

Chemistry : Elements of Group 1 and Group 2

INTRODUCTION

- ❑ Hydrogen is the first element in the periodic table.
- ❑ It has the simplest atomic structures having only one proton and one electron.
- ❑ The elemental form of diatomic (H_2) molecule is called dihydrogen.
- ❑ Hydrogen combines with other elements by losing, gaining or sharing of electrons.
- ❑ Hydrogen is third most abundant on the surface of earth.
- ❑ Its name hydrogen was proposed because it produces water on burning with oxygen (In Greek *Hydro* = water, *gen* = producing)

OCCURRENCE

- i) Dihydrogen is the main element of the solar systems.
- ii) In the combined form it constitutes about 15.4% of earth crust and ocean.
- iii) The earth's atmosphere contains about 0.15% of hydrogen by mass.
- iv) It occurs in plant and animal tissues as carbohydrates and proteins.
- v) It is present in hydrides, hydrocarbons and many other compounds.
- vi) Planets like Jupiter and Saturn consists mostly hydrogen.

POSITION OF HYDROGEN IN THE PERIODIC TABLE

- ❑ It is first element in the periodic table.
- ❑ The position of hydrogen is not definite in the periodic table because it resembles both the alkali metals (Group -1) as well as halogens (Group 17).
- ❑ At the same time it differs from both in many characteristics. Thus it is a rogue element.

- ❑ Loss of electrons from H atom results in nucleus size of $H^+ = -1.5 \times 10^{-3}$ Pm is extremely small as compared to normal atomic and ionic sizes of 50 to 200 Pm. Hence H^+ does not exist freely and is always associated with other atoms/molecules.

- ❑ It means H is unique behaviour, therefore, best placed separately in periodic table.

• Electronic configuration

- ❑ Atomic number of H is one.
- ❑ Its electronic configuration is $1s^1$ similar to the outermost electronic configuration of alkali metals ns^1 . It forms univalent ion similar to alkali metal ions.
- ❑ It forms oxides, halides and sulphides like alkali metals.
- ❑ Hydrogen resembles halogens of group 17 in the properties like high ionisation enthalpy (ΔH of $H_2 = 1312$ kJ/mole), formation of uninegative ion (H^+), formation of hydrides with many elements (NaH), formation of large number of covalent compounds (HCl , H_2O), existence as a diatomic molecule (H_2)
- ❑ Hydrogen is less reactive than halogens.

ISOTOPES OF HYDROGEN

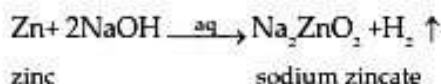
- i) Hydrogen has three isotopes (a) Protium (${}_1H^1$), (b) Deuterium (${}_1H^2$ or D) and (c) Tritium (${}_1H^3$ or T)
- (a) **Protium/Hydrogen (${}_1H^1$)** : Which is a predominant form of isotope. It has no neutron in its nucleus.
- (b) **Deuterium (${}_1H^2$ or D)** : Which is known as heavy hydrogen. It has one neutron in its nucleus.
- (c) **Tritium (${}_1H^3$ or T)** : Which is a radioactive isotope with half life 12.4 years and β -particle emitter. It has two neutrons in its nucleus.
- ii) Since these isotopes have identical electronic configuration and chemical properties. They have different physical properties due to different masses. This effect is known as isotopic effect.

- iii) The heavy isotopes, deuterium and tritium are used for nuclear fusion, and as tracers in the study of reaction mechanism.
- iv) The concentration of tritium is about one atom per 10^{10} atoms of protium.

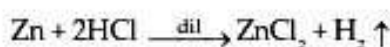
PREPARATION OF DIHYDROGEN

A) Laboratory method

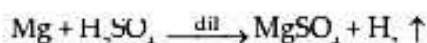
- i) Zinc reacts with aqueous alkali gives sodium zincate and hydrogen.



- ii) Granulated zinc reacts with dil. HCl gives zinc chloride and dihydrogen.



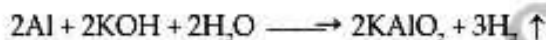
- iii) Magnesium ribbon reacts with dil. H_2SO_4 gives magnesium sulphate and dihydrogen.



- iv) Sodium hydride reacts with water gives sodium hydroxide and H_2 gas.



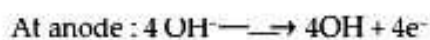
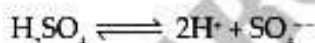
- v) **Uyeno's method**: Scrap aluminium or silicon reacts with potassium hydroxide and water gives potassium aluminate and H_2 gas.



B) Commercial method

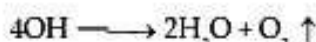
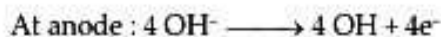
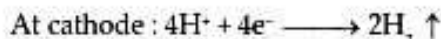
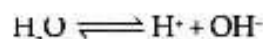
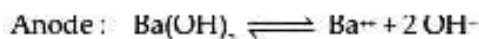
- i) **Electrolytic method**: On large scale, dihydrogen is prepared by electrolysis of acidified water (water + dil. H_2SO_4) using platinum electrode.

- Dihydrogen is liberated at cathode and dioxygen is liberated at anode. During electrolysis acidic medium

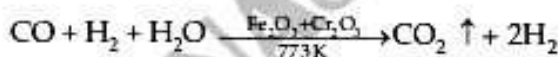


SO_4^{2-} ions are not discharged at the anode as their discharge potential is very much higher than that of H^+ ion.

- ii) High purity of dihydrogen (> 99.96%) is obtained by electrolyzing warm aqueous solution of Ba(OH)_2 between Ni electrode.

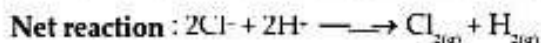
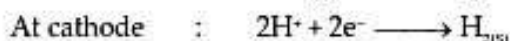
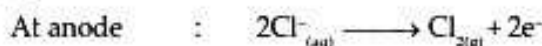


- iii) **Bosch process**: When water gas ($\text{CO} + \text{H}_2$) is mixed with twice the volume of steam (H_2O) and passed over heated catalyst (Fe_2O_3) at 773 K in presence of promoter Cr_2O_3 / ThO_2 / CO is oxidized, to CO_2 which is removed by dissolving in water under pressure (20-25 atm) and H_2 left behind is collected.



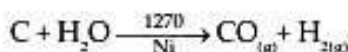
Water gas

- iv) H_2 is obtained as a by product in the manufacture of NaOH and Cl_2 by the electrolysis of brine (NaCl) solution.

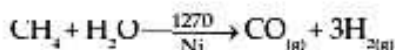


Na^+ and OH^- ions remain in the solution which gives NaOH .

- v) When coke (c)/hydrocarbon (CH_4) is passed with steam at high temperature at 1270 K in presence of Ni gives water gas ($\text{CO} + \text{H}_2$)



coke steam

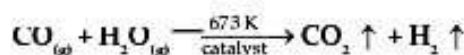


- Water gas ($\text{CO} + \text{H}_2$) is used for synthesis of methanol and number of hydrocarbons called as synthesis / syngas. $\text{CO} + 2\text{H}_2 \xrightarrow{\Delta} \text{CH}_3\text{OH}$

- Syngas is produced from sewage, saw dust, scrap and newspapers etc.

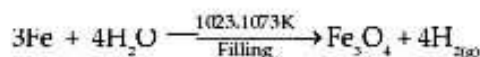
- The process of producing syngas from coal is called as coal gasification.

- ❑ Carbon monoxide of syngas mixture with steam in presence of iron chromate to give H_2



vi) **Lane's process (from steam)**

- ❑ When superheated steam is passed over iron (Fe) filings heated to 1023-1073 K gives H_2 gas.



Iron steam Ferric trioxide (Hemetite)

PHYSICAL PROPERTIES OF DIHYDROGEN

- Dihydrogen is colourless, odourless, tasteless, non-poisonous combustible gas.
- It is non supportive of combustion.
- It is lighter than air.
- It is insoluble in water.
- It is neutral to litmus.

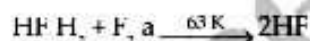
• **Chemical properties of dihydrogen**

- ❑ Chemical reactivity of dihydrogen involving the breaking of H-H bond.
- ❑ The bond dissociation enthalpy of H-H bond is very high (435.8 kJ/mole) so **very high energy** is required to break the H-H bond.
- ❑ Therefore dihydrogen is not very reactive under normal condition. It is inert at room temperature.

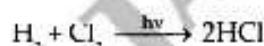
i) **Reaction with halogens**: Dihydrogen reacts with X_2 gives HX .



- ❑ Fluorine reacts with violently with H_2 even in dark and at very low temperature to form

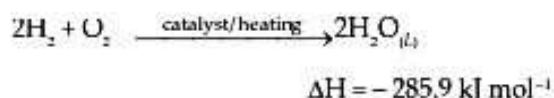


- ❑ Chlorine reacts with H_2 in presence of UV light gives HCl .



- ❑ Iodine requires in presence of a catalyst.

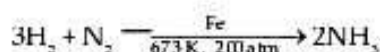
ii) **Reaction with dioxygen**: Dihydrogen reacts with dioxygen to form water and the reaction is highly exothermic.



iii) **Reaction with dinitrogen: Haber's process**

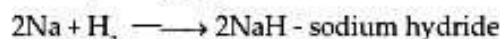
Dihydrogen reacts with dinitrogen in presence of Fe

at 673 K under 200 atm pressure gives ammonia, is known as Haber's process.



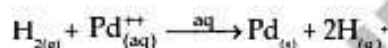
$$\Delta H = -92.6 \text{ W mol}^{-1}$$

iv) **Reaction with metals**: Dihydrogen reacts with many metals (like Na) at high temperature to give corresponding hydrides.



v) **Reaction with metal ion and metal oxide**:

Dihydrogen is reducing agent. It reduces some metal ions in aqueous solutions gives corresponding metal.



Dihydrogen reduces with oxides of metal to give corresponding metal.



vi) **Reaction with organic compounds**:

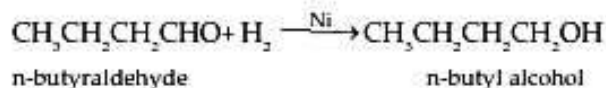
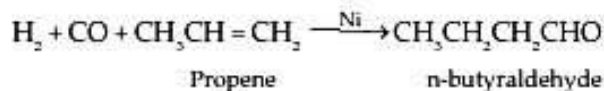
Dihydrogen reacts with unsaturated organic compounds in presence of catalyst to form saturated organic compound (hydrogenated) is called as hydrogenation.

- ❑ Hydrogenated compound gives some useful products of commercial importance,

e.g. Hydrogenation of vegetable oil (unsaturated triglycerides) in presence of Nickel gives edible fats (margarine and vanaspati ghee) (saturated triglycerides)



- Hydrogenation of alkenes (olefins) first gives aldehydes which is further undergo reduction.



USES OF DIHYDROGEN

- It is used in the manufacture of vanaspati ghee (fat) by hydrogenation of polyunsaturated vegetable oil like soyabean, cotton seed etc.
- It is used in the preparation of ammonia by Haber's process, ammonia is used in the manufacture of HNO_3 , nitrogenous, fertilizers.

- iii) It is used in the manufacture of methanol, HCl, metal hydride (ionic, covalent, interstitial hydrides)
- iv) It is used in fuel cells for generating electrical energy.
- v) It is used in metallurgical process to reduce oxides of heavy metals.
- vi) It is used as rocket fuel in space research, liquid H_2 mixed with liquid O_2 is used as rocket fuel.
- vii) It is used in atomic hydrogen and oxyhydrogen torches find use for cutting and welding purpose.

ALKALI METALS AND ELEMENTS OF GROUP 2

Electronic configuration

- s-block elements, the last electrons enters the s- subshell belonging to the outermost shell i.e. ns Hence their general electronic configuration can be written as [Noble gas] ns^{1-2} .

Therefore ns^1 is the configuration of group IA and ns^2 that of group IIA. Their actual electronic configuration as follows.

Occurrence

- i) **Group - 1** : Sodium and potassium are most abundant and lithium, rubidium, caesium have less abundant and francium is highly radioactive and has half life period of only 21 minutes, (short lived)
- ii) **Group - 2** : Mg and Ca are most abundant, strontium and barium have much lower abundance, Beryllium is rare and radium is the rarest of all igneous rocks.

Elements	Symbol	At. No.	Electronic configuration	of group 1 elements	Valence shell Electronic configuration (ns^1)
			Electronic configuration	Electronic configuration w.r.t. nearest Noble gas	
Hydrogen	H	1	$1s^1$		$1s^1$
Lithium	Li	3	$1s^2, 2s^1$	[He] $2s^1$	$2s^1$
Sodium	Na	11	$1s^2, 2s^2, 2p^6, 3s^1$	[Ne] $3s^1$	$3s^1$
Potassium	K	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$	[Ar] $4s^1$	$4s^1$
Rubidium	Rb	37	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$	[Kr] $5s^1$	$5s^1$
Caesium	Cs	55	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 6s^1$	[Xe] $6s^1$	$6s^1$
Francium	Fr	87	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6, 7s^1$	[Rn] $7s^1$	$7s^1$

Elements	Symbol	At. No.	Electronic configuration w.r.t. nearest Noble gas	Valence shell Electronic configuration (ns^2)
Beryllium	Be	4	[He] $2s^2$	$2s^2$
Magnesium	Mg	12	[Ne] $3s^2$	$3s^2$
Calcium	Ca	20	[Ar] $4s^2$	$4s^2$
Strontium	Sr	38	[Kr] $5s^2$	$5s^2$
Barium	Ba	56	[Xe] $6s^2$	$6s^2$
Radium	Ra	88	[Rn] $7s^2$	$7s^2$

• **Anomalous properties of lithium**

i) Alkali metal cations, lithium has smallest size and highest polarizing power (i.e. ionic charge 152 Pm/ionic radius ratio). Due to lithium is different from other of its family member. Therefore lithium shows anomalous nature.

ii) Lithium is soluble in organic solvents.

• **Points of difference between lithium and other alkali metals**

i) Lithium is hard metal, its melting point and boiling point are higher than alkali metals.

ii) Lithium is strongest reducing agent and least reactive among all alkali metals.

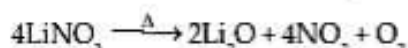
iii) Lithium combustion with air to forms Li_2O (lithium monoxide) and Li_3N (lithium nitride). This formation is not possible for other alkali metals.

iv) Lithium chloride (LiCl) is deliquescent (water absorb). It crystallizes as a hydrate ($\text{LiCl} \cdot 2\text{H}_2\text{O}$). Other alkali metal chlorides do not form hydrates.

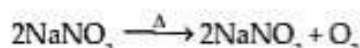
v) Lithium hydride (LiH) is the stablest as compared to other alkali metal hydrides.

vi) Lithium hydroxide (LiOH) is a weak base while other alkali metal hydroxides are strong bases.

vii) When lithium nitrate (LiNO_3) is heated (decompose) gives Lithium monoxide (Li_2O)



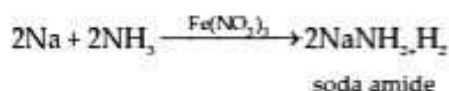
While other alkali metal nitrates decompose to give the corresponding nitrites.



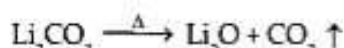
viii) Li_2CO_3 , LiF , Li_3PO_4 (Lithium carbonate, fluoride and phosphate) are sparingly soluble in water while salts of other alkali metals are soluble in water.

ix) Lithium hydrogen carbonate (LiHCO_3) is not solid but other alkali metal hydrogen carbonates are solid.

x) Lithium combines with ammonia to form lithium imide (Li_2NH) while other alkali metals combines with ammonia to form metal amide ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$)



xi) Lithium carbonate decomposes on heating to evolve CO_2 while other alkali metal carbonates do not.



PERIODIC TRENDS OF ALKALI METALS

□ The alkali metals show regular trends in their physical and chemical properties with increasing atomic number depends upon following:

i) **Electronic configuration** : All the alkali metals have one valence electron (i.e. ns^1). All these elements produce monovalent ions (M^+) by losing electron and hence never found in free state in nature.

ii) **Atomic and ionic radii**

• Alkali metal atoms have largest size in their respective periods of the periodic table.

• Atomic and ionic radii increases with increase in atomic number from Li to Cs. (except Fr)

• The monovalent ions (M^+) are smaller than the parent atoms (M)

e.g. Metallic radius :

$\text{M} = \text{Na} = 186 \text{ Pm}, \text{Li} = 152 \text{ Pm}$ Ionic radius :

$\text{M}^+ = \text{Na}^+ = 102 \text{ Pm}, \text{Li}^+ = 76 \text{ Pm}$

iii) **Ionization enthalpy (energy)**

Low values of I.E. are -

• Due to increase in atomic number, size, nuclear charge and screening effect.

e.g. Ionization enthalpy of Li is 520 kJ/mol and Cs is 376 kJ/mol.

• All alkali metals are good reducing agent.

• Ionisation energy of these elements is low and gradually decreases from Li to Cs.

• Therefore electropositive or metallic character increases from Li to Cs.

CHEMICAL REACTIVITY

□ Alkali metals are highly reactive due to their large size and low ionization enthalpy. The chemical reactivity of these elements increases from Li to Cs (down the group.) (Not Fr because radioactive)

a) **Reaction with oxygen (air)** : Alkali metals have strong affinity for oxygen and readily tarnish in air due to the formation of oxide. To prevent any reaction of alkali metals with air or moisture these are stored under kerosene or paraffin oil.

i) Alkali metal oxides react with moisture to hydroxides.

ii) Alkali metals burn in oxygen forming their oxides. Lithium forms monoxide ($4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O}$) Sodium forms peroxide ($2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$)

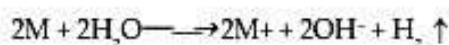
The other metals form superoxide.

($\text{K}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{KO}_2$) Potassium superoxide (O_2^-)

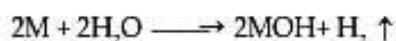
- iii) In all these oxides the oxidation state of alkali metal is +1.

b) Reaction with water

- The alkali metals react with water to form hydroxides and loss of dihydrogen.



(M = alkali metal)



- i) Except lithium, other alkali metals react explosively with water.
- ii) Lithium has the most negative E° (standard potential) value, its reaction with water is less vigorous than that of sodium which has the less negative E° value among the alkali metals.
- iii) Chemical reactivity increases with the increase in electropositive character of metal.



(Lower the standard potential and higher reducing agent)

c) Reactivity towards hydrogen (dihydrogen)

- The alkali metals react with dihydrogen at about 673 K (lithium at 1073 K) to form ionic hydrides such ionic hydrides are solids with high melting point.

- i) The reactivity of alkali metals towards hydrogen decreases as $Li > Na > K > Rb > Cs$
- ii) The lattice energy of these hydrides decreases as the size of the metal cation increases.
- iii) The stability of metal hydrides decreases from LiH to CsH ($M + H_2 \rightarrow MH$)
- iv) Li and Na form complex hydrides like $LiAlH_4$ (Lithium aluminium hydride) and $NaBH_4$ (sodium borohydride) which are powerful reducing agents.

d) Reaction with halogens

- All alkali metals react with halogens vigorously to form corresponding ionic crystalline halides.



Where M = Na, K, Rb, Cs and X = Cl, Br, I or F.

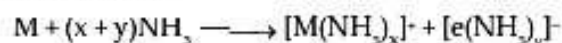
e) Reducing nature

- i) The reactivity of alkali metal towards a particular halogen increases in the order $Li < Na < K < Cs$
- ii) Lithium halide, however, have some partial covalent character.
- iii) Li^+ ion is very small in size and has a tendency to distort electron cloud around the negative halide ion. Since the anion with large size can be easily distorted.

- LiF is ionic compound, $LiCl$, $LiBr$, LiI are covalent compounds. Remaining Na, K, Rb, Cs halides are ionic compounds.

f) Solution in liquid ammonia :

- Elements of group 1 reacts with liquid ammonia gives deep blue coloured solution which show electrical conductivity.



- The blue colour changes to bronze and the solution becomes diamagnetic.

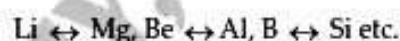


(Here am = solution in ammonia)

DIAGONAL RELATIONSHIP

- **Points of similarities between Lithium and magnesium**

Lithium and Beryllium of Group I and Group II show some properties are different from other members of respective groups. Such anomalous properties resemble the second element of the group. The similarities are



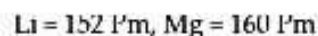
- i) This diagonal similarity is commonly called as diagonal relationship in the periodic table.

- ii) The diagonal relationship is due the similarity in

- Ionic size (ionic radii)



- Charge / Radius (Radii)



Electronegativity of $Li = 1.00$, $Mg = 1.20$

- Polarising power of Li^+ and Mg^{2+} are nearly the same.
- Hi) Li and Mg are harder than other elements in respective group.

- iv) $LiCl$ and Mg are dissolve in ethyl alcohol and they are deliquescent (water absorb) solids and crystallize from their aqueous solution as hydrates. $LiCl \cdot 2H_2O$ and $MgCl_2 \cdot 8H_2O$.

- v) They combine with oxygen to form monoxides like H_2O and MgO . The Li_2O and MgO do not combine with excess of oxygen to give super oxide.

- vi) $LiOH$ and $Mg(OH)_2$ are weak bases.

- vii) Li and Mg combine with nitrogen to give respective nitrides i.e. Li_3N , Mg_3N_2 .

- viii) The carbonates of Li and Mg decompose easily on heating to form their oxides and CO_2 .

- ix) Li and Mg hydrogen carbonates are not solid form.

- x) Li and Mg decompose water only on heating.

$$\text{Mg} + 2\text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$$
- **Screening effect**: The effect of inner electrons on the outermost electrons is called as **screening effect**.
 - **Ionization enthalpy**: The amount of **energy** required to remove the most loosely held (**bound**) electron from an isolated gaseous atom in its ground state is called ionization enthalpy.

USES OF ALKALI METALS

• Uses of Lithium

- It is used in the manufacturing of alloy like Li-Pb (used for making toughened bearing)
- Li-Al (used for aircraft construction.)
- Li-Mg - (used for armour plate and aerospace components.)
- It is used for producing thermonuclear energy for propelling rockets and guided missiles.
- LiOH is used in removing CO_2 from exhaled air in submarines and space vehicles.
- LiBr is used in medicine as sedative while LiCl is used in air conditioning system (plants) to regulate humidity.

• Uses of sodium

- Sodium is used to make Na/Pb alloy needed to make PbEt₂ and PbMe₄. These are antiknocking additives in petrol.
- Liquid sodium metal is used as coolant in fast breeder nuclear reactors.
- It is used as a reducing agent in the extraction of B and Si.
- It plays an important role in Wurtz reaction (as reagent)
- It is used in making sodium vapour lamp.

• Uses of potassium

- It is used in biological system.
- KCl is used as a fertilizer.
- KOH is used in the manufacture of soft soap and an excellent absorbent of CO_2 .
- Potassium superoxide (KO_2) is used as a source of oxygen in submarine, space shuttles and in emergency breathing apparatus.

The moisture of breath reacts with superoxide to liberate oxygen and KOH.



Potassium hydroxide thus formed removes CO_2 as it is exhaled thereby allowing the breathing apparatus

(oxygen mask) to be continuously operated.



• Uses of caesium

It is used in devising photo electric cells.

BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

• Importance of sodium and potassium in biological system

- Na and K play a vital role in the biological system.
- They are highly mobile unipositive ions forming soluble salts. Common salt which is our daily need-of food contains sodium whereas potassium is present in the coffee, tea, milk, banana, potatoes, etc.
- Daily requirement of NaCl is minimum 5-10 gm and KCl is 4 gm approximately.

• Functions of sodium and potassium ions in human cell

- Na^+ is major cation in blood plasma of vertebrate (outside the cells) and potassium is major cation in cytoplasm (inside the cells)
- Hence inside the cell and tissue, there is a higher concentration of K^+ and low concentration of Na^+ (143 mg L^{-1}) and low concentration of K^+ (5 mg L^{-1})
- Where as RBC (red blood cell) has concentration of Na^+ is 10 mg L^{-1} and K^+ is 105 mg L^{-1} .
- This difference in concentration inside and outside the cell creates a potential difference across the cell membranes. This helps nerve fibre to conduct impulses and the contraction of muscles.
- They are required to maintain osmotic pressure on either side of cell wall.
- They help regulating acid-base balance of body fluids.
- Both ions (Na^+ and K^+) are required for smooth working of muscles and nervous system. They maintain the sensitivity of nerves and control muscles.
- If Na^+ ions depress the muscles activity then K^+ ions contact it and permit the heart muscles to relax between the beats. They are structures promoters for protein and polynucleic acids.
- Deficiency of Na**: Reduction in fat deposition, atrophy of muscles and testies, lungs infection, retarded bone growth and reduction in steroid tissues, reduction in blood pressure causes circulatory failure.
- Deficiency of K**: Reduction in heart beats, scarring of heart muscles, hypertrophy of kidney and paralysis of muscles.

- **Group II Elements : Alkaline Earth Metals**

The group II elements include Be, Mg, Ca, Sr, Ba, Ra.

- These elements except Be are called alkaline earth metals as they form alkaline oxides and hydroxides, which occurs in earth's crust.

- **Electronic configuration**

- It has two electrons in s-orbital of valence shell configuration with respect to nearest noble gases in ns^2 .

- **Atomic and ionic radii**

- Atomic and ionic radii of these elements are smaller as compared to alkali metal of same period and it increases with the increase in atomic number (from Be to Ba).

- **Ionization enthalpies**

- The amount of energy required to remove the most loosely held (bound) electron from an isolated gaseous atom in its ground state is called ionization enthalpies.

- Alkaline earth metals have large atomic size and their ionization enthalpies are low.
- It decreases down the group from Be to Ba due to increase in atomic size.
- The first ionization enthalpies of the alkaline earth metals are higher than their smaller atomic size than alkali metals.
- The second ionization enthalpies of the alkaline earth metals are smaller than those of corresponding alkali metals. Because of low ionization enthalpies they are strongly electropositive in nature.

- The electropositive character increases down the group from Be to Ba.

- **Chemical reactivity**

- Chemical reactivity is less as compared to alkali metals.

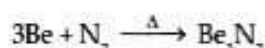
- It increases from Be to Ba due to increase in electropositive character of the metals with increasing atomic number.

- Because of small size, high electronegativity and enthalpy, mostly Be forms covalent compounds.

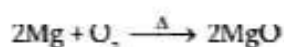
- The compound of Mg are partly ionic and partly covalent while those of Ca, Sr, Ba are purely ionic.

- **Reaction with oxygen** : Be and Mg are kinetically inert to the reaction with oxygen.

- Powdered Be burns brilliantly on ignition in air to produce BeO and Be₃N₂ (beryllium nitride)



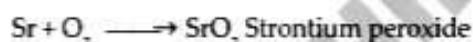
- Mg is more electropositive than Be. It burns with dazzling brilliance in air to produce MgO and Mg₃N₂.



- When Be, Mg and Na are heated with pure O₂ gives corresponding oxides



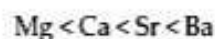
- When Sr, Ba and Ra are heated with pure O₂ gives peroxides



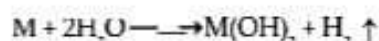
The affinity of metals towards oxygen increases down the group.

- **Reaction with water** : Be does not react even with boiling water, Mg reacts with boiling water while Ca, Sr, Ba react vigorously even with cold water.

- The order of reactivity of the metal with water increases from Mg to Ba.



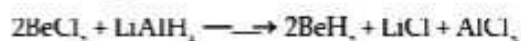
Mg reacts with water gives Mg(OH)₂ and loss of H₂ gas



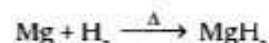
where M = Mg, Ca, Sr, Ba.

- **Reaction with hydrogen**

- However BeCl₂ reduced with LiAlH₄ gives BeH₂, LiCl and AlCl₃



- All the alkaline earth metals except Be, directly heated with hydrogen gives metal hydride. (MH₂)



Similarly Ca, Sr and Ba forms CaH₂, SrH₂ and BaH₂

- BeH₂ is covalent, MgH₂ is partly ionic but the CaH₂, SrH₂ and BaH₂ are ionic solids.

- CaH₂ is called hydrolith.

- All the hydrides react with water to evolve hydrogen and metal hydroxide (strong reducing agents)

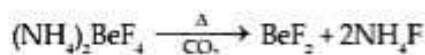


• Reactivity towards halogens

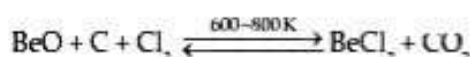
- All alkaline earth metals heated at high temperature with halogens forming (except BeF_2) corresponding metal halides.



- a) Thermal decomposition of ammonium fluoberyllate $(\text{NH}_4)_2\text{BeF}_4$ in presence of CO_2 gives BeF_2 and NH_4F .

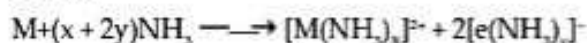


- b) BeCl_2 is prepared from BeO and carbon in the presence of chlorine between 600–800 K.



- 1 **Reducing nature** : All elements of group 2 have high negative value of standard reduction potential (E°) and strong reducing agent. However their reducing power is less than those of alkali metals.

- **Solution in ammonia** : Alkaline earth metals reacts with high liquid ammonia gives deep blue black colour.



• Anomalous properties of Beryllium

- Be shows anomalous behaviour as compared to Mg and other members of group II because of its smaller atomic and ionic radii, higher electronegativity.

- Be differs from other members of group II as follows

- Be is hard and other alkaline earth metals are soft.
- Be is least metallic in its group and forms covalent bonds due to high ionization enthalpy and small size.
- Melting and boiling point of Be are highest of all the alkaline earth metals.
- BeO and $\text{Be}(\text{OH})_2$ are amphoteric in nature while other alkaline earth metal oxides and hydroxides are basic in nature.



Sodium beryllate

- Be does not liberate H_2 from acids (HCl , H_2SO_4) while other metals react with acid and to liberate H_2 .
- Be does not show co-ordination number more than four, as in its valence shell there are only four orbitals ($\text{Be} = 2s^2, 2p_x, 2p_y, 2p_z$). The remaining members of the group can have a coordination number of six by making use of d-orbitals ($\text{Mg} = 3s^2, 3p_x, 3p_y, 3p_z, 3d^0$).

• Uses of alkaline earth metals

1) Uses of beryllium

- It is used in the manufacture of Cu-Be alloy used in the preparation of high strength springs.
- Metallic beryllium is used for making windows of X-ray tubes.

2) Uses of magnesium

- Mg is light metal, its alloys (Mg + Al + Zn) with Al and Zn are used in aircraft construction.
- An alloy of Mg + Zn used in construction of aircraft. Mg + Al alloy used in construction of aircraft.
- Suspension of $\text{Mg}(\text{OH})_2$ is used as an antacid in medicine.
- MgCO_3 is an ingredient of toothpaste.

3) Uses of calcium

- Ca is used to remove air from vacuum tubes, sulphur from petroleum and last traces of water from alcohol.
- It is used as a reducing agent in the extraction of metals from their oxides.
- Compounds of Ca such as limestone (CaCO_3) and gypsum (CaSO_4) are used as constituents of cement and mortar.
- Ca reacts with oxygen and nitrogen at high temperature. It is used to remove last traces of air from vacuum tubes.

4) Uses of barium

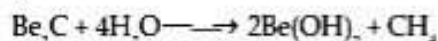
- Ba reacts with oxygen and nitrogen at high temperature, hence it is used to remove air from vacuum tubes.
- BaSO_4 is insoluble in water and opaque to X-ray. It is used as barium meal to scan the X-ray of human digestive system.

• Diagonal relationship between Be and Al

- Due to diagonal relationship and nearly same charge to radius ratio, Be (0.064) and Al (0.064). Ionic radius of Be^{2+} is 31 pm and Al^{3+} is 53.5 pm show certain similarities they are as follows :

- Be and Al have strong tendency to form covalent compounds.
- Both Be and Al do not react with acids due to oxide film present on its surface.
- $\text{Be}(\text{OH})_2$ dissolves in excess alkali gives beryllate ion $[\text{Be}(\text{OH})_4]^{2-}$ whereas $\text{Al}(\text{OH})_3$ gives aluminate ion $[\text{Al}(\text{OH})_4]^-$.

- iv) Carbides of both Be and Al on hydrolysis with H_2O give methane



Beryllium carbide



Aluminium carbide

- v) Anhydrous $BeCl_2$ and $AlCl_3$ are incomplete octet molecules and acts a Lewis acid. They are soluble in organic solvent and used as catalysts in Friedel-Craft reaction.
- vi) Be and Al form complexes like BeF_4^{2-} and AlF_6^{3-}
- vii) BeO and Al_2O_3 or $Be(OH)_2$ and $Al(OH)_3$ are amphoteric in nature.

SOME IMPORTANT COMPOUNDS OF SODIUM

(Preparation and properties)

Sodium carbonate (Washing soda = Na_2CO_3)

- Na_2CO_3 is generally prepared by solvay or ammonia soda process.
- Raw materials are ammonia, $NaCl$ and milk of $[Ca(OH)_2]$ lime.
- Ammonium bicarbonate is obtained by passing CO_2 through a solution of ammonia

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$
- NH_4HCO_3 reacts with $NaCl$ gives sodium hydrogen carbonate ($NaHCO_3$) and NH_4Cl

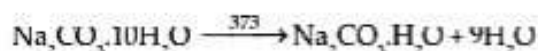
$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$
- Sodium bicarbonate being slightly soluble, gets precipitated due to common ion effect and separated. It is strongly heated to give sodium carbonate.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$
- NH_4Cl obtained in the above reaction is treated with milk of lime to give $CaCl_2$, NH_3 and water.

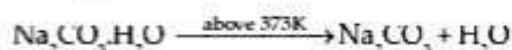
$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3$$
- K_2CO_3 cannot be obtained by this process because $KHCO_3$ being highly soluble in water can not be precipitated.

• Properties of Na_2CO_3

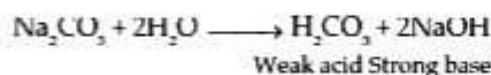
- It is soluble in water crystallizes from water as a decahydrate ($Na_2CO_3 \cdot 10H_2O$), called washing soda.
- On heating decahydrate losses water to form monohydrate.



- Further heating above 373 K (> 373 K) monohydrate becomes completely anhydrous and changes to a white powder called as soda ash.



- CO_3^{2-} ion of Na_2CO_3 gets hydrolysed by water to form an alkaline solution.



- On passing CO_2 through aqueous solution sodium hydrogen carbonate is formed



• Uses of Na_2CO_3

- It is used in paper, paints and textile industries.
- It is used to prepare glass, soap, borax and caustic soda.
- It is used in water softening in laundry and cleaning.
- It is used as important reagent for qualitative and quantitative analysis.

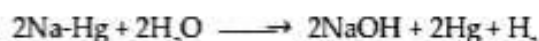
SODIUM HYDROXIDE (NAOH) (CAUSTIC SODA)

• Preparation :

- It is prepared through commercially by the electrolysis of $NaCl$ (brine solution) in Castner-Kellner cell.
- Electrolysis is conducted through mercury cathode and carbon (graphite rod) anode which sodium metal is discharges at cathode. Combine with Hg forming Na-Hg and evolution of Cl_2 gas at anode.

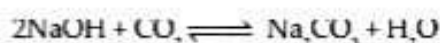


- The Na-Hg is treated with water to give $NaOH$ and H_2 gas.



• Physical properties :

- It is a white, translucent solid.
- It melts at 391 K.
- It is soluble in water gives strong alkali solution.
- Solution of $NaOH$ at the surface reacts with CO_2 in air to form Na_2CO_3 .



- **Uses**

- It is used in purification of bauxite.
- It is used in the manufacture of soap, paper, artificial silk and many chemical compounds.
- It is useful in petroleum refining.
- It is used in the textile industries for mercerizing cotton fabrics.
- It is laboratory reagent and used in preparation of pure fats and oils.

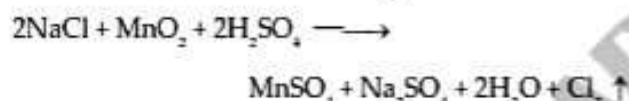
(C) **Sodium chloride (NaCl)**

- **Preparation**

- Sodium chloride is prepared by evaporation of sea water which contains CaSO_4 , CaCl_2 and MgCl_2 as impurities and is deliquescent. Which on passing through HCl gas gives pure NaCl (crude).
- Approximately 50 lakh tons of salt is produced annually in India by solar evaporation.

- **Properties**

- It melts at 1081 K.
- It is highly soluble in water. It has solubility of 36.09g in 100 g of water at 273 K
- When NaCl is heated with conc H_2SO_4 and MnO_2 it oxidised and liberates chlorine gas.



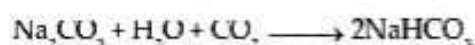
- **Uses**

- It is used as a common salt or table salt for domestic purpose.
- It is used for the preparation of Na_2O_2 , NaOH , Na_2CO_3 etc.
- It is used as a preservative for meat, fish etc.
- It is used in the salting process of soap in the freezing mixture to lower down temperature of ice.

(D) **Sodium hydrogen carbonate (NaHCO_3)**

Preparation

- It is prepared by saturated solution of sodium carbonate with CO_2 .
- The white crystalline powder of sodium hydrogen carbonate, being less soluble, gets separated out.



NaHCO_3 compound is also known as baking soda.

- **Properties**

- NaHCO_3 is heated at 373 K gives Na_2CO_3 and CO_2
- $$2\text{NaHCO}_3 \xrightarrow{373\text{ K}} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

- Its aqueous solution is alkaline due to hydrolysis.



- **Uses**

- It is used in the fire extinguisher.
- It is used as a constituent of baking powder.
- It is used in medicine to minimize the acidity of stomach (antacid)
- Baking powder is a mixture of starch, NaHCO_3 and potassium hydrogen tartarate.
- It is used in baking of cakes, breads etc. as due to heating of CO_2 is evolved which makes the cake and breads spongy porous cakes etc.

IMPORTANT COMPOUNDS OF CALCIUM

- Important compounds of calcium are CaO and CaCO_3 .

a) **Calcium oxide / Quick lime (CaO)**

- **Preparation :** It is prepared commercially on large scale by heating limestone (CaCO_3) in, a reverberatory kiln at 1070-1270 K gives CaO and CO_2 gas.

- The CO_2 is removed immediately so that reaction can proceed to completion.



Limestone quick lime

- **Properties**

- CaO (quick lime) is a white amorphous solid.
- It has a melting point of 2270 K.
- When CaO is exposed to atmosphere it absorb moisture of CO_2



- Quick lime is basic oxide on heating with NH_4Cl gives CaCl_2 , NH_3 and H_2O

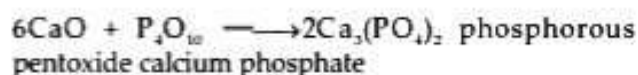


Quick lime

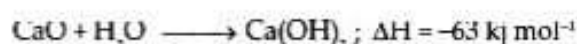
- Quick lime (basic oxide) combines with acidic oxides at high temperature.



Silica oxide calcium silicate



- Quick lime is added to limited water gives slaking of lime



Quick lime slaking of lime

vii) When dry slaked lime is reacts with chlorine gives bleaching powder



- It is used in the manufacture of Na_2CO_3 from NaOH . (caustic soda)
- It is an important primary material for large scale production of cement. It is the cheapest form of alkali.
- It is used in the manufacture of dye stuff and purification of sugar.

- **Preparation :** CaCO_3 occurs in many forms like chalk, lime stone, marble slate, calcite etc.

- i) It is prepared by passing CO_2 through slaked lime
 $\text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
 slaked lime

Controlled addition of CO_2 is essential. Excess quantity of CO_2 leads to the formation of water soluble calcium hydrogen carbonate.



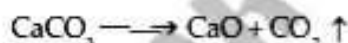
- ii) Sodium carbonate is added to calcium chloride gives calcium carbonate and NaCl.



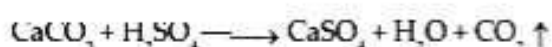
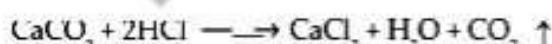
i) It is white fluffy powder.

- ii) It is almost insoluble in water.

- iii) When CaCO_3 is heated at 1200 K, it decomposes to evolve CO_2 .



- iv) CaCO_3 reacts with dil. acid (HCl or H_2SO_4) to liberate CO_2 gas.



- **Uses**

- It is used in the manufacture of quick lime CaO .
- It is used as a building material in the form of marble.
- The mixture of CaCO_3 and MgCO_3 is used as a flux in the extraction of iron metal.
- Specially precipitated CaCO_3 is used in the

v) It is a kind of antacid.

- vi) It is used as mild abrasive in tooth paste.

- vii) It is one of the constituent of chewing gum.

- **Biological importance of Mg and Ca**
Biological importance of Ca

- Adult body contains 1200 gm of calcium out of which 90% is present in bones and teeth.
- The daily requirement in the human body has been estimated to be 200-300 mg of calcium.
- Calcium play important roles in neuromuscular function, cell membrane integrity and blood coagulation and interneuronal transmission.
- Concentration of Ca in one litre of plasma is regulated to 100 mg.
- Deficiency of Ca causes rickets, osteoporosis, osteomalacia.

Biological importance of Mg

- i) Adult body contains 25 gm of Mg.
- ii) The main pigment for the absorption of light in plants is chlorophyll which contains Mg and helps ; in photosynthesis.
- iii) Mg is the co-factor of all enzymes that utilize **ATP** (Adenocine triphosphate) in phosphate and : transfer and energy release.
- iv) Deficiency of Mg results into convulsion, neuromuscular irritation.

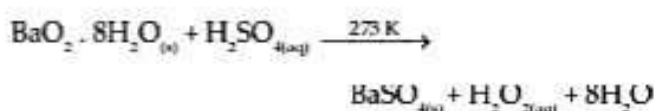
1) Molecular formula is H_2O_2 and called %s oxygenated water.

- ii) It was discovered by French Chemist Thenard in 1818.

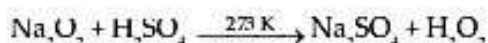
- Preparation of H_2O_2

- i) **Laboratory method**

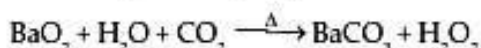
When hydrated barium peroxide is acidified with dil. H_2SO_4 , gives H_2O_2 along with a white ppt of BaSO_4 .



- a) Insoluble BaSO_4 is filtered off.
 - b) Excess water is removed by evaporation.
 - c) Anhydrous BaO_2 can not be used in this method since BaSO_4 forms a protective layer around unreacted BaO_2 and prevent further reaction.
- ii) **Merck's Method** : Sodium peroxide is reacted with dil. acids (H_2SO_4) gives sodium sulphate and H_2O_2 .

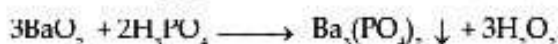


- iii) When carbon dioxide is bubbled through a thin plate of barium peroxide (BaO_2) in ice cold water, gives H_2O_2



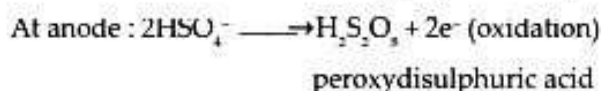
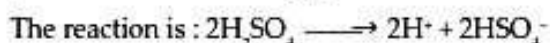
Barium peroxide ppt of
in ice cold water barium carbonate

- iv) When barium peroxide is reacted with phosphoric acid gives H_2O_2 and insoluble barium phosphate:



Barium phosphoric Barium
peroxide acid phosphate (ppt)

- v) **Electrolysis method**: On large scale, H_2O_2 is obtained by electrolysis of 50% solution of H_2SO_4 using platinum at anode and graphite at cathode



Peroxydisulphuric acid is distilled with water under pressure, low boiling hydrogen peroxide distills over along with water leaving behind boiling H_2SO_4



Peroxydisulphuric acid Peroxymono sulphuric acid



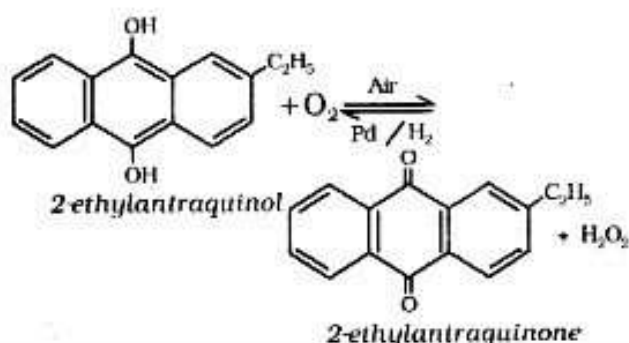
This method is now used for the laboratory preparation of D_2O_2 .



Pot. deuterium sulphate Deuterium
peroxide

- vi) **Industrial method**: This method used in USA. Industrially H_2O_2 is prepared by autooxidation of 2-ethylanthraquinol. (10% solution in benzene + cyclohexanol)

- a) When 2-ethylanthraquinol (Benzene and cyclohexanol mixture) passed in air is bubbled, it oxidizes to give 2-ethylanthraquinone and H_2O_2 .



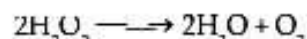
- b) 2-ethylanthraquinone is dissolved in benzene and hydrogen gas is passed through the solution in presence of Pd gives reduction product.

- c) It is an example of alternate oxidation and reduction called as auto-oxidation reaction.

- d) **Concentration of H_2O_2** : 1% H_2O_2 is obtained by this method. It is extracted with water and distilled under reduced pressure pure H_2O_2 is obtained by freezing out the remaining water.

• **Storage of H_2O_2**

- a) H_2O_2 decomposes slowly on exposure to light:



- b) The presence of metal surfaces or glass bottles which contains traces of alkali, catalyses the decomposition of H_2O_2 . Hence it cannot be stored in metallic containers or glass bottles.

- c) H_2O_2 stored in paraffin wax coated plastic or teflon bottles which are kept in dark. Small amount of acid, glycerol, alcohol, acetamide or phosphoric acid (H_3PO_4) are used as stabilizers to prevent the decomposition of H_2O_2 .

- **Strength of H_2O_2** : Strength of H_2O_2 solution is expressed either as (i) percentage strength (ii) volume strength

- (i) **Percentage strength**: It indicates weight of H_2O_2 in 100 ml solution,

e.g. 3% H_2O_2 solution = 3 g H_2O_2 in 100 ml solution,

- (ii) **Volume strength**: The volume of O_2 in litre at STP obtained by decomposition of litre of the sample.

Thus 10 volume H_2O_2 = 1 litre of H_2O_2 on decomposition gives 10 litres of O_2 at STP

A 10 volume of H_2O_2 has a normality 1/9 and is approximately 3% w/v (or 3.05 w/v exact value)

- Equivalent weight of H_2O_2

$$= \frac{\text{Molecular weight}}{\text{Acidity}} = \frac{34}{2} = 17$$

- Normality of H_2O_2

$$= \frac{\text{Percentage strength}}{\text{Equivalent weight of } \text{H}_2\text{O}_2} \times 10$$

- Volume strength of H_2O_2 = Normality \times 5.6

- Volume strength of H_2O_2 = Normality \times 11.2

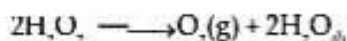
- Normality = Molarity $\times \frac{34}{17}$ = Molarity \times 2

- Molarity = $\frac{\text{Normality } N}{2} = \frac{N}{2}$

Problem : Calculate the strength of 20 volume of solution of hydrogen peroxide.

Sol.: 20 volume of solution of H_2O_2 =

1 litre H_2O_2 will give 20 litre of O_2 at STP



$2 \times 34 \text{ gm} = 22.4 \text{ litre at STP}$

$\therefore 22.4 \text{ litre of } O_2 \text{ at STP is produced from } H_2O_2$
= 68 gm

20 litre of O_2 at STP produced from.....?

$$\frac{20 \times 68}{22.4} = 60.71 \text{ g/litre}$$

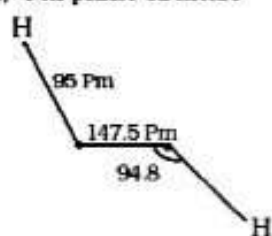
• **Physical properties of H_2O_2**

- Pure H_2O_2 is pale blue liquid.
- It is miscible with water and forms a hydrate, $H_2O_2 \cdot H_2O$ having melting point 221 K.
- Its boiling point (extrapolated) at 423 K.
- Its density in liquid form is 1.44 gm/cm^3 at 298 K.

• **Structure of H_2O_2**

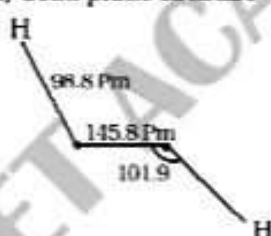
- Hydrogen peroxide is non polar open book (skew) structure.
- The bond length and angles are slightly different in gas, liquid and solid phases due to H-bonding.

1) Gas phase structure



H-O-H bond angle = 111.5°

2) Solid phase structure

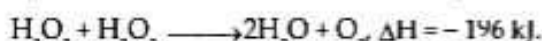


H-O-H bond angle = 90.2°

• **Chemical properties of H_2O_2**

i) **Autooxidation reduction of H_2O_2 :**

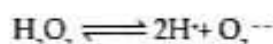
H_2O_2 decomposes rapidly on heating in presence of light, dust, carbon, Ca, Fe, Cu, Au, Ag, Pt, MnO_2 etc.



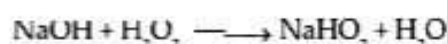
In this reaction one molecule of H_2O_2 is oxidized to O_2 (oxidation number of O^{-1} to O^0) and other molecule of H_2O_2 reduced to H_2O (oxidation number O^{-1} to O^{-2})

- It is diamagnetic and exhibits dipole moment 2.1 D.
- It acts as a weak acid (dissociation constant $= 1.55 \times 10^{-12}$ at 293 K)

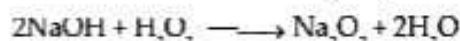
- It forms two series of salts like hydroperoxide (acidic salts) and peroxides (normal salts)



It neutralizes alkalies



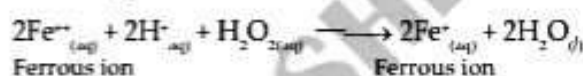
Sodium hydroperoxide (acidic salt)



Sodium peroxide (normal salt)

- H_2O_2 acts as an oxidising and reducing agent in both acidic and alkaline media.

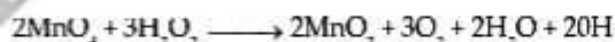
a) **Oxidising action in acidic medium**



b) **Oxidising action in basic medium**



c) **Reducing action in alkaline medium (basic medium)**



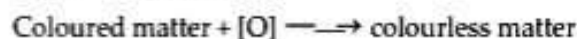
d) **Reducing action in acidic medium**



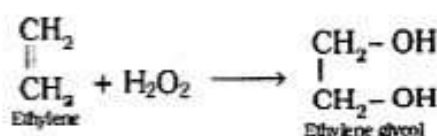
e) **Reducing action in basic medium**



- H_2O_2 acts as bleaching agent : It decomposes to give nascent oxygen which oxidizes the colouring matter to colourless matter



iv) **Formation of glycols :**



LITHIUM ALUMINIUM HYDRIDE ($LiAlH_4$)

- It is commonly abbreviated as LAH. It has chemical formula $LiAlH_4$.

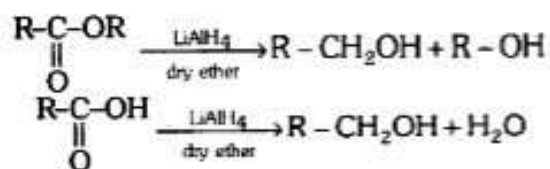
❑ **Preparation :**



❑ **Properties :** It is colourless solid. It reacts violently with water and even atmospheric moisture.

Uses :

- i) LAH is a source of hydride and therefore used as reducing agent in organic synthesis.



- ii) LAH is Useful to prepare PH_3 (phosphine)

