

Hydrogen

(3)

- lightest element known
- first element of Periodic Table
- outermost e⁻ configuration is 1s¹
(due to which it is kept with IA metal)
However 'H' matches with halogen as well
in many respect
 - high I.E.
 - formation of H⁺ ion
 - Non-metallic character
 - existence in form of H₂
- Most abundant element in universe
- On earth, it is rare in free dihydrogen (H₂) form due to lower molecular wt.
However in combined form, in earth surface,
in water, in hydrocarbon, organic comp.
& inorganic comp., H present in large amount
 - * Hydrogen is most abundant element in compound.

#

Preparation of H₂

① Lab prep.

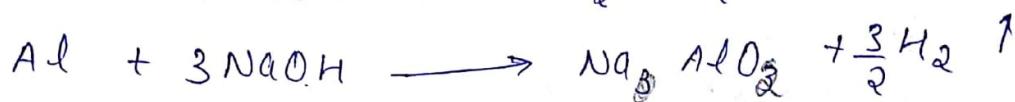
- (i) Active metal + Acid/H₂O → Metal salt/hydroxide + H₂↑
(Metal ≠ Cu, Ag, Au, Hg, Pt etc) → which lie
below Hydrogen in the electrochemical series.

Eg:-



(ii)

By action of amphotetic metal on bases



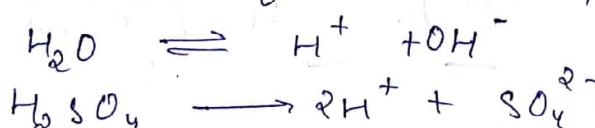
(iii) By action of H_2O on metal hydrides



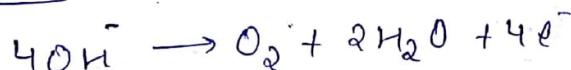
Industrial Prep

(i) By electrolysis of H_2O containing 10 to 20% acid or alkali.

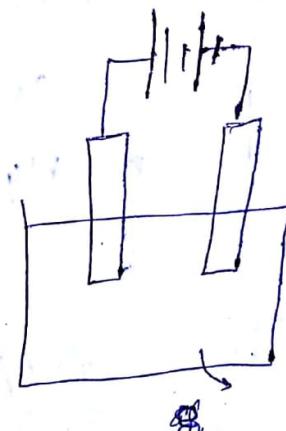
in presence of acid H_2SO_4



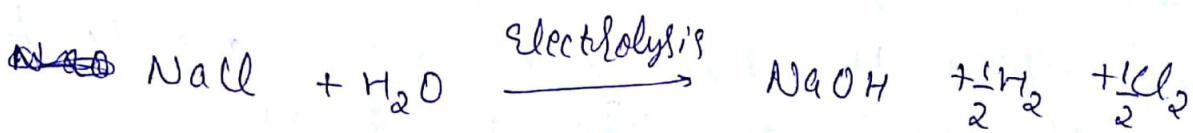
At Anode



At cathode



In prep' of NaOH by electrolysis of Brine (NaCl)

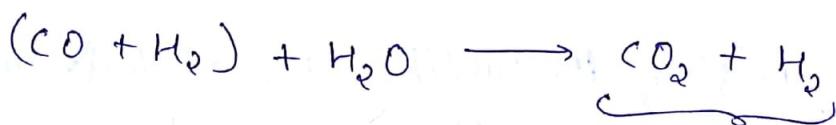


i) from water gas / synthetic gas - 'syngas'

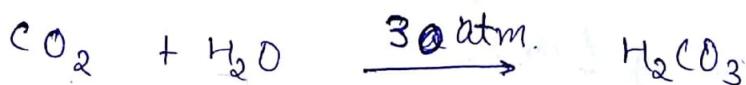
Equimolar mixture of CO & H₂ is called water gas.



Water gas is heated over super-heated steam (180°C) in presence of catalyst like Fe₂O₃ & promoter like Cr₂O₃ at about temp. 400 - 500°C.

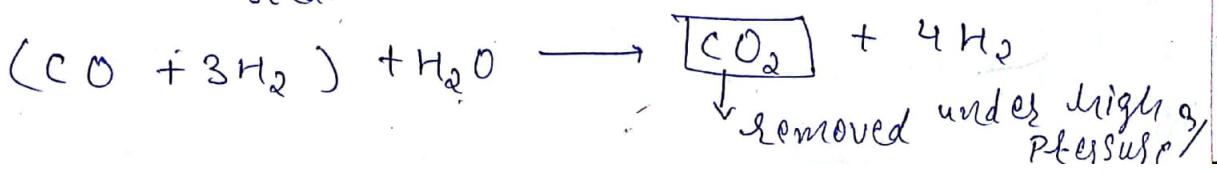
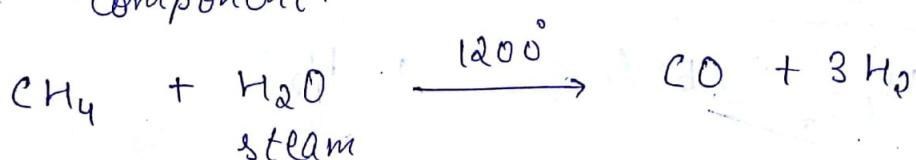


CO₂ can be removed by passing with steam under high pressure.



(iv) from Natural Gas

A mixture of hydrocarbon (mainly CH₄) produced in extraction of petroleum component.

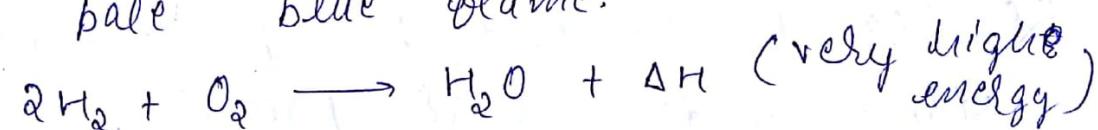


Physical Properties of H₂

- ① Pure H₂ is colourless, odourless gas but impure H₂ has fishy smell due to presence of impurities like PH₃ & AsH₃.
- ② H₂ is lightest gas known.
- ③ H₂ has very low critical temp. & hence it can't be liquified easily. It makes transportation of H₂ tough & uneconomical. So, H₂ is transported in the form of C₂H₂ (Methylhydride)
- ④ H₂ is slightly adsorbed on metal surface like Ni, Pd, Pt.

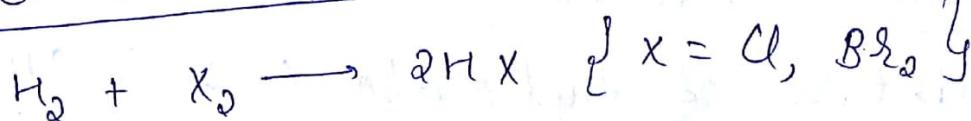
Chemical Properties of Hydrogen

- ① H₂ is highly combustible gas & burns with a pale blue flame.



non-polluting fuel

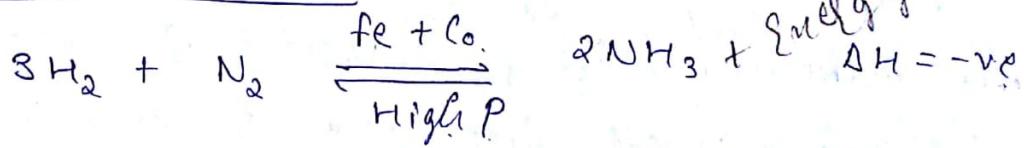
- ② Reacⁿ with X₂



- ③ Reacⁿ with S



Reaⁿ with N₂

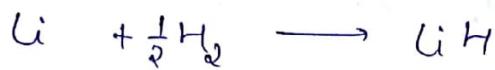


Favorable condⁿ for ^{max} yield of NH₃

- (i) High Pressure
- (ii) Low Temp.

⑤

Reaⁿ with Metal



⑥

H₂ has reducing property & it reduces metal oxide like CuO, SnO, PbO, Fe₂O₃



#

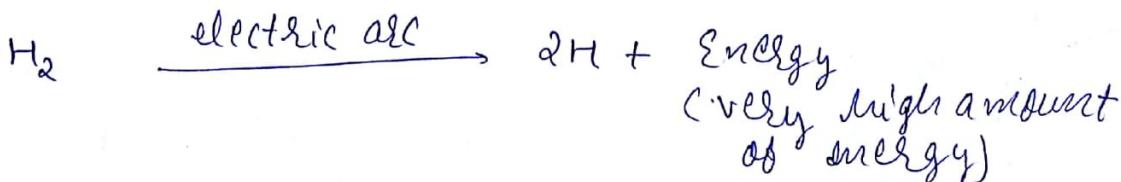
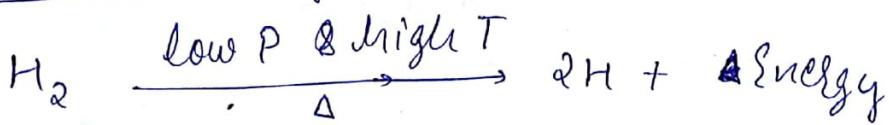
Uses of H₂

- ① In prepⁿ of NH₃, HCl, CH₃OH, Gasoline.
- ② In hydrogenation of vegetable oil.
- ③ An non-polluting fuel
- ④ In metrological purpose.

#

Type of Hydrogen

Atomic Hydrogen

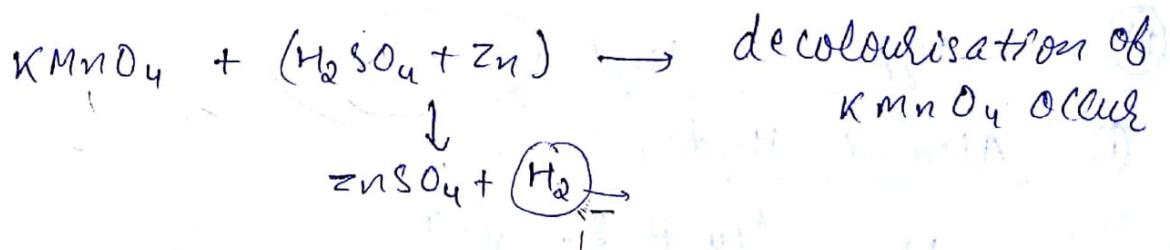
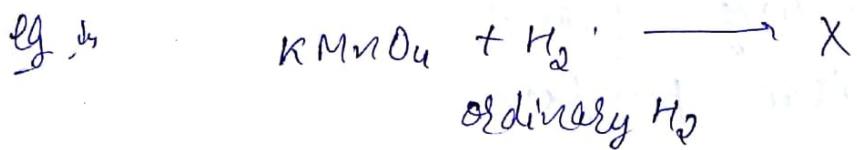


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high amount of energy associates with $H-a$
 \checkmark
 which make it highly energetic & reactive.
 It has very small life time &
 combine
 together to form H_2 producing
 energy so
 high that temp. rises to 4000°C.
 Atomic H combine at metal surface, then
 metal surface glow with intense light.
 It is the principle of atomic hydrogen
 torch.

- * Atomic H combine with all non-metal except N_2 .
- * Atomic H combine with metal to form metal hydrides.

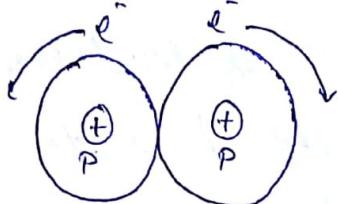
(2) Nascent Hydrogen is Hydrogen at the instant
 of production is called nascent H. It
 is more reactive than ordinary hydrogen.



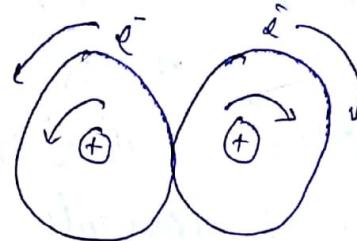
Ortho & Para H₂

H₂ contain 2e⁻ & 2P

e⁻ will spin opp. dirⁿ acc. to pauli exclusion principle



If P moves in same dirⁿ, then it is called ortho H₂.



If P moves in opp. dirⁿ, then it is called para H₂.

At normal condⁿ,

stability ortho H₂ > para H₂



Isotopes of H

There are three isotopes of H

① ^1H (Protium) ; ② ^2H (Deuterium) ; ③ ^3H (Tritium)

No. of P = 1

No. of P = 1

No. of P = 1

No. of n = 0

No. of n = 1

No. of n = 2

% abundance = 99.985%

0.015 %

$10^{-15}\%$

(stable)

(stable)

radioactive

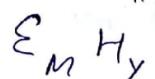
All has electronic conf. is $1s^1$. chemical properties are identical. There is only diff. in rate of reacⁿ because heavier isotopes form slightly stronger bond.

Compounds of Hydrogen

Hydrides \rightarrow Hydrogen has ability to combine with almost all elements at diff. pressure & temps. except noble gas.

Binary compounds of hydrogen with other elements are called hydrides

General formula \rightarrow ~~E~~ EH_x



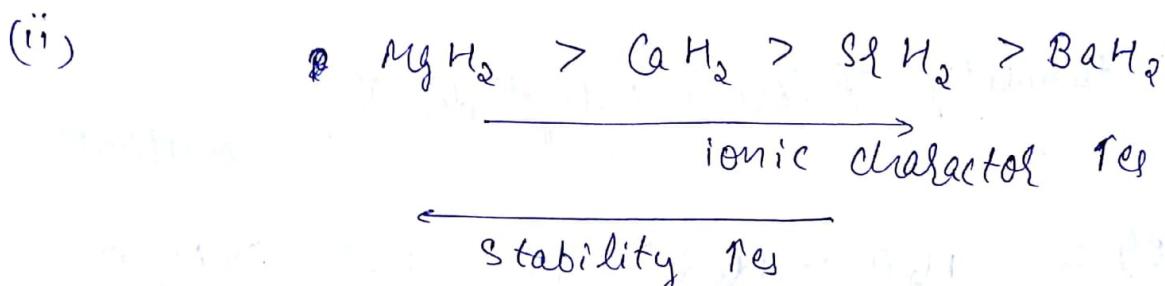
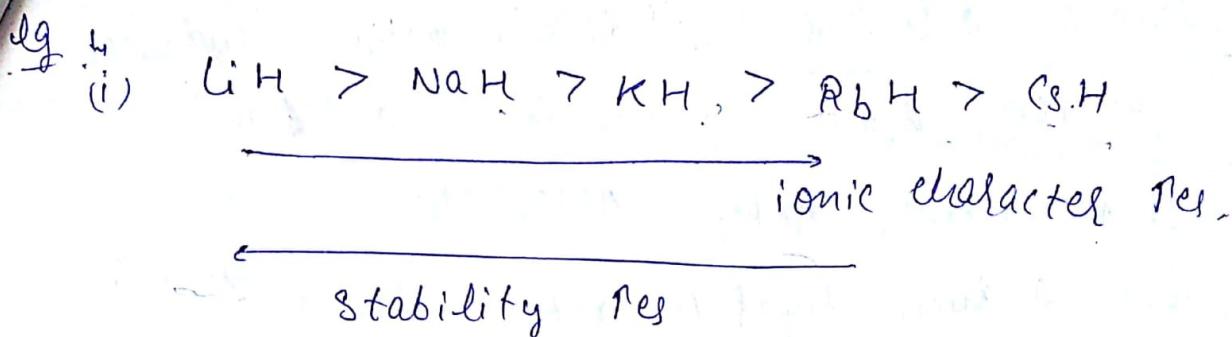
There are three types of hydrides

- ① Ionic Hydrides / Saline (salt like) Hydrides
- ② Covalent Hydrides
- ③ Interstitial Hydrides / Non-stoichiometric Hydrides

① Ionic Hydrides \rightarrow

- * formed by most electropositive elements (IA & IIA metals) except Mg, Be
- * These are stoichiometric compds. in which hydrogen is present in the form of H⁻.
- * The presence of H⁻ is indicated by evolution of H₂ gas at anode through oxidation.
- * Such hydrides are ionic solid & hence they are non-conductors in solid state. However, in molten state or in aq. solⁿ they are conductors due to presence of free ion.

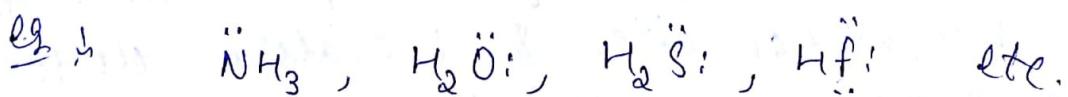
Stability of Hydrides $\propto \frac{1}{\text{size of cation}}$



② Covalent Hydrides

- * Such Hydrides are formed by metals & non-metals of P-block with Be & Mg.
- * They are stoichiometric compound & H is attached to element through covalent bond.
- * There are three type of covalent hydrides

① (i) Electron-rich Hydrides : that hydride which contain lone pair of eg.



These are also known as Lewis base.

(ii) Electron-sufficient Hydrides : the hydrides in which all atoms have completed their octet. ~~steplet~~

e.g. CH_4 , C_2H_4 , C_2H_6 etc.

more
to

(iii). Electron deficient Hydrides in more hydrides which have incomplete octet.

e.g. BH_3 , BeH_2 , AlH_3 etc

{ Such hydrides act as Lewis acid }

④ Stability of covalent hydrides $\propto \frac{1}{\text{size of atom}}$

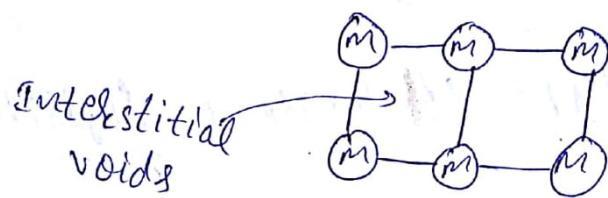
e.g. $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te} > \text{H}_2\text{Po}$

$\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

⑤ Interstitial hydrides

* formed by D & f-block metals

⑥ Metal \rightarrow Lattice



→ H due to its small size occupies some of the interstitial sites & therefore these are known as interstitial hydrides

→ These hydrides are always non-stoichiometric i.e. they will have variable composition e.g. $\text{TiH}_{1.5-1.8}$, $\text{ZrH}_{1.3-1.75}$

non-stoichiometric hydrides

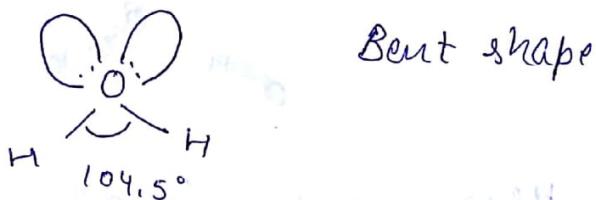
These hydrides exhibit properties similar to metal. So, they are also called metallic hydrides.

Note 2: Among d-block metals, metals of group 7, 8 & 9 do not form hydrides & this is known as 'Hydride Gap'

#

Water (H_2O)

- water is covalent hydride of great importance
- structure of H_2O

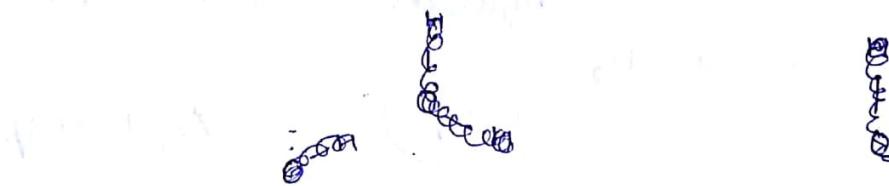


- Capable of H-bonding, have ~~at~~ high dielectric const.
- water is good solvent for ionic compds.
i.e. water is a universal solvent.
- Ionic compds. are soluble if $(\Delta H_{\text{hyd}}) >$ lattice energy of ionic solid
- Covalent compds. like ~~alcohols~~ alcohols are soluble in H_2O due to H-bond formation.

* H_2O has f.p. = 0°C , b.p. = 100°C

$$\rightarrow d_{\text{ice}} < d_{\text{H}_2\text{O}(\ell)}$$

Reason: \rightarrow Ice has a cage like hexagonal lattice (at normal condⁿ) in which each H_2O molecule is attached to 4 other H_2O molecule through H-bond. The cage like stf. of ice is responsible for its low density.

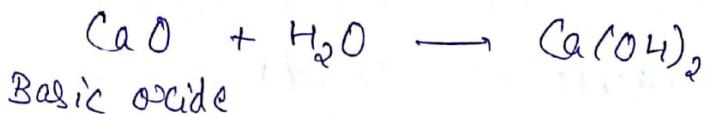
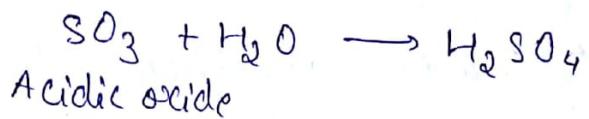


Heavy water (D_2O)

- All characteristics are almost same.
- All physical properties of D_2O (except dielectric const.) is higher than those of H_2O .
- Chemical properties are similar. However due to stronger D-O bond than H-O bond, rate of reacⁿ differ. Such effect in rate due to difference in isotopic mass is called isotopic effect.
- $\overset{m}{\text{D}_2\text{O}}$ is harmful for small organism, however for human being, it is not harmful at all.
- D_2O is used as moderator (to slowdown the neutron) in nuclear reactor.

Chemical properties of H_2O

Water is amphoteric in nature & hence it reacts with both acid & base



(2) Water also acts as oxidising as well as reducing agent.

e.g.



(3)

Hydrolysis of salts



(4) Hydrates formation

H_2O attach itself to ionic solid & form hydrates

e.g. $CuSO_4 \cdot 5H_2O$, $MgCl_2 \cdot 6H_2O$, $Na_2CO_3 \cdot 10H_2O$

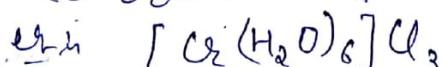
The H_2O present in hydrates are called water of crystallisation.

Hydrates



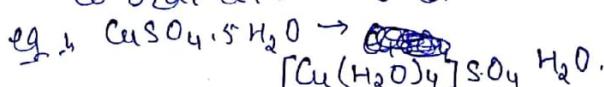
Cationic Hydrates

Water is attached to cation through co-ordinate bond



Anionic Hydrates

Water is attached to anion through H-bond & to cation through co-ordinate bond



Lattice Hydrates

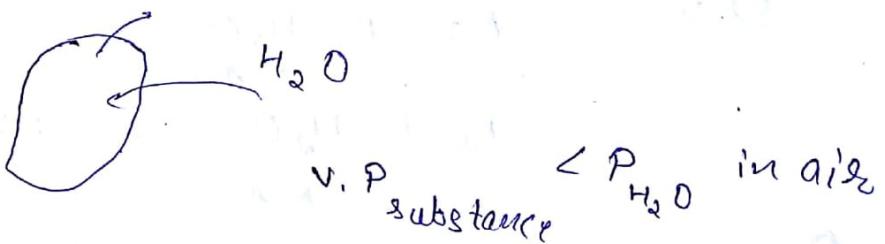
H_2O is present in interstitial space making the crystal stable

(#) Water absorber / releaser

* Some ionic solid absorbs H_2O from atmosphere. Such ionic solids are called hygroscopic solid. If the water absorption occurs to greater extent, then such solids are called deliquescent solids.

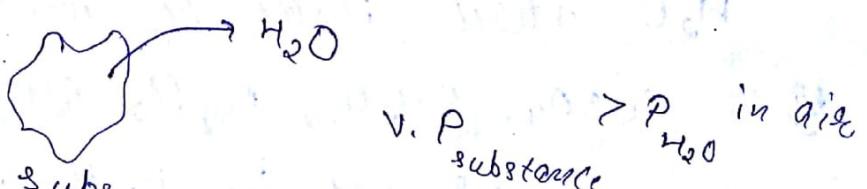
Eg. $NaCl$, $MgCl_2$

~~Def~~ Deliquescent occurs when



* Some ionic solid releases H_2O to atmosphere. Such ionic solids are called efflorescent material.

Efflorescent occurs when

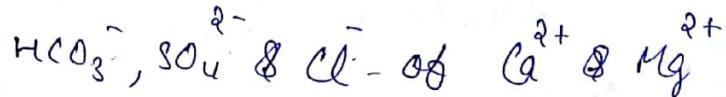


Hard water & soft water

Hard water is that sample of H_2O which doesn't give lather easily with soaps or detergent. Hence, hard water can't be used for laundry purpose.

* Hardness of water

is due to



Hardness

Temporary hardness

presence of HCO_3^- of Ca^{2+} & Mg^{2+} causes temporary hardness.

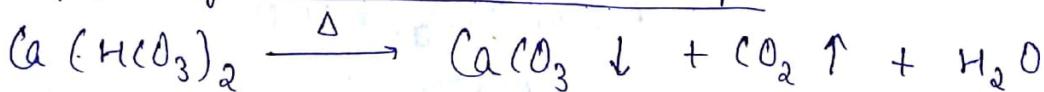
Permanent hardness

presence of Cl^- & SO_4^{2-} of Ca^{2+} & Mg^{2+} cause permanent hardness.

⇒ Removal of hardness of H_2O

① Temporary hardness is removed by

(i) Boiling the water sample

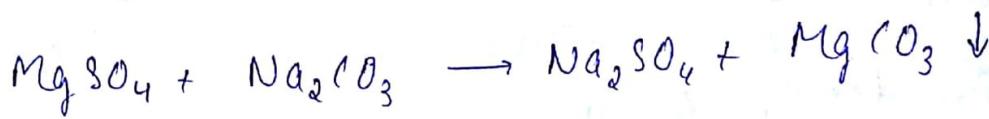
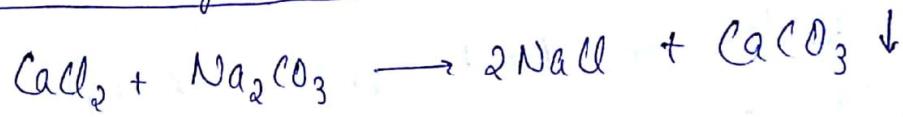


(ii) By reacting with CaO or $Ca(OH)_2$



② Permanent hardness is removed by following methods

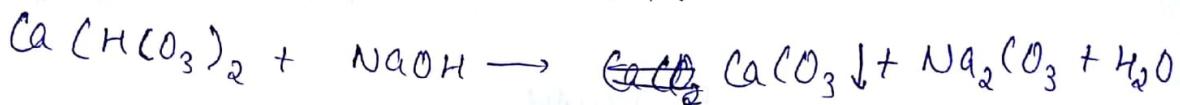
(i) By reacting with Na_2CO_3



BUT

and

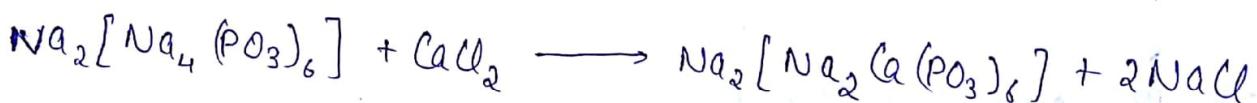
(ii) If both permanent & temporary hardness are present, then hardness is removed by heating with NaOH .



(iii) Calogen Method

Sodium hexametaphosphate: $\text{Na}_6\text{P}_6\text{O}_{18}$

$\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$



(iv) Zeolite Method (Permutit Process)

zeolite: sodium aluminium orthosilicate

$\text{NaAlSi}_3\text{O}_8 \cdot x\text{H}_2\text{O}$

NaZe



* Note: CaZe_2 can be converted back into NaZe

by treating with NaCl as



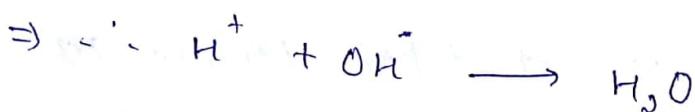
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By passing water through ion-exchange resin in

hard water — (cation exchange resin) — (Anion exchange resin)
* insoluble organic molecule
containing COO^- & SO_3^{2-}
group replaces Na^+ , Ca^{2+} ,
 Mg^{2+} by H^+
* insoluble org. molecule
containing $-\text{NH}_2$, $-\text{OH}$
group

- * After passing through cation exchange resin, water sample becomes acidic

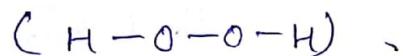
In anion exchange resin, anions like SO_4^{2-} , Cl^- , HCO_3^- are replaced by OH^- ion



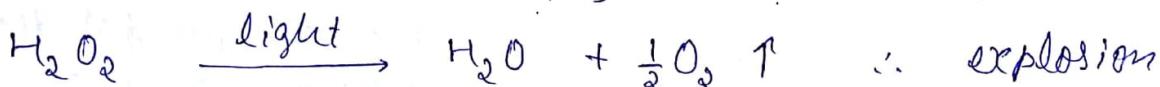
So, such sample of water is free from all cation & anion called demineralized water.

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H_2O_2 (Hydrogen peroxide)

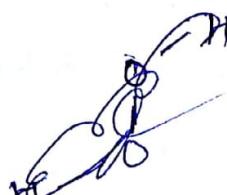


Due to peroxide bond, H_2O_2 is very unstable.



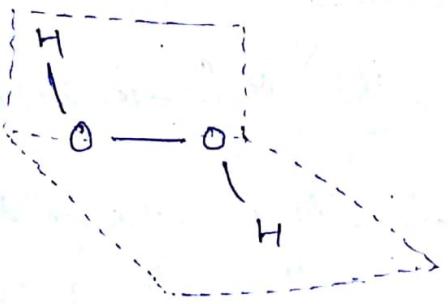
So, H_2O_2 (ℓ) is stored in dark coloured wax lined bottle to cut off the light & remove rough surface. Also small amount of glycerine, acetanilide is also added which act as anti-catalyst for decomposition.

- * Structure of H_2O_2



3D structure

17

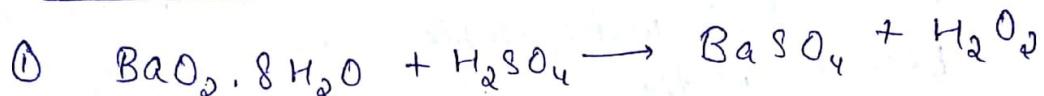


(3D structure
open-book structure)

(in gaseous & solid form)

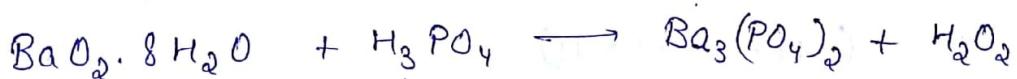
Prep. of H_2O_2

Lab prep.

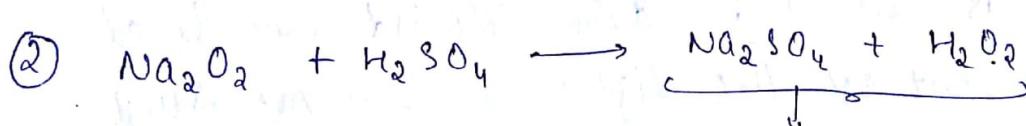


Note (i) Anhydrous BaO_2 is not taken because ~~as~~ protective coating of $BaSO_4$ deposit on BaO_2 , which prevent further sol^n .

(ii) H_2SO_4 act as catalyst for decomposition of H_2O_2 . So, H_3PO_4 is preferred over H_2SO_4 .



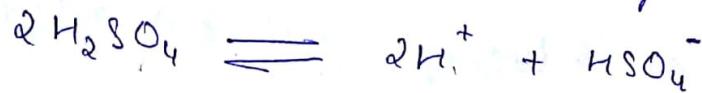
H_3PO_4 act as anti-catalyst for decomposition of H_2O_2



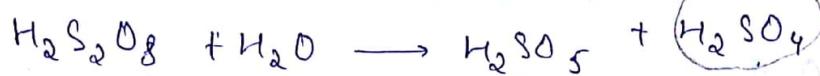
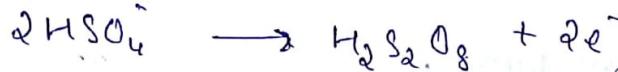
Always contain Na_2SO_4 as impurity & so each sample of H_2O_2 is used for bleaching purpose.

Industrial preparation

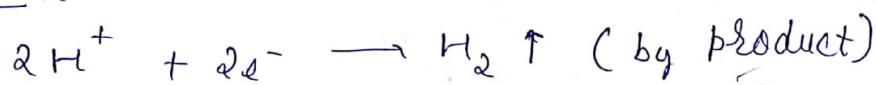
① By electrolysis of H_2SO_4 ~~using light~~



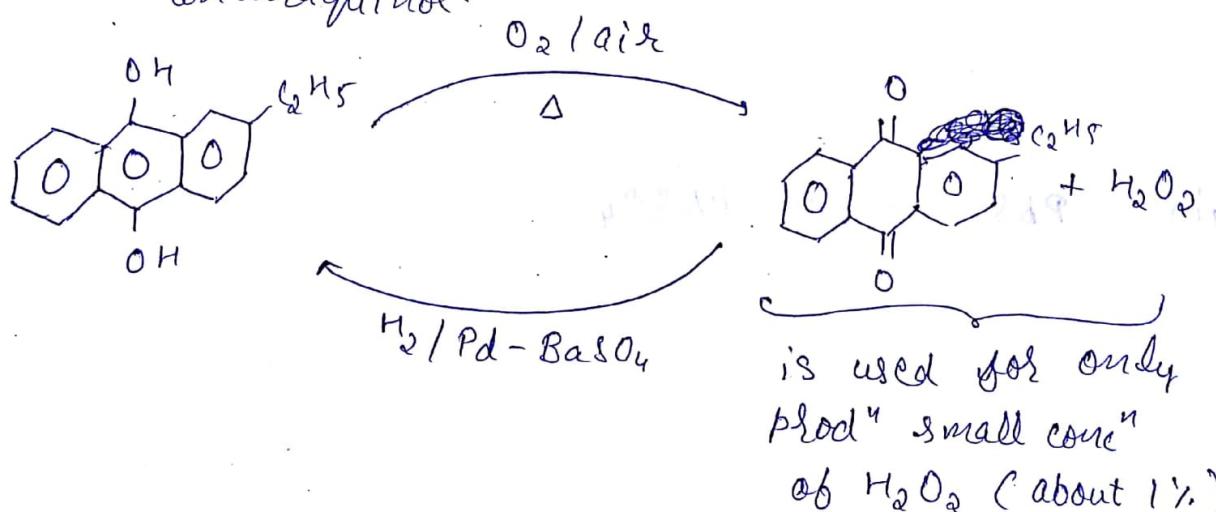
At anode ↗



At cathode ↗



② By cyclic oxidation-reduction of 2-ethyl anthraquinol.



Physical Properties

- ① It is pale blue oily liquid.
- ② It is a good polar solvent due to high dielectric ~~const.~~ const.
- ③ Extent of H-bonding in H_2O_2 is greater than ~~that~~ that in H_2O .

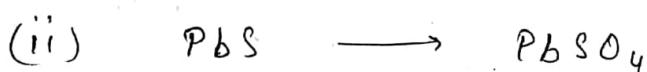
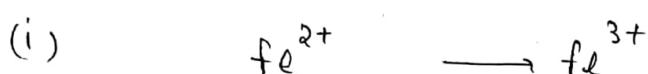
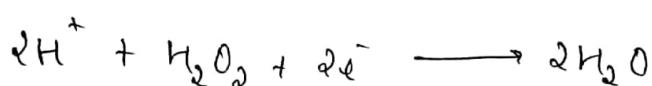
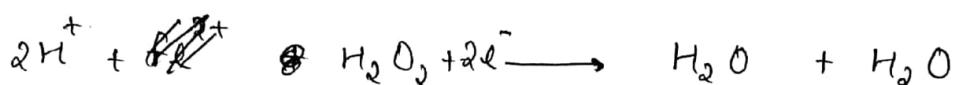
Chemical Properties

In H_2O_2 , O is in -1 ^{odd} state.

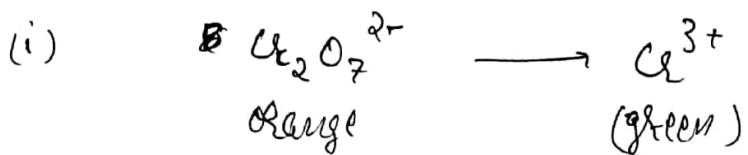
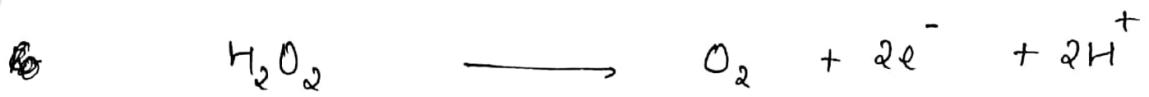
So, it acts as reducing agent & oxidising agent both in acidic & basic medium.

① In acidic medium,

As O.A

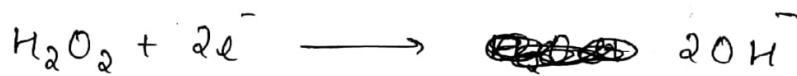


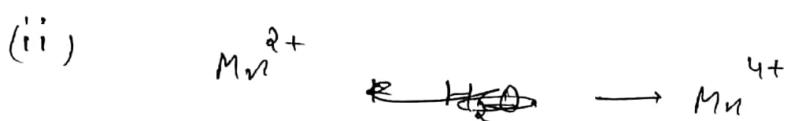
Reducing agent,



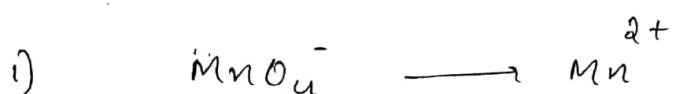
② In basic medium,

AB O.A

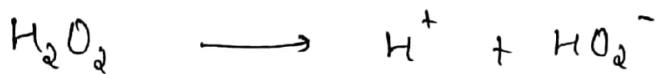




A8 R.A



Acidic character of H_2O_2



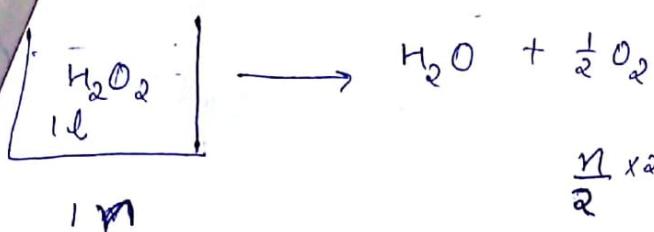
→ H_2O_2 has bleaching property & is due to oxidation of H_2O_2 & hence bleaching by H_2O_2 is permanent.

Uses of H_2O_2

- ① As bleaching agent for wool, clothes.
- ② As antiseptic under the name of perhydrol.
- ③ To restore old dead painting.

④

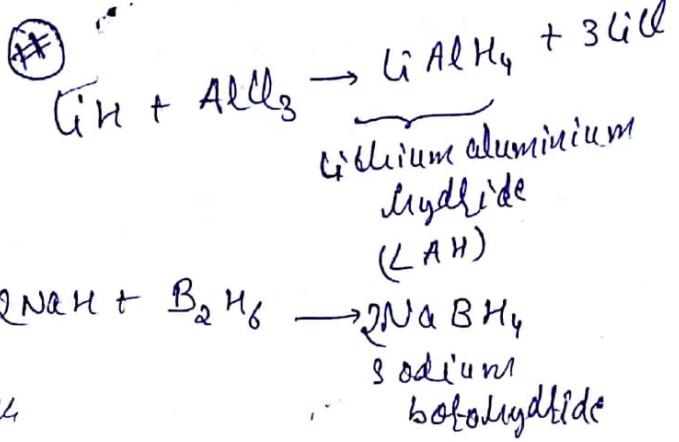
volume strength of H_2O_2



$$\frac{n \times 22.4}{2}$$

$$11.2 \times M = \text{volume strength}$$

$$M = \frac{\text{volume strength}}{11.2}$$



$11.2 \times \frac{N}{2} = \text{volume strength}$

$$N = \frac{\text{volume strength}}{5.6}$$

Problem

$$N = \frac{20}{5.6}$$

Cal. the normality of 20 volume hydrogen peroxide soln.

Soln $3.5 = N$

find the vol. strength of 1.6 N H_2O_2 soln.

Soln $N = \frac{\text{volume strength}}{5.6}$

=

8.96 ✓

Q Why I.E of hydrogen lies in the range of halogen?

Solⁿ Hydrogen is non-metallic like halogen. They both have tendency to accept one electron to form a⁻ ion. So, I.E of hydrogen lie in the range of halogen.

Q Explain, why H₂ is not produced from action of metal on H₂SO₄ or HNO₃?

Solⁿ H₂SO₄ & HNO₃ are acid as well as oxidising agent. So, when metals are reacted with H₂SO₄ or HNO₃, metal oxides are formed which form a protective layer on metal. It avoids further reacⁿ with metal.

Q Why for getting pure H₂, Ba(OH)₂ solⁿ of H₂O is preferred over NaOH solⁿ?

Solⁿ In most of the hydroxide are contaminated with metal carbonate by absorption of CO₂ from air. However, Ba(OH)₂ solⁿ is free from its carbonate because BaCO₃ is insoluble in water.

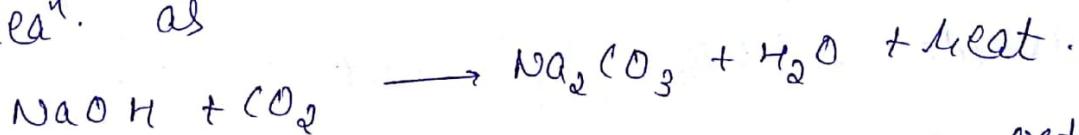
Q How do you expect the metallic hydrides to be useful for H₂ storage? Ans

Solⁿ There are some metals, Pt, Pd, Ni adsorbs very high volume of H₂ gas in finely

divided state. H_2 from these metals can be easily obtained by heating, which is used in reduction; these metals are used for combustion purpose. So, these metals are used for H_2 -storage & it is called 'Hydrogen Economy'.

- ⑤ why the fire produced in H_2 production from saline hydrides with water is not extinguished by CO_2 ?

Solⁿ $NaH + H_2O \rightarrow NaOH + H_2 \uparrow + \text{heat}$
the heat produced in above H_2 production can't be extinguished by CO_2 because $NaOH$ reacts with CO_2 which is also an exothermic reacⁿ. as

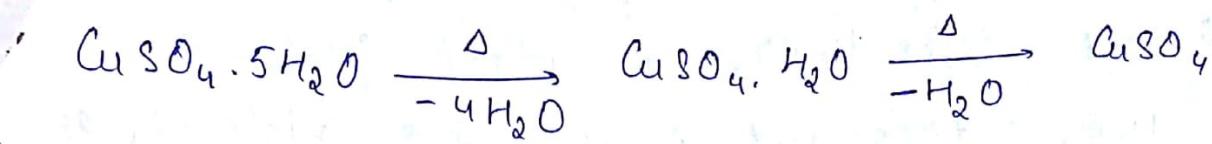


In this case, sand particles are used to extinguish the fire.

- ⑥ why only 4 H_2O molecules are removed initially when $CuSO_4 \cdot 5H_2O$ is dehydrated?

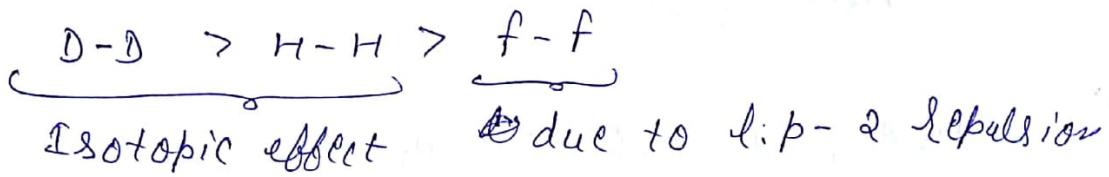
Solⁿ is $CuSO_4 \cdot 5H_2O$ is an anionic hydrate & in which 4 H_2O molecules are attached to Cu^{2+} ion through weak co-ordinated bond ~~part~~, & 1 H_2O molecule is attached to SO_4^{2-} ion through H-bond.

MCE,



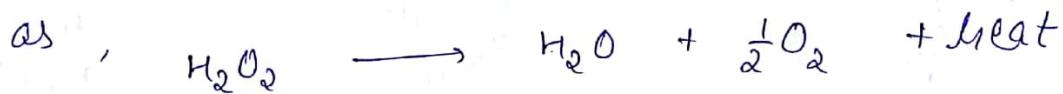
- (7) Arrange the bond F-F, H-H & D-D in increasing order of bond strength.

Solⁿ



- (8) Why should a bottle of H_2O_2 be cooled before opening?

Solⁿ H_2O_2 kept in a bottle is partially dissociated as



To avoid this dissociation & heat produced, it is first cooled before opening.

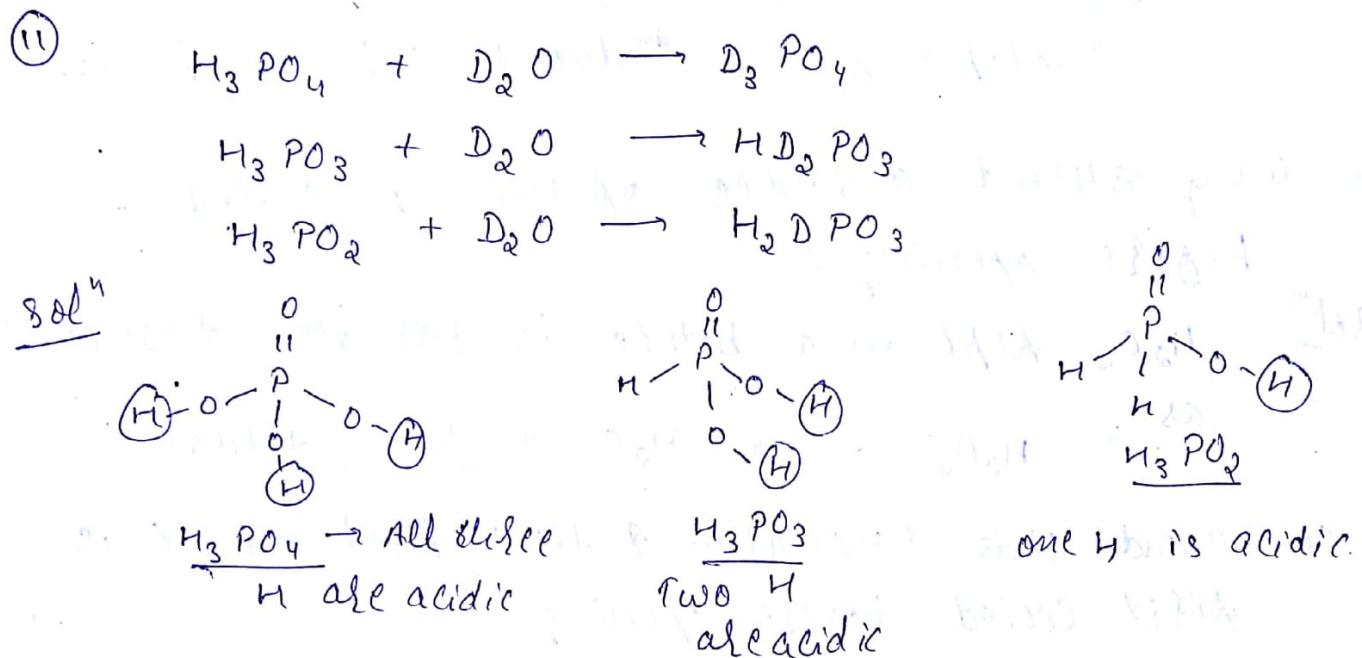
- (9) What do you expect the nature of hydrides if formed by elements of atomic number 15, 19, 23 & 44 with dihydrogen?

Solⁿ

At. No.	Nature of element	Type of hydrides
15	P (non-metal)	covalent hydrides
19	K (metal)	Ionic hydrides
23	V (transition metal)	Metallic hydrides
44	.	.

(10) In the preparation of H_2O_2 , temp. is kept low & acid like H_3PO_4 is added. Explain?

Solⁿ H_2O_2 dissociates in H_2O & O_2 violently at high temp. So, temp. is kept low & anti-catalyst like H_3PO_4 is added to H_2O_2 soln.



(12) Is rain water, distilled water, demineralised water good for drinking?

Solⁿ No, because these water samples don't contain the ions which are important for human body.

(13) Which one is good bleaching agent? H_2O_2 or Cl_2 ?

Solⁿ H_2O_2 is better bleaching agent than Cl_2 , because H_2O_2 is not a pollutant whereas Cl_2 is a pollutant.