9. HYDROGEN

HAIZEL G. ROY H.S.S.T. (HG) CHEMISTRY GOVT. H.S.S. KALAMASSERY ERNAKULAM.



ABOUT HYDROGEN

Hvdroaen

1.0079

•Hydrogen is the most abundant element in the universe. It is the lightest of all known elements. 1 Operived from two Greek words 'Hydro' means water **Cand 'gene' means producing.** • The meaning of the word hydrogen is 'water producer'. •The name hydrogen was given to the gas by Lavoisier. In 1766, Henry Cavendish discovered hydrogen.

POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. Its electronic configuration is 1S¹. It shows similarities to both alkali metals and halogens. Therefore, its position in the periodic table is anomalous.



RESEMBLANCE WITH ALKALI METALS

- Both have 1 electron in the valence shell and forms unipositive ions.
- Like alkali metals, Hydrogen also loses its one electron to form Hydrogen Ion, H⁺.
- 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 (H₂)
- Combines with metals to form hydrides.
- Combines with non-metals to give covalent compounds.
- Hydrogen has very high ionisation enthalpy.

OCCURRENCE OF HYDROGEN

- Dihydrogen is the most abundant element in the universe.
- It is the main element in the solar atmosphere.
- The giant planets Jupiter and Saturn consist mostly of hydrogen.
- It occurs in plants and animal tissues.
- In the combined form it exists in the form of carbohydrates, proteins, hydrocarbons, hydrides and many other compounds.

ISOTOPES OF HYDROGEN

Hydrogen has three isotopes with mass numbers 1, 2 and 3.
They are Protium (¹₁H), Deuterium (²₁H or ²₁D) and Tritium (³₁H or ³₁T).
Tritium is radioactive.

Isotopes	Protons	Neutrons	Electrons
$^{1}_{1}H$	1	0	1
² ₁ H	1	1	1
³ ₁ H	1	2	1

PREPARATION OF DIHYDROGEN

LABORATORY PREPARATION

Dihydrogen is prepared by the action of dil. HCl on granulated Zn.

 $\rm Zn+2HCl \rightarrow ZnCl_2 + H_2$

 Dihydrogen can also be prepared by the reaction of Zinc with aqueous alkali.

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

COMMERCIAL PRODUCTION

ELECTROLYSIS OF WATER

- Water containing Small amount of acid is electrolysed using platinum electrodes.
- Hydrogen is liberated at the cathode and oxygen at the anode.

$$2H_2O \xrightarrow{Electrolysis} 2H_2 + O_2$$

ELECTROLYSIS OF BRINE SOLUTION

• Obtained as a byproduct in the manufacture of NaOH by the electrolysis of brine solution.

During electrolysis the following reactions takes place.

- At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
- At Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- Overall Cell Reaction: 2Cl[−] + 2H₂O → Cl₂ + H₂ + 2OH[−]

BOSCH PROCESS OR WATER GAS PROCESS

- In this process, super-heated steam is passed over red hot coke at 1270K.
- A 1:1 mixture of carbon monoxide and hydrogen, known as water gas is Obtained.

$$C + H_2O \rightarrow CO + H_2$$

- The water gas is then mixed with excess of steam.
- It passed over heated Iron Chromate catalyst at 673K to form CO₂ and H₂.

• This is called Water gas Shift Reaction.

$$\text{CO} + \text{H}_2\text{O} \xrightarrow{673\text{K/FeChromate}} \text{CO}_2 + \text{H}_2$$

• The above mixture of gas is passed through water under pressure.

• It dissolves the more soluble CO₂ leaving behind hydrogen.

SYNTHESIS GAS OR SYN GAS

A mixture of CO and H₂ used for the synthesis of methanol and a number of hydrocarbons is called synthesis gas or Syngas.



COAL GASIFICATION

The process of producing Syngas from coal is called coal gasification.



PROPERTIES OF DIHYDROGEN

PHYSICAL PROPERTIES

• Dihydrogen is a colourless, odourless, tasteless and combustible gas.

- It is lighter than air.
- It is insoluble in water.



1. REACTION WITH HALOGENS

Dihydrogen reacts with halogens to give hydrogen halides.

 $H_{2} + X_{2} \rightarrow 2HX$ $H_{2} + Cl_{2} \xrightarrow{\text{Sunlight}} 2HCl$ $H_{2} + F_{2} \xrightarrow{\text{Dark}} 2HF$ $H_{2} + Br_{2} \xrightarrow{670K} 2HBr$ $H_{2} + I_{2} \xrightarrow{\text{Catalyst}} 2HI$

2. REACTION WITH DIOXYGEN

Dihydrogen reacts with dioxygen to form water.

$$\rm 2H_2 + O_2 \rightarrow 2H_2O$$

3. REACTION WITH DINITROGEN

Dihydrogen reacts with dinitrogen to form ammonia.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

4. REACTION WITH METALS

With many metals, dihydrogen combines at high temperature to yield corresponding hydrides.

> $H_2 + 2M \rightarrow 2MH$ $H_2 + 2Na \rightarrow 2NaH$

5. REACTION WITH METAL IONS & METAL OXIDES

Dihydrogen reduces some metal ions in aqueous solution to corresponding metals.

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

Dihydrogen reduces oxides of metals, less active than iron into corresponding metals

 $WO_3 + 3H_2 \longrightarrow W + 3H_2O$

6. REACTION WITH ORGANIC COMPOUNDS

HYDROGENATION

Unsaturated hydrocarbons combine directly with hydrogen to produce saturated hydrocarbons.

$$CH_{2} = CH_{2} \xrightarrow{H_{2}/Ni/470K} CH_{3} - CH_{3}$$
$$CH \equiv CH + 2H_{2} \xrightarrow{Ni/470K} CH_{3} - CH_{3}$$

When hydrogen gas is bubbled through vegetable oils in presence of finely divided Ni, at about 470K, they are converted to solid fats known as 'Vanaspati'. reaction is This called hydrogenation or hardening of oils.







- Alkenes react with hydrogen and carbon monoxide to form an aldehyde.
- Aldehyde further undergo reduction to give alcohols.
- This reaction is called hydroformylation.

$$H_2 + CO + R - CH = CH_2 \rightarrow R - CH_2 - CH_2 - CHO$$

 $\mathrm{H}_2 + \mathrm{R} - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CHO} \rightarrow \mathrm{R} - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{OH}$

USES OF HYDROGEN

- In the hydrogenation of oils to make vanaspati.
- In the production of synthetic petrol from coal.
- In the manufacture of ammonia by Haber process.
- In the manufacture of hydrogen chloride and hydrochloric acid.
- In the production of oxyhydrogen flame for cutting and welding purposes.
- In the manufacture of organic chemicals particularly methanol.
- In the manufacture of metal hydrides.
- Hydrogen is used as a rocket fuel.

HYDROGEN ECONOMY

- The basic principle of hydrogen economy is the storage and transportation 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.
- Hydrogen is also used in fuel cells for generation of electric power.
- Hydrogen has the potential for use as a non-polluting fuel of the near future.



HYDROGEN AS A FUEL

ADVANTAGES

- 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.

DISADVANTAGES

- Generation of pollutants like oxides of dinitrogen.
- Requires massive and insulated tanks for storage.

COMPOUNDS OF HYDROGEN

HYDRIDES

- Dihydrogen, under certain conditions combine with almost all elements, except noble gases to form binary compounds, called hydrides.
- Hydrides can be represented as EH_x or $E_m H_n$.
- Eg:- NaH, CaH_2 , MgH_2 , B_2H_6 etc.

CLASSIFICATION OF HYDRIDES

IONIC OR SALINE OR SALT LIKE HYDRIDES

- Binary compounds of dihydrogen formed with most of the
- s-block elements.
- which are highly electropositive in character.
- The ionic hydrides are crystalline, non volatile and non conducting in solid state.
- Eg:- NaH, LiH etc.
COVALENT HYDRIDES

- Binary compounds of dihydrogen formed with most of the pblock elements.
- They are generally soft and have low melting and boiling points.
- They are poor conductors of electricity.
- They are soluble in organic solvents.
- Eg:- CH_4 , NH_3 , H_2O , HF etc.

CLASSIFICATION OF COVALENT HYDRIDES

1. ELECTRON DEFICIENT HYDRIDES These hydrides have too few electrons for writing its conventional Lewis structure. Eg:- B₂H₆

2. ELECTRON PRECISE HYDRIDES

These compounds have the required number of electron to write their conventional Lewis structures. Eg:- All elements of group 14.

3. ELECTRON RICH HYDRIDES

These compounds have excess electrons which are present as lone pairs.

Eg:- Elements of group 15 to 17. $(NH_3, H_2O, HF etc.)$

METALLIC OR INTERSTITIAL HYDRIDES

- These are binary compounds of dihydrogen with d-block elements of group 3,4,5 and 6 (CrH) and f-block elements.
 The metals of group 6 except Cr, 7, 8 and 9 do not form hydrides.
- Due to this, the region of the periodic table from groups 6 to 9 is called hydride gap.

- In metallic hydrides, the hydrogen occupies interstitial position in the metal lattices.
- Most metallic hydrides are good conductors of electricity.
- Conductivity decreases with increase in temperature.
- Eg:- ScH₂, TiH₂, VH, NiH, CrH, LaH₂ etc.



- Water is one of the most abundant and important compounds known to man.
- It is an important constituent of all animal and plant matter.
- About 65% of the human body and 95% of many plants is water.
- About 3/4 th of the earth's crust is covered by water.
- Water can exist in three states namely solid (ice), Liquid (water) and gas (water vapour).

PHYSICAL PROPERTIES

- Water is a colourless, odourless and tasteless liquid.
- Due to hydrogen bonding,water has
- high freezing point
- high boiling point
- high heat of vaporization
- high heat of fusion.

ICE

• The crystalline form of water is ice.

- At atmospheric pressure, ice crystallizes in the hexagonal form.
- At very low temperature, it condenses to cubic form.
- Density of ice is less than that of water.
- Therefore, an ice cube floats on water.
- In winter season, ice is formed on the surface of a lake.
- It provides thermal insulation which helps in the survival of the aquatic life.

- Ice Has a Highly ordered three dimensional hydrogen bonded structure.
- X-ray analysis shows that each oxygen atom is surrounded tetrahedrally by other four oxygen atoms at a distance of 276 pm.
- Hydrogen bonding gives ice an open type structure with wide holes.



CHEMICAL PROPERTIES

AMPHOTERIC NATURE

- Water has the ability to act as an acid as well as a base.
- i.e., it behaves as an amphoteric substance.
- Eg:- With ammonia water can act as an acid.
- With H₂S, water can act as a base.

 $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$

 $H_2O + H_2S \rightleftharpoons H_3O^+ + HS^-$

• The self ionisation of water takes place as follows.

 $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

Acid Base Conjugate Conjugate acid base

REDOX REACTIONS INVOLVING WATER

- With highly electropositive metals, water can act as an oxidising agent.
- Whereas with highly electronegative element water can act as a reducing agent.

 $2Na + 2H_2O \rightarrow 2NaOH + H_2$

 $2\mathrm{Cl}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{H}\mathrm{Cl} + \mathrm{O}_2$

HYDROLYSIS REACTION

Water can hydrolyse many metallic and non-metallic compounds.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

 $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

HYDRATE FORMATION

 From aqueous solutions, many salts can be crystallized as hydrated salt.

Such an association of water is of different types.

* Coordinated water

- Eg:- [Cr(H₂O)₆]³⁺ 3Cl⁻
- * Interstitial water

Eg:- $BaCl_2.2H_2O$

* Hydrogen bonded water

Eg:- CuSO₄.5H₂O $[Cu(H_2O)_4]^{2+} SO_4^{2-}.H_2O$

HARD AND SOFT WATER

- Water which gives a ready and permanent lather with soap solution is called soft water.
- Eg:- Rainwater, Distilled water etc.
- Water which does not produce a ready lather with soap solution is called hard water.
- Eg:- Sea water, River water etc.
- The hardness of water is due to the presence of dissolved bicarbonates, chlorides and sulphates of Ca and Mg.

TYPES OF HARDNESS

TEMPORARY HARDNESS

- This is due to the presence of dissolved bicarbonates of Ca or Mg.
- It can be removed by boiling.
- Hence it is known as temporary hardness.

PERMANENT HARDNESS

- This is due to the presence of chlorides and sulphates of Ca or Mg.
- It cannot be softened by simple boiling.
- Hence the name permanent hardness.

Hard water does not produce a ready lather with soap. Why?

Soaps are sodium or potassium salts of higher fatty acids like stearic acid

- ($C_{17}H_{35}COOH$), palmitic acid ($C_{15}H_{31}COOH$) etc.
- When hard water is used for washing, the Ca²⁺ and Mg²⁺ ions present in it react with soap producing the corresponding metal salts as insoluble precipitates.

$$2C_{17}H_{35}COONa + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca$$

• Thus a large amount of soap is used up in precipitating the Ca and Mg salts.

Only after their complete precipitation, lather is formed.

REMOVAL OF TEMPORARY HARDNESS

BY BOILING

- During boiling, the soluble magnesium bicarbonate is converted into insoluble magnesium hydroxide.
- Calcium bicarbonate is converted to insoluble calcium carbonate.
- These precipitates can be removed by filtration.

$$Mg(HCO_3)_2 \xrightarrow{\text{heating}} Mg(OH)_2 + 2CO_2$$
$$Ca(HCO_3)_2 \xrightarrow{\text{heating}} CaCO_3 + H_2O + CO_2$$

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.

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

REMOVAL OF PERMANENT HARDNESS

TREATMENT WITH WASHING SODA

Washing soda reacts with soluble Ca and Mg chlorides and sulphates in hard water to form insoluble carbonates.

$$CaCl_{2} + Na_{2}CO_{3} \longrightarrow CaCO_{3} + 2NaCl$$

$$MgCl_{2} + Na_{2}CO_{3} \longrightarrow MgCO_{3} + 2NaCl$$

$$CaSO_{4} + Na_{2}CO_{3} \longrightarrow CaCO_{3} + Na_{2}SO_{4}$$

$$MgSO_{4} + Na_{2}CO_{3} \longrightarrow MgCO_{3} + Na_{2}SO_{4}$$

CALGON'S METHOD

- Calgon is sodium hexa meta phosphate $(Na_6P_6O_{18})$.
- When calgon, is added to hard water, the following reactions takes place.

$$Na_{6}P_{6}O_{18} \longrightarrow 2Na^{+} + Na_{4}P_{6}O_{18}^{2-}$$
$$M^{2+} + Na_{4}P_{6}O_{18}^{2-} \longrightarrow [Na_{2}MP_{6}O_{18}]^{2-} + 2Na^{+} \quad [M = Ca, Mg]$$

ION EXCHANGE METHOD

- This method is also called zeolite process or permutit process.
- Zeolite is sodium aluminium silicate (NaAlSiO₄).
- Sodium aluminium silicate can be written as NaZ.
- When zeolite is added to hard water, exchange reactions take

place.

$$2NaZ + M^{2+} \longrightarrow MZ_2 + 2Na^+$$
 [M = Ca, Mg]

HYDROGEN PEROXIDE

Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.





PREPARATION

FROM BARIUM PEROXIDE

H_2O_2 is prepared in the laboratory by the action of ice cold dilute sulphuric acid on hydrated barium peroxide.

$$BaO_2.8H_2O + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 + 8H_2O_2$$

FROM SODIUM PEROXIDE

- Sodium peroxide reacts with ice cold dilute sulphuric acid to form Hydrogen Peroxide.
- This method is called Merck's Process.

 $Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$

- The resulting solution is cooled below 273K.
- Na₂SO₄ crystallizes out as Na₂SO₄ .10H₂O.
- These crystals are removed.
- A 3% solution of H₂O₂ is obtained.

PHYSICAL PROPERTIES

- H₂O₂ is a colourless, odourless, oily liquid, very pale blue in bigger bulks.
- It is miscible with water, alcohol and ether in all proportions.
- It is highly associated through hydrogen bonding than in water.
- Due to this, its density and boiling point are higher than those of water.

STRUCTURE OF HYDROGEN PEROXIDE

- Hydrogen peroxide has a non-polar and non-linear dihydroxy structure.
- The two oxygen atoms are lying on the spine of a book opened at an angle of 111.5°.
- The hydrogen atoms are placed one on each cover.
- Each of the H—O—O— bond angle is 94.8°.
- The length of the O—O bond is about 147.5 pm.
- The length of the O—H bond is 95 pm.
- The structure of H_2O_2 in the gas phase and solid phase is given below



STRENGTH OF HYDROGEN PEROXIDE

The strength of H₂O₂ is expressed in terms of the volume of O₂ evolved at STP by one volume of H₂O₂ on heating.
Eg:- 10 volume of H₂O₂ means that 1 ml of the sample gives 10

ml of O_2 a STP.

STORAGE OF HYDROGEN PEROXIDE

- H₂O₂ must be stored in coloured wax lined plastic or glass bottles in dark.
- Rough glass surface, presence of light etc may cause the decomposition of H_2O_2 .
- A small amount of urea can be added as a stabilizer.
- A small amount of negative catalyst like glycerol or phosphoric acid is usually added to H₂O₂ to retard its decomposition.

USES OF HYDROGEN PEROXIDE

- It is used for bleaching silk, wool, ivory etc.
- It is used in medicine as an antiseptic and germicide.
- It is used for restoring the colour of lead paintings.
- 90% H₂O₂ is used as a fuel in rockets, submarines etc.


CHEMICAL PROPERTIES

DECOMPOSITION

• Pure H_2O_2 is unstable and decomposes on standing or on heating.

• The decomposition is accelerated by catalysts like finely divided platinum, MnO₂, silver, gold etc. rough surfaces and light.

$$2\mathrm{H}_{2}\mathrm{O}_{2} \rightarrow 2\mathrm{H}_{2}\mathrm{O} + \mathrm{O}_{2}$$

ACIDIC PROPERTY

- H₂O₂ is a mild acid, turning blue litmus to red.
- It neutralizes bases like NaOH, Ba(OH), Sr(OH), etc to form
 - corresponding salts called peroxides.

 $2NaOH + H_2O_2 \rightarrow NaO_2 + 2H_2O$

 $Ba(OH)_2 + H_2O_2 \rightarrow BaO_2 + 2H_2O$

 $Sr(OH)_2 + H_2O_2 \rightarrow SrO_2 + 2H_2O$

BLEACHING PROPERTY H₂O₂ is a mild bleaching agent. It bleaches silk, wool, ivory etc by oxidation.

OXIDATION H₂O₂ oxidises ferrous salt to ferric salt in acid medium.

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

REDUCTION It reduces permanganate ion to Mn²⁺.

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

HEAVY WATER (D₂0)

0

Heavy Water

or Deuterium Oxide

D

D

Η

Regular Water

- water is deuterium Heavy oxide (D₂O). It is a form of water that contains a large amount of hydrogen isotope deuterium rather than the common
 - hydrogen-1 isotope.

PREPARATION OF HEAVY WATER

It can be prepared by the exhaustive electrolysis of water.

Preparation of heavy water



USES OF HEAVY WATER

- It is used as a moderator in nuclear reactors.
- It is used in the study of reaction mechanism.
- It is used for the preparation of other deuterium compounds.

ATOMIC HYDROGEN TORCH

- It involves the formation of atomic hydrogen atoms.
- The atomic hydrogen atoms are produced by the dissociation of dihydrogen with the help of an electric arc.
- The atomic hydrogen so produced immediately recombine to form molecular hydrogen.
- This liberates a tremendous amount of heat.
- This heat is used for cutting and welding purpose in the form of atomic hydrogen or oxy-hydrogen torches.



RESTORATION OF THE COLOUR OF LEAD PAINTINGS

- Hydrogen peroxide acts as an oxidizing agent, giving water as the reduction product.
- The oxidizing ability of hydrogen peroxide is used for the restoration of old lead paintings.
- The H₂S present in the air combines with the lead darkens in time.
- This is due to the formation of black lead sulfide.
- Hydrogen peroxide converts PbS to $PbSO_4$, which is white.

