3) **Tritium** ($_1H^3$) - Has 2 neutrons. It is ***radioactive***. (1 x 10^{-15}%)

Dihydrogen (H_2)

In the normal elemental form, hydrogen exists as diatomic H_2.

Preparation

A. Laboratory preparation:

i. The reaction between **granulated zinc** and **dilute HCl**.

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$

ii. The reaction of **Zn** with **aqueous alkali**

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

Sodium zincate

B. Commercial production:

i. Electrolysis of **acidified water** using **platinum electrodes**.

$$2H_2O_{(l)} \xrightarrow{\text{electrolysis}} 2H_{2(g)} + O_{2(g)}$$

ii. Pure H_2 is obtained by electrolysing warm **aqueous barium hydroxide solution** between **nickel electrodes**.

iii. H_2 is obtained as a byproduct in the manufacture of NaOH and Chlorine by the electrolysis of ***Brine*** (NaCl solution).

The overall reaction is-

$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2Na^+_{(aq)} + 2OH^-_{(aq)}$$

iv. By the reaction of **steam on hydrocarbons or coke** at high temperature (1270K) in the presence of catalyst.

$$C_{(s)} + H_2O_{(g)} \longrightarrow \underbrace{CO_{(g)} + H_{2(g)}}_{\textit{Water gas}}$$

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

> The process of producing 'syngas' from coal is called ***'coal gasification'***.

Water-gas shift reaction- The production of H_2 can be increased by reacting CO of syngas mixtures with steam in the presence of **iron chromate** as catalyst.

$$CO_{(g)} + H_2O_{(g)} \xrightarrow[\text{Catalyst}]{673K} CO_{2(g)} + H_{2(g)}$$

Properties

Physical:

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

Chemical:

- ✓ H_2 is relatively **inert** at room temperature *due to the high H–H bond enthalpy*. However, it forms compounds with almost all elements **at high temperature** or in the **presence of catalyst**.

Reactions:-

a. Reaction with halogens: Dihydrogen reacts with halides to form *hydrogen halides* (HX).

$$H_{2(g)} + X_{2(g)} \rightarrow 2HX_{(g)}$$

b. Reaction with O_2: H_2 reacts with dioxygen to **form water**.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

c. Reaction with N_2: Forms *ammonia* (*Haber process*)

$$3H_{2(g)} + N_{2(g)} \xrightarrow[\text{Fe}]{673K,\ 200\ atm} 2NH_{3(g)}$$

d. Reaction with metals: H_2 combines with metals (alkali) at higher temperature to form **metal hydrides**.

$$2M + H_2 \rightarrow 2MH$$

e. Reaction with organic compounds: Form **hydrogenated compounds** of commercial importance (vanaspati, aldehyde, alcohols etc.).

Uses of H_2

a) H_2 is mainly used for the **synthesis of ammonia** which is used in the manufacture of **nitric acid** and **nitrogenous fertilizers**.
b) It is used in the manufacture of **vanaspathi fat** by the hydrogenation (using nickel as catalyst) of vegetable oils.
c) It is used for the **manufacture of metal hydrides**
d) It is used for the preparation of **hydrogen chloride, methanol** etc.
e) In **metallurgical processes**, it is **used to reduce** heavy metal oxides to metals.
f) Atomic hydrogen torch are used for **cutting** and **welding purposes** (due to high H–H **bond dissociation enthalpy** of dihydrogen).
g) H_2 gas is used as a **rocket fuel** and for providing clean **drinking water to the astronauts**.
h) It is used in **fuel cells** for generating electrical energy.

Hydrogen as a Fuel

- ➢ The proposal of using H_2 as alternative source of energy refers to **hydrogen economy**.
- ➢ **Advantage**
  - It can release **more energy** than petrol (on mass for mass basis)
  - **Pollution less** combustion (product is water).
  - Used in **fuel cells** for generation of electric power.
- ➢ **Disadvantage**
  - Generation of pollutants like **oxides of dinitrogen** (due to the presence of dinitrogen as impurity with dihydrogen)
  - Requires **massive** and **insulated tanks** for storage.

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Hydrides (H^-)

Binary compounds of the elements (metals or non-metals) with hydrogen are called **Hydrides**. They are classified into 3:-

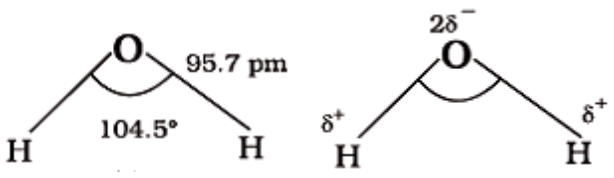
Ionic or Saline hydrides:	**Covalent or Molecular hydrides**:	**Metallic or Interstitial hydrides**
✓ They are hydrides of **s-block elements** ✓ **Crystalline solids** having M^{n+} and H^- ions in lattice. ✓ Non-volatile ✓ Conduct electricity in the molten state E.x: NaH, BeH_2 etc.	✓ They are hydrides of **p-block elements** ✓ Have molecular lattice; the molecules are held by van der Waal's force of attraction. ✓ Volatile ✓ Non-conductors E.x: B_2H_6, CH_4, HF.	✓ They are hydrides of **d-block** and **f-block elements** ✓ In these hydrides the hydrogen atom is occupied in the metal lattice. ✓ They conduct heat and electricity. E.x: $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $PdH_{0.6-0.8}$

Water (H_2O)

Water is the most common and abundantly available substance. It is of a great chemical and biological significance.

Structure

The water molecule is highly polar in nature due to its bent structure.



Properties

Physical:

- ✓ Water is a colourless and tasteless liquid.
- ✓ It has high boiling point (*due to extensive H-bonding*).
- ✓ It has a higher specific heat capacity, thermal conductivity, surface tension, dipole moment, dielectric constant etc.

When **ice** is formed from liquid water, some **air gap** is formed in its crystalline structure. 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*.

Chemical:

The polar nature of water makes it:

- ✓ to act as an **amphoteric** (acid as well as base) substance;
- ✓ a very **good solvent** for ionic and partially ionic compounds;
- ✓ to **form hydrates** of different types.

Hard and soft water

Soft water: Water which **foam easily with soap**. It is free from soluble salts of calcium and magnesium.
Ex: Distilled water, rain water

Hard water: Water which does **not easily foam with soap**. It is due to the presence of calcium and magnesium salts in the form chlorides, sulphates and bicarbonates.
Ex: River water, sea water, tap water.

Types of hardness of water

There are two types of hardness of water –

I. Temporary Hardness

Due to the presence of **bicarbonate of Ca** and **Mg**. It is called so since it can be easily removed by simply boiling and filtering the water.

It can be removed (***softened***) by-

(i). ***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.

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$
$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

(ii). ***Clark's method***: Adding calculated amount of lime. 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

Due to the presence of soluble **chlorides** and **sulphates of Ca** and **Mg** in water. It is called so since it cannot be removed simply by boiling. It can be removed by-

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

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl \qquad (M = Mg, Ca)$$
$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$$

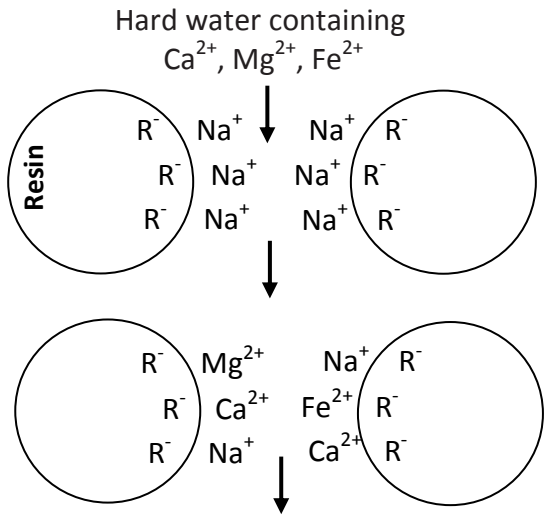
(ii) **Calgon's method**: ***Calgon*** (which means ***cal***cium ***gon***e) i.e., *Sodium hexameta-phosphate*- $Na_6P_6O_{18}$, when added to hard water, the Ca^{2+} and Mg^{2+} in hard water give soluble complex salts.

$$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$$
$$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+ \qquad (M = Mg, Ca)$$

(iii) **Zeolite/permutit process**: Zeolite /permutit (hydrated sodium aluminium silicate), when added to hard water, exchange basic radical which helps in softening it.

$$2NaZ + M^{2+} \rightarrow MZ_2 + 2Na^+ \qquad (\text{where M = Mg, Ca})$$
Zeolite *Insoluble*

(iv) **Synthetic resins method**: Ion exchange resin (RSO_3H) is changed to RNa by treating it with NaCl. The resin exchanges Na^+ with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft.

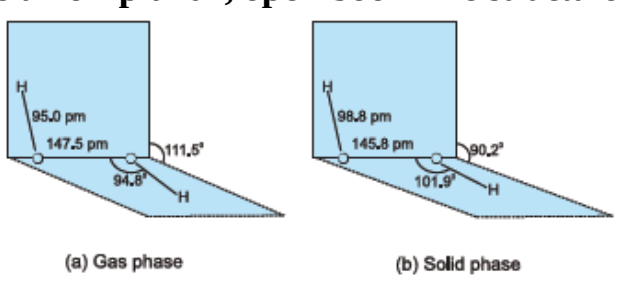


Hydrogen Peroxide (H_2O_2)

It is the hydride of oxygen. In traces, it is found in atmosphere and plants, snow etc.

Structure

It has a **non-planar, open book-like** structure



(a) Gas phase (b) Solid phase

Preparation

(i) It can be prepared by adding ice cold **dil. H_2SO_4** to a paste of **barium peroxide**

$$BaO_2.8H_2O_{(s)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + H_2O_{2(aq)} + 8H_2O_{(l)}$$

(ii) *Industrially* H_2O_2 is prepared by the auto-oxidation and reduction of **anthraquinols**.

2-ethylanthraquinol $\underset{H_2/Pd}{\overset{O_2}{\rightleftharpoons}}$ H_2O_2 + oxidised product

PROPERTIES

Physical:

- ✓ H_2O_2 is a **pale blue coloured** liquid.
- ✓ It is **soluble in water**.

Chemical:

- ✓ H_2O_2 is a **powerful oxidising agent** as well as a **poor reducing** agent in both acidic and alkaline media.
- ✓ H_2O_2 decomposes on exposure to light.

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

It is, therefore, *stored* in **wax-lined glass or plastic vessels** in dark.

REACTIONS:-

(i) Oxidising action in acidic medium

$$2Fe^{2+} + 2H^{+} + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$$

(H_2O_2 oxidises acidified *ferrous sulphate* to *ferric sulphate*)

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

Black *White*

(H_2O_2 oxidises lead sulphide to lead sulphate, used in refreshing old oil paints which is blackened by atmospheric H_2S)

(ii)Reducing action in acidic medium

$$2MnO_4^{-} + 6H^{+} + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

Pink *Colourless*

(H_2O_2 decolourise pink $KMnO_4$)

$$HOCl + H_2O_2 \rightarrow H_3O^{+} + Cl^{-} + O_2$$

Hypochlorous acid

(It reduces hypohalous acid to halide ion in acidic medium)

(iii) Oxidising action in alkaline medium

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^{-}$$

(H_2O_2 oxidises *ferrous salt* to *ferric salts* in alkaline medium)

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^{-}$$

Colourless *Black*

(It oxidises *manganese salt* to *manganese dioxide*)

(iv)Reducing action in alkaline medium

$$I_2 + H_2O_2 + 2OH^{-} \rightarrow 2I^{-} + 2H_2O + O_2$$

(H_2O_2 reduces *halogens* to *halide ions*)

$$2MnO_4^{-} + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^{-}$$

(It reduces *Potassium permanganate* to *manganese dioxide*)

USE:-

a) Hydrogen peroxide is used as **hair bleach** and as a **disinfectant**.
b) It is used to manufacture chemicals like **sodium perborate** and **per-carbonate**, which are used in high quality detergents.
c) It is used in the synthesis of **hydroquinone**, **tartaric acid** and certain food products and pharmaceuticals (***cephalosporin***) etc.
d) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats etc.
e) In **pollution control treatment** of domestic, restoration of aerobic conditions to sewage wastes, etc. (in Green Chemistry).

Heavy Water (D_2O)

It is deuterium oxide.

PREPARATION

By repeated electrolysis of normal water with alkali.

USE:-

a) It is used as a **moderator** in nuclear reactors.