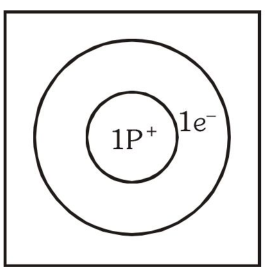
# Hydrogen

## INTRODUCTION

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

Lightest metal – Li

Lightest non metal – H




Structure of H–atom

Electronic Configuration – $1s^1$

for this configuration required –
- one shell → n = 1 or K
- one subshell → s
- one orbital → s

**Discovery of H-atom :**

Discovered by **"Covendish"** $\xrightarrow{\text{called}}$ **"Inflamable" air**

Term Hydrogen given by "Lavoisier" (Father of chemistry)

Hydrogen –
- Hydra–Water
- Genns–Maker

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

**Relative abundance :**

$$\underbrace{\text{Universe (92\%)} > \text{Sun atomosphere}}_{\text{Atomic form}} > \underset{\substack{\downarrow \\ \text{as different compounds}}}{\text{Earth}}$$

* Hydrogen is most abundent element in the universe, i.e. 70% of the universe total mass.

* Hydrogen is highly reactive element as single atomic form but less reactive in their molecular state.

* Due to their high Bond energy.

* with respect to all diatomic (Homo atomic, Heteroatomic) molecule, hydrogen contain maximum bond energy (exception HF)

* Due to their small size of atom, $H_2$ contain high bond energy.

## Method of preparation

**By acids :** The metal which are placed about $H_2$ in electrochemical series react with dil acids they liberate $H_2$.

**Ex.** $$Fe + \underset{\text{(dil)}}{H_2SO_4} \rightarrow FeSO_4 + H_2$$

$$Cu + H_2SO_4 \rightarrow \times \text{ (No reaction)}$$

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

$$\underset{\text{(impure)}}{Zn} + \underset{\text{(dil)}}{H_2SO_4} \rightarrow ZnSO_4 + H_2$$

**By alkalies :** Only (Be, Zn, Al, Sn, Pb) (Amphoteric metal) react with boiling NaOH or KOH they evolve $H_2$.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$$
(sodium zincate)

$$2Al + 2NaOH + 2H_2O \longrightarrow NaAlO_2 + 3H_2\uparrow$$
(sodium meta aluminate)

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$$
(sodium stannate)

$$Pb + 2NaOH + H_2O \longrightarrow Na_2PbO_3 + 2H_2\uparrow$$
(sodium plumbate)

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$
(sodium beryliate)

## Solved Examples

**Ex.1** Element which does not reach with NaOH.

(i) Mg (ii) Be (iii) Al (iv) Zn

(1) 1,3 (2) 1, 2, 3 (3) 1, 4 (4) 1, 3, 5

**Sol. Ans.** (1)

**Ex.2** Element which give $H_2$ gas with caustic soda (NaOH).

(1) Zn (2) Al (3) Na (4) Ag

**Sol. Ans.** (2)

**From water :** All the metals which are placed above than $H_2$ when react with water the evolve $H_2$.

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

Three type of water is used

(i) **Cold water :** The temperature of cold water is 7 to 25°C this water is used for highly reactive metals.

Such as Li, K, Ba, Sr, Ca, Na, means alkali metals of alkalic earth metals.

The reaction with alkali metals are vigorous to minimum 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 :** The temperature of hot water is 25°C to 90°C. This water is used for reactive metals, such as Mg, Al, Mn, Zn, Cr.

(iii) **Steam :** The temperature of steam is more than 100°C. This form of water is used for very less reactive metals like Fe, Cd, Co, Ni, Sn, Pb.

**Condition for best yield of Hydrogen**

(i) Cold water $\longrightarrow$ With highly reactive metals.

(ii) Hot water $\longrightarrow$ With reactive metals

(iii) Steam $\longrightarrow$ With less reactive metals.

## Solved Examples

**Ex.3** Which process does not form $H_2$ gas.

(1) Zn + ice cold $H_2O$ (2) Zn + $H_2SO_4$

(3) Na + ice cold $H_2O$ (4) Mg + Hot $H_2O$

**Sol. Ans. (1)**

**On Ionic hydride :** Whenever ionic hydride reacts with water then form $H_2$.

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

### Method to prepare pure hydrogen

(i) **Electrolysis of water :** To prepare pure hydrogen we use impure water (i.e. having 15-20% solution of alkali or acid)

$$4H_2O \rightleftharpoons 4H^+ + 4OH^-$$

at cathode $4H^+ + 4e^- \longrightarrow 2H_2$

at anode $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

The $SO_4^{-2}$ or $K^+$ ion present in acid or alkali does not move towards anode or cathode as their discharge potential is higher than of $OH^-$ ions or $H^+$ ions respectively.

(ii) **By reaction of Magnesium with dilute $H_2SO_4$ :**

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

(iii) **By reaction of NaH with water :**

$$NaH + H_2O \longrightarrow NaOH + H_2$$

(iv) **Uyeno method :** This method is used for military purpose.

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2\uparrow$$
(Potassium meta aluminate)

**Note :** By this reaction we can prepare $H_2$ in a rapid manner.

## Commercial or industrial method to prepare $H_2$

(i) **Lane's process :** In this process, steam is passed over hot iron. Iron decomposes steam with the formation of magnetic oxide ($Fe_3O_4$) and hydrogen. The temperature of iron is maintained between 550 to 800°C. This reaction is termed gassing reaction and time alloted for this reaction is about 10 minutes.

$$\underset{\text{}}{3Fe} + \underset{\text{Steam}}{4H_2O} \longrightarrow \underset{\text{Magnetic oxide}}{Fe_3O_4} + 4H_2\uparrow \text{ Gassing}$$

Iron is regenerated by reducing magnetic oxide with water gas ($CO + H_2$). This reaction is called **vivifaction** and time alloted for this reaction is about 20 minutes.

$$FeO_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

This iron is again used for decomposition of steam. In order to make the process contiunuous, the above two reactions are carried out alternatively using two or more furnaces.

(ii) **Bosch's process :** The maximum quantity of commercial hydrogen is obtained by the use of this method. Water gas is produced first by passing steam over hot coke at 1000°C. The temperature is not allowed to fall below 1000°C.

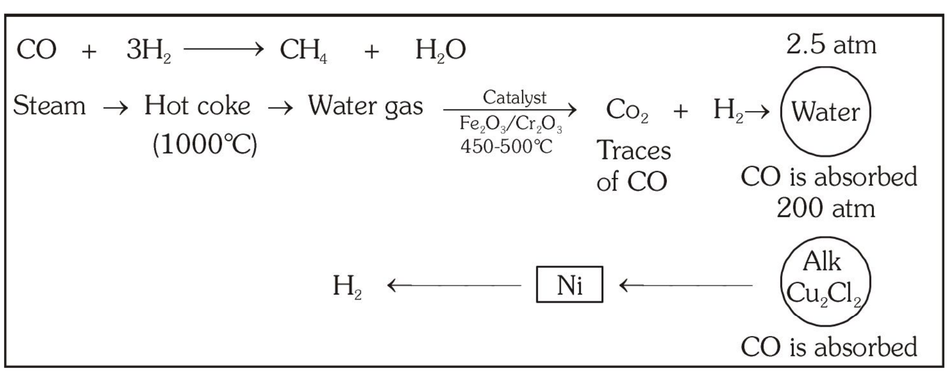
$$C + H_2O \longrightarrow CO + H_2$$

Water gas is mixed with twice the volume of steam and passed over a mixture of ferric oxide and chromium oxide heated to 500°C. The mixture acts as a catalyst and helps in the conversion of carbon monoxide to carbon dioxide.

$$\underset{\text{Water gas}}{H_2 + CO} + \underset{\text{Steam}}{H_2O} \xrightarrow{\text{Catalyst}} CO_2 + 2H_2$$

$CO_2$ dissolves in water under pressure. The mixture of $CO_2$ and $H_2$ is passed through water under the pressure of 25 – 30 atmospheres. $CO_2$ dissolves completely in water. Traces of CO present in hydrogen are removed by passing the gas through ammonical cuprous solution under a pressure of 200 atmospheres.

The hydrogen manufactured by this method is utilized for the synthesis of ammonia in which CO acts as a poison for the catalyst. To make hydrogen completely free from CO, it is passed over nickel catalyst then all CO present is converted into methane.




(iii) **From Natural gas :** $C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n+1)H_2$

## Solved Examples

**Ex.4** Acid used in formation of $H_2$ gas ?

(1) Concentrated $H_2SO_4$ (2) Dilute $H_3PO_4$

(3) Dilute $H_2CO_3$ (4) Dilute HCl

**Sol. Ans.** (4)

**Ex.5** Which of following reaction do not form $H_2$ ?

(1) $Fe + H_2SO_4$ (2) $Sn + H_2SO_4$

(3) $Cu + H_2SO_4$ (4) $Zn + H_2SO_4$

**Sol. Ans.** (3)

**Ex.6** What happen when NaH is dissolved in water (solvent) ?

(1) $NaH \longrightarrow Na^+ + H^-$

(2) $H^- + \underset{H\quad H}{O} \longrightarrow H_2 + OH^-$

(3) $HO^- + Na \longrightarrow NaOH$

**Sol. Ans.** (2)

**Ex.7** Species or ion which doesnot exist in nature.

(1) $H^+$ (2) $H_3O^+$ (3) $H_2^+$ (4) 1,3 both

**Sol. Ans.** (4)

$H^+$ ion doesnot exist in nature, because $H^+$ is without $e^-$ species of size of $H^+$ ions is negligible.

$H_2^+$ does not exist, because its bond order is 0.5.

**Ex.8** Ion which is not present in dilute HCl.

(1) $H^+$ (2) $H_3O^+$ (3) $Cl^-$ (4) HCl

**Sol. Ans.** (1)

### Physical Properties of Hydrogen

* Hydrogen is a lightest colourless, odourless and tasteless gas. It is sparingly soluble in water. It is inflammable and less reactive gas.
* Its freezing point ($-259.2^0C$) and boiling point ($-252^0C$) are very low, indicating less intermolecular attraction. Due to low melting point, liquid hydrogen is used as a **cryogenic fluid** (to produce low temperature).
* H – H bond energy [ 104 Kcal $mol^{-1}$] and 436 KJ $mol^{-1}$
* H – H bond length [ 74 pm] so hydrogen is less reactive and require high temperature for reaction

### Chemical Property

(i) $3H_2 + N_2 \rightleftharpoons 2NH_3$ (Haber Process)

(ii) $H_2 + X_2 \rightleftharpoons 2HX$

(iii) $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

(iv) Vegetable oil unsaturated fats $\rightarrow$ Vagetable ghee (Vanaspati ghee) saturated fats.

**Uses**

1. Hydrogenation of vegetable oil to form solid fats i.e. vanespati ghee.
2. In the oxyhydrogen torch and atomic hydrogen torch for welding process.
3. In liquid form as a rocket fuel.
4. In aeroplanes and in balloons mixture of Hydrogen & Helium is used as fuel [15% $H_2$ + 85% He]

## ISOTOPIC EFFECT

* Effect which can change physical & chemical properties of isotopes is called isotopic effect.
* By isotopic effect, maximum change occur in physical property of isotopes but minimum change occur in chemical property of isotopes.

**Physical property :** melting point, boiling point, density etc.

**Chemical property :** Rate of chemical reaction.

* Isotopic effect is found only in Hydrogen isotope because maximum mass number difference present in hydrogen isotopes.

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

${}_1H^1$ ${}_1H^2$ ${}_1H^3$ ✓

Double

Triple

**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

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

## ISOTOPES OF HYDROGEN

| Property | Protium or ordinary hydrogen | Deuterium or heavy hydrogen | Tritium |
|---|---|---|---|
| Atomic number | 1 | 1 | 1 |
| Mass number | 1 | 2 | 3 |
| Exact atomic mass | 1.008123 | 2.0142 | 3.0170 |
| Symbol | ${}_{1}^{1}H$ | ${}_{1}^{2}H$ or ${}_{1}^{2}D$ | ${}_{1}^{3}H$ or ${}_{1}^{3}T$ |
| Molecular formula | $H_2$ | $D_2$ | $T_2$ |
| No. of protons in the nucleus | 1 | 1 | 1 |
| No. of neutrons in the nucelus | Nil | 1 | 2 |
| No. of electron | 1 | 1 | 1 |
| Electronic configu. | $1s^1$ | $1s^1$ | $1s^1$ |
| Relative abundance | 99.984% | 0.016% | $10^{-15}$ % |
| Stability | Stable | Stable | Unstable (Radioactive) |

**Physical Properties of isotopes of hydrogen**

| Physical contants | $H_2$ | $D_2$ | $T_2$ |
|---|---|---|---|
| M.P. | – 259$^0$C | – 254.3$^0$C | – 252.4$^0$C |
| B.P. | – 252.6$^0$C | – 249.3$^0$C | – 248.0$^0$C |
| Bond length (H– H) | 74 pm | 74 pm | 74 pm |
| B.E. (H—H) | 436.0 KJ mol$^{-1}$ | 443.3 KJ mol$^{-1}$ | 446.9 KJ mol$^{-1}$ |
| Heat of fusion & vaporisation | Minimum | H < D < T | Maximum |

| | |
|---|---|
| Stability of Isotopes according to availibility. | P – P > D – D > T – T |
| Stability of Isotopes on the basis of reaction with $Cl_2$. | T – T > D – D > P – P |
| Stability of Isotopes according to bond energy. | T – T > D – D > P – P |
| On the basis of their physical properties. | T – T > D – D > P – P |

### 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.

## *Solved Examples*

**Ex.9** Normally hydrogen placed in

(1) IA (2) IVA (3) VIIA (4) All of these

**Sol. Ans.** (1)

**Ex.10** Hydrogen can be placed :

(1) IA (2) IVA

(3) VIIA (4) both (1) and (3)

**Ans.** (4) Normally hydrogen is placed in IA group because of properties (Valence shell electronic configuration) is similar with IA group element

**Properties of hydrogen similar with IA group :**

| | | Hydrogen | IA |
|---|---|---|---|
| * | Oxidation state | +1 ($H^+$) | +1($M^+$) |
| * | Valence shell $e^-$ configuration | $ns^1$ | $ns^1$ |
| * | Electron releasing tendency | ($H \rightarrow e^- + H^+$) | ($M \rightarrow e^- + M^+$) |

* H is strong reducing agent like I[st] A group elements but reduce only below element. (In ECS)

**Properties of hydrogen with VIIA group :**

| | | H | VII[th] A |
|---|---|---|---|
| * | Oxidation state | 1 ($H^-$) Hydride (NaH) | –1($X^-$) (NaX) Halide |
| * | Diatomic nature | $H_2$ | $X_2$ |

* Ionisation polential of H gas similar with halogen.
* In electrolysis of metals halides and metal hydrides from diatomic gas, both halogen and hydrogen will liberate at anode.

$2H^- \longrightarrow 2e^- + H_2\uparrow$ and $2X^- \longrightarrow 2e^- + X_2\uparrow$

**Properties of hydrogen with IVA group :**

Both hydrogen and IVA group elements have half filled valence shell.

$$\left.\begin{array}{l} H \rightarrow 1s^1 \text{ or } ns^1 \\ C \rightarrow 1s^2 2s^2 2p^2 \text{ or } ns^2 np^2 \end{array}\right\} \text{Half filled}$$

**Different form of hydrogen**

(i) **Atomic hydrogen (H) :** Atomic hydrogen are also classified in three categories -

**Simple atomic hydrogen :** $H-H\,(H_2) \rightleftharpoons 2H$

* Formed by dissociation of $H_2$ gas and dissociation of $H_2$ gas is an endothermic process.
* An ideal condition for this is high temperature and low pressure.

**Nascent Hydrogen :**

* It is formed by specific chemical reaction i.e. formation of nascent hydrogen by base, acid and water

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + \underset{\text{Nascent ( unstable)}}{2H} \rightarrow H_2\uparrow$$

* Simple atomic hydrogen and nascent hydrogen are good reducing agent.

$FeCl_3 + [H] \longrightarrow FeCl_2 + HCl$

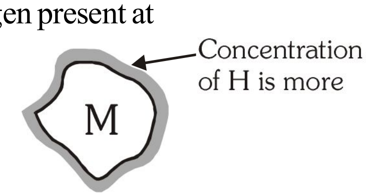
## Solved Examples

**Ex.11** Which of the following process form nascent $H_2$ gas ?

(1) $C_2H_5OH$ (Acid) + Na (2) Al + NaOH
(3) Zn + dilute $H_2SO_4$ (4) All of these

**Sol. Ans.** (4)

**Adsorbed/Occluded hydrogens :** Adsorbed H is hydrogen present at




the outer surface of metal.

**Occlusion :** The property of metal to adsorb any gas is called occlusion.

(ii) **Molecular hydrogen :** (Ortho & Para /Nuclear isomers/Proton spin isomer)

Ortho & Para isomerism present in only diatomic molecule with atomic number odd value ($N_2$, $H_2$, $F_2$, $D_2$) but absent in $O_2$

**Ortho hydrogen :** Molecular form of hydrogen with same spin of proton is called ortho hydrogen.

Total spin of proton

$$\left[+\frac{1}{2}+\frac{1}{2}=+1 \quad \text{or} \quad -\frac{1}{2}-\frac{1}{2}=-1\right]$$

**Para hydrogen :** Molecular form of hydrogen with opposite spin of proton is called para hydrogen.

Total spin of proton = 0

**Internal energy :** Normally internal energy of ortho hydrogen is more then the para hydrogen because ortho hydrogen have same spin of proton or greater repulsion of proton.

**Stability :** At high temperature, ortho is more stable then para but at low temperature para is more stable than ortho.

$$P_{H_2} \underset{\text{Temperature}\downarrow}{\overset{\text{Temperature}\uparrow}{\rightleftharpoons}} O_{H_2}$$

| Temperature | Ortho | Pera |
|---|---|---|
| 25°C/ 298° K | 75% | 25% |
| –273°C/20° K | 0% | 100% |

**Note :** Pure para or 100% para may be possible. But 100% ortho is not possible because at high temperature molecular form of hydrogen is converted into atomic form.

**Reactivity of reducing property :**

Simple hydrogen > Nascent hydrogen > Adsorbed hydrogen > Molecular hydrogen

## *Solved Examples*

**Ex.12** Which of the following process form Nascent H :

(1) Al + NaOH (2) Zn + $H_2SO_4$

(3) Na + $C_2H_5OH$ (4) All of the above

**Ans.** (4) All of these

## Hydrides :

The compounds of hydrogen with different elements are called hydrides. These are of three types :

**(1) Ionic/Salt like/Saline hydrides :**

Compounds of hydrogen with s-block elements except berylium & magnesium are called ionic hydrides.

LiH, NaH, KH, RbH, CsH, $CaH_2$, $SrH_2$, $BaH_2$

$BeH_2$, $MgH_2$ are covalent polymeric hydride.

* Structure of these hydrides are similar to rock salt, so they are also called salt like/saline hydrides.
* Down the group size↑ Lattice energy↓ stability↓ Melting point↓ Boiling point↓
* On electrolysis of these hydrides, hydrogen is liberated at anode.
* On reaction with water these hydrides will form hydrogen

$NaH + H_2O \longrightarrow NaOH + H_2$

* These hydrides forms complex hydrides which are very good reducing agents.

$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$

$NaBH_4 \longrightarrow$ Sodium borohydride

$LiAlH_4 \longrightarrow$ Lithium aluminium hydride.

**(2) Mettalic / Interstitial hydrides :**

They are the compounds of d & f-block elements.

In these hydrides hydrogen occupies interstitial sites present in metallic lattice, so they are called interstitial hydrides.

* Properties of these hydrides are similar to parent metals, so they are also known as metallic hydrides.
* These hydrides are non. stochiometric in nature (i.e. having variable composition)

ZrHx (x = 1.3 – 1.75)

TiHx (x = 1.8 – 2)

* Metals of group 7,8,9 donot form any hydrides so this particular part of periodic table is known as hydride gap.

**(3) Covalent/Molecules hydrides**

* They are the compounds of hydrogen with p-block elements $CH_4$, $NH_3$, $H_2O$, HF, etc.
* These hydrides exist as molecules, so they are also known as molecular hydrides. There hydrides are non-conductor of electricity.

Nomenclature – element + Suffix (ane)

$PH_3 \longrightarrow$ Phosphane

$NH_3 \longrightarrow$ Azane

$H_2O \longrightarrow$ Oxidane

These hydrides are again divides into 3 categories.

(a) Electron deficient hydrides :

* They are the hydrides of group 13 elements.

$BH_3$, $AlH_3$, $GaH_3$ – In these hydrides central element does not have complete octet. i.e. why they are called electron deficient compounds.

(b) Electron precise hydrides – They are the hydrides of group 14 element.

**Ex.** $CH_4$, $SiH_4$, $GeH_4$

In these type of hydrides central elements has $8e^-$ in their outer most shell.

(c) Electron rich hydrides : These are the hydrides of group 15, 16, 17

**Ex.** $\dot{N}H_3$, $H_2\ddot{O}:$, $H\ddot{F}:$ etc.

In these hydrides lone pair are present on central atom which can be given to others. So they are called electron rich hydrides.

## Water ($H_2O$)

Water act both as oxidising and reducing agent.

| | | | | |
|---|---|---|---|---|
| Na | + | $H_2O \longrightarrow$ | NaOH + | $\frac{1}{2}H_2$ |
| Reducing agent | | Oxidising agent | | |
| $2F_2$ | + | $2H_2O \longrightarrow$ | 4HF | $+ O_2$ |
| $3F_2$ | + | $3H_2O \longrightarrow$ | 6HF | $+ O_3$ |
| Oxidising agent | | Reducing agent | | |

### Physical Property

(i) Pure water is colour less, test less and odour less.

(ii) It freezes at $0^0C$ and boil at $100^0C$

(iii) Density of water is 1 at $0^0C$

(iv) Density of ice < density of $H_2O$ ( $4^0C$ maximum)

(v) Volume of ice > $H_2O$

(vi) Pure water is a bad conductor of electricity due to very low degree of ionisation.

(vii) In absance of Hydrogen Bond boiling point of $H_2O$ about – 100°C.

### Chemical property

(i) Water is considered as most **convenient solvent**. Because its dielectric constant is high.

**Ex.** 81 and it is a polar molecule. Due to these properties salts are highly ionised in water.

(ii) The solubility of ionic compounds in water is also due to liberation of a large amount of hydration energy due to interaction between the ions of solute and the polar water molecules.

(iii) Water is not good solvent for covalent compounds because in this case less amount of energy is released which can not overcome even the weak van der Waals' force of attraction of the covalent compound what to say of breaking of hydrogen bonds in water.

(iv) Solubility of some covalent compounds. **Ex.** alcohols, acids, amines, carbohydrates etc. in water is due to their capability of forming hydrogen bonding with water.

For pure water pH = 7

$[H^+] = [OH] = 10^{-7}$ at $25^0C$ $\quad$ $Kw = 10^{-14}$

(v) **Reaction :**

$$C + H_2O \longrightarrow [CO + H_2]$$
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

water gas $\qquad$ Hypchlorous acid

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
$$2Cl_2 + 2H_2O \xrightarrow{\text{Sun light}} 4HCl + O_2$$

(vi) **Hydrolysis :**

$$\text{Ester} + H_2O \rightleftharpoons \text{acid} + \text{alcohol}$$

(vii) **Reaction with carbides :**

By reaction with $H_2O$ & carbides form of difference type of hydrocarbon (Alkane, Alkyne, Alkene).

(i) $CaC_2 \rightarrow [Ca^{2+} + C_2^{-2}] \xrightarrow{2H^+} C_2H_2$

(ii) $Al_4C_3 \longrightarrow [4Al^{+3}]^{+12} + C_3^{-12} \xrightarrow{12H^+} C_3H_{12}(\text{unstable}) \longrightarrow 3CH_4$

(iii) $Mg_2C_3 \longrightarrow [2Mg^{+2}]^{+4} + C_3^{-4} \longrightarrow C_3H_4 \left\langle \begin{array}{l} H_2C{=}C{=}CH_2 \\ HC{\equiv}C{-}CH_3 \end{array} \right.$

Silicon caibide will not react with $H_2O$ because of its diamond like structure.

(viii) **Reaction with Non-metal oxide :**

Non-metal oxide + $H_2O \longrightarrow$ Oxyacid.

$N_2O_5 + H_2O \longrightarrow 2HNO_3$

$SO_3 + H_2O \longrightarrow H_2SO_4$

(ix) **Reaction with Metal oxide :**

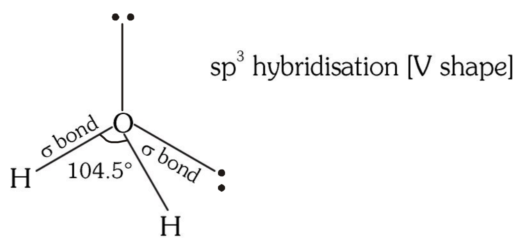
Metal oxide + $H_2O \longrightarrow$ Hydroxide

$Na_2O + H_2O \longrightarrow 2NaOH$

**Test of water :**

$CuSO_4 + H_2O \longrightarrow$ Blue colour

**Structure of water :**




**Hard and Soft water**

Water from rivers, springs or even 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.

$$CaCl_2 + 2C_{17}H_{35}COONa \longrightarrow Ca(C_{17}H_{35}COO)_2\downarrow + 2NaCl$$

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

**Note :** Hard water is not always harmful for drinking purposes. However it is disadvantageous in the laundry work.

**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 :**

**Method for temporary Hardness :**

(i) **By Boiling**

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

$CaO (s) + H_2O \longrightarrow Ca(OH)_2$
(quick lime) (Slaked lime)

**Note :** Here $Ca(OH)_2$ can not used as excess quantity because $Ca(OH)_2$ by absorbing $CO_2$ further formation of $Ca(HCO_3)_2$.

**Method for permanent Hardness :**

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

**Method for Both temporary as permanent hardness:**

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

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

(A) Inorganic process (B) Organic process
(C) Calgon process

(A) **Inorganic process :**

**Permutit process :** For this process used inorganic salt like hydrates of sodium & aluminium silicates.

$[Na_2Al_2Si_2O_8 . xH_2O]$ this compound also called "Zeolite" Zeolite is a water softner & shape selective catalyst.

Formation by $Na_2CO_3$, $Al_2O_3$, $SiO_2$ etc.

This general formula of its – $Na_2Z$

here, $Z = Al_2Si_2O_8 . x H_2O$

In this process column chromatography always used.

$Na_2Z + CaCl_2 \rightarrow CaZ + 2NaCl$

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

**Cation exchanger :** exchange only hard cation.

**Ex.** $R - COO^-H^+$

$2RCOO^-H^+ + Ca^{+2} \longrightarrow (R-COO)_2Ca\downarrow + 2H^+$

**Anion exhanger :** exchange only hard anion.

**Ex.** $R - NH_2^{\oplus} - OH^-$

$2R-NH_2^{\oplus}-OH^- + Cl^- \longrightarrow R-NH_2^{\oplus}Cl^-\downarrow + OH^-$

## Solved Examples

**Ex.13** Which of the following substance produce hardness in water.

(1) $CaCO_3$ (2) $CaCl_2$

(3) $Na_2CO_3$ (4) $Na_2(HCO_3)_2$

**Sol. Ans.** (2)

**Key Point**

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.

(C) **Calgon Process** : Calgon is the trade name of sodium hexameta-phosphate, $Na_2(Na_4(PO_3)_6]$. The $Ca^{2+}$ and $Mg^{2+}$ ions present in hard water react with calgon to form complex anions, which are very inactive and do not form precipitate with soap.

$Na_2[Na_4(PO_3)_6] + 2Ca^{2+} \longrightarrow Na_2[Ca_2(PO_3)_6] + 4Na^+$

soluble complex

## $D_2O$ (Heavy water)

Heavy water is deuterium oxide ($D_2O$). It was discovered by **Urey (1932)**. One part of $D_2O$ is present in about 6000 parts of $H_2O$. Theoritically six different types of heavy water are possible in terms of three different isotopes of oxygen

**Ex.** $H–O^{16}–D$, $H–O^{17}–D$, $H – O^{18} – D$ and $D–O^{16}–D$, $D–O^{17}–D$, $D–O^{18}–D$.

**Chemical property**

Chemical property of $H_2O$ and $D_2O$ are same but rate of chemical reaction of $H_2O > D_2O$. because bond energy of $O–D > O–H$ Like water but process is slow due to high bond energy.

$2D_2O \xrightarrow{\text{Electrolysis}} 2D_2 + O_2$ $2Na + 2D_2O \longrightarrow 2NaOD + D_2$

Sodium deutroxide

$SO_3 + D_2O \longrightarrow D_2SO_4$

Heavy sulphuric acid

$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 2CD_4$

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

It is injurious to living organism and does not support life so well. It also retards the growth of living organism, plants and animals.

**Uses**

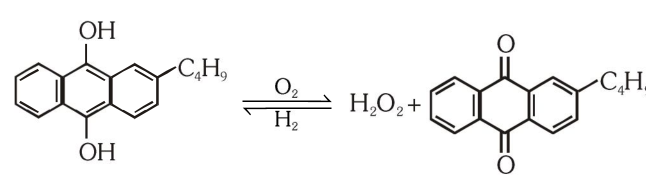
(i) It is used in production of heavy hydrogen, and deutero compounds, as a tracer compound and as a moderator in atomic reactors.

(ii) Used as a Moderator

## $H_2O_2$ (Hydrogen Peroxide)

**Industrial Method**

(i) **Auto oxidation of 2 butyl anthraquinol ( cyclic process) :**



(ii) **Oxidation of isopropyl alcohol :**

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + O_2 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H_2O_2$$

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

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

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

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

Peroxo disulphhuric acid

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

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

**Note :** Now a day use 50% $(NH_4)_2SO_4$ with 50% $H_2SO_4$.

## Physical Property

(i) Pure $H_2O_2$ is colour less, odourless liquid and impure with bluish layer.

(ii) It has more Hydrogen bonding then $H_2O$, So order of boiling point. $H_2O_2 > D_2O > H_2O$

(iii) It is soluble in $H_2O$, alcohol and ether

(iv) It has bitter test and harmful for skin

(v) It is a dibasic weak acid

(vi) It has a oxidising as well as reducing property

(vii) $H_2O_2$ easily decompose in presence of light and temperature, So $H_2O_2$ always kep in dark bottles and kept at cool places.

(viii) 30% solution of $H_2O_2$ is called **Perhydrol**.

## Chemical Property

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

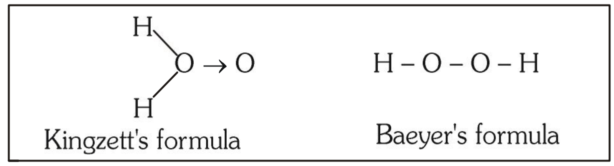
**Note :** Nascent oxygen working as colourless agent

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

**Note :** This is retarded by R–OH, acetenilide glycerol acelerates by **Pt, Au, Ag, MnO$_2$**

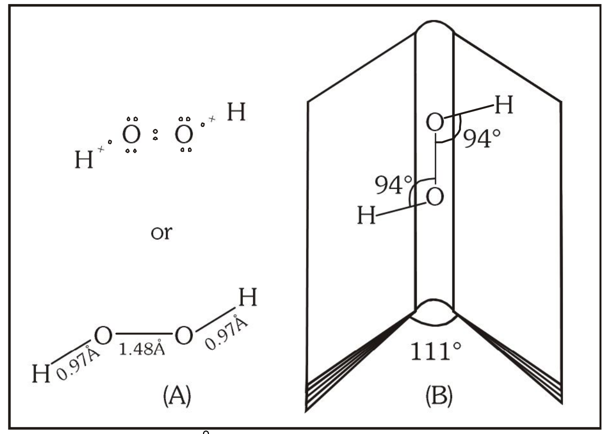
## Structure of Hydrogen Peroxide

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.

The calculated value of the single bond O–O




distance is 1.48Å and X-ray measurements shows what in hydrogen peroxide, O–O bond distance is 1.46 + 0.03Å. The value of dipole moment of $H_2O_2$ is 2.1 D. This suggests that all the four atoms do not lie in the same plane. The molecule can be pictured as lying on the spine of a book open to an angle of 111°. The hydrogen atoms are present one on each cover and H–O bonds making angles of 94° with the O–O bond as shown in fig. The bond distance between O–H is 0.97Å.

**Precautions :**

(i) $H_2O_2$ can not be stored in simple glass bottles since rough surface of glass [alkali oxides present in it] excited by light and decomposed $H_2O_2$.
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.

**Uses**

(i) Bleaching agent

(ii) Hair dying

(iii) $H_2O_2 + N_2H_4$ as Rocket propellent

(iv) $H_2O_2$ as oxidant and reductant

(v) Antiseptic