Notes of

Chapter 9 🧨🔥

Hydrogen

Chemistry Class 11th

CHAPTER-9

HYDROGEN

Dihydrogen, H_2

1. Accurence

- Most abundant element in universe (70%)
  0.15% by mass in earth's atmosphere
- Constitutes 15.4% of earth's crust & oceans in combined form.

2. Isotopes

Three isotopes -

(i) Protium, ^1_1H, no neutrons, predominant form
(ii) Deuterium, ^2_1H, 1 neutron, known as heavy hydrogen, 0.0156% of terrestrial hydrogen
(iii) Tritium, ^3_1H, 2 neutrons, conc. is about 1 atom per 10^{18} atoms of ^1_1H, radioactive & emits low energy β^- particles.

- All isotopes have same chemical properties bt rates of rxns. is different due to different bond dissociation enthalpies.
  Physical properties differ due to mass.

Preparation of H_2

1. Laboratory

(i) $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$ (H^+: dilute HCl)

(ii) $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$ (NaOH: aqueous alkali)

2. Commercial

(i) Electrolysis of acidified H_2O using Pt electrods

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

(ii) Highly pure (>99.95%) H_2 is obtained by electrolysing warm aqueous $Ba(OH)_2$ solution b/w nickel electrodes.

(iii) A byproduct in chlor-alkali process.

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

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

(iv) Rxn. of steam on hydrocarbons or coke at high temp. in presence of catalyst.

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

- Mixture of CO & H_2 is called 'water gas'. $(CO + H_2)$ is used for synthesis of methanol & a no. of hydrocarbons, it is also called 'synthesis gas' or 'syngas'.
- Production of syngas from coal → coal gasification

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

H_2 production is increased by reacting CO of syngas with steam in presence of iron chromate as a catalyst.

- $$CO(g) + H_2O(g) \xrightarrow[\text{catalyst}]{673K} CO_2(g) + H_2(g)$$

This is called 'water-gas shift' rxn.

CO_2 is removed by scrubbing with sodium arsenite solution.

Properties of H_2

1. Physical

Colourless, odourless, tasteless, combustible gas. Lighter than air & insoluble in water.

2. Chemical

(i) Rxn. with halogens -

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

(ii) with O_2

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

$$\Delta H^\circ = -285.9 \text{ kJ mol}^{-1}$$

(iii) with N_2

$$3H_2(g) + N_2(g) \xrightarrow[Fe]{673K,\ 200atm} 2NH_3(g)$$

$$\Delta H^\circ = -92.6 \text{ kJ mol}^{-1}$$

(iv) with metals

$$H_2(g) + 2M(g) \longrightarrow 2MH(s)$$

where M is alkali metal

(v) with metal ions (in aqueous form) & metal oxides (less active than Fe)

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

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

(vi) with organic compounds

(a) Hydrogenation of vegetable oils using Ni catalyst

(b) $H_2 + CO + RCH=CH_2 \rightarrow RCH_2CH_2CHO$

$H_2 + RCH_2CH_2CHO \longrightarrow RCH_2CH_2CH_2OH$

Hydroformylation of olefins to aldehydes & further to alcohols.

Uses of H_2

1. Synthesis of ammonia for manufacture of HNO_3 & nitrogenous fertilizers.
2. Hydrogenation of polyunsaturated vegetable oils.
3. Manufacture of methanol

   $$CO(g) + 2H_2(g) \xrightarrow{\text{Co \& catalyst}} CH_3OH(l)$$
4. Manufacture of metal hydrides
5. Preparation of HCl.
6. Used to reduce heavy metal oxides in metallurgical processes.
7. Used as rocket fuel in space research.
8. Used in fuel cells for generating electricity.

Hydrides

It is the binary compound of H with any element.
Can be represented as EH_x or E_mH_n.
There are 3 categories of hydrides –

1. Ionic or Saline Hydrides

These are stoichiometric compounds of H_2 with most of s-block elements.

- These are crystalline, non-volatile & non-conducting in solid state. Their melts conduct electricity & on electrolysis liberate H_2 at anode.

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

React violently with water.

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

LiH, BeH_2 & MgH_2 have significant covalent character.

- LiH is unreactive at moderate temp. with O_2 or Cl_2. It is used in synthesis of other hydrides –

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

$$2LiH + B_2H_6 \longrightarrow 2LiBH_4$$

2. Covalent or Molecular Hydride

They are formed b/w H_2 & p-block elements.
Being covalent, they are volatile in nature.
They are further of 3 types based on their Lewis structures –

(i) e^- deficient –
They are formed by grp 13 elements, act as Lewis acids.
Octet of central atom is incomplete.
Eg. – BH_3, AlH_3 etc.

(ii) e^- precise –
formed by grp 14 elements
Complete octet of central atom, tetrahedral geometry.
Eg. CH_4

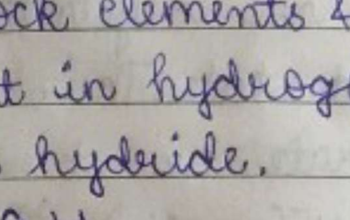
(iii) e^- rich –
formed by elements of grp 15-17
Excess e^- on central atom which are present as lone pairs, act as Lewis bases
Eg. NH_3, H_2O, HF etc.

3. <u>Metallic</u>/<u>Non-stoichiometric</u>/<u>Interstitial Hydrides</u>

- These are formed by d- and f- block elements & always non-stoichiometric, deficient in hydrogen.
- Metals of grp 7, 8 & 9 do not form hydride. From grp 6, only chromium forms CrH.
- They don't conduct heat & electricity efficiently as their parents do.
- Eg. $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$ etc.

<u>Hydrogen Storage</u>

- As metals exist in lattice form & they are rigid spheres. It was thought that hydrogen occupies interstices without ~~por~~ producing any change in its type. So, they were named 'interstitial hydrides'.



- Some metals (eg. Pd, Pt) can accomodate a very large volume of hydrogen & can be used as its media. This property has high potential for hydrogen storage & as a source of energy.

<u>Physical Properties of Water</u>

- Colourful & tasteless liquid, excellent solvent
- The unusual properties of water in condensed phase are due to extensive H-bonding b/w water molecules.

Structure of Water

- In gas phase, water has bent shape with bond angle = 104.5°, and O–H bond length = 95.7 pm, has sp^3 hybridisation. It is a highly polar molecule.
- In liquid phase, H_2O molecules are associated together by hydrogen bonds.
- The crystalline form of water is ice. At atm, ice crystallise in hexagonal form, but at very low temp. it condenses to cubic form.
- In winter season ice formed on surface of lake provides thermal insulation which ensures survival of aquatic life.

Structure of Ice

- Ice has highly ordered 3-D hydrogen bonded structure. Each O is surrounded tetrahedrally by 4 other O atoms at a distance of 276 pm.
- Hydrogen bonding gives ice a open type structure with wide holes which can hold some other molecules of appropriate size interstitially.
- Density of water is max. at 4°C.
  Temp. above 4°C, intermolecular hydrogen bonding starts breaking due to which volume increases & hence density decreases.
  Below 4°C temp., water's cage like structure begins to form & density again falls.

Chemical Properties of Water

1. Amphoteric Nature

It acts as acid as well as base in Brönsted sense.
Auto-protolysis (self-ionization) of water –

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

2. Redox rxns involving water

Water is reduced to H_2 by metals.

$2H_2O(l) + 2Na(s) \longrightarrow 2NaOH(aq) + H_2(g)$

$6CO_2(g) + 12H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$

With F also, it is oxidised to O_2.

$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

3. Hydrolysis Rxn

Due to high dielectric constant, it has a very strong hydrating tendency.

It dissolves many ionic compounds bt certain ionic & covalent compounds are hydrolysed in water.

$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$

$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$

$N^{3-}(s) + 3H_2O(l) \longrightarrow NH_3(g) + 3OH^-(aq)$

4. Hydrates formation

From aqueous solutions many salts can be crystallised as hydrated salts viz

(i) coordinated water eg. $[Cr(H_2O)_6]^{3+}3Cl^-$

(ii) interstitial water eg. $BaCl_2 \cdot 2H_2O$

(iii) hydrogen-bonded water eg. $CuSO_4 \cdot 5H_2O$

Soft water

It lathers well with soap and is free from free Ca^{2+} & Mg^{2+} ions.

Hard water

It contains the Ca & Mg salts in form of chloride, sulphates & hydrogencarbonates in water.

It do not lathers well with soap & forms scum.

$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \longrightarrow (C_{17}H_{35}COO)_2M\downarrow + 2Na^+$

where M is Ca / Mg

(i) Temporary Hardness

It is due to the presence of Mg & Ca hydrogencarbonates

It can be removed by -

(a) Boiling -

$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$

$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$

Precipitates can be removed by filtration.

(b) Clark's method -

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

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

(ii) Permanent Hardness

It is due to presence of Mg / Ca sulphates & chlorides in water. It can be removed by -

(a) $MCl_2 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + 2NaCl$ $(M = Mg, Ca)$

$MSO_4 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + Na_2SO_4$

(b) Calgon's method -

$Na_6P_6O_{18}$ - Sodium hexametaphosphate (calgon)

When it is added to hard water,

$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$

$M^{2+} + Na_4P_6O_{18}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$ $(M = Ca / Mg)$

(c) Ion - exchange method -

Also called zeolite / permutit process.

zeolite is lattice of aluminium silicate

Sodium aluminium silicate ($NaAlSiO_4$) - NaZ

When it is added in hard water,

$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^+(aq)$

Zeolite is said to be exhausted when all Na in it is used up. It is regenerated by following rxn. -

$MZ_2(s) + 2NaCl(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$

where M = Ca / Mg

(d) Synthetic Resins Method -

This is more efficient than zeolite process.

Cation exchange resins contain large organic molecule with $-SO_3H$ group & are insoluble. Ion exchange resin (RSO_3H) is changed to RNa by NaCl.

$$2RNa(s) + M^{2+}(aq) \longrightarrow R_2M(s) + 2Na^+(aq)$$

Here R is resin anion.

Pure demineralised water is obtained by passing water successively through a cation exchange (H^+) & an anion exchange (OH^-) resins -

$$2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$$

It makes water acidic.

In anion exchange process -

$$RNH_2(s) + H_2O(l) \rightleftharpoons RNH_3^+.OH^-(s)$$

$$RNH_3^+.OH^-(s) + X^-(aq) \rightleftharpoons RNH_3^+.X^-(s) + OH^-(aq)$$

OH^- exchanges for anions like Cl^-, HCO_3^- and SO_4^{2-} present in water.

Hydrogen Peroxide (H_2O_2)

1. Preparation

(i) Acidifying Ba peroxide & removing excess water by evaporation under reduced P.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O$$

(ii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate sol. at high current density, on hydrolysis.

$$2HSO_4^-(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H(aq) \xrightarrow{\text{hydrolysis}} 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$$

It is also used for prep. of D_2O_2.

$$K_2S_2O_8(s) + 2D_2O(l) \longrightarrow 2KDSO_4(aq) + D_2O_2(l)$$

(iii) Industrially it is prepared by auto-oxidation of 2-alkylanthraquinols.

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

Physical Properties

- In pure state, H_2O_2 is almost colourless (very pale blue) liquid.
- It is miscible with water in all proportions & forms a hydrate $H_2O_2 \cdot H_2O$.
- 1 ml of 30% H_2O_2 sol. gives 100 mL of Oxygen at STP. Commercially marketed sample is 10 V (3% H_2O_2).
- H_2O_2 has a non-planar structure.

Chemical Properties

It acts ~~as~~ as oxidising & reducing agent in both acidic & alkaline media.

(i) Oxidising action in acidic medium

$$PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$$

(ii) Reducing action in ~~ba~~ acidic medium

$$HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$$

(iii) Oxidising action in basic medium

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

(iv) Reducing action in basic medium

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

Storage

- H_2O_2 decomposes slowly on exposure to light.

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

In the presence of metal surfaces or traces of alkali, the above rxn. is catalysed.
- It is stored in wax-lined glass or plastics in dark. Urea can be added as a stabilizer.
- It is kept away from dust.

Uses

Used as hair bleach & mild disinfectant.
As an antiseptic (perhydrol).
Used in synethesis of hydroquinone, tartaric acid, pharmaceuticals (cephalosporin) & food products.
Used in environmental (Green) chemistry.
Used in industries as bleaching agent for paper pulp, textiles, leather, oils, fats etc.

Heavy water, D_2O

- Used as moderator (dec. the speed of fast going rxn. in nuclear reactors (fission mainly).
- Its rxns. proceed as water.

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$
(Ca carbide)

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

$$Al_4C_3 + 12\,D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$$

Hydrogen Economy

- It is the transportation & storage of energy in the form of liquid or gaseous H_2.
- Its advantage is that energy is transmitted in form of H_2, not electric power.
- For 1st time in history of India, Pilot project using H_2 as fuel was launched in Oct. 2005 for running automobiles.
  Initially 5% H_2 was mixed in CNG for use in 4-wheeler vehicles. The percentage of H_2 would be gradually increased to reach optimum level.
- Nowadays, it is also used in fuel cells for generation of electric power.