

# The s-Block Elements

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## The s-Block Elements

### 10.1 Introduction:

The long form of the periodic table has been conveniently divided into four blocks i.e., s, p, d and f-blocks, depending upon the filling of a particular shell. The s-block elements are those in which the last electron enters the outermost s-orbital. As the s-orbital can accommodate only two electrons, this block includes only two groups; group 1 (or 1A) and group 2 (or II A). They have one or two electrons in their outermost s-subshell respectively.

The elements of group 1 are called alkali metals and those of group 2 are called alkaline earth metals. Therefore, **alkali metals and alkaline earth metals constitute s-block.**

### 10.2 Abundance and occurrence:

The alkali and alkaline earth metals are the most violently active of all the metals. These are readily oxidized and therefore, are not found in the free state in nature. These are found in the combined form with halide, sulphate, carbonate, silicate ions, etc.

The abundance of alkali and alkaline earth metals in the earth's crust shows a good range. Among these, **calcium** is the fifth most abundant element in the earth's crust and hence, the third most abundant metal after aluminum and iron. Vast sedimentary deposits of  $\text{CaCO}_3$  occur over large parts of the earth's surface. **Magnesium** is the sixth and **sodium** is the seventh most abundant element in the crustal rocks. These are fourth and fifth most abundant metals after Al, Fe and Ca. **Potassium** (eighth) is the next most abundant element after sodium. There is unlimited supplies of NaCl in natural brines and oceanic waters. The occurrence of other metals in the earth's crust is very poor. Strontium and barium have much lower abundances. *Francium and radium are radioactive* and have rare terrestrial abundance. Francium is highly radioactive and its longest lived isotope  $^{223}\text{Fr}$  has a half life of only 21 minutes. Beryllium is rare and radium is the rarest of all comprising only  $10^{-10}$  per cent of igneous rocks.

### 10.3 Anomalous properties of first element in each group:

The elements in a group show similar physical and chemical properties. However, the first member of each group differs from its succeeding member (called **congeners**). For example, lithium shows an anomalous behavior as compared to sodium and rest of the family members of the alkali metal family. It is mainly due to the following reasons:

- (i) Small size of the atom and its ion.
- (ii) High ionization enthalpy and electronegativity.
- (iii) Non-availability of d-orbitals.

Let us study the effect of above factors on the chemistry of first element as compared to other elements (specially second). The first member differs from its succeeding members in some of the properties as given below:

- (i) As we go down a group, the size goes on increasing, therefore, the first member of each group has the smallest size in its group.
- (ii) Because of small size the first member has largest ionization enthalpy and ionization enthalpy decreases down the group.
- (iii) All the elements of second period has abnormally low electron affinity than the second member. For example, the electron affinity decreases as we move down a group but the first member has abnormally lower electron affinity than the second because of its small size.
- (iv) The small size of the atom results in relatively high cohesive properties associated with relatively strong intermetallic bonding. On the other hand, large atoms usually form weak bonds, therefore, the bond strengths of the compounds decrease as we move down the group. For example, lithium has relatively high heat of atomization, melting and boiling points, density and hardness.
- (v) The first member has higher electronegativity as compared to other members of the group. Therefore, it has greater tendency to form covalent bonds. Forexample,

lithium halides are covalent while halides of other members of group 1 are ionic in nature.

- (vi) Because of very small size of the cation of second period (e.g.,  $\text{Li}^+$ ,  $\text{Be}^{2+}$ ), it has high hydration energy and as a result, it acts as an excellent reductant in aqueous solution.
- (vii) The first member of the group has no vacant d, orbitals in its valence shell. Therefore, it can have maximum of four co-ordination number i.e., only four electron pair. On the other hand, the elements of third period (second member of the group) have vacant 3d-orbitals in its valence shell. Therefore, these can have co-ordination number more than four. In other words, elements of second period cannot extend their octets while the elements of higher periods can extend their octets. For example, beryllium forms  $\text{BeF}_4^{2-}$  while aluminium forms  $\text{AlF}_6^{3-}$  in solution.

The specific characteristics of distinction between **lithium** and **sodium** (group 1) and **beryllium** and **magnesium** (group 2) are discussed later in discussion of groups.

#### 10.4 Diagonal relationship:

It has been observed that some elements of second period show similarities with the elements of the third period present diagonally to each other, though belonging to different groups. This is called **diagonal relationship**.

Thus, the similarity in properties of elements present diagonally is called diagonal relationship. This is shown below:

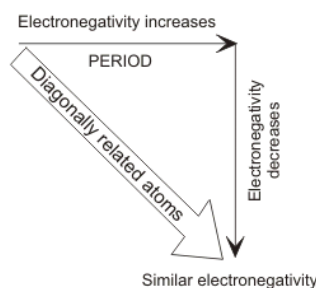
|               | Group 1 | Group 2 | Group 13 | Group 14 |
|---------------|---------|---------|----------|----------|
| Second period | Li      | Be      | B        | C        |
| Third period  | Na      | Mg      | Al       | Si       |

For example, lithium resemble with magnesium, the elements of group 2.

**Cause of diagonal relationship.** The cause of diagonal relationship is the similarity in properties such as electronegativity, ionization enthalpy, size or charge/radius ratio, etc. between the diagonal elements. For example, on moving from left to right across a period, the electronegativity increases and while moving down a group electronegativity decreases. Therefore, on moving diagonally, the two opposing tendencies almost cancel out and the electronegativity values remain almost same as we move diagonally. Thus, the diagonal pairs have many similar properties.

**Three important diagonal pairs.** The following pairs exhibit diagonal similarity:

##### (i) Lithium - magnesium



##### (ii) Beryllium – aluminium

##### (iii) Boron – silicon.

The specific characteristics of diagonally related pairs such as Li – Mg and Be-Al are discussed later in the discussion of groups.

## 10.5 Group 1; Elements-The Alkali Metals

### 10.5.1 The Electronic Configurations of Alkali Metals:

| Element   | Symbol | Atomic number | Electronic Configuration | Abundance in earth's crust (ppm) |
|-----------|--------|---------------|--------------------------|----------------------------------|
| Lithium   | Li     | 3             | [He] 2s <sup>1</sup>     | 65                               |
| Sodium    | Na     | 11            | [Ne] 3s <sup>1</sup>     | 28,300                           |
| Potassium | K      | 19            | [Ar] 4s <sup>1</sup>     | 25,900                           |
| Rubidium  | Rb     | 37            | [Kr] 5s <sup>1</sup>     | 310                              |
| Caesium   | Cs     | 55            | [Xe] 6s <sup>1</sup>     | 7                                |
| Francium  | Fr     | 87            | [Rn] 7s <sup>1</sup>     | -                                |

- All these elements are metallic in nature and are known as **alkali metals** because their hydroxides are strong bases or alkalies.

### 10.5.2 General Physical Characteristics of Alkali Metals:

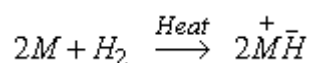
- Atomic Radii.** The **atomic radii** of alkali metals are largest in their respective periods. The atomic radii increase on moving down the group from top to bottom.
- Ionic Radii.** Alkali metals change into positively charged ions by losing their outermost electron. These ions are considerably smaller than the parent atoms. Ionic radii increase on moving down the group.
- Density.** Alkali metals have **low densities** due to their large atomic size. Densities increase on going down the group from top to bottom. Potassium is, however, lighter than sodium.
- Ionization Energy.** The first **ionization energies** of alkali metals are very low as compared with the other elements of the same period.
- Electropositive Character.** On account of their low ionisation energies, these metals have a strong tendency to lose their valence electrons and thus change into positive ions. Consequently, **alkali metals are strongly electropositive or metallic in character.** As this tendency for losing electrons increases down the group, the electropositive character increases.
- Oxidation State.** Alkali metals exhibit an **oxidation state** of + 1.
- Reducing Character.** Alkali metals are very **good reducing agents** because of their great tendency to lose electrons. The reducing character increases from Na to Cs. Li is however, stronger reducing agent than Na due to greater hydration energy.
- Cohesive Forces.** Because of weak metallic bond, alkali metals have very **weak cohesive forces** and can be cut with the help of knife. Softness of alkali metals increases with increase in atomic number.
- Melting and Boiling Points.** Alkali metals have very **low melting and boiling points** due to weak cohesive forces.
- Photoelectric Effect.** Alkali metals exhibit **photoelectric effect** due to their low ionization energies. Because of this property potassium and caesium are used as cathodes in photoelectric cells.
- Flame Colouration.** Alkali metals impart characteristic colours to the flame when they are heated in a Bunsen burner flame.

- **The compounds of alkali metals are diamagnetic.** Superoxides of alkali metals are, however, paramagnetic.
- **Hydration.** All the simple salts of alkali metals dissolve in water. In solutions alkali metal ions are hydrated.

### 10.5.3 Chemical Properties Of Alkali Metals

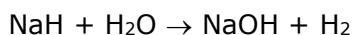
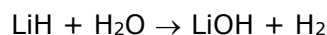
- **The alkali metals are highly reactive elements.** The reactivity of alkali metals is due to
  - low value of ionization energy; and
  - low heat of atomization.
- **The reactivity of alkali metals increases from Li to Cs.**

**1. Hydrides.** Alkali metals react with dry hydrogen to form hydrides.



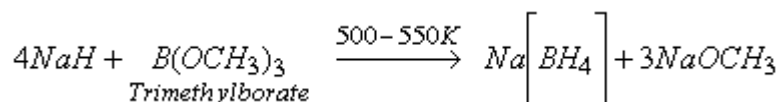
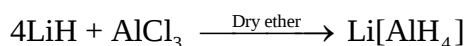
-These hydrides are ionic in nature and exist as crystalline solids.

-These hydrides of alkali metals react with water to form corresponding hydroxides and hydrogen gas.

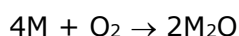


-These hydrides are **strong reducing agents** and their reducing nature **increases down the group**.

-Alkali metals also form complex hydrides such as  $LiAlH_4$  and  $NaBH_4$ , which are also good reducing agents.

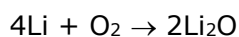


**2. Oxides.** Alkali metals on reaction with air form different kinds of oxides. For example, the alkali metals on reaction with limited quantity of oxygen form normal oxides of the formula,  $M_2O$ .

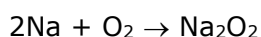


(Where  $M = Li, Na, K, Rb, Cs$ ).

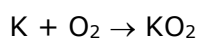
However, when heated with excess of air, lithium forms **normal oxide**,  $Li_2O$ , sodium forms **peroxide**,  $Na_2O_2$ , whereas potassium, rubidium and caesium form **superoxides** having general formula  $MO_2$ .



Lithium oxide

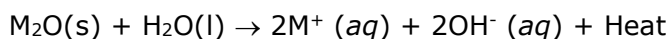


Sodium peroxide

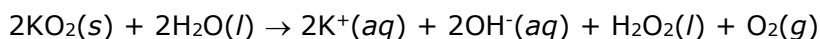
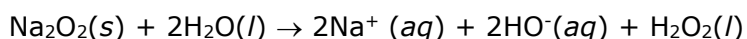


Potassium superoxide

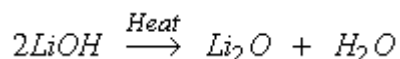
The **normal oxides** of alkali metals dissolve readily in water to form hydroxides and a large amount of heat is produced.



The **peroxides** and **superoxides** are also readily hydrolysed by water



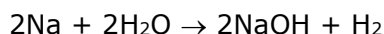
- **Basic nature of Alkali Metal Hydroxides.** The hydroxides of alkali metals are strong bases, all of which are highly soluble in water as well as in alcohol and are stable to heat.



The **basic character of alkali metal hydroxides increases in going down the group**. This can be explained in terms of decreasing ionization energies in moving down the group. The decrease in ionization energies leads to weakening of the bond between alkali metal and hydroxide ion. This results in the increased concentration of hydroxyl ions in solution, i.e., **increased basic character**. Thus, the basic character of alkali metal hydroxides is in the order

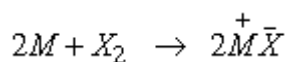


- **Reaction with Water.** Alkali metals react with water and other compounds containing acidic hydrogen atoms such as hydrogen halides (HX) and acetylene (C<sub>2</sub>H<sub>2</sub>) and liberate hydrogen gas.



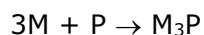
All the alkali metals when exposed to atmosphere react with oxygen and moisture to form oxides and hydroxides and therefore their surface gets tarnished. In order to protect from atmosphere oxygen and water, *these metals are stored under kerosene oil*.

- **Reaction with Halogens.** Alkali metals react with halogens to form metal halides, which are ionic crystalline solids having general formula M<sup>+</sup>X<sup>-</sup>.

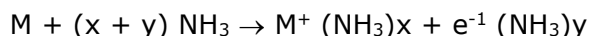


All the halides of alkali metals **except lithium fluoride** are freely soluble in water. The low solubility of lithium fluoride is attributed to greater force of attraction between lithium ions and fluoride ions in the crystal lattice.

- **Reaction with Non-Metals.** Alkali metals, on heating react with non-metals such as sulphur and phosphorus to form sulphides and phosphides respectively.



- **Solubility in Liquid Ammonia.** All alkali metals dissolve in liquid ammonia giving *dark blue* solutions which are conducting in nature. These solutions contain ammoniated cations and ammoniated electrons as shown below.



- **Complex Compounds.** The alkali metal ions form fewer complex compounds than any other group of metal ions. This is due to their large atomic size and weak effective nuclear charge. The complex forming ability decreases in the order.



### Anomalous Behaviour Of Lithium And Its Diagonal Relationship With Magnesium

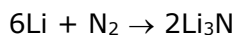
The properties of lithium are quite different from the properties of other alkali metals. On the other hand, it shows greater resemblance with magnesium, which is diagonally opposite element of group 2. The main reasons for the anomalous behavior of lithium as compared to other alkali metals are:

- The extremely small size of lithium atom and its ion.
- Greater polarizing power of lithium ion ( $\text{Li}^+$ ), due to its small size which results in the greater covalent character in the compounds.
- Least electropositive character and highest ionization energy as compared to other alkali metals.

The reason for resemblance of properties of lithium with magnesium is that these two elements have almost same polarizing power.

The following points illustrate the anomalous properties of lithium and its diagonal relationship with magnesium:

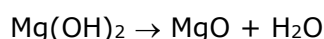
- The melting point and boiling point of lithium are comparatively high.
- Lithium is much harder than the other alkali metals. Magnesium is also a hard metal.
- Lithium reacts with oxygen least readily to form normal oxide whereas other alkali metals form peroxides and super-oxides. Magnesium also forms normal oxide.
- $\text{LiOH}$  like  $\text{Mg}(\text{OH})_2$  is a weak base. Hydroxides of other alkali metals are strong bases.
- Due to their appreciable covalent nature, the halides and alkyls of lithium and magnesium are soluble in organic solvents.
- Unlike other alkali metals but like magnesium, lithium forms nitride with nitrogen.



- Unlike other alkali metals lithium reacts directly with carbon to form ionic carbide. Magnesium also forms similar carbide.



- The carbonates, hydroxides and nitrates of lithium as well as magnesium decompose on heating.



The corresponding salts of other alkali metals are stable towards heat.

- $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ,  $\text{LiF}$  and  $\text{Li}_3\text{PO}_4$  are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.
- The lithium ion and its compounds are more heavily hydrated than those of other alkali metals. Lithium chloride, like magnesium chloride, separates out from aqueous solutions as hydrated crystals,  $\text{LiCl} \cdot 2\text{H}_2\text{O}$ . Sodium and other alkali metal chlorides do not form hydrates at ordinary temperature,  $\text{LiCl}$  and  $\text{MgCl}_2$  are deliquescent.

## 10.6 Elements of alkali metals and Their Compounds

### 10.6.1 Lithium (Li) and its compounds

#### Important ores-

**Petalite**  $LiAl(Si_2O_5)_4$  – 2.7 – 3.7%

**Spodummene**-  $LiAl(SiO_3)_2$  – 4 – 6%

**Triphylite**-  $(Li, Na)_3PO_4 \cdot (Fe, Mn)_3(PO_4)_2$  – 4%

**Lepidolite** or **Lithia mica**-  $(Li, Na, K)_2, Al_2(SiO_3)_3, (F, OH)_2$  – 1.5%

**10.6.1.1 Physical Properties Of Lithium:** Silvery white metal; harder than Na or K;

Lightest metal known (density 0.634)

#### 10.6.1.2 Chemical properties Of Lithium:

**(i) With air:** No effect by dry air

When heated air,  $Li + O_2 \xrightarrow{200^\circ C} Li_2O$

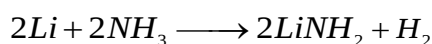
**(ii) With water**  $2Li + 2H_2O \xrightarrow{Cold} 2LiOH + H_2 \uparrow$

**(iii)** Reacts **with dil. acids** to liberate hydrogen

**(iv) With non-metals** (e.g.,  $H_2, N_2, S$  and  $X_2$  etc.) form hydride, nitride, sulphide and halides, etc.,  $LiH, Li_3N, Li_2S, LiX$ .

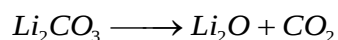
**(v) With  $NH_3$** -dark blue solution with liquid  $NH_3$  however when  $NH_3$  is passed over molten

$Li \rightarrow LiNH_2$  is formed as



#### 10.6.1.3 Compounds of Li

**1.  $Li_2O$ :** Prepared by burning Li in oxygen or air. However obtained in pure condition from  $LiCO_3, LiOH, LiNO_3, Li_2SO_4$ , etc., heating, as:

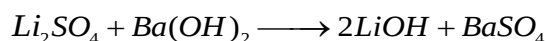


$Li_2O$  is a white solid, that reacts slowly with water to form LiOH. It resembles other alkali hydroxides is possessing caustic properties.

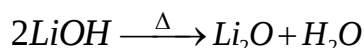
**2.  $Li_2O_2$ :** It is prepared by adding  $H_2O_2$  and alcohol to a concentrated solution of LiOH. It appears as white precipitate as  $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ .

When dehydrated over  $P_2O_5$  it loses water as well as  $H_2O_2$  thus leaving behind  $Li_2O_2$ .

**3.  $LiOH$ :** Prepared by the action of **Baryta water** [ $Ba(OH)_2$ ] on lithium sulphate as:



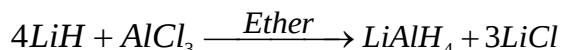
It is less soluble and much less thermally stable. It decomposes on heating as:



4. **LiH**: Prepared by heating metal Li in a current of  $\text{H}_2$ .

White solid substance, m.p. - 680°; electrovalent' reduces  $\text{CO}_2$  to C; with water liberates  $\text{H}_2$ .

5. **LiAlH<sub>4</sub>**: Prepared by reacting  $\text{AlCl}_3$ (anhy.) + LiH (in ethereal solution), powerful reducing agent.



6. **LiCl**: Prepared by burning metal in  $\text{Cl}_2$  or by adding  $\text{HCl}$  to  $\text{LiOH}$  or  $\text{Li}_2\text{CO}_3$ , white crystalline solid extremely soluble in water also soluble in alcohol and pyridine.

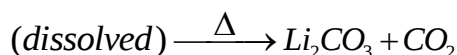
7. **LiNO<sub>3</sub>**: Prepared by dissolving  $\text{Li}_2\text{CO}_3$  in dil.  $\text{HNO}_3$ . Highly soluble in water and alcohol, on heating gives  $\text{NO}_2 + \text{O}_2$

8. **Li<sub>2</sub>CO<sub>3</sub>**: Prepared by  $(\text{NH}_4)_2\text{CO}_3$  + salt of Li(soluble)  $\longrightarrow \text{Li}_2\text{CO}_3$  (ppt.)

White stable powder on heating above 600° decomposes it to give oxide.

Sparingly soluble in water (  $\approx$  Ca and Mg).

Carbonate + passing of  $\text{CO}_2$  in solution  $\longrightarrow \text{LiHCO}_3$



**Lithia water**: Solution of  $\text{LiHCO}_3$  used for gout and rheumatism.

#### 10.6.1.4 Tests for Li:

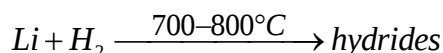
1. **Flame test**: Crimson red.

2. **Phosphate test**: Sodium hydrogen phosphate +  
 $\text{Li salt} \longrightarrow (\text{Na}_2\text{HPO}_4) + \text{Li}_3\text{PO}_4 \downarrow + \text{HCl}$   
 White

3. **Carbonate test**: White ppt. wit ammonium carbonate. ( $\text{Li}_2\text{CO}_3$ ) white

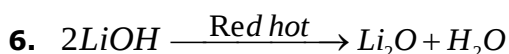
#### 10.6.1.5 Anomalous behaviour of Li: Li differs in

- Li hardest, its boiling point and melting point highest among the group
- Li  $\rightarrow$  least reactive,
- Only alkali metals which reacts directly with  $\text{N}_2$  to give nitride ( $\text{Li}_3\text{N}$ ).
- LiH  $\rightarrow$  much more stable



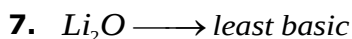
(Remaining hydrides are formed at 350-430°C)

5. With air or  $\text{O}_2$  it only gives  $\text{Li}_2\text{O}$ , i.e., monoxide while remaining gives  $\text{M}_2\text{O}_2$  (peroxide) and  $\text{MO}_2$  (superoxide) also.



Others hydroxides  $\xrightarrow{\text{Red hot}}$  no reaction

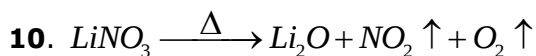
$\text{LiOH} \longrightarrow$  lowest solubility



8. Fluoride, phosphates, oxalate and carbonates of Na, K  $\longrightarrow$  freely soluble

9. Carbonates and hydroxide of Li  $\longrightarrow$  least stable (thermally)

Carbonates and hydroxide of other alkalis  $\longrightarrow$  highly stable (thermally)



$\text{NaNO}_3 \longrightarrow \text{NaNO}_2 + \text{O}_2 \uparrow$  (Thermally stable)

(Nitrates of other alkali metals also give same reactions)

11. Lithium sulphate  $\longrightarrow$  does not form alums.

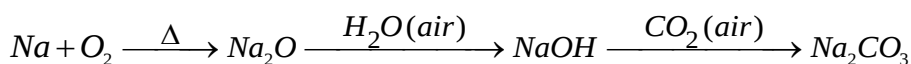
### 10.6.2 Sodium(Na) and its compounds

**Important ores**-NaCl (Rock salt);  $\text{NaNO}_3$  (Chilesaltpetre);  $\text{Na}_3\text{AlF}_6$  (Cryolite);  $\text{NaAlSi}_3\text{O}_8$  (Felspar)

#### 10.6.2.1 Properties of Sodium:

**(i) Physical:** Soft, silvery white metal; density 0.972 g/cc; m.p. = 97.8°C; b.p. = 883°C, malleable and ductile.

**(ii) Chemical: (a) With air:** Tarnished by moist air because firstly



When heated in dry air  $\longrightarrow$  mixture of oxides (monoxide + peroxide)

**(b) With water:** Hydroxide +  $\text{H}_2 \uparrow$

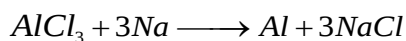
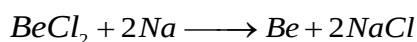
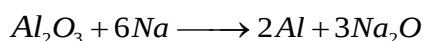
**(c) With acids:**  $\text{H}_2 \uparrow$

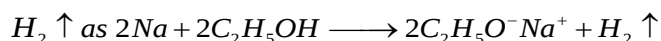
**(d) With  $\text{H}_2$ :** Electrovalent hydride

**(e) With  $\text{NH}_3$ :** Deep blue solution and when heated in a current of  $\text{NH}_3 \longrightarrow \text{NaNH}_2$

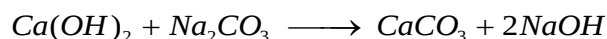
**(f) With non-metals:** With  $\text{Cl}_2$ , S and P forming NaCl,  $\text{Na}_2\text{S}$ , and  $\text{Na}_3\text{P}$

**(g) Reducing action:** Strong, e.g.,



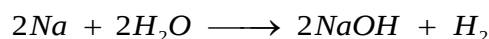
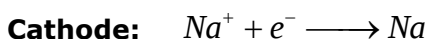
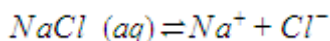
**(h) With alcohols:****10.6.2.2 Compounds of Sodium(Na)****10.6.2.2.(a) Sodium Hydroxide NaOH (Caustic soda):****Preparation by electrolysis of NaCl [brine]**

Until World War II, the principal method of producing sodium hydroxide, NaOH, involved conversion of  $Ca(OH)_2$  to  $CaCO_3$  using  $Na_2CO_3$

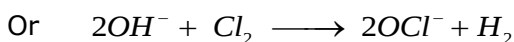


The reaction goes to completion as is evident by measuring pH of the solution after reaction.

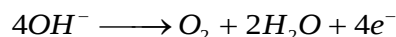
- Electrolysis of aqueous NaCl gives NaOH at cathode



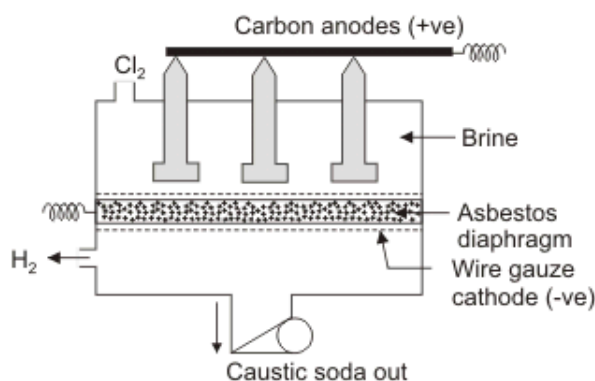
Side reaction may also occur if the products formed mix with one each other.



And following reaction may also occur at the anode to a smaller extent:

**Nelson Cell (Diaphragm cell)**

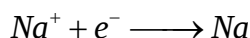
If  $H_2$  and  $Cl_2$  gases mix, they react with explosion. A porous diaphragm of asbestos is used to keep the  $H_2$  and  $Cl_2$  (and thus cathode and anode) gases separated from one another. Product in this cell is a mixture of 11% NaOH and 16% NaCl. Concentration in a steam evaporator gives solution containing 50% NaOH and 1% NaCl. (Fig)



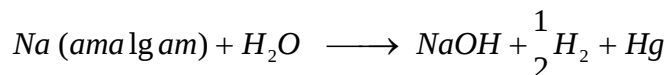
**Fig.** A Diaphragm Cell

### Mercury Cathode Cell (Castner-Kellner Cell)

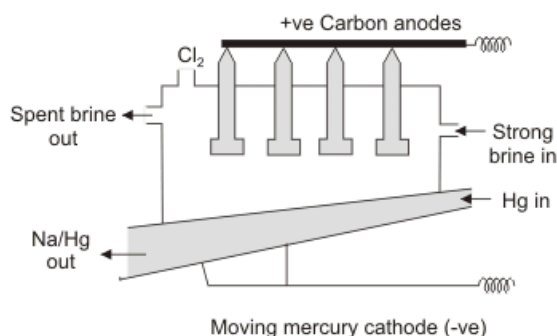
During the electrolysis of brine,  $\text{Na}^+$  is discharged at cathode



If the cathode is made of mercury, the Na atoms produced are dissolved in mercury to a different compartment and water reacts to form NaOH.

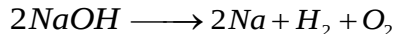


Originally the anodes were made of graphite, but because traces of oxygen are produced in a side reaction, they become pitted with corrosion. The anodes are now made of steel coated with titanium (Fig).



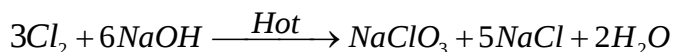
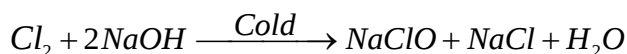
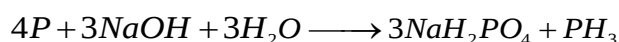
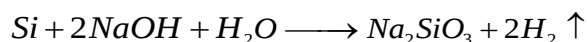
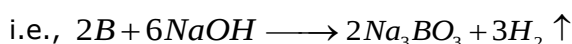
**Fig.** The Castner-Kellner Cell

**Properties:** White solid, m.p. =  $318^\circ\text{C}$ . Decomposes at  $1300^\circ$  as

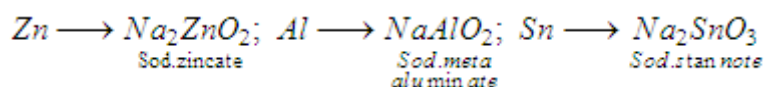


Hygroscopic, highly soluble in water,  $\longrightarrow$  gives strongly alkaline solution. Sparingly soluble in alcohol but less soluble than KOH.

- **With non-metals** (e.g., B, Si white P, S and halogens)  $\longrightarrow$  sod. Salt of oxyacid of non-metal.



- **Weakly electropositive metals** dissolved in NaOH and evolve  $\text{H}_2$ . After forming complexes like



- Precipitates hydroxide from many salt solutions, e.g., it precipitates  $\text{Fe}(\text{OH})_2$  from  $\text{FeSO}_4$  solution.
- **With CO** under pressure it gives sodium formate.

#### 10.6.2.2.(b) Sodium chloride (Common salt), NaCl.

**Preparation.** The most abundant source of sodium chloride is sea water which contains 2.7 – 2.9% by mass. In tropical countries like India, common salt is generally obtained by evaporation of sea water. In India, about 50 lakh tons of salt are produced annually by solar evaporation. Crude sodium chloride obtained by crystallization of brine solution contains impurities of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), calcium sulphate ( $\text{CaSO}_4$ ), calcium chloride ( $\text{CaCl}_2$ ) and magnesium chloride ( $\text{MgCl}_2$ ). Since  $\text{MgCl}_2$  and  $\text{CaCl}_2$  are deliquescent (absorb moisture easily from the atmosphere), therefore, impure common salt gets wet in rainy season. To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride (HCl) gas when crystals of pure sodium chloride separate out. The calcium and magnesium chloride being more soluble remain in the solution.

**Properties.** Sodium chloride melts at 1081 K. Its solubility is 36.0 g per 100 g of  $\text{H}_2\text{O}$  at 273 K. However, the solubility does not increase appreciably with rise in temperature.

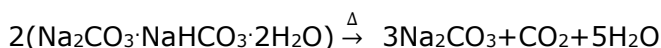
**Uses.**

(i) It is used as a common salt or table salt for domestic purposes.

(ii) It is used in the preparation of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{O}_2$ .

#### 10.6.2.2.(c) Sodium carbonate $\text{Na}_2\text{CO}_3$ : ("Washing soda" or "soda ash")

From pre-historic times a natural deposit called Trona,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  (sesqui-carbonate) has been obtained from dried-up lake beds in Egypt. Trona is sometimes called sodium sesqui-carbonate (sesqui means one and half) and on heating it,  $\text{Na}_2\text{CO}_3$  is obtained.



**Manufacture by solvay ammonia process.** The process involving following three steps:

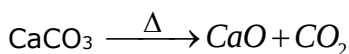
**Step (1)**  $\text{CO}_2$  is passed through a solution of  $\text{NH}_3 \longrightarrow \text{NH}_4\text{HCO}_3$  is produced

**Step (2)**  $\text{NH}_3 \longrightarrow \text{NH}_4\text{HCO}_3$  is then reacted with

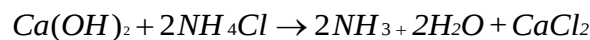


**Step (3)** Bicarbonate  $\xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$

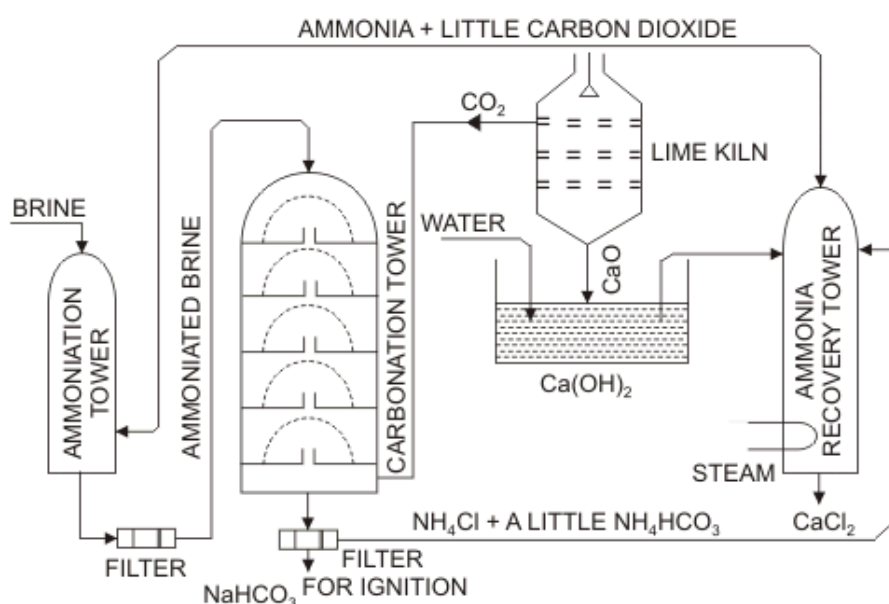
- $\text{CO}_2$  is obtained by the decomposition of  $\text{CaCO}_3$



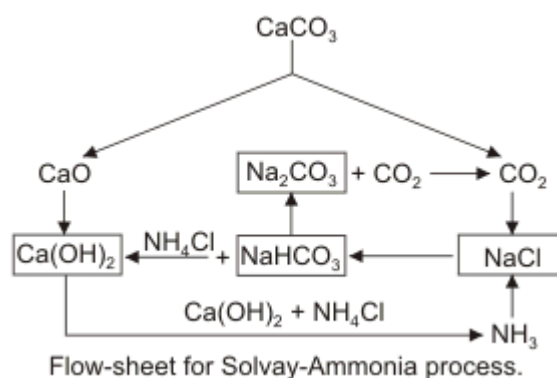
- $\text{CaO}$  (aq) can decompose  $\text{NH}_4\text{Cl}$  to form  $\text{NH}_3$  which can be reused



Thus,  $\text{NH}_3$  is required in first instance only; it is recycled in further cycles. It is shown in the fig



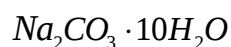
Solvay-Ammonia process for the manufacture of sodium carbonate.



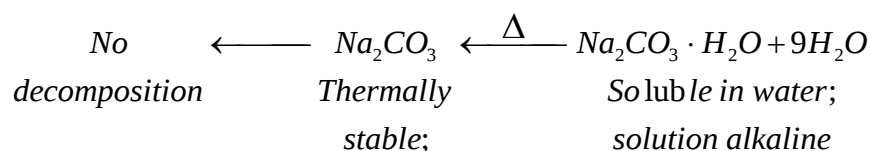
Flow-sheet for Solvay-Ammonia process.

**Raw Materials:**  $\text{NaCl}$ ,  $\text{NH}_3$  and limestone (for  $\text{CO}_2$ ) Most of  $\text{NH}_3$  can be recovered in the process  $\text{CaCl}_2 \longrightarrow$  only by-product.

**Properties:** Crystallizes as decahydrate



$\downarrow$  Gives on exposure to air



- Fusion mixture**  $\longrightarrow \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$  mixture (as these two carbonates are thermally stable in nature)

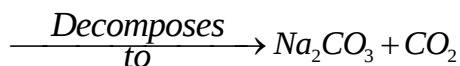
#### 10.6.2.2.(d) $\text{NaHCO}_3$ : (Sodium bicarbonate)

**Manufacture by Solvay process in lab.**  $\text{NaHCO}_3$  is prepared by saturating a solution of  $\text{Na}_2\text{CO}_3$  (cold) with  $\text{CO}_2 \longrightarrow \text{NaHCO}_3$  separates as white crystals (Due to its poor solubility in water).

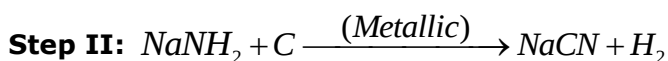
**Properties:**

(a) Sparingly soluble in water; solution, mild alkaline

(b) If heated (solid or solution)



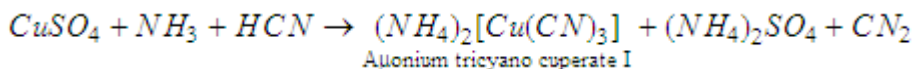
Produces  $\text{CO}_2$  that's why used as constituent of "**baking powder**" and effervescent drinks.

**10.6.2.2.(e) NaCN: (Sodium cyanide)****Step I**

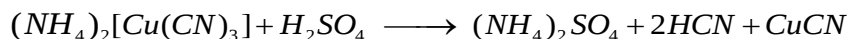
(ii) **From calcium cyanamide:** Through crude calcium cyanamide



(iii) From coal gas in its purification where HCN and  $\text{NH}_3$  are evolved as impurities. These impurities are treated with  $\text{CuSO}_4$  as,



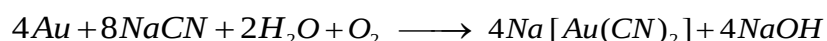
When all the copper salt has been converted into the complex cyanide, dil.  $\text{H}_2\text{SO}_4$  is added to it. The HCN gas evolved is absorbed in NaOH solution to form NaCN as,

**Properties**

- Colourless solid, readily soluble in water, solution alkaline due to hydrolysis of  $\text{CN}^-$  ion. Highly poisonous, smell of bitter almonds.
- Forms soluble complex cyanides with salts of transition elements like Cu, Au, Ag, Cd, Zn, Fe, etc., as



- **Dilute solution of NaCN can dissolve Au or Ag in the presence of air or oxygen forming soluble complex cyanide as**



$\text{Na}[\text{Au}(\text{CN})_2]$  is sodium dicyano aurate (I)

- Large quantities of NaCN is used in the extraction of Au and Ag, along with, it is also employed for the **electroplating of Au and Ag** which involves electrolysis of their complex cyanides. On account of its highly poisonous character, it is also used as germicide.

**10.6.2.2.(f) Sodamide  $\text{NaNH}_2$  :**

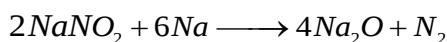
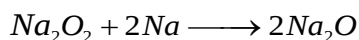
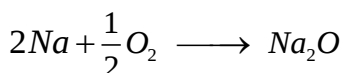
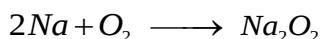
**Preparation:** Steam of dry  $\text{NH}_3$  over metal Na (iron retorts)  $300-400^\circ\text{C}$ .

**Properties:** Waxy solid, m.p.  $210^\circ\text{C}$ ;

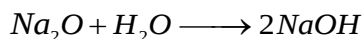
- (a) With water  $\longrightarrow \text{NaOH} + \text{NH}_3$ ;
- (b) With dry  $\text{H}_2 \longrightarrow (150-300^\circ) \longrightarrow \text{NaH} + \text{NH}_3$
- (c) With CO  $\longrightarrow \text{NaCN} + \text{NaOH} + \text{NH}_3$
- (d) With  $\text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{CN} \cdot \text{NH}_3 + \text{H}_2\text{O}$
- (e) With  $\text{N}_2\text{O} \longrightarrow \text{NaN}_3$  (sodium azide) +  $\text{H}_2\text{O}$

**10.6.2.2.(g) Sodium oxide and peroxide( $\text{Na}_2\text{O}$  and  $\text{NaO}$ )**

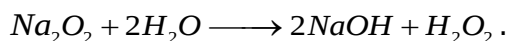
- Sodium peroxide alongwith sodium oxide is formed when sodium burns in air or with  $\text{NaNO}_2$



- $\text{Na}_2\text{O}$  is colourless ionic solid and aqueous solution is a strong base.

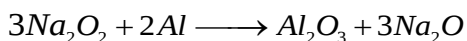


- $\text{Na}_2\text{O}_2$  is diamagnetic (all electrons paired) and is regarded as a salt of dibasic acid  $\text{H}_2\text{O}_2$ .

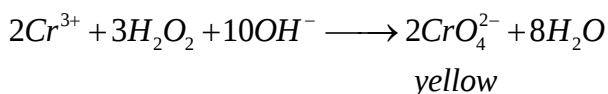
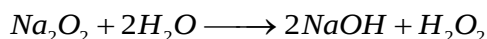


- $\text{Na}_2\text{O}_2$  is colourless in pure form but is pale yellow in colour due to presence of sodium superoxide  $\text{NaO}_2$  and is an oxidizing agent.

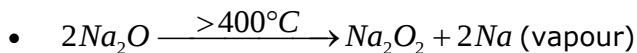
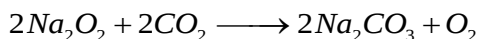
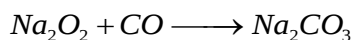
- Al is oxidised to  $\text{Al}_2\text{O}_3$



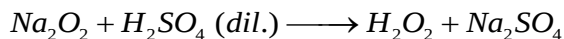
- $\text{Cr}^{3+}$  salt is oxidised to  $\text{CrO}_4^{2-}$  (yellow)



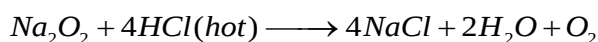
Because it reacts with  $\text{CO}_2$  in the air, it has been used to purify air in submarines and confined spaces, as it both removes  $\text{CO}_2$  and produces  $\text{O}_2$ .



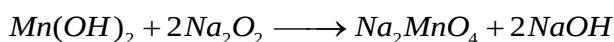
- $\text{Na}_2\text{O}_2$  gives  $\text{H}_2\text{O}_2$  with dilute acids



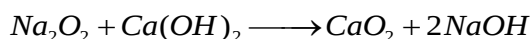
- $\text{O}_2$  is formed when  $\text{Na}_2\text{O}_2$  reacts with hot acids



- $\text{Na}_2\text{O}_2$  oxidises  $\text{Mn}(\text{OH})_2$  to  $\text{MnO}_4^{2-}$  (green)



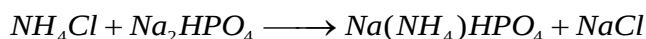
When mixture of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O}_2$  is compressed,  $\text{CaO}_2$  is formed.



#### 10.6.2.2.(h) Microcosmic salt, $\text{Na}(\text{NH}_4)\text{HPO}_4$

**Preparation** of microcosmic salt can be describe as:

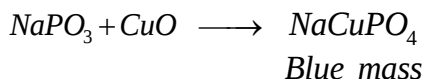
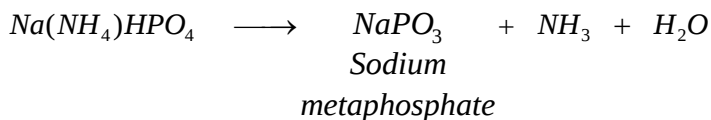
- It is prepared by dissolving ammonium chloride and disodium hydrogen phosphate in molecular proportion in hot water.



- The sparingly soluble microcosmic salt separates out. It is filtered and purified by recrystallisation.

#### Properties

- It is colourless crystalline solid, sparingly soluble in water.
- When heated, it melts to form a clear transparent mass which has the property of combining with metallic oxides to form coloured orthophosphates.

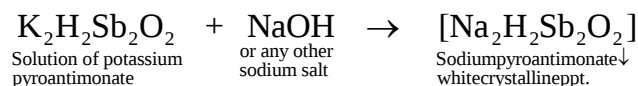


- On account of this property, microcosmic salt is used for the detection of coloured ions. The test is similar to borax bead test. The salt is heated on a loop of platinum wire as the result, a transparent bead is formed. When hot bead is brought in contact with coloured substance and strongly heated, a coloured bead is formed if the substance contains  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , etc. It is especially used for testing silica with which a cloudy bead containing floating properties of silica is obtained.

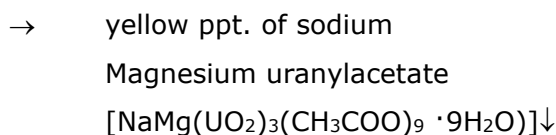
### 10.6.2.3 Tests of Na.

(a) **Flame test** : yellow colour.

(b) **Pyroantimonate test** :



(c) Sodium salt + solution of magnesium uranyl acetate



### 10.6.3. Potassium(K):

Symbol K is derived from german word **Kali**. Important ores are

**Carnallite** --  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

**Polyhalite** --  $\text{K}_2\text{SO}_4, \text{MgSO}_4, \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

**Kainite** --  $\text{KCl}, \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$

**Schonite** --  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$

**Felspar** --  $\text{KAlSi}_3\text{O}_8$ ;

**Norwegian salt petre** --  $\text{KNO}_3$ ;

**Longbenite** --  $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$

- Resembles Na in its physical and chemical properties (softer and chemically more reactive) slightly radioactive.

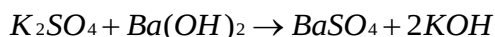
#### 10.6.3.1 Compounds of potassium:

##### 10.6.3.1.(a) Potassium hydroxide(KOH)

**Preparation** :

(i) It is prepared by the electrolysis of KCl solution or from potassium carbonate by caustification process.

(ii) Pure KOH is obtained by adding potassium sulphate to a hot saturated solution of  $\text{Ba}(\text{OH})_2$ .  $\text{BaSO}_4$  is filtered off and filtrate is evaporated in a silver dish.



**Properties:**

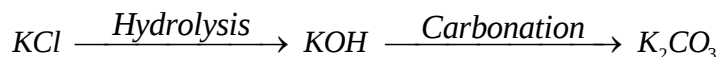
- It purified like NaOH by dissolving in alcohol.
- It is white crystalline, highly deliquescent solid, extremely soluble in water; m.p.  $360.4^\circ\text{C}$ . Its action as an alkali, is stronger than that of NaOH.
- Absorbs  $\text{CO}_2$  from air to form  $\text{K}_2\text{CO}_3$ .

- More soluble in alcohol than NaOH.

#### 10.6.3.1.(b) Potash or pearl ash ( $K_2CO_3$ ):

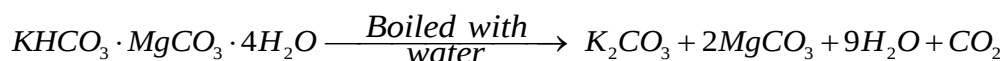
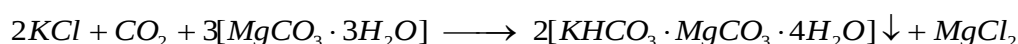
##### Preparation:

(i) From **Leblanc** process (It is an oldest process.)



(ii) **Manufacture through Engel-Precht process:**

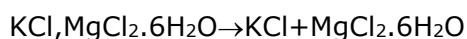
By passing  $CO_2$  in  $MgCO_3 \cdot 3H_2O$  and KCl.



- **Properties:** White hygroscopic solid, m.p.  $-900^\circ C$  very soluble in water, thermally stable.

**10.6.3.1.(c) Potassium chloride(KCl):** Its principal source is **stassfurt salt** where it occurs as **syilvine KCl**, and also as carnallite  $KCl \cdot MgCl_2 \cdot 6H_2O$ . **Dried sea weeds contain 90% KCl.**

KCl is prepared from fused carnallite-nearly pure KCl separates from the melt, leaving fused  $MgCl_2$  behind.

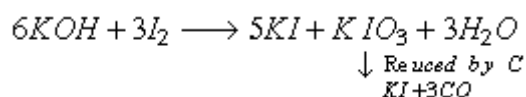


##### Properties

It is colourless cubic crystal like solid soluble in water. Its solubility increases almost linearly with temperature.

**10.6.3.1.(d) Potassium iodide(KI):** It is prepared:

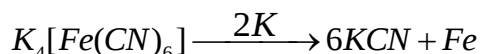
(i) From KOH



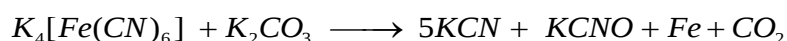
#### 10.6.3.1.(e) Potassium cyanide(KCN):

- KCN can be prepared by:

(i) By drying  $K_4[Fe(CN)_6]$  to white heat or with metallic K as:



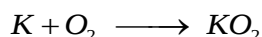
(ii) By the reaction of  $K_4[Fe(CN)_6]$  with  $K_2CO_3$  as:



- KCN is white crystalline solid, highly hygroscopic and very soluble in water, its aqueous solution is alkaline; **a deadly poison.**

#### 10.6.3.1.(f) Potassium superoxide ( $KO_2$ )

**Preparation:** It is formed as a chrome-yellow (orange) powder by burning potassium in excess of moisture-free oxygen or air.

**Example:**

What is the most reactive alkali metal and why?

**Solution:**

The most reactive alkali metal is caesium due to its lowest first ionization enthalpy and lowest electronegativity.

**Example:**

The alkali metals have low densities. Explain.

**Solution:**

The alkali metals have low densities due to their large atomic sizes. In fact, Li, Na and K are even lighter than water.

**Example:**

The metallic lustre exhibited by sodium is explained by

- (A) Diffusion of sodium ions      (B) Oscillation of loose electrons  
(C) Excitation of free protons      (D) Existence of body-centered cubic lattice

**Solution:**

(B)

**10.6.4 Biological Importance of Sodium and Potassium**

A typical human being weighing about 70 kg contains about 90 g of Na, 170 g of K, 5 g of Fe and 0.06 g of Cu.

Although  $Na^+$  and  $K^+$  ions have similar chemical properties but surprisingly their biological functions are quite different. Whereas  $Na^+$  ions are primarily found outside the cells in blood plasma and other interstitial fluids,  $K^+$  ions are present inside the cells. These ions help in transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into the cells.

Since  $K^+$  ions are the most abundant cations within the cell fluids, they activate many enzymes and participate in the oxidation of glucose to produce ATP (adenosine triphosphate).

There is a very large variation in the concentration of  $Na^+$  and  $K^+$  ions found on the opposite sides of cell membranes. For example, in blood plasma,  $Na^+$  ions are present to the extent of  $143 \text{ mmol L}^{-1}$  while the concentration of  $K^+$  ions is only  $5 \text{ mmol L}^{-1}$  within the red blood cells. These concentrations change to  $10 \text{ mmol L}^{-1}$  ( $Na^+$ ) and  $105 \text{ mmol L}^{-1}$  ( $K^+$ ). These ionic gradients called the *sodium-potassium pump* operate across the cell membranes which consume more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human being.

## 10.7 Group- 2; Elements-The Alkaline-Earth Metals

### 10.7.1 The Electronic Configurations of Alkaline-Earth Metals

| Element          | Symbol | Atomic number | Electronic Configuration | Abundance in earth's crust in (ppm) |
|------------------|--------|---------------|--------------------------|-------------------------------------|
| <b>Beryllium</b> | Be     | 4             | [He] 2s <sup>2</sup>     | 6                                   |
| <b>Magnesium</b> | Mg     | 12            | [Ne] 3s <sup>2</sup>     | 20,900                              |
| <b>Calcium</b>   | Ca     | 20            | [Ar] 4s <sup>2</sup>     | 36,300                              |
| <b>Strontium</b> | Sr     | 38            | [Kr] 5s <sup>2</sup>     | 300                                 |
| <b>Barium</b>    | Ba     | 56            | [Xe] 6s <sup>2</sup>     | 250                                 |
| <b>Radium</b>    | Ra     | 88            | [Rn] 7s <sup>2</sup>     | 1.3 x 10 <sup>-6</sup>              |

All these elements are metallic in nature. These are known as **alkaline earth metals** because oxides of these metals were called **alkaline earths** as they existed in the earth and were alkaline in nature.

### 10.7.2 General Physical Characteristics of Alkaline-Earth Metals

**Atomic Radii.** The **atomic radii** of alkaline earth metals are quite larger but are smaller than those of alkali metals.

**Density.** The **densities** of alkaline earth metals are larger than those of alkali metals. This is due to stronger metallic bond. Density of alkaline earth metals first decreases from Be to Ca and then increases from Ca to Ra.

**Cohesive Forces.** Cohesive forces in alkaline earth metals are stronger than alkali metals due to smaller atomic radii and greater nuclear charge. Alkaline earth metals are harder than alkali metals due to stronger metallic bond.

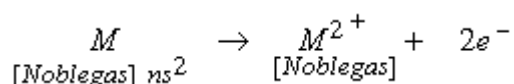
**Melting and Boiling Points.** The melting and boiling points of alkaline earth metals are quite low but are higher than those of alkali metals.

**Ionization Energy.** The alkaline earth metals owing to their large size of atoms have fairly low values of **ionization energies** as compared to the *p*-block elements. However, within the group, the ionization energy, decreases as the atomic number increases.

A comparison of ionisation energies of elements of groups 1 and 2 shows that the members of group 2 have higher values. This is due to smaller size and higher nuclear charge of alkaline earth metals due to which the electrons in their outermost shell are tightly held.

It is interesting to note that although first I.E. of alkaline earth metals are higher than those of alkali metals, the second I.E. values are much lower than those of alkali metals.

- **Electropositive Character.** Alkaline earth metals are fairly **electropositive** in nature; however, due to their greater ionization energies these are less electropositive than alkali metals. In general, among the family members the electropositive character increases from Be to Ba.
- **Oxidation States.** The alkaline earth metals have two electrons in their valence shell and by losing these electrons; these atoms acquire the stable noble gas configuration. Thus, alkaline earth metals exhibit + 2 oxidation state in their compounds.



**Reducing Properties.** All the members of group 2, owing to their low ionization energies have a tendency to lose their valence electrons and thus act as strong reducing agents. Reducing character increases on moving down the group from top to bottom. However, the members of this group are weaker reducing agents than the alkali metals. *It is because of higher ionization energy of alkaline earth metals as compared to alkali metals.*

**Flame colouration:** Among the members of this group except Be and Mg other members give characteristics colouration to the flame.

|           |             |              |             |
|-----------|-------------|--------------|-------------|
| Ca        | Sr          | Ba           | Ra          |
| Brick red | Crimson red | Grassy green | Crimson red |

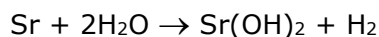
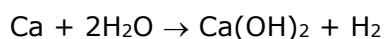
Beryllium and magnesium do not impart any colour to the flame because of their small size and higher ionisation energies. Due to this, the energy of flame is insufficient to cause the excitation of their valence electrons to higher shells.

**Solubility in liquid ammonia:** all these metals dissolve in liquid  $\text{NH}_3$ . Dilute solutions are bright blue in colour while concentrated solutions are bronze coloured. These solutions on evaporation yield hexammineates of metals which slowly decompose to give metal amides

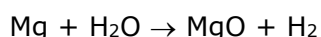


### 10.7.3 Chemical Characteristics of Alkaline–Earth Metals

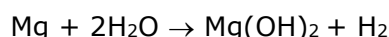
- Alkaline earth metals are **quite reactive** elements due to their *low ionization energies* and *high* electropositive character. The reactivity of these elements increases with increase in atomic number.
- Alkaline earth metals are less reactive than alkali metals.
- Reaction with Water.** Ca, Sr and Ba react with cold water, liberating hydrogen gas



Magnesium decomposes hot-water



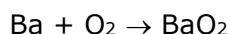
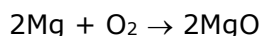
Or



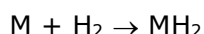
Beryllium does not react with water.

*Order of Reactivity:*  $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$

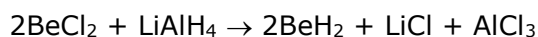
- Reaction with Oxygen.** All the alkaline earth metals burn in oxygen to form oxides. Be, Mg and Ca form oxides whereas Ba and Sr form peroxides.



- Hydrides.** All the members of the group, except beryllium, combine with hydrogen on heating to form metal hydrides,  $\text{MH}_2$ .

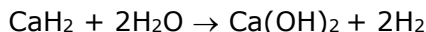


$\text{BeH}_2$  can, however, be produced by reduction of  $\text{BeCl}_2$  with  $\text{LiAlH}_4$ .

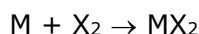


$\text{BeH}_2$  and  $\text{MgH}_2$  are covalent in nature and are polymeric, while  $\text{CaH}_2$ ,  $\text{SrH}_2$  and  $\text{BaH}_2$  are ionic in nature.

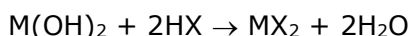
The hydrides are good reducing agents and are hydrolyzed by water with evolution of H<sub>2</sub> gas



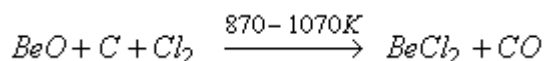
- **Hydroxides.** The hydroxides of these elements can be formed either by dissolving metal oxides in water or by reaction of these elements with water.
- Be(OH)<sub>2</sub> is amphoteric. The **hydroxides** of magnesium, calcium, strontium and barium are **bases** and their strength increases from magnesium to barium.
- These hydroxides are less soluble in water as compared to the alkali metal hydroxides.
- The solubility of the hydroxides in water increases with the increase in atomic number. Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are almost insoluble, Ca(OH)<sub>2</sub>, is sparingly soluble while Sr(OH)<sub>2</sub> and Ba(OH)<sub>2</sub> are increasingly more soluble.
- **Halides.** Alkaline earth metals react with halogens directly to form halides having general formula, MX<sub>2</sub>.



These halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides.



Beryllium chloride is prepared indirectly, from its oxide as follows:

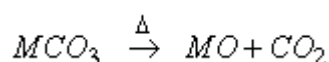


***Beryllium chloride exists as monomer or dimer in vapour state but exists as polymer in solid state.***

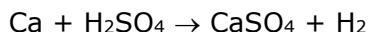
- **Carbonates.** Carbonates of alkaline earth metals are insoluble in water. These can be precipitated by addition of sodium or ammonium carbonate solution to the solution of salts of these metals. For example,



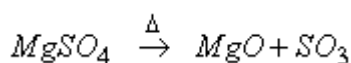
- All the carbonates decompose on heating to give carbon dioxide and metal oxide.



- However, as the atomic number increases, the stability of the carbonates towards heat **increases**. Beryllium carbonate is unstable and can be kept only in an atmosphere of CO<sub>2</sub>.
- **Sulphates.** Sulphates of alkaline earth metals can be prepared by the reaction of H<sub>2</sub>SO<sub>4</sub> with the metals, their oxides, hydroxides or carbonates.

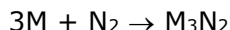


- The sulphates of alkaline earth metals are less soluble than the corresponding salts of alkali metals. Their solubilities decrease on going down the group.
- All these sulphates decompose on heating

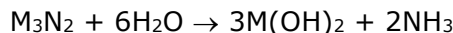


The thermal stability of sulphates increases on moving down the group from top to bottom.

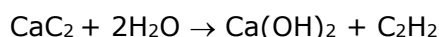
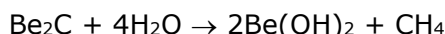
- **Nitrides.** Alkaline earth metals burn in nitrogen to form nitrides,  $M_3N_2$  which are ionic in nature.



Nitrides on reactions with water are hydrolysed and ammonia is released.



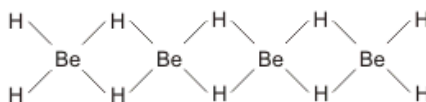
- **Carbides.** BeO when heated with C at about  $2000^\circ\text{C}$   $\text{Be}_2\text{C}$  is formed. The metals Mg, Ca, Sr and Ba form carbides of the formula  $\text{MC}_2$ . These carbides are formed when the metal or the metal oxide is heated with carbon in an electric furnace.
- These carbides are ionic in nature.
- $\text{Be}_2\text{C}$  yields methane on hydrolysis whereas carbides of other metals yield acetylene



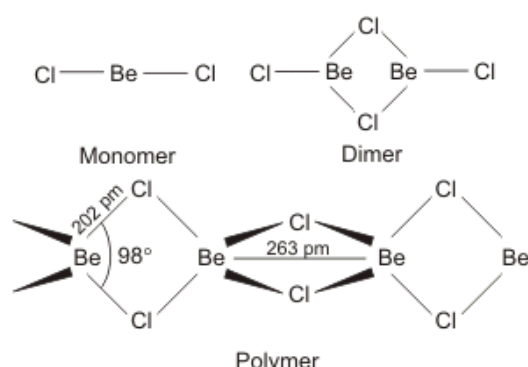
- **Complex Compounds.** Alkaline earth metals have a tendency to form stable complexes. Their ability to form complexes is more as compared to alkali metals. This is because of the smaller size and higher charge of the alkaline earth metal ions as compared to alkali metal ions. Among the elements of group 2, beryllium and magnesium, have greater tendency of complexation.
- Carbides of both Al and Be give methane on hydrolysis.
- $\text{BeCl}_2$  like  $\text{Al}_2\text{Cl}_6$  has a bridged polymeric structure.
- The salts of beryllium as well as aluminium are extensively hydrolysed.
- Beryllium hydride is electron deficient and polymeric with multicentre bonding, just like aluminium hydride but unlike hydrides of other alkaline earth metals.

#### 10.7.4 Some more important points about alkaline earth metal compounds are:

1. **BeO :** Very hard solid (4 : 4 coordination); rest oxides are with 6 : 6 co-ordination. These oxides are highly stable due to their large ionic crystal lattice energies. BeO and MgO are almost insoluble in water. **Due to their high melting points, MgO and CaO are used as basic lining of furnaces.**
2. The basic character and solubility of hydroxides increases down the group. **The aqueous suspension of  $\text{Mg(OH)}_2$  is called milk of magnesia and used as anti acid drug (antacid).**  $\text{Ba(OH)}_2$  is almost as strong as the alkali hydroxides and most soluble among all hydroxides.
3.  $\text{BeH}_2$  and  $\text{MgH}_2$  are known to have polymeric bridge structure with hydrogen present as bridge between two metal atoms.



4.  $\text{BeCl}_2$  shows polymeric bridge structure in its solid state which it is monomeric in vapour phase with zero dipole moment.



5. Sulphate, carbonates, nitrates and hydroxides of these metals decompose on heating to yield oxides.

#### 10.7.5 Main ores of alkaline earth metals are:

1. **Be** : In complex silicates *e.g.*, **felspar** and **mica**.

**beryl** –  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$

2. **Mg**: **Magnesite** –  $\text{MgCO}_3$ ; **dolomite** –  $\text{MgCO}_3 \cdot \text{CaCO}_3$ ; **carnallite** –  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

**Asbestos** –  $\text{CaMg}(\text{SiO}_3)_4$

3. **Ca**: Largely as carbonates *e.g.*, limestone, chalk, calcite, marble, dolomite etc. and sulphates *e.g.*, gypsum, anhydrite ( $\text{CaSO}_4$ ) alongwith fluorspar ( $\text{CaF}_2$ ), calcium silicate ( $\text{CaSiO}_3$ ) etc.

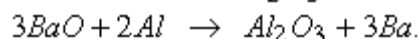
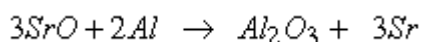
4. **Sr**: **Celestine** ( $\text{SrSO}_4$ ); **strontianite**  $\text{SrCO}_3$ .

5. **Ba** :  $\text{BaCO}_3$  (witherite) ;  $\text{BaSO}_4$  (barytes)

6. **Ra**: Pitchblende and carnotite.

#### Outlines of extraction of various alkaline earth metals are:

- Be** ores are first oxidized to give  $\text{BeO}$  which is then reduced with the help of Cu and coke to get Be.
- Mg** is usually extracted by the electrolysis of fused  $\text{MgCl}_2$  or  $\text{MgO}$ . Carnallite is used as the source of  $\text{MgCl}_2$  and magnesite for  $\text{MgO}$ . From  $\text{MgO}$  the metal can also be obtained through its reduction by C, Si or Al at about  $2000^\circ\text{C}$  in vacuum. In the modern process (**pidgeon process**) mixture of ferrosilicon and Al is used as reducing agent.
- Ca**: By the electrolysis of fused  $\text{CaCl}_2$  mixed with about 12%  $\text{CaF}_2$  in graphite vessel.
- Sr and Ba** – By reduction of their oxides on heating with Al (alumino-thermic process) at  $1200^\circ\text{C}$ .

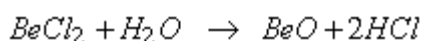


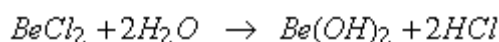
##### 10.7.5.1 Some important compounds of Be and their important characteristic include:

1. **BeO** : Prepared by burning Be in air or by heating hydroxide, carbonate or nitrate of Be.

White powder, insoluble in water, partly ionic, amphoteric, unchanged by heating in air, On heating with carbon, silicon or boron it yields : Carbide ( $\text{Be}_2\text{C}$ ) ; silicide ( $\text{BeSi}$ ) or boride ( $\text{Be}_3\text{B}_2$ ) ; with high m.p. ( $2570^\circ$ )  $\rightarrow$  used as refractory material.

2. **BeCl<sub>2</sub>** : Prepared by burning metal in  $\text{Cl}_2$  or by  $\text{HCl}$  + metal, white crystalline solid, m. p.  $44^\circ$ , fumes in air like  $\text{PCl}_5$  and very readily hydrolysed in the presence of water.





$\text{BeCl}_2 \rightarrow$  Dissolves freely in water (exothermic)  $\rightarrow [\text{Be}(\text{H}_2\text{O})_4]^{2+}$  on crystallization  $[\text{Be}(\text{H}_2\text{O})_4\text{Cl}_2]$  is deposited

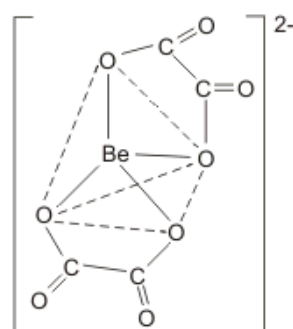
- 3.  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  :** Prepared by dissolving BeO in hot conc.  $\text{H}_2\text{SO}_4$ . Crystallites as tetrahydrate.

Tetrahydrate loses water at  $400^\circ\text{C}$ ; anhyd.  $\text{BeSO}_4$  decomposes above  $500^\circ\text{C}$ .

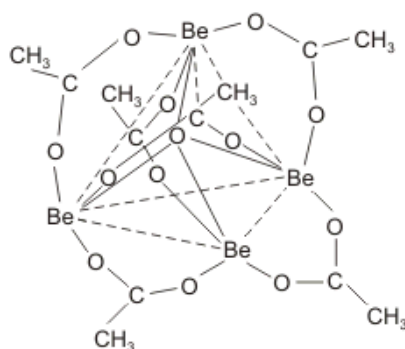
$\text{BeSO}_4 \xrightarrow{\Delta} \text{BeO} + \text{SO}_3$ . Tetrahydrate  $\rightarrow$  Very soluble; Anhydr.  $\rightarrow$  almost (insoluble in water (cold)); with hot water insoluble anhyd is converted into tetrahydrate (soluble).

Be gives Be oxalate ion with oxalic acid.

Be gives Be acetate with acetic acid  $[\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6]$ .



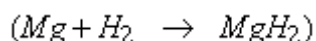
Structure of beryllium oxalate ion  $[\text{Be}(\text{OX})_2]^{2-}$



Structure of basic beryllium acetate,  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$

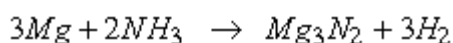
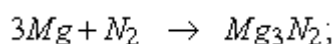
### 10.7.5.2 Some important compounds of Mg and their important characteristics

- 1.  $\text{MgH}_2$  :** Preparation by passing  $\text{H}_2$  under pressure on heated Mg powder

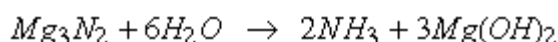


Light grey solid, gives out  $\text{H}_2$  on treatment with  $\text{H}_2\text{O}$ . Fairly stable and decomposes only when strongly heated.

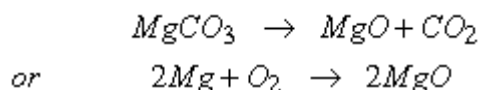
- 2.  $\text{Mg}_3\text{N}_2$  :** Preparation by heating Mg to redness in  $\text{NH}_3$  or  $\text{N}_2$



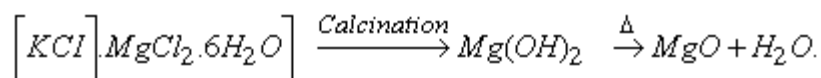
Light yellow solid; reacts with water as



**3. MgO** : Preparation when magnesite is heated to high temperature as

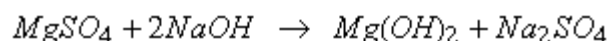


Also preparation from



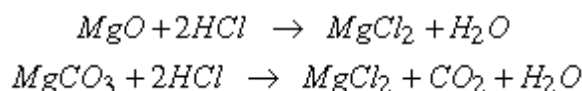
White powder melts at 2300° C; basic; changes gradually to Mg (OH)<sub>2</sub> in water; **used as refractory material in furnaces.**

**4. Mg(OH)<sub>2</sub>** : Preparation by the action of an alkali with Mg salt.



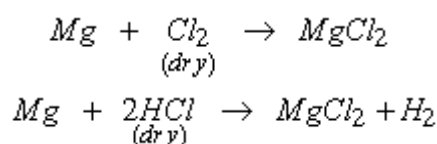
Sparingly soluble in water; ppt. by NH<sub>4</sub>OH in the presence of NH<sub>4</sub>Cl. Weak base when heated at high temperature changes to MgO.

**5. MgCl<sub>2</sub>** : Obtained in laboratory in its hydrate form by dissolving MgO(OH)<sub>2</sub> or MgCO<sub>3</sub> in dilute HCl as :

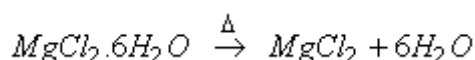


Anhydrous MgCl<sub>2</sub> cannot be prepared by heating the hydrated salt because on heating it undergoes partial hydrolysis. Thus it is obtained.

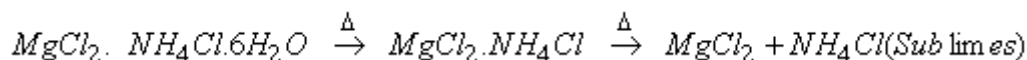
(i) By heating Mg in current of dry chlorine or HCl gas as :



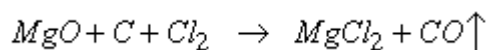
(ii) By heating MgCl<sub>2</sub> . 6H<sub>2</sub>O in vacuum as



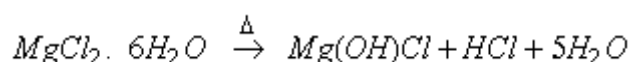
(iii) By igniting the double salts of Mg and NH<sub>4</sub>Cl. NH<sub>4</sub>Cl sublimes leaving the anhydrous salt as



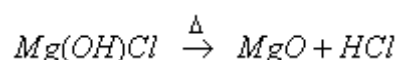
(iv) By heating a mixture of MgO and C in a current of dry Cl<sub>2</sub>



**Properties of MgCl<sub>2</sub>** include colourless, crystalline solid, highly deliquescent, exceedingly soluble in water, crystallises as MgCl<sub>2</sub> . 6H<sub>2</sub>O. On heating basic magnesium chlorides of variable composition are obtained as



On strong heating MgO is obtained as,



When a saturated solution of  $MgCl_2$  is mixed with  $MgO$  the resulting paste sets to a hard marble like mass having the composition  $MgCl_2 \cdot 5MgO \cdot xH_2O$ . It is called as **magnesia cement** or **sorel cement**. This cement is **uses** as

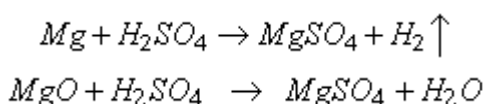
- (a) Dental filling
- (b) A finish for plaster due to its high polish
- (c) For cementing glass and porcelain
- (d) For making artificial stones

**NOTE:**

**When sorel cement is mixed with saw dust, cork waste etc, a fairly weather proof wood like material called xylotite is obtained which is used as covering for floor, laboratory tables etc.**

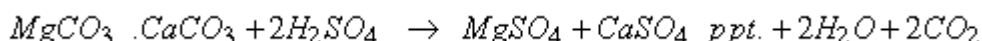
**6.  $MgSO_4$  :** Occur as  $MgSO_4 \cdot 7H_2O$ , commonly called Epsom salt (Epsom = Name of place where huge amounts of  $MgSO_4$  seen). It is prepared

(i) In lab by the action of dil.  $H_2SO_4$  with  $MgO$  or  $Mg$  metal as



The solution on concentration gives crystals of  $MgSO_4 \cdot 7H_2O$ .

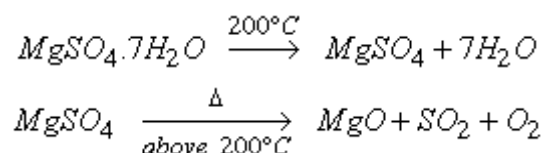
(ii) By dissolving dolomite in boiling dilute  $H_2SO_4$



Insoluble  $CaSO_4$  is removed by filtration.

(iii) Commercially it is prepared by dissolving mineral **kiesserite** in boiling water and then crystallising the resulting solution.

Colourless, efflorescent, soluble in water, bitter in taste, isomorphous with  $ZnSO_4 \cdot 7H_2O$ , can easily form double salts like  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ . On heating to  $200^\circ C$  all water of crystallisation is lost. On further heating  $MgO$  and  $SO_2$  are obtained as



**Test of Mg:**

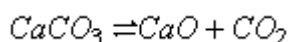
**(a)Charcoal cavity test:** Here, the  $Mg$  salt is heated till it is converted into white residue in charcoal cavity. This white residue on moistening with cobalt nitrate solution is converted into pale pink mass of  $MgO \cdot CaO$ .

**(b)**  $Mg$  salt +  $\alpha$ -nitrosobenzene-azo- $\beta$ -naphthol+  $NaOH \rightarrow$  Blue coloured solution is obtained.

**10.7.5.3 Some important compounds of Ca and their important characteristics**

**1.  $CaO$  (quick lime)**

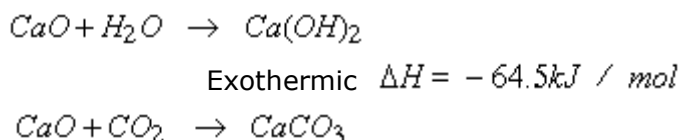
**Preparation** by heating limestone to  $1000^\circ C$  in lime lines as



reversible reaction, proceeds efficiently in forward direction when  $CO_2$  is allowed to escape from the system.

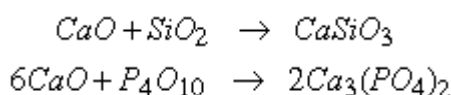
**Properties :** Amorphous white solid, with high melting point (2273K), usually obtained in the form of hard lumps and when heated in oxyhydrogen flame emits a bright light called **lime light**.

Easily absorbs  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as



The addition of limited quantity of water converts limp of lime to slaked lime (as the process is called **slaking**) Similarly, if we use soda in the place of water the product is called **soda lime (NaOH/CaO)**

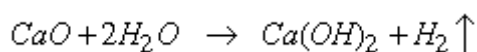
Combines with solid acidic oxides at high temperature to give their salts as :



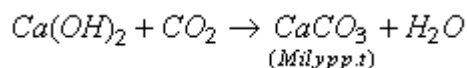
Very useful as drying agent, in bleaching powder production (as used for the preparation of slaked lime) and as a constituent of **mortar**.

## 2. $\text{Ca(OH)}_2$ (slaked lime)

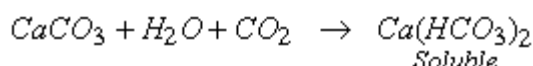
**Preparation** by adding water to quick lime as



White powder, sparingly soluble in water, **aqueous solution called lime water and aqueous suspension is called milk of lime**.  $\text{CO}_2$  has the ability to turn lime water milky as



This milkiness disappears with excess of  $\text{CO}_2$  as soluble calcium hydrogen carbonate is formed:



Being basic in nature it reacts with acids and acidic gases forming their salts.

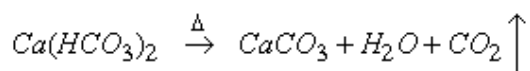
On reaction with chlorine, it forms hypochlorite a constituent of bleaching powder as :



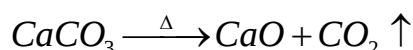
Slaked lime is used in mortar production, lime water production, disinfectant, bleaching powder production etc.

## 3. $\text{CaCO}_3$ (Limestone)

Commonest form of  $\text{CaCO}_3$  is lime stone and it is also found as chalk, marble, coral, calcite, aragonite etc. A precursor of quick lime and slaked lime. It is prepared as:



Easily decomposed on heating as:



**4.  $\text{CaSO}_4$  :**  $\text{CaSO}_4$  usually occur as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (**Gypsum** or **alabaster** or **selenite**)

It forms compounds like  $\text{CaSiO}_3$  and  $\text{Ca}(\text{AlO}_2)_2$  with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  respectively.

**5. Portland cement**

Mixture of Ca silicates and Ca aluminates with small amount of gypsum.

**Composition:**  $\text{CaO} = 50\text{-}60\%$ ,  $\text{SiO}_2 = 20\text{-}25\%$ ,

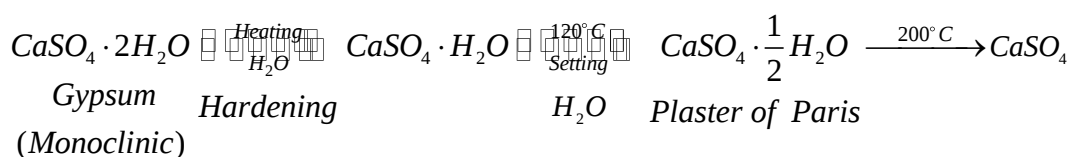
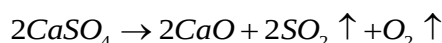
$\text{Al}_2\text{O}_3 = 5\text{-}10\%$ ;  $\text{MgO} = 2\text{-}3\%$ ,  $\text{Fe}_2\text{O}_3 = 1\text{-}2\%$ ;  $\text{SO}_3 = 1\text{-}2\%$

**Essential raw materials-limestone** for  $\text{CaO}$ , etc., **clay** for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , etc.

**6. Plaster of Paris,  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  or  $(\text{CaSO}_4)_2\text{H}_2\text{O}$**

It occurs in nature as gypsum and the anhydrous salt as anhydride. It is prepared by precipitating a solution of calcium or nitrate with dilute sulphuric acid.

The effect of heat on gypsum or the dehydrate presents a review of interesting changes. On heating the monoclinic gypsum is first converted into orthorhombic form without loss of water. When the temperature reaches  $120^\circ\text{C}$ , the hemihydrate or plaster of paris is the product. The latter losses water becomes anhydrites above  $200^\circ\text{C}$  and finally above  $400^\circ\text{C}$ , it decomposes into calcium oxide.

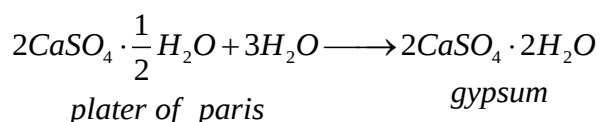


The following conditions are necessary

- (i) The temperature should not be allowed to rise above 393 K because above this temperature the whole water of crystallization is lost. The resulting anhydrous  $\text{CaSO}_4$  is called dead burnt plaster because it loses the properties of setting with water.
- (ii) The gypsum should not be allowed to come in contact with carbon containing fuel otherwise some of it will be reduced to calcium sulphite.

**Properties**

It is a white powder. On mixing with  $1/3^{\text{rd}}$  its weight, it forms a plastic mass which sets into a hard mass of interlocking crystals of gypsum within 5 to 15 minutes. It is due to this reason that it is called plaster. The addition of common salt accelerates the rate of setting, while a little borax or alum reduces it. The setting of plaster of paris is believed to be due to rehydration and its reconversion into gypsum.



**Uses:**

- (i) Plaster of paris is used for producing moulds for pottery and ceramics & casts of statues & busts.
- (ii) It is used in surgical bandages used for plastering broken or fractured bones.
- (iii) It is also used in dentistry.

### 10.7.5.3.1 Industrial Uses of Lime, Slaked Lime and Limestone

#### Uses of lime

Calcium oxide is called lime or quick lime. Its main industrial uses are.

- (i) It is used in steel industry to remove phosphates and silicates as slag.
- (ii) It is used to make cement by mixing it with silica, alumina or clay.
- (iii) It is used in making glass.
- (iv) It is used in lime soda process for the conversation of  $Na_2CO_3$  to  $NaOH$  & Vice versa.
- (v) It is used for softening water, for making slaked lime  $Ca(OH)_2$  by treatment with water and calcium carbide  $CaC_2$ .

#### Uses of slaked lime $[Ca(OH)_2]$

- (i) Slaked lime is used as a building material in form of mortar. It is prepared by mixing 3-4 times its weight of sand and by gradual addition of water. It sets into a hard mass by loss of  $H_2O$  and gradual absorption of  $CO_2$  from air.
- (ii) In manufacture of bleaching powder by passing  $Cl_2$  gas.
- (iii) In making glass and in the purification of sugar and coal gas.
- (iv) It is used in softening of had water.

#### Uses of lime stone ( $CaCO_3$ )

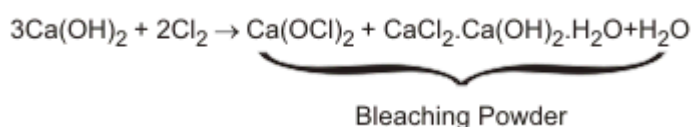
- (i) It is used as building material in form of marble.
- (ii) In manufacture of quick lime.
- (iii) It is used as a raw material for the manufacture of  $Na_2CO_3$  in solvay- ammonia process.
- (iv) Commercial limestone contains iron oxide, alumina, magnesia, silica & sulphur with a  $CaO$  content of 22-56%  $MgO$ ,  $MgO$  content upto 21%. It is used as such as a fertilizer.

### 10.7.6 Bleaching Powder

The exact chemical composition of bleaching powder is not yet known but it behaves as if it contains calcium hypochlorite  $Ca(OCl)_2$  and basic calcium chloride,

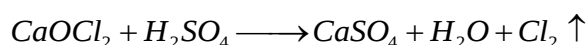
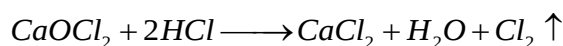


**Preparation:** It is prepared by passing chlorine over slaked lime



#### Properties:

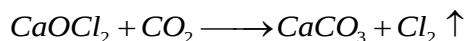
- (i) Reaction with dilute acids: with dilute acids, it gives chlorine which is known as available chlorine.



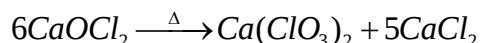
(ii) When treated with water it decomposes into calcium chloride and calcium hypochlorite.



(iii) Bleaching powder reacts with  $\text{CO}_2$  (atmospheric) and gives chlorine which accounts for its oxidizing and bleaching actions.



(iv) Action of heat: On heating bleaching powder gives a mixture of chlorate and chloride.



### 10.7.7 Biological Importance of Magnesium and Calcium

Magnesium and calcium ions play important role in biological processes. An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of Fe and 0.06 g of Cu. the daily requirement of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions is 200-300 mg.  $\text{Mg}^{2+}$  ions are concentrated animal cells and  $\text{Ca}^{2+}$  ions are concentrated in the body fluids outside the cell, in much the same way as  $\text{K}^+$  concentrates inside the cell and  $\text{Na}^+$  outside.

$\text{Mg}^{2+}$  ions catalyse a number of enzymatic reactions. We know that energy is stored in form of phosphate linkages in ATP. The formation of these linkages, i.e., storage of energy is catalysed by  $\text{Mg}^{2+}$  ions. Conversely, hydrolysis of phosphate linkages is accompanied by release of energy. This process is also catalysed by  $\text{Mg}^{2+}$  ions.

$\text{Mg}^{2+}$  ions are present in chlorophyll – a green colouring pigment in plants which absorbs light and is essential for photosynthesis.

About 99% of body calcium is present in bones and teeth as apatite,  $\text{Ca}_3(\text{PO}_4)_2$  and the enamel on teeth as fluorapatite  $[\text{3 Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$   $\text{Ca}^{2+}$  ions are also important in blood clotting and are required to trigger the contraction of muscles and to maintain the regular beating of the heart. The concentration of  $\text{Ca}^{2+}$  ions in blood plasma is about  $100 \text{ mg L}^{-1}$ . This concentration is maintained by two hormones called **calcitonin** and **parathyroid**. Do you know that bone is not an inert and unchanging substance? The calcium ions in bones are continuously dissolving into and redepositing from the blood plasma to the extent of 400 mg per day in man. In normal adult this exchange is in balance, but in elderly people, especially women, there is sometimes net loss of bone calcium, leading to the diseases called **osteoporosis**.

## Quick Chapter Recap

### SOME KEY FACTS TO REMEMBER

- The general electronic configuration of s-block elements is (Noble gas)  $ns^2$ .
- Alkali metals are soft having low melting and boiling points. This is due to weak intermetallic bonding.
- All alkali metals are paramagnetic but their salts are diamagnetic.
- Alkali metals give characteristic flame colourations due to their low ionization enthalpies.
- Alkali metals (except Li) exhibit photoelectric effect.
- Alkali metals are strong reducing agents and reducing character increases down the group (except Li, which is strongest reducing agent due to its high oxidation potential).
- Alkali metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ...) are diamagnetic because they have no unpaired electron but alkali metals are paramagnetic because they have one unpaired electron.
- Basic character :  $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CaOH}$
- Solution of alkali metals in liquid  $\text{NH}_3$  are highly conducting and deep blue in colour. The blue colour is due to the presence of ammoniated electrons.
- Li forms oxide ( $\text{Li}_2\text{O}$ ), Na forms peroxide ( $\text{Na}_2\text{O}_2$ ) and other alkali metals form superoxides also ( $\text{MO}_2$  :  $\text{M} = \text{K}, \text{Rb}, \text{Ca}$ ).
- Alkali metals are kept under kerosene oil because they readily combine with oxygen and moisture of the air.
- Ionic mobility in water :  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Ca}^+$  because of degree of hydration.
- The elements showing diagonal relationship, Li-Mg, Be-Al, B-Si.
- Alkaline earth metals also (except Be and Mg) give characteristic colour to flame.
- Basic character :  $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$ .
- $\text{Mg}(\text{OH})_2$  is called milk of magnesia and is used as antacid.
- $\text{Ca}(\text{OH})_2$  is called milk of lime.
- Solubility decreases :  $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{CsSO}_4$  ;  
 $\text{BaCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
- $\text{BeCl}_2$  is covalent while  $\text{MgCl}_2$  and  $\text{CaCl}_2$  are ionic.
- $\text{BeCl}_2$  and  $\text{AlCl}_3$  behave as strong Lewis acids and are soluble in organic solvents.
- Both Be and Al form fluoro complex ions i.e.  $\text{BeF}_4^{2-}$  and  $\text{AlF}_4^-$  in solution.
- Quicklime is  $\text{CaO}$ . On adding water to it, calcium hydroxide is formed. This process is called slaking of lime.
- When  $\text{CO}_2$  is passed through lime water, milkiness is formed (due to  $\text{CaCO}_3$ ) and on further passing  $\text{CO}_2$  gas, milkiness disappears [due to  $\text{Ca}(\text{HCO}_3)_2$ ].
- Plaster of Paris is  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . On mixing with water it forms a plastic mass which sets into a hard solid mass (gypsum). This is called setting of Plaster of Paris.
- $2\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
Gypsum
- $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.