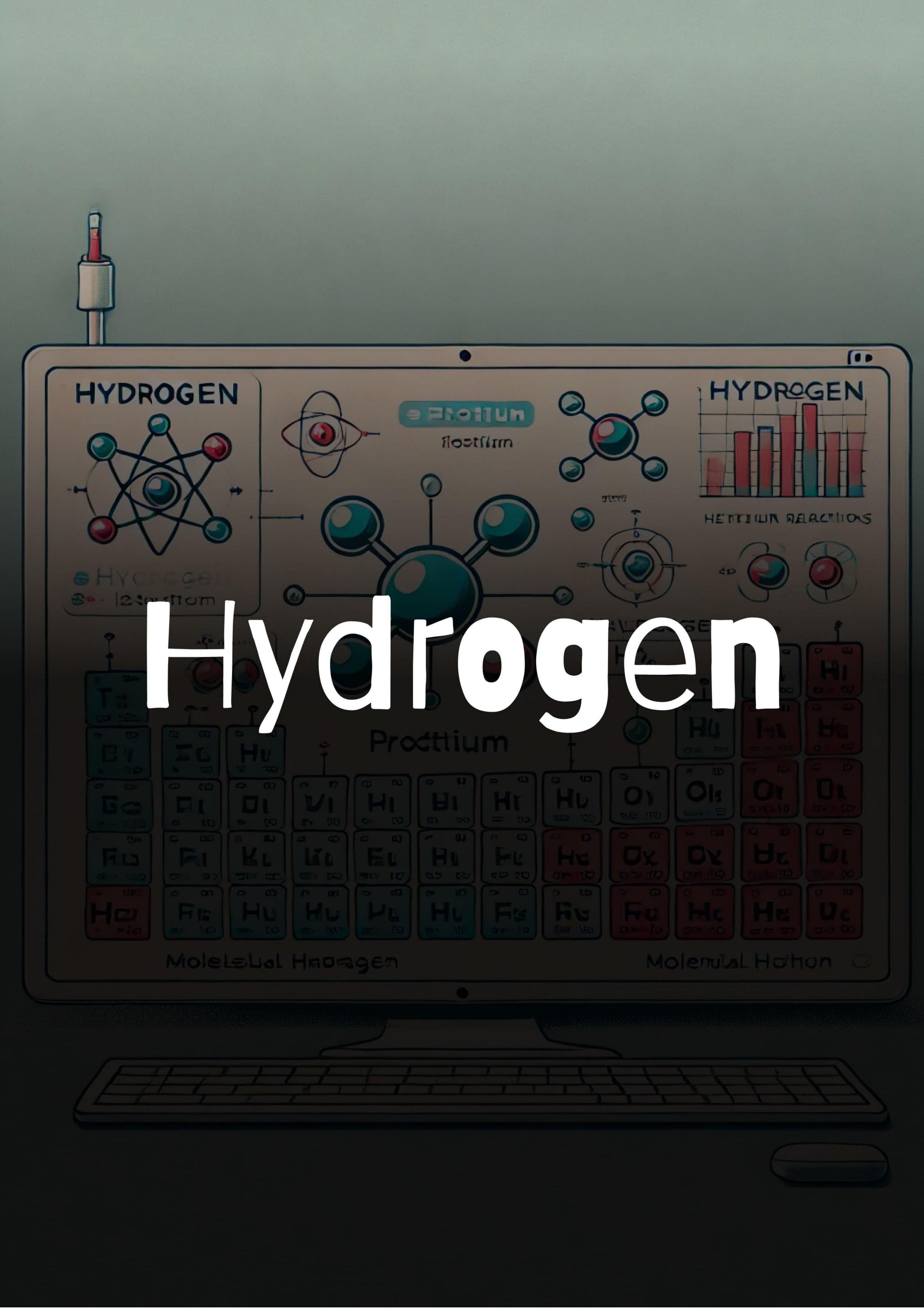
# Hydrogen



# * Hydrogen *

→ most abundant element in Universe
→ Simplest atomic str. → $1s^1$
→ 1 proton, 1 electron, 0 neutron.
→ In elemental state it exists as $H_2$ (Dihydrogen)

## * Position of Hydrogen in Periodic Table

→ Electronic configuration $1s^1$, similar to $ns^1$ which belongs to group 1.
→ It is short by $1e^-$ to complete its octet, so it resembles with group 17.
→ Hydrogen resembles to alkali metals which loose 1 electron to form unipositive ion
As well as it gains one electron to form Uni-negative ion, which resembles with Group 1
→ In terms of ionisation energy it resembles with Grp 17.
$\Delta H$ of Li = 520 kJ/mol
IE of H = 1312 kJ/mol
$\Delta H$ of F = 1680 kJ/mol
→ like Group 17 Hydrogen has tendency to form diatomic molecule.
→ It is unique in behaviour, and placed separately in P.T

## * Di-Hydrogen $H_2$

→ most abundant element in universe
→ Jupiter & saturn consist of $H_2$ (majorly)

## * Isotopes of $H_2$

Three isotopes
1) Protium $^1_1H$ → 0 neutron – most abundant
2) Deuterium $^2_1H$ D → 1 neutron – also known Heavy hydrogen
3) Tritium $^3_1H$ T → 2 neutron – Radioactive emits $\beta^-$ particle

## * Preparation of $H_2$

① Laboratory preparation

→ prepared by reaction of granulated zinc with dil. HCl

$$Zn + 2H^+ \longrightarrow Zn^{+2} + H_2 \uparrow$$
(HCl)

→ Prepared by reaction of zinc with base.

$$Zn + NaOH \longrightarrow Na_2ZnO_2 + H_2 \uparrow$$
soluble sodium zincate

② Commercial preparation.

i) Electrolysis of acidified water using platinum electrodes gives Hydrogen gas

$$2H_2O\,(l) \xrightarrow[\text{pt electrode}]{\text{electrolysis}} H_2(g) + O_2(g)$$

ii) High Purity (>99.95 %) $H_2$ gas is obtained by electrolysing warm aqueous Barium Hydroxide in presence of Nickel electrodes

③ It is obtained as a biproduct in manufacture of Sodium hydroxide and chlorine by electrolysis of Brine solution.

anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

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

(4) Reaction of steam on Hydrocarbon on coke at high temp. and in presence of catalyst.

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

n=1

$$CH_4 + H_2O(g) \xrightarrow[Ni]{1270k} \boxed{CO + 3H_2}$$

water gas

# $$C(s) + H_2O(g) \xrightarrow{1270k} \boxed{CO(g) + H_2(g)}$$

Syn gas / synthesis gas

→ This is coal gasification

# $CO_2$ and $H_2$ mixture is used for synthesis of methanol

# The production of $H_2$ gas can be increased by reaction of CO gas of syn gas mixture with steam in presence of iron chromate catalyst

$$CO(g) + H_2O(g) \xrightarrow[catalyst]{673k} CO_2(g) + H_2\uparrow$$

more abundant

→ water gas shift Reaction

* Physical properties
→ odorless, tasteless, colourless & combustible gas
→ Lighter than air & insoluble in water

* Chemical properties
→ H-H bond enthalpy is highest for a single bond
H-H dissociation is only 0.081 % at 2000 k
" " " 95.5 % at 5000 k

Relatively inert at room temp due to high H-H bond energy

# So, atomic hydrogen is produced at very high temp in electric arc or under U-V radiation

$H_2$ undergoes reaction in 3 ways.
① Loss of electron to give $H^+$
② Gain of electron to form $H^-$
③ Sharing of electron to form single covalent bond.

* Reaction of $H_2$ → 6 Reaction.

1) Reaction with Halogen → Form$^n$ of Hydrogen Halide (HX)

$$H_2(g) + X_2(g) \longrightarrow 2HX(g)$$

X = F, Cl, Br, I

'F' reaction occur even in dark
'I' reaction requires catalyst.

2) Reaction with dioxygen ($O_2$) → water → Highly exothermic

$$2H_2(g) + O_2(g) \xrightarrow[\Delta]{catalyst} 2H_2O(l)$$

water

$\Delta H = -285.9$ kJ/mol.

3) Reaction with Di-nitrogen. Ammonia $NH_3$ → Haber's process

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

exothermic
$\Delta H = -92.6$ kJ/mol

4) Reaction with Metal - Metal hydride → at high Temp

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

5) Reaction of $H_2$ with metal ion and metal oxide
Reduces metal ion and metal oxide (less active than iron)
$H_2 + Pd^{+2}(aq) \longrightarrow Pd(s) + 2H^+(aq)$

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

6) Reaction with organic compound
→ Hydrogenation of vegetable oil using Ni catalyst gives edible fat (margarine and vanaspati ghee)

→ Hydroformylation of olefins gives aldehyde which on reduction produces alcohol.
$CO + H_2 + RCH{=}CH_2 \longrightarrow RCH_2CH_2CHO$

$RCH_2CH_2CHO + H_2 \longrightarrow RCH_2CH_2CH_2OH$
aldehyde                alcohol

* Uses of $H_2$
→ Used in $NH_3$ formation & $NH_3$ is used in making of $HNO_3$ (nitric acid) and nitrogenous fertilizer
→ Used in making vanaspati ghee.
→ making of organic chemicals like methanol
$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{\text{cobalt}} CH_3OH(l)$
→ Preparation of HCl
→ Atomic H & oxy H are used for cutting & welding
→ Rocket fuel & also used in fuel cell for energy generation. It doesn't produce any pollution & release greater energy

## * Hydride.

$H_2$ gas combines with almost all element except noble gas to form Hydride.

→ 3 types

1) Ionic or saline or salt like Hydride
2) Covalent or Molecular Hydride
3) Metallic or Non Stoichiometric Hydride

### 1) Ionic / Saline Hydride

→ Stoichiometric compound of $H_2$ formed with s-Block element

| | |
|---|---|
| $LiH$ | $BeH_2$ |
| $NaH$ | $MgH_2$ |
| $KH$ | $CaH_2$ |
| $RbH$ | $SrH_2$ |
| $CsH$ | $BaH_2$ |

($LiH$, $BeH_2$, $NaH$, $MgH_2$) → Significant covalent character

→ $BeH_2$ & $MgH_2$ → Polymeric nature.

→ ionic hydrides are Crystalline, non volatile, non conducting in solid state. But their melts conduct electricity.

→ on electrolysis it liberates $H_2$ gas at anode.

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

→ It reacts with $H_2O$ to produce gas

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

→ $LiH$ is unreactive at moderate temp so it is used to make other hydride

$$LiH + Al_2Cl_6 \rightarrow LiCl + LiAlH_4$$

$$LiH + B_2H_6 \rightarrow LiBH_4$$

2) Covalent / molecular Hydride.

→ compounds of $H_2$ formed with p Block.

$CH_4$, $NH_3$, $H_2O$, HF etc.

3 types (on the basis of no. of e⁻ in lewis str.)

| 1) e⁻ deficient | 2) e⁻ precise | 3) e⁻ rich. |
| --- | --- | --- |
| Has too few electron for writing conventional lewis structure. | Has required no. of e⁻ to write lewis str. | Have excess e⁻ which are present as lone pair |
| → $B_2H_6$ | → $CH_4$ | $\ddot{N}H_3$ $H_2\ddot{O}:$, $H\ddot{F}:$ |
| → Formed by G-12 elements. | → Formed by G-14 elements. | Formed by G15-G17 elements |
| → acts as lewis acid | → Tetrahedral Geometry | → act as lewis base. |

3) Metallic / non stoichiometric / interstitial.

→ Formed by d & f block elements.

→ G6, G7, G8, G9 do not form hydride except Cr (CrH)

→ It conducts heat & electricity.

→ They are non stiochiometry $LaH_{2.87}$, $YbH_{2.55}$ etc.

→ It is called interstitial hydride because Hydrogen occupies interstices in metal lattice.

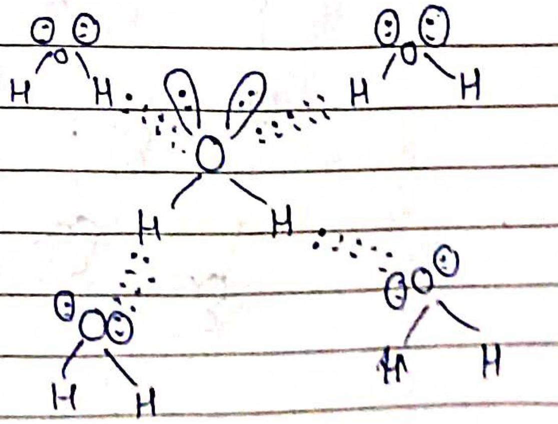
* Water

→ Universal solvent

→ Colorless & tasteless liquid

→ H Bond occurs

→ High freezing point, High Boiling Point, High Heat of Vapourization due to H Bond as compared to $H_2S$ & $H_2Se$

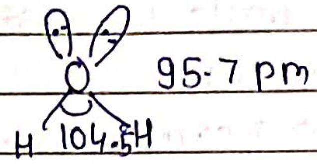


→ As compared to other liq. water have high specific heat, thermal conductivity, surface Tension, dipole moment, dielectric constant.

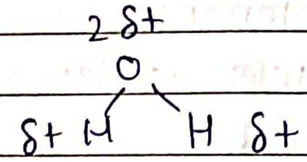
→ Due to H bond with polar molecule covalent comp. like alcohol and carbohydrate dissolve in water

## * Structure of $H_2O$:

→ In gas phase $H_2O$ is a bent molecule



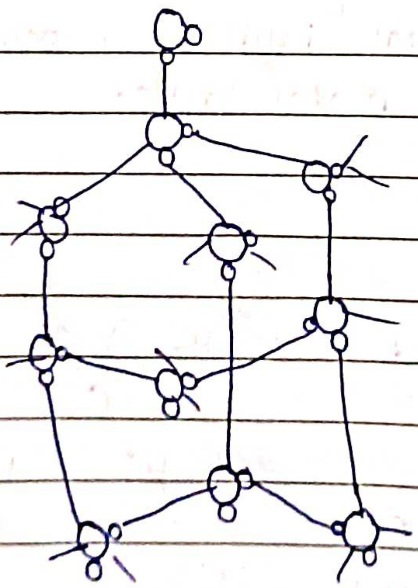

→ It is a polar molecule because it acts like a dipole




→ In liquid phase it shows H bonding.

## * Ice

Crystalline form of $H_2O$ is called ice.



→ Highly Ordered 3 dimensional Hydrogen Bonded Str.

→ Each water molecule forms 4 Hydrogen bond.

→ 2 H Bond → due to H
2 H bond → due to lone pair

→ Each oxygen molecule is surrounded tetrahedrally by 4 other oxygen atom at a distance of 276 pm

→ at atmospheric pressure ice crystallizes in hexagonal form.
→ at very low temp ice condenses to cubic form.
→ open cage like structure.
→ Density of ice is less than $H_2O$ so ice floats on water
→ In winter ice formed on surface of lake provides thermal insulation due to which aquatic life survives

## * Chemical Reaction of $H_2O$.

① Amphoteric nature. → It acts as acid as well as base.

[Acid] $H^+$ donate ← $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

[Base] $H^+$ accept ← $H_2O_{(l)} + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$

$H_2O$ undergoes self ionization (auto protolysis)

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

② Redox Reaction of $H_2O$

Highly electropositive metal reduce $H_2O$ to $H_2$.

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

water is oxidised to $O_2$ during photosynthesis
↓

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

~~with Flo.~~

with Flourine also, $H_2O$ is oxidised to $O_2$

$$F_2(g) + H_2O(l) \longrightarrow HF(aq) + O_2$$

③ Hydrolysis Reaction

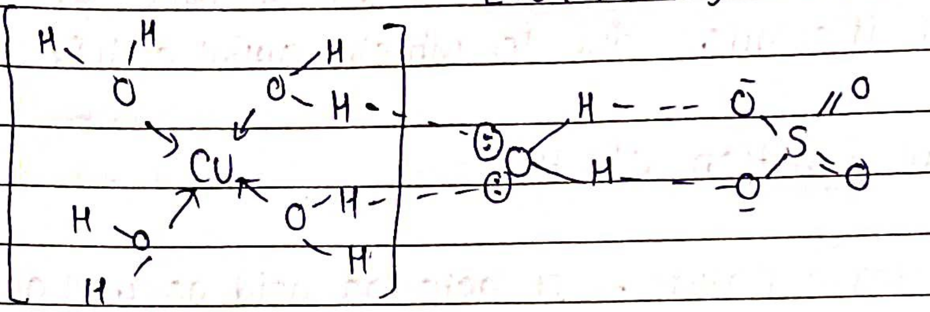
$$\overset{+5}{P_4}O_{10} + H_2O \longrightarrow H_3\overset{+5}{P}O_4$$

$$SiCl_4 + H_2O \longrightarrow SiO_2 + HCl$$

$$N_3^- + 3H_2O \longrightarrow NH_3 + 3OH^-$$

④ Hydrate Formation

1) Cordinate water → $[Cr(H_2O)_6]^{+3}\ 3Cl^-$
2) Interstitial water → $BaCl_2 \cdot 2H_2O$
3) H Bonded Water → $CuSO_4 \cdot 5H_2O$ · Blue vitriol
$[Cu(H_2O)_4]^{+2}\ H_2O\ SO_4^{-2}$




* Hard & Soft Water

→ water becomes hard due to presence of Hydrogen Carbonate (soluble), Chlorine (soluble), Sulphate (soluble) of calcium & Magnesium

→ Hard water doesn't give lather with soap.

→ water free from soluble salt of Ca & Mg is called soft water.

→ Soft water gives lather with soap.

→ Hard water forms scum / precipitate with soap.

→ soap contains large organic molecule ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca & Mg.

$$2\,C_{17}H_{35}COONa + M^{+2}(aq) \longrightarrow \underset{\text{scum / Precipitate}}{(C_{17}H_{35}COO)_2M} + 2Na^+$$

$M = Ca, Mg$

→ Hardness is unsuitable for laundary.

→ Harmful for boiler because of deposition of salt in boiler (Precipitate / Scum)

→ Hardness of water is of two types.
1) Temporary Hardness - presence of Hydrogen carbonate Ca & Mg
2) Parmanent Hardness - Presence of soluble salt of Ca & Mg Chloride & Sulphate

# Temporary Hardness can be Removed in 2 ways

① Boiling - During boiling soluble $Mg(HCO_3)_2$ is converted to insoluble $Mg(OH)_2$ and soluble $Ca(HCO_3)_2$ is converted to insoluble $CaCO_3$
Insoluble $Mg(OH)_2$ and $CaCO_3$ is precipitated.

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

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

soluble → insoluble
"it is precipitated out

② Clark's method - Calculated amount of lime is added to Hard water. insoluble $Mg(OH)_2$ & $CaCO_3$ is precipitate

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

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

soluble → Insoluble

# Removal of Parmanent Hardness → 4 ways
① Treating with washing Soda ($Na_2CO_3$)
② Calgon's method
③ Ion exchange method
④ Synthetic Resin method

① Treatment with washing soda:

$Na_2CO_3$ reacts with soluble Ca & Mg chloride & sulphate in hardwater to form insoluble carbonate

$$MCl_2 + Na_2CO_3 \longrightarrow NaCl + \boxed{MCO_3}$$

$$MSO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + \boxed{MCO_3}$$

soluble M = Mg & Ca Insoluble Precipitate formed

② Calgon's method

$Na_6P_6O_{18}$ Sodium hexa metaphosphate

↳ commercially it is known as calgon

when ~~coto~~ calgon is added to water

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

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

③ Ion exchange method

also called as zeolite / permutit process

zeolite → $NaAlSiO_4$ → NaZ

when zeolite is added in $H_2O$, exchange reaction takes place

$$NaZ + M^{+2} \longrightarrow MZ_2 + 2Na^+ \quad M = Mg \text{ \& } Ca$$

when all sodium is used, then zeolite is said to be exhausted it is further regenerated by treating with aq. NaCl.

$$MZ_2 + NaCl \longrightarrow NaZ + MCl_2$$

④ Synthetic Resin method

→ more efficient than zeolite.

→ It contains large organic molecule with $SO_3H$ group ($R$-$SO_3H$)

→ $RSO_3H$ is converted to RNa by reaction with aq. NaCl.

→ RNa resin exchanges $Na^+$ with $Ca^{+2}$ & $Mg^{+2}$ in hardwater to make it soft water.

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

→ Resin is regenerated by reaction with aq. NaCl

# To obtain pure water (free from all soluble mineral salt)

→ water is successively passed through a cation and anion exchange Resin.

#Cation exchange Resin ($R\overline{SO_3}H$)

$RH + M^{+2} \longrightarrow MR_2 + H^+\,(aq)$

# anion exchange Resin

$R\overset{+}{N}H_3\,\overline{OH} + X^- \rightarrow R\overset{+}{N}H_3\,X^- + OH^-\,(aq)$

$$H^+\,(aq) + OH^-\,(aq) \rightarrow H_2O\,(l)$$

# Some synthetic water is also formed

$H^+ + OH^- \longrightarrow H_2O$

→ Properties

| | $H_2O$ | $D_2O$ |
|---|---|---|
| F.P | 0°C | 3.8°C |
| B.P | 100°C | 101.4°C |
| Density | 0.98° (1) | 1.1 |
| Latent heat of Vapourisation | 536 cal/gm | 557 cal/gm |
| Latent heat of fusion | 80 cal/gm | 75.5 cal/gm |

* Preparation of $H_2O$·

1) Sodium peroxide is treated with ice cold dil· $H_2SO_4$

$$Na_2O_2 + H_2SO_4 \longrightarrow H_2O_2 + Na_2SO_4.$$

2) From hydrated barium peroxide ($BaO_2$) is treated with ice, cold. dil· $H_2SO_4$

$$\underset{\text{Hydrate of Barium peroxide}}{BaO_2 \cdot 8H_2O} + \underset{(dil\cdot)}{H_2SO_4} \longrightarrow \underset{(dil\cdot)}{H_2O_2} + \underset{(PPt)}{BaSO_4} + 8H_2O$$

a) $BaSO_4$ (PPt) is separated by filteration

b) Anhydrous $BaO_2$ is not used for preparation of $H_2O_2$ Because $BaO_2$ reacts with dil· $H_2SO_4$ to form insoluble layer of $BaSO_4$ on its surface and no further chemical reaction

3) By electrolysis of 50%. solution of $H_2SO_4$

$$H_2SO_4 \xrightarrow[\text{electrolysis}]{Pt} H^+ + HSO_4^{\ominus}$$

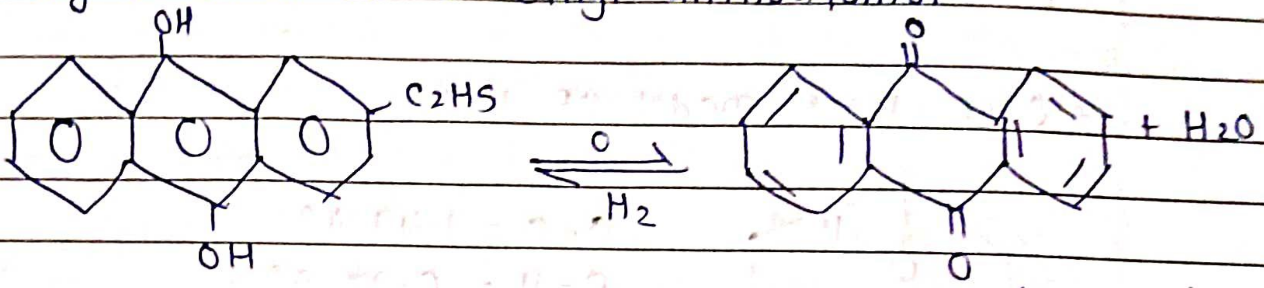
→ Anode (+) : $2HSO_4^- \longrightarrow 2HSO_4 \longrightarrow H_2S_2O_8 + 2e^-$

$$H_2S_2O_8 + 2H_2O \longrightarrow H_2O_2 + 2H_2SO_4$$

→ Cathode (-) : $2H^+ + 2e^- \longrightarrow H_2\uparrow$ gas

# Modern method for preparation of $H_2O_2$:

→ By oxidation of 2-ethyl anthraquinol.




Anthraquinone

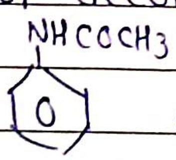
# Physical properties

1) Light blue colour syrupy liquid.
2) B.P → 152°c   M.P − 0.89°c
3) Form intermolecular Hydrogen bonding.
4) Bent polar molecule with dipole moment of 2·1 debye

# Chemical properties

→ Stability − $H_2O_2$ is unstable liquid decompose in water

$$H_2O_2 \longrightarrow H_2O + [O]$$

→ To stop decomposition some amount of $H_3PO_4$, glycerine. Urea,  acetanilide are mixed with $H_2O_2$. It acts as −ve catalyst and stop the decomposition



# Oxidizing properties of $H_2O_2$.

$$H_2O_2 \longrightarrow H_2O + [O]$$

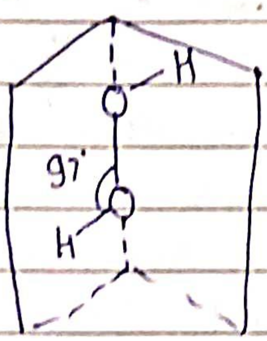
→ It is strong oxidising agent.

i) Turns PbS Black in $PbSO_4$ white

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

Imp - oil paintings made up of Pb. After sometime it reacts with sulphur to form black layer of PbS by treatment of $H_2O_2$ the black layer is removed

→ Open - Book model of $H_2O_2$:




O - O = 1.49 A°
O - H = 0.97 A°
→ It is non polar Bent molecule
→ Dipole moment is 2.1 Debye