INTRODUCTION

Hydrogen is a lightest gas and lightest element of periodic table and it contain 1e, 1p and zero neutron.

- Hydrogen is called hydrogen because maximum quantity of Hydrogen is used in preparation of H_2O.

Method of Preparation of H_2

(a) By acids : The metals which are placed above H in electrochemical series react with dil. acids like HCl or H_2SO_4 to liberate H_2.

Ex. $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
(dil)

$Cu + H_2SO_4 \rightarrow \times$ (No reaction)

Note: Mn and Mg react with dil. HNO_3 and evolves H_2. HNO_3 is not commonly used ,as being good oxidising agent, it forms an oxide layer on the surface of metal.

Lab preparation – When impure Zn reacts with dil. H_2SO_4 it forms H_2

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
(impure) (dil)

$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + H_2$ no reaction as HNO_3 reduces

(b) By alkalies : Only (Be, Zn, Si, Al, Sn, Pb) Amphoteric metals react with boiling NaOH or KOH to evolve H_2.

$M + 2NaOH \rightarrow salt + H_2\uparrow$

Na_2MO_2

M = Zn, Sn, Pb

$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

(c) From water : All the metals which are placed above H when react with water to evolves H_2.

$Zn + H_2O \longrightarrow ZnO + H_2\uparrow$

Three type of water can be used:

(i) ***Cold water :*** Cold water (7 to 25°C) is used for highly reactive metals.

Such as Li, K, Ba, Sr, Ca, Na, means alkali metals or alkaline earth metals.

The reaction with alkali metals are vigorous.

To minimise the rate of reaction these metals are used in the form of amalgam.

$2Na(Hg) + H_2O \longrightarrow 2NaOH + H_2\uparrow$

(ii) ***Hot water :*** Hot water (25°C to 90°C) is used for moderate reactive metals, such as Mg, Al, Mn, Zn, Cr.

Ex. $Mg + H_2O \xrightarrow{Boil} MgO + H_2$

(iii) ***Steam :*** The steam (>100°C) is used for very less reactive metals like Fe, Cd, Co, Ni, Sn, Pb.

Ex. $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2\uparrow$

(iv) ***From Ionic hydride :*** Whenever ionic hydride reacts with water they form H_2.

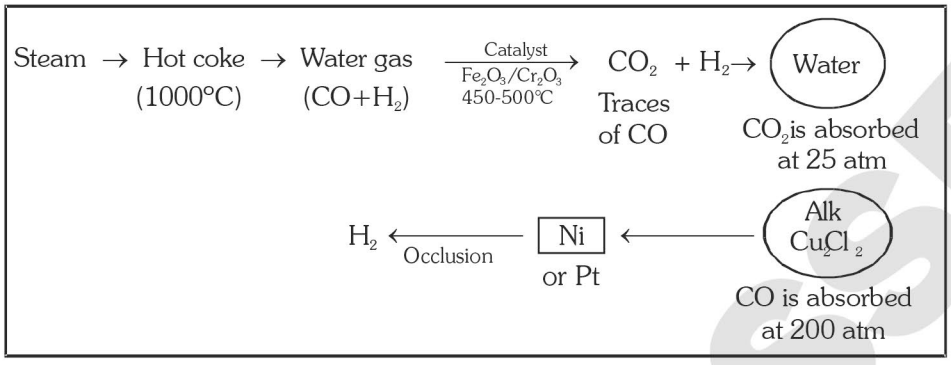
$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2$
(Hydrolith)

(d) Commercial or industrial method to prepare H_2

(i) ***Lane's process :*** In this process, steam is passed over hot iron.

$$\underset{\text{Hot}}{3Fe} + \underset{\text{Steam}}{4H_2O} \longrightarrow \underset{\text{Magnetic oxide}}{Fe_3O_4} + 4H_2\uparrow \; ; \quad \Delta H = -160.7 \text{ kJ}$$

(ii) ***Bosch's process :*** The maximum quantity of commercial hydrogen is obtained by the use of this method.



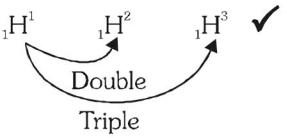
1. Formation of water gas from Coke is known as coal gasolification.
2. Seperation of H_2 from water gas is known as water gas shift reaction $(CO + H_2) + H_2O \rightarrow CO_2 + H_2$

(iii) ***From Natural gas :*** $C_nH_{2n+2} + nH_2O \xrightarrow{Ni/1000°C} nCO + (2n+1)H_2$ [Steam reforming process]

ISOTOPIC EFFECT

- Effect which can change physical & chemical properties of isotopes is called isotopic effect.
- Isotopic effect is found only in Hydrogen isotope because maximum mass number difference present in hydrogen isotopes.

$_7N^{14}$, $_7N^{15}$ ✗ $\qquad$ $_8O^{16}$, $_8O^{17}$, $_8O^{18}$ ✗



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Note : Application of isotopes is not isotopic effect (Except H)

(i) Co_{60} in cancer treatment.

(ii) Iodine in thyroid gland treatment.

Example of isotopic effect :

(i) $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (fast)

(ii) $CD_4 + Cl_2 \rightarrow CD_3Cl + DCl$ (slow)

Bond energy of C–D > C–H

$$\text{Bond energy} \propto \frac{1}{\text{Rate of reaction}}$$

POSITION OF HYDROGEN IN PERIODIC TABLE

Position of H is not fixed in Periodic Table because properties of hydrogen are similar with different groups i.e. IA, VIIA etc. so it is considered as ***rogue element*** of periodic table.

HYDRIDES

Compounds of hydrogen are known as hydrides

Types :

1. Ionic hydrides : Hydrides of s-block elements (in these hydrides oxidation number of H is –1).

$\overset{+}{N}a\overset{-}{H}$ $\quad$ $\overset{+}{K}\overset{-}{H}$

CaH_2 = Hydrolith

$2NaH \xrightarrow{2H_2O} 2NaOH + 3H_2$

2. *Covalent or molecular hydrides :-*

Hydrides of p-block elements are covalent hydrides

(a) Electron deficient : having less than $8e^-$ at central atom

BCl_3, $AlCl_3$, $GaCl_3$

(b) Electron rich : $\ddot{N}H_3$ $H_2\ddot{O}$ $R-\ddot{O}-H$ $R-\ddot{N}H_2$

having $8e^-$ and at least $1\ell p$ at central atom

(c) Electron precise : Having $8e^-$ at central atom and $\ell p = 0$ CH_4 SiH_4 GeH_4

These are bad conducter of electricity.

3. *Metallic or interstitial hydrides :-*

Hydrides of d and f-block elements are known as metallic or intertitial hydrides there are not stoichiometric hydrides and do not obey law of constant proportion.

Ex. $ZrH_{x(1.3-1.75)}$ $TiH_{x(1.3-1.5)}$

- Their conductivity is similar to metals.
- ***Reactivity of reducing property :***

Simple atomic hydrogen > Nascent hydrogen > Adsorbed hydrogen (occluded hydrogen) >Molecular hydrogen

Water

Hard and Soft Water

Water from rivers, springs or even from wells contains a certain amount of dissolved mineral substances. Water containing soluble calcium and magnesium salts such as bicarbonates, chlorides, sulphates is termed ***hard water*** and if these salts are absent, the water is called ***soft water***.

Hard water is one which does not easily lathers with soap (Na or K salts of higher fatty acids). This is due to the formation of precipitate of Ca or Mg stearate while a sample of water which lathers easily with soap is called soft water.

$$\underset{\text{present in hard water}}{CaCl_2} + \underset{\text{sodium stearate (soap)}}{2C_{17}H_{35}COONa} \longrightarrow \underset{\text{Calcium Stearate}}{Ca(C_{17}H_{35}COO)_2}\downarrow + 2NaCl$$

Types of Hardness

Temporary Hardness : Due to presence of Ca and Mg bicarbonate like $Ca(HCO_3)_2$, $Mg(HCO_3)_2$

Permanent Hardness : Due to presence of Ca and Mg Chlorides and Sulphates like $CaCl_2$, $MgSO_4$ etc.

Removing Hardness from Water [Water Softening]

(1) Methods for Removal of temporary Hardness :

(i) ***By Boiling***

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} CaCO_3\downarrow + CO_2 + H_2O$$

(ii) ***By Clark's process*** [Using $Ca(OH)_2$]

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

$$\underset{\text{(quick lime)}}{CaO\ (s)} + H_2O \longrightarrow \underset{\text{(Slaked lime)}}{Ca(OH)_2}$$

Note : Here $Ca(OH)_2$ can not used in excess quantity because $Ca(OH)_2$ by absorbing CO_2 further leads to the formation of $Ca(HCO_3)_2$.

(2) *Methods for Removal of Permanent Hardness and temporary hardness also removed.*

(i) ***By Na_2CO_3*** (washing soda)

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

(3) *Method for Both Temporary and Permanent Hardness :*

(a) ***Lime and soda process :*** In this process both $Ca(OH)_2$ and Na_2CO_3 are added together to hard water.

(b) ***By Ion exchange process :***

(i) Inorganic process (ii) Organic process (iii) Calgon process

(i) ***Inorganic process :***

$$Na_2Z + CaCl_2 \rightarrow CaZ + 2NaCl$$

(ii) ***Organic Process :*** In organic process, always organic substance is used like.

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

The water obtained so is free from all type of ions and known as deionised water.

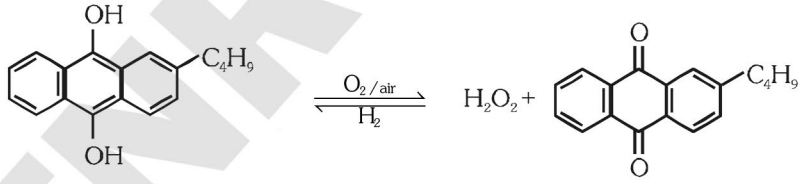
(iii) ***Calgon Process*** : Calgon is the trade name of sodium hexameta-phosphate, $Na_2(Na_4(PO_3)_6]$.

GOLDEN KEY POINTS

- Hard water is not always harmful for drinking purposes. However it is disadvantageous in the laundry work.
- Ethylene diaminetetraacetic acid (EDTA) is a versatile complexing agent hence it can remove hardness of water by forming stable complexes with metal ions. It is also used for estimating the hardness of water, volumetrically.

H_2O_2 (HYDROGEN PEROXIDE)

(a) Thenard discovered H_2O_2 and named it as oxygenated water.



2-butyl anthraquinol

(b) ***Electrolytic Process :*** Used 50% H_2SO_4 in electrolytic cell using Pt as anode and graphite as cathode.

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^{\ominus}$$

At Cathode $2H^+ + 2e^- \longrightarrow H_2 \uparrow$

At Anode $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

Peroxo disulphuric acid

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

- Now a days 50% $(NH_4)_2SO_4$ with 50% H_2SO_4 is used.

(c) ***By action of H_2SO_4 over Barium peroxide–***

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

Chemical Property

(i) It is unstable in nature, decompose on standing and heating. It is an example of auto oxidation-reduction Reaction ; $H_2O_2 \rightarrow H_2O + O$

(ii) Decomposition of H_2O_2 ; $2H_2O_2 \rightleftharpoons 2H_2O + O_2$

- This is retarded by R–OH, acetanilide, glycerol and accelerated by ***Pt, Au, Ag, MnO_2***.

(iii) Acidic nature:

Pure H_2O_2 is weak dibasic acid, it turns blue litmus to red but aqueous solution of H_2O_2 is neutral towards litmus paper.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$HO_2^- \rightleftharpoons H^+ + O_2^{-2}$$

(iv) Oxidizing nature:

It is more powerful oxidant in acidic medium than in alkaline medium.

In acidic medium $H_2O_2 + 2H^+ + 2e^- \xrightarrow{\text{Fast}} 2H_2O$; $E^0_{RP} = +1.77V$

In alkali medium $H_2O + OH^- + 2e^- \xrightarrow{\text{Slow}} 3OH^-$; $E^0_{RP} = +0.87V$

(v) Reducing nature:

It is better reductant in basic medium than in acidic medium.

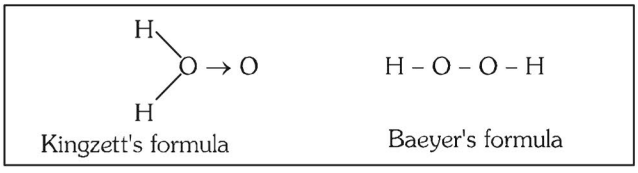
$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^- \quad \text{(in acid)}$$

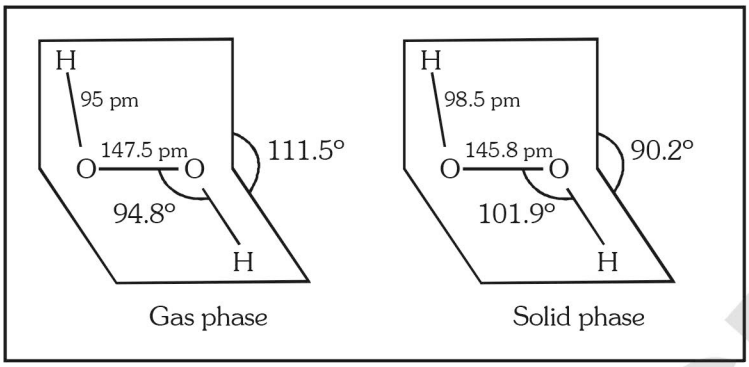
$$H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^- \quad \text{(in alkali)}$$

Ex. H_2O_2 → $KMnO_4/H^+$ → Mn^{+2}; H_2S → S; $FeSO_4/H^+$ → Fe^{+3}; $NaNO_2$ → $NaNO_3$

Structure of Hydrogen Peroxide

The vapour density as determined by Victor Meyer method at 90°C is 17. Hence, the molecular mass of H_2O_2 is 34. Two formulae have been suggested for hydrogen peroxide.





Storage of H_2O_2

(i) So the H_2O_2 usually stored in coloured, paraffin wax coated, plastic bottle.

(ii) Always with H_2O_2 add small quantity of inhibitor or negative catalyst to stay decomposition of H_2O_2. like H_3PO_4, acetanilides etc.

GOLDEN KEY POINTS

- It is not possible to determine the boiling point of H_2O_2 at atmospheric presseure because it decomposes vigorously on heating.
- Decomposition of H_2O_2 is favoured by certain metal ions (e.g., Fe^{2+}, Fe^{3+}), metal surface (Co, Au, Ag, Pt, etc.) and metal oxides (e.g.) MnO_2 strongly catalyze the reaction. Even carbon, rough surfaces, exposure to light, and traces of alkali (present in glass) catalyze its decomposition.