# THE s-BLOCK ELEMENTS (ALKALI AND ALKALINE EARTH ELEMENTS)

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#### 6.1 Introduction

The elements are divided into four blocks namely s, p, d and f in the modern periodic table. We shall study s-block elements of the periodic table in this unit. s-block elements are those elements in which the last electron, enters into the outermost s-orbital. Only two electrons can be accommodated in s-orbital, so there are two groups (1 and 2) (Old I-A and II-A) in s-block.

The elements of first group-1 (group I-A) of periodic table are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr). These elements are collectively known as alkali metals. This word is derived from arabic word 'Alguis' which means ash of shrubs, because sodium and potassium carbonate salts are in larger proportions in the ash of shrubs or plants. The other reason is that they react with water and form the hydroxides which are alkaline in nature (property).

In the elements of Group-2 (II-A) are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra).

These elements, except beryllium, are generally known as alkaline earth metals because their oxides and hydroxides are alkaline in nature (property) and the oxides of these metals are available in the \*crust.

# 6.2 Alkali Metals : Occurrence, Atomic and Physical Properties

Amongst alkali metals, sodium and potassium are in greater abundance. The proportion of sodium and potassium in the composition of the soil is about 4%. The proportion of lithium, rubidium and cesium is very less. Even then they are available in many minerals. (Table 6.1) Francium is highly radioactive. The half life period of its isotope <sup>223</sup>Fr is having longest life of only 21 minutes.

\* The thin outer sphere of earth is called crust of the earth.

Calcium and magnesium amongst the alkaline earth metals have their abundance order as fifth and sixth in the crust of the earth. The abundance of strontium and barium is much less. Beryllium is rare and radium is the rarest. Its proportion is only  $10^{-10}$  percent in igneous rocks.

The electronic configurations of s-block elements are [noble gas] ns¹ for alkali metals and [noble gas] ns² for alkaline earth metals. The first elements of group-1 and group-2 lithium and beryllium show some properties which are different from those of other elements in that group. These elements having anomalous properties show similarities with elements in the second group following them. Thus lithium (group-1) and beryllium (group-2) show similarity in many of their properties and magnesium (group-2) with aluminium (group-3) respectively. This type of diagonal similarity is generally expressed as "Diagonal relationship" in the periodic table.

This diagonal relationship is due to ionic size and/or charge/radius ratio of the elements. The monovalent sodium and potassium ions and divalent magnesium and calcium ions are available in large proportion in biological fluid. These ions perform important biological functions like maintenance of equilibrium of ions and nerve impulse conductions.

The chief minerals and the compositions of elements of group-1 elements are as follows:

(i) Lithium : Spodumine- Li(AlSiO<sub>3</sub>)<sub>2</sub> Lapidolyte-

(Li, Na, K), Al, (SiO<sub>2</sub>), [F(OH)],

(ii) Sodium : Rock salt- NaCl,

Carnite-  $Na_2B_4O_7$  4H<sub>2</sub>O, Borax-  $Na_2B_4O_7$  10H<sub>2</sub>O,

Chilie Saltpetre- NaNO<sub>3</sub>

(iii) Potassium: Sylvine- KCl,

Carnalite- KCl, MgCl,, 6H,O.

The atomic and physical properties of alkali metal elements are given in table 6.1

Table 6.1

Properties	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Cesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (gmol <sup>-1</sup> )	6.94	22.99	39.10	85.47	132.91	223
Electronic Configuration	[He]2s <sup>1</sup>	[Ne]3s <sup>1</sup>	[Ar]4s <sup>1</sup>	[Kr]5s <sup>1</sup>	[Xe]6s <sup>1</sup>	[Rn]7s <sup>1</sup>
Ionization enthalpy (kJmol <sup>-1</sup> )	520	496	419	403	373	-375
Hydration enthalpy (kJmol <sup>-1</sup> )	-506	-406	-330	-310	-270	I
Metallic radius (pm)*	152	186	227	248	265	ı
Ionic radius (pm)*	76	102	138	152	167	(180)
m. p. (K)	454	371	336	312	302	
b. p. (K)	1615	1156	1032	961	944	-
♦ Density (gcm <sup>-3</sup> )	0.53	0.97	0.86	1.53	1.90	
Standard potentials E <sup>0</sup> (V) for (M <sup>+</sup> /M)	-3.04	-2.714	-2.925	-2.930	-2.927	=
Occurrence in lithosphere	18*	2.27**	1.84**	78.12**	2.6*	10 <sup>-18*</sup>

<sup>\*</sup> ppm (parts per milion or parts per ten lacs. \*\* percentage by weight, \*pm = picometer = 10<sup>-12</sup> meter (\*) Lithosphere - outerlayer of earth : Its crust and upper mantle portion. ◆ SI unit of density is kgm<sup>-3</sup>

<sup>\*\*</sup> A type of rock formed from magma (Molten rock) that has cooled and has become hard.

It will be seen from table 6.1 that alkali metal elements possess one electron in their outermost orbit that is ns1. As this electron possesses weak attraction, it can be easily removed and positive ions can be formed. Their ionization enthalpy is low and form easily monovalent ions. Hence, they are called highly electropositive metals. As they lose the electron easily, they are not available in free state in nature but are available in large abundance in the salts having monovalent ions. All the elements are silvery white but their surface becomes dull in air having moisture because a layer of oxide (hydroxide) is formed on their surface. These metals are light. Their low melting points and high electrical conductivity indicate weak bond in solid state.

These metals give different colour flames in oxidising (blue) flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson	Yellow	Violet	Red	Blue
	red			violet	violet
λ (nm)	670.8	589.2	766.5	780.0	455.5

 $(nm = 10^{-9} meter)$ 

**Activity:** Light a match stick. After some time blow it out. Dip its upper black part in water and wet it. Keep it in salt (sodium chloride) so that salt will stick. Now, start your cooking gas in the house and put it in oxdising (blue) flame. Note what you observe. You will see yellow colour flame which tests the presence of Na<sup>+</sup> in the salt. This is known as flame test in qualitative analysis.

Because of low ionization enthalpy, the outermost electron in s-orbital absorbs energy and gets excited, and goes to higher energy level. Afterwards, in instantaneous time the excited electron returns to its original orbital (ground state) and the absorbed energy is emitted through radiation having specific wave lengths. As the radiations are of different wavelengths, they give different colour flames. Due to this the flame test is carried out in qualitative analysis.

The amounts of Na and K can be determined with the help of instruments like flame photometer or atomic absorption spectrophotometer. Cesium and potassium are used in photoelectric cells because of this property.

Their densities are low because of their larger sizes. The density increases as we move from Li to Cs. Their melting and boiling points

are low which indicate that they possess weak metallic bonds which is due to only one valence electron.

#### 6.3 Atomic Size and Ionic Size

The sizes of atoms of alkali metals are highest compared to atomic sizes of other elements in any period of the periodic table. With the increase in atomic number the atom becomes bigger. Monovalent ions (M<sup>+</sup>) are smaller in size as compared to their parent atoms. The atomic and molecular radii of alkali metals increase as we go down in the group. i.e. as we move from Li to Cs, their sizes and radii increase.

# 6.4. Reaction Enthalpy of Elements

**6.4.1 Ionization enthalpy (energy):** The ionization enthalpy is lowest for alkali metals as compared to elements of any other group of the periodic table. It decreases as we move from Li to Cs because the nuclear attraction of electron in valence orbit decreases because of their bigger atomic sizes and the electron is easily removed.

Because of high electropositive nature of alkali metals, they can easily form ionic bonds with elements having higher electronegativity e.g. NaCl. As these elements are good conductors of heat, some of them are used as coolants in atomic reactor.

**6.4.2 Hydration enthalpy (energy):** The hydration enthalpy of alkali metals decreases with increase in their ionic sizes.

$$Li^+> Na^+> K^+> Rb^+> Cs^+$$
.

The degree of hydration of Li is the highest due to which lithium salts are mainly hydrated. e.g.  $\text{LiCl} \cdot 2\text{H}_2\text{O}$ .

# 6.5 Chemical Reactivity (reactions) of Alkali Metals

Alkali metals are very reactive because of their large size and low ionization enthalpy. The reactivity of these elements increases as we go down in the group.

#### Chemical reactions:

# (i) Reactivity towards air or oxygen:

The alkali metals get tarnished in dry air because of the formation of their oxides which further react with moisture and form hydroxides. They burn vigorously in air and form oxides. Lithium forms monoxide.

$$4\text{Li}_{(s)} + O_{2(g)}$$
 (Limited amount)  $\xrightarrow{\Delta} 2\text{Li}_2O_{(s)}$ 

Lithium oxide

Sodium forms peroxide.

$$4\text{Na} + \text{O}_2 \text{ (Enough amount)} \xrightarrow{\Delta} \text{Na}_2\text{O}_2$$

(Sodium peroxide)

The other metals form superoxides. Superoxide ions  $(O_2^{1-})$  ion) are stable only in presence of big cations like- K, Rb, Cs.

$$4\text{Li}_{(S)} + O_{2(g)} \rightarrow 2\text{Li}_2O_{(S)}$$
 (Oxide)

$$2Na_{(S)} + O_{2(g)} \rightarrow Na_2O_{2(S)}$$
 (Peroxide)

$$M_{(S)}+O_{2(g)} \rightarrow MO_{2(s)}$$
 (Super oxide)

$$(M = K, Rb, Cs)$$

The oxidation state of alkali metal in all these oxides is +1.

Lithium, as an exception, also forms lithium nitride (Li<sub>3</sub>N) by direct reaction with nitrogen of air. Alkali metals are kept in kerosene because of their high reactivity.

# 6.6 Oxide and Hydroxide Compounds and Reactivity (reactions) towards dihydrogen, dihalogen, water, ammonia

# (i) M<sub>2</sub>O type oxides of alkali metal react with water and gives strong basic solutions:

$$M_2O_{(s)} + H_2O_{(l)} \rightarrow 2MOH_{(l)}$$

The peroxides of these metals give basic solution with water. MOH type basic hydroxides being very strong bases are called alkalies. Sodium hydroxide is called caustic soda and potassium hydroxide is called caustic potash. It burns the skin. LiOH is sparingly soluble in water while the hydroxides of Na, K, Rb and Cs are soluble in water.

#### (ii) Reactivity towards water:

Alkali metals react with water and form hydroxides and dihydrogen (hydrogen molecule) -  $H_2$ .

$$2M_{(s)} + 2H_2O_{(l)} \rightarrow 2M^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)}$$
  
(M = alkali metal)

Here, it is necessary to note that the value of reduction potential, Lithium (E<sup>0</sup>) is negative (Table 6.1) but it reacts less vigorously than sodium which has the lowest value of reduction potential. This behaviour of lithium is

considered due to its small size and high hydration enthalpy. The other metals of the group react violently with water. They also react with proton donors like alcohol, gaseous ammonia and alkyne.

## (iii) Reactivity towards dihydrogen:

Alkali metals, when heated with dihydrogen, form their hydrides which on reaction with water release dihydrogen gas.

$$\begin{array}{lll} 2M_{(s)} + H_{2(g)} & \rightarrow & 2MH_{(s)} \;\; (\text{Metal hydride}) \\ MH_{(s)} + H_2O_{(I)} & \rightarrow & MOH_{(aq)} + H_{2(g)} \end{array}$$

#### Reduction nature:

Alkali metals are strong reducing agents (table 6.1). Lithium is the strongest and sodium is the least strong reducing agent. The standard electrode potential (E<sup>0</sup>) determines the strength as reducing agent.

$$M_{(s)} \rightarrow M_{(g)}$$
 (Sublimation enthalpy)  
 $M_{(g)} \rightarrow M^{+}_{(g)} + e^{-}$  (Ionisation enthalpy)  
 $M^{+}_{(g)} + H_{2}O_{(l)} \rightarrow M^{+}_{(aq)} + OH^{-}$  (Hydration enthalpy)

With the lowest size of its own ion, lithium, with its highest hydration enthalpy and high negative value of E<sup>0</sup> possesses high reducing strength.

# (iv) Reactivity towards halogens:

Alkali metals react instantaneously and violently with halogens and form ionic halides M<sup>+</sup>X<sup>-</sup>. Lithium halide is somewhat covalent. The reason for this is the high polarization capability of lithium ions. The distortion in electron cloud of electron produced by cation is called polarization. Li<sup>+</sup> ion is very small in size and distorts the electron cloud around halide ion. The anions with large size easily get destroyed and so lithium iodide amongst halides is more covalent. Halogens act as oxidising agent in formation of halides.

The halide compounds of alkali metals are colourless, crystalline, solids having high melting point and are stable ionic compounds. The melting points and boiling points of any alkali metal is in order fluoride > chloride > bromide > iodide. All halide compounds except lithium fluoride are soluble in water.

### (v) Reactivity towards liquid ammonia:

The alkali metals dissolve in liquid ammonia and give deep blue coloured solutions which are electric conductor in nature.

 $\mathbf{M}_{\text{(S)}} + (\mathbf{x} + \mathbf{y}) \ \mathbf{N} \mathbf{H}_{3(I)} \longrightarrow [\mathbf{M}(\mathbf{N} \mathbf{H}_3)_x]^+_{(am)} + [\mathbf{e}(\mathbf{N} \mathbf{H}_3)_y]^-_{(am)}$ 

The blue colour of the solution is due to ammoniated electron, which absorbs light from visible spectrum and gives blue colour to solution. These solutions are paramagnetic and liberate dihydrogen gas slowly on standing and form amide.

 $M^+_{(am)} + e^- + NH_{3(l)} \rightarrow MNH_{2(am)} + \frac{1}{2}H_{2(g)}$  where 'am' indicates solution which is in ammonia. The blue colour in strong solutions changes to bronze colour and becomes diamagnetic.

When dry ammonia gas is passed over sodium metal at 573-673K temperature sodamide is formed and dihydrogen gas is liberated.

#### (vi) Salts of oxo acids:

Oxo-acids are such acids in which acidic proton is in hydroxyl group and the oxo group is combined with the same atom. e.g. Carbonic acid  $H_2CO_3^-$  (OC(OH)<sub>2</sub>), Sulphuric acid  $H_2SO_4^-$  (O<sub>2</sub>S(OH)<sub>2</sub>). Alkali metals form salts with all oxo acids. They are generally soluble in water and are thermally stable. Their carbonates (M<sub>2</sub>CO<sub>3</sub>) and most of the hydrogen carbonates (bicarbonates) are more stable towards heat. As we go down in the group the stability of carbonates and hydrogen carbonates increases. Lithium carbonate is not so stable towards heat. Lithium, being small in size, decomposes into Li<sub>2</sub>O and CO<sub>2</sub>. Its hydrogen carbonate does not exist as solid.

# 6.7 Diagonal Relationship and Irregularity (Lithium and Magnesium)

**6.7.1 Diagonal relationship of lithium** with magnesium: The similarities between lithium (group-1) and magnesium (group-2) is surprising. The reason for its existence is their similar sizes.

Atomic radii Li =152 pm Mg = 160 pm Ionic radii Li<sup>+</sup> = 76 pm Mg<sup>2+</sup> = 72 pm

# The main points of the similarity are as follows:

- Lithium and magnesium elements are harder but softer than the other elements of the corresponding groups.
- (ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are very less soluble in water. Their hydroxides decompose on heating.

(iii) Lithium and magnesium both combine with nitrogen directly and form nitrides (Li<sub>3</sub>N and Mg<sub>3</sub>N<sub>2</sub>)

- (iv) The oxides Li<sub>2</sub>O and MgO do not give superoxides by combining with more oxygen.
- (v) On heating carbonates of lithium and magnesium, decompose easily and give oxides and carbon dioxide. Solid hydrogen carbonates are not formed by lithium and magnesium.
- (vi) Both LiCl and MgCl, are soluble in ether.
- (vii) Both LiCl and MgCl<sub>2</sub> are hygroscopic and crystallise, as LiCl 2H<sub>2</sub>O and MgCl<sub>2</sub> 8H<sub>2</sub>O from their aqueous solutions.

# 6.7.2 Anomalous behavior of lithium from other elements of the group:

- (i) Lithium is very hard. Its melting point and boiling point are higher than those of other alkali metals.
- (ii) Lithium is least reactive amongst alkali metals. Monoxide Li<sub>2</sub>O and nitride Li<sub>3</sub>N are formed. This does not happen in other alkali metals.
- (iii) LiCl is deliquescent and crystallises as hydrate LiCl 2H<sub>2</sub>O while other alkali metals do not form hydrates.
- (iv) Lithium hydrogen carbonate (lithium bicarbonate) is not obtained in solid form while all other elements form solid hydrogen carbonates (bicarbonates.)
- (v) Lithium unlike other alkali metals does not form ethynide by reaction with ethyne.
- (vii) LiF and Li<sub>2</sub>O are very less soluble in water compared to the corresponding compounds of their metals.

# 6.8 Diagonal Relationship and Irregularity (Beryllium and aluminium)

**6.8.1 Diagonal relationship of beryllium** with aluminium: The ionic radius of Be<sup>2+</sup> is about 31 pm. The ratio of charge/radius of Be<sup>2+</sup> ion is almost nearer to that of Al<sup>3+</sup> ion. Hence, beryllium possesses similarities in certain cases. **Some of such similarities are as under:** 

 Beryllium like aluminium does not react very fast with acid because of the oxide layer on the surface of metal.

- (ii) Beryllium hydroxide becomes soluble in excess alkali forming beryllate ion. [BeOH)<sub>4</sub>]<sup>2-</sup> which is similar to aluminate ion. [Al(OH)<sub>4</sub>]<sup>-</sup> is formed by aluminium hydroxide with excess alkali.
- (iii) The chlorides of both beryllium and aluminium possess -Cl bridge in their vapour state. Chlorides of both are soluble in organic solvents and are strong Lewis acids. AlCl<sub>3</sub> is used as Friedel-Crafts catalyst.
- (iv) Beryllium and aluminium ions have greater tendency to form complexes. e.g.  $[BeF_4]^{2-}$ ,  $[AIF_4]^{3-}$
- Beryllium like aluminium is passive towards nitric acid.
- (vi) Aluminium carbide Al<sub>4</sub>C<sub>3</sub> and beryllium carbide Be<sub>2</sub>C give methane gas.

**6.8.2** Anomalous behavior of beryllium from other elements of the group: Beryllium, the first element of second group elements, shows anomalous behaviour as compared to other members of the group.

- (i) Beryllium as an exception has small atomic and ionic sizes and so it can not be compared with other elements of the group. Its compound that it forms are mostly covalent because of their high ionization enthalpy and small size and consequently hydrolyse easily.
- (ii) Beryllium has four electrons in its orbital and so there are four orbitals and therefore it can not exhibit coordination numbers more than four. Other elements of the group can utilize d-orbitals and obtain co-ordination number six.
- (iii) Oxide and hydroxide of beryllium are amphoteric compared to other members of the group. Oxides and hydroxides of other members are basic in nature.

# 6.9 Lithium (Occurrence, Properties and Uses)

The chief minerals of lithium and their compositions are as follows:

- (i) Spodumine LiAl (SiO<sub>3</sub>)<sub>2</sub>,
- (ii) Lepidolite (Li, Na, K)<sub>2</sub> Al<sub>2</sub> (SiO<sub>3</sub>)<sub>3</sub> (F,OH)<sub>2</sub>,
- (iii) Amblygonite Li<sub>2</sub>Al (PO<sub>4</sub>) F(OH).

**Extraction:** The extraction of lithium from its minerals is carried out by the following two steps:

- (i) To obtain LiCl from mineral and (2) electrolysis of LiCl. In the first step, the mineral is heated at 1373 K and then it reacts with sulphuric acid at 573 K temperature and then mixed with water it converts in to Li<sub>2</sub>SO<sub>4</sub>, 2H<sub>2</sub>O. Then reacts with sodium carbonate and finally reacting with hydrochloric acid LiCl is formed.
- (ii) In the second step, the molten mixture of 55% LiCl and 45% KCl is electrolysed giving lithium containing 1% impurity of K.

## Properties:

- (i) Lithium is silvery white and softer metal than lead, but harder than sodium.
- (ii) Being smallest in the size of the elements of group-1 the values of its melting point, boiling point and ionization enthalpy are the highest.

### Uses:

It is used

- (i) As reducing agent.
- (ii) In formation of alloys.
- (iii) In aeronautic industry.
- (iv) In formation of Armeour plate.
- (v) In formation of very strong and corrosion resistant alloy (1% Mg + 14% Li)

# 6.10 Sodium (Occurrence, Properties and Uses)

Sodium metal, being very reactive, is not available free in nature but it can lose one electron easily and form stable monovalent ion. So it is available in large abundance in combined form in the crust of earth, sea water etc. Its chief minerals and their compositions are as follows:

(i) Rock Salt (NaCl) (ii) Chilie salt petre (NaNO<sub>3</sub>) (iii) Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O)

**Extraction:** On electrolysis of aqueous solutions of sodium salts, dihydrogen gas instead of sodium metal is obtained at the cathode, because the reduction potential of sodium metal is more negative than that of dihydrogen. Hence, the salts of sodium are melted and then electrolysed, so that sodium metal is obtained at the cathode. The industrial production of sodium is carried out via Down cell by electrolysis of sodium chloride melted at 1123 K. In the Down cell, anode is inert graphite and steel or iron is cathode. Sodium metal

is obtained at cathode. Chlorine gas is liberated at anode. In the Down cell, a protective membrane is kept between the two electrodes so that there is no reaction between sodium and chlorine. Sodium is kept in kerosene so as to keep it away from the reaction with air and water.

### Cell reaction:

Anode :  $2Cl_{(l)}^{-} \rightarrow Cl_{2(g)} + 2e^{-}$  (Oxidation) Cathode :  $Na_{(l)}^{+} + e^{-} \rightarrow Na_{(s)}$  (Reduction)

### Properties:

Physical: Sodium is a silvery shining and soft metal. It gets tarnished when kept in open air because it is very reactive. (If it is cut with a knife, its inner part will shine). It is kept in kerosene because it is very reactive.

#### Chemical:

Reactivity towards dioxygen: Sodium metal reacts very fast with dioxygen and gives peroxide in presence of excess of dioxygen.

$$\begin{array}{ccc} 2Na_{(s)} \,+\, O_{2(g)} & \rightarrow & Na_2O_{2(s)} \\ & & (Sodium\ peroxide) \end{array}$$

(ii) Reactivity towards water: Sodium metal reacts very fast and vigorously with water and sometimes there is explosion and it gives sodium hydroxide and dihydrogen gas.

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

 $2Na_{(s)}+2H_2O_{(l)}\rightarrow 2NaOH_{(aq)}+H_{2(g)}$  (iii) Reactivity towards dihydrogen : Sodium reacts with dihydrogen and forms sodium

$$2Na_{(s)} + 2H_{2(g)} \rightarrow 2NaH_{(s)}$$
 (Sodium hydride)

(iv) Reactivity towards halogen: Sodium reacts very fast with halogens and forms halides.

$$2Na_{(s)} + X_{2(g)} \rightarrow 2NaX_{(s)} (X = F, Cl, Br, I)$$

Uses: Sodium is used

- as reducing agent (i)
- as liquid coolant in atomic reactor (ii)
- in dye industry
- (iv) as vapour in sodium light (yellow colour street lights)
- in the test of elements in organic compounds (v) Lassigne test.

# 6.11 Alkaline Earth Metals (Occurrence, Physical Properties and Electronic Structure)

Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra) are the elements of group-2 (II-A). They follow alkali metals in the periodic table. These elements, except beryllium, are called alkaline earth metals. The first element beryllium differs from other elements of the group but possesses diagonal relationship with second element of the next group. The chief minerals of these elements are mentioned in table 6.2. These metals are not available free in nature. Calcium and magnesium are available in greater abundance and strontium and barium in very small proportion, radium is radioactive and is obtained in very less proportion in the combined form.

Table 6.2

Element	Chief minerals and composition
Beryllium	Oxide Beryl: 3BeOAl <sub>2</sub> O <sub>3</sub> , 6SiO <sub>2</sub> (15%BeO)
	Oxide crenaside: BeOAl <sub>2</sub> O <sub>3</sub> (7% BeO)
	Oxide bromalite: BeO (45% BeO)
Magnesium	Magnesite: MgCO <sub>3</sub> , Epsom salt: MgSO <sub>4</sub> 7H <sub>2</sub> O
	Criserite: MgSO <sub>4</sub> · H <sub>2</sub> O, Carnalite: MgCl <sub>2</sub> KCl · 6H <sub>2</sub> O
	Crinite: K <sub>2</sub> SO <sub>4</sub> , MgSO <sub>4</sub> , MgCl <sub>2</sub>
	Dolomite CaCO <sub>3</sub> MgCO <sub>3</sub>
Calcium	Lime stone, Chalk, Marble : CaCO <sub>3</sub>
	Gypsum : CaSO <sub>4</sub> · 2H <sub>2</sub> O, Flourspar : CaF <sub>2</sub>
	Flourapatite : [Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F], Chlorapatite : [Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl]
Strontium	Strontianide: SrCO <sub>3</sub> , Silastine: SrSO <sub>4</sub>
Barium	Witherite: BaCO <sub>3</sub> , Baryte: BaSO <sub>4</sub>
Radium	In combined salt form in minerals like Pitchblende, Carnalite

-			-	-
1	h	a	6.	-
-				-

Property	Beryllium B e	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol <sup>-1</sup> )	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He]2s <sup>2</sup>	[Ne]3s <sup>2</sup>	[Ar]4s <sup>2</sup>	[Kr]5s <sup>2</sup>	[Xe]6s <sup>2</sup>	[Rn]7s <sup>2</sup>
First ionization enthalpy (kJmol <sup>-1</sup> )	899	737	590	549	503	509
Second ionization enthalpy (kJmol <sup>-1</sup> )	1157	1450	1145	1064	965	979
Hydration enthalpy (kJmol <sup>-1</sup> )	-2494	-1921	-1577	-1443	-1305	_
Metallic radius (pm)	111	160	197	215	222	_
Ionic radius (pm) (M <sup>2+</sup> ion)	31	72	100	118	135 <sup>-</sup>	148
Melting point (K)	1560	924	1124	1062	1002	973
Boiling point (K)	274	1363	1767	1655	2078	(1973)
Density (g cm <sup>-3</sup> )	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential (E <sup>(-)</sup> for M <sup>2+</sup> /M)V	-1.97	-2.36	-2.84	-2.89	-2.92	-2.02
Lithosphere	2*	2.76**	4.6**	3.84*	3.90*	10-6*

<sup>\*</sup> ppm (Parts per million \*\* Percentage by weight)

Electronic configuration: It is clear from table 6.3 that the general electronic configuration of these elements can be shown as [noble gas] ns<sup>2</sup> and have two electrons in their outermost orbital. As these electrons can be easily lost, they are mainly ionic.

**Ionization enthalpy:** The reason for low ionization enthalpy of alkaline earth metals is to some extent due to their large size. The first ionization enthalpy  $(M \to M^{1+} + e^-)$  of alkaline earth metals is more than that of corresponding group-1 metals. The reason for this is that their size is smaller in comparison to corresponding alkali metals. It is interesting to note that the second ionization enthalpy of alkaline earth metals  $(M^{1+} \to M^{2+} + e^-)$  is less than that of their corresponding alkali metals.

Hydration enthalpy: Like alkali metal ions, the hydration enthalpy of alkaline earth metal ions is more than alkali metal ions. Hence the compounds of alkaline earth metals get hydrated extensively as compared to alkali metal compounds. e.g. MgCl<sub>2</sub> and CaCl<sub>2</sub> exist as MgCl<sub>2</sub>•6H<sub>2</sub>O and CaCl<sub>2</sub>•2H<sub>2</sub>O respectively while NaCl and KCl do not form hydrates.

# 6.12 Related trend between Physical Properties

Alkaline earth metals are generally white, shiny and soft but hard in comparison to alkali metals. Beryllium and magnesium appear somewhat like ash colour. They are ductile and malleable. The melting points and boiling points of these metals are higher than the corresponding alkali metals. Because they are small in size, this trend is not systematic. Due to low ionization

enthalpy they are strongly electropositive in nature. This characteristic increases as we move from Be to Ba. Calcium, barium and strontium give characteristic flames. Calcium-Brick red, Barium-Light green and Strontium-Crimson red. The electron in the outermost orbit gets excited to higher energy level when kept in flame and on returning of electron the emitted energy absorbs colour from the visible spectrum. The electrons of beryllium and magnesium are so strongly bonded that they do not get excited in flame. Ca, Sr and Ba are detected by flame test in qualitative analysis. The quantitative analysis of calcium can be done with flame photometer or atomic absorption spectrophotometer. The alkline earth metals are good conductors of heat and electricity because of the higher electrical and thermal conductivity. This is a specific characteristic of these metals.

# 6.13 Chemical Properties: Reactivity (reactions) of Dioxygen and Water with Metals

The alkaline earth metals are less reactive as compared to alkali metals. The reactivity increases as we go down in the group.

Beryllium and magnesium are inert from reactivity point of view because there is an oxide layer on their surfaces, but powdered beryllium burns brightly in air and gives BeO and Be<sub>3</sub>N<sub>2</sub>. Magnesium being more electropositive burns in air brightly giving shining light and gives MgO and Mg<sub>3</sub>N<sub>2</sub>. Calcium, strontium and barium quickly get attacked by air and give oxides and nitrides. They react quickly with water and form hydroxides.

# 6.14 Oxide and Hydroxide Compounds

Alkaline earth metals form oxides of the type MO which are white coloured compounds. The oxides of beryllium and magnesium are sparingly soluble in water, while solubility of oxides of remaining metals increases gradually. Beryllium oxide is amphoteric while other oxides are strongly basic and absorb moisture and carbon dioxide of air.

$$MO_{(s)} + H_2O_{(l)} \rightarrow M(OH)_{2(aq)}$$

Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> can be obtained by reaction of NaOH with their water soluble salts. They are less basic than oxides of alkali metals. As we go down in the group there is gradual decrease in the solubility of the hydroxides. Beryllium hydroxide is amphoteric, so it reacts with base and acid respectively.

$$\text{Be(OH)}_{2(s)} + 2\text{OH}^{-}_{(aq)} \rightarrow [\text{Be(OH)}_{4}]^{2-}$$
  
beryllate ion.

$$\mathrm{Be(OH)}_{2(\mathrm{s})} + 2\mathrm{HCl}_{(\mathrm{aq})} \to \mathrm{BeCl}_{2(\mathrm{aq})} + 2\mathrm{H}_2\mathrm{O}_{(l)}$$

### 6.15 Halide Compounds

### Reactivity towards halogens:

All the alkaline earth metals at high temperature combine with halogens and form their halides.

$$M + X_2 = MX_2$$
 (X = F, Cl, Br, I)

The best reaction of formation of  $BeF_2$  is the decomposition of  $(NH_4)_2 BeF_4 BeCl_2$ . It can be prepared easily from its oxide.

$$BeO + C + Cl_2 \stackrel{600-800 \text{ K}}{\rightleftharpoons} BeCl_2 + CO$$

All the halides of alkaline earth metals with exception of beryllium halide are ionic in nature. Beryllium halide is chiefly covalent and soluble in organic solvents. The form of beryllium chloride in solid state is chain-like.

BeCl<sub>2</sub> in vapour state forms a dimer having chloro-chloro (Cl-Cl) bridge.

$$Cl$$
 Be  $Cl$  Be  $-Cl$ 

It dissociates into monomer at about 1200 K. The tendency of formation of halide hydrates decreases gradually as we go down in the group. e.g. MgCl<sub>2</sub>·8H<sub>2</sub>O, CaCl<sub>2</sub>·6H<sub>2</sub>O, CrCl<sub>2</sub>·6H<sub>2</sub>O, BaCl<sub>2</sub>·2H<sub>2</sub>O. The dehydration of hydrated chloride, bromide and iodide of barium, calcium and strontium can be carried out by heating, but the corresponding hydrated halides of Be and Mg undergo hydrolysis. Fluorides are relatively less soluble than chlorides. The reason for this is their higher lattice energy.

# 6.16 Solubility and Thermal Stability of Oxosalts

Alkaline earth metals form salts of oxo acids. Some of them are as follows:

**Sulphates:** Sulphates of alkaline earth metals can be obtained by reaction of sulphuric acid with carbonates of metals.

$$MCO_{3(s)} + H_2SO_{4(aq)} \rightarrow MSO_{4(s)} + H_2O_{(l)} + CO_{2(g)}$$
  
(M = Alkaline earth metal)

It is a white solid substance and thermally stable. BeSO<sub>4</sub> and MgSO<sub>4</sub> dissolve readily in water. The solubility decreases as we move from

CaSO<sub>4</sub> to BaSO<sub>4</sub>. The hydration enthalpy of Be<sup>2+</sup> and Mg<sup>2+</sup> ions is more than the lattice enthalpy and so they are soluble in water.

**Nitrates:** Nitrates can be obtained by reaction of dilute nitric acid with metal carbonates. Magnesium nitrate crystallizes as magnesium nitrate with molecules of water, while barium nitrate crystallizes as anhydrous salt. This also shows that with increase in ionic size and with decreasing hydration enthalpy, there is a decrease in tendency of formation of hydrates. All of them, when heated, decompose into oxides like lithium nitrate.

2M (NO<sub>3</sub>)<sub>2(s)</sub> 
$$\rightarrow$$
 2MO<sub>(s)</sub> + 4NO<sub>2(g)</sub> + O<sub>2(g)</sub> (M = Be, Mg, Ca, Sr, Ba)

Carbonates: The carbonates of alkaline earth metals are insoluble in water. They can be precipitated by adding sodium carbonate or ammonium carbonate to aqueous solutions of their soluble salts. With the increase in atomic number, the solubility of carbonate salts gradually decreases.

### Reduction nature of metals:

The alkaline earth metals like alkali metals are strong reducing agents. This is indicated by their more negative reduction potentials (Table 6.3). Their power as reducing agent is less than that of their corresponding alkali metals. In comparison to other alkaline earth metals, the value of beryllium is less negative. Its reducing nature is associated with its higher hydration enthalpy which is in accordance with its (Be<sup>2+</sup>) small size and higher value of metal atomic enthalpy.

**Solutions in liquid ammonia:** Alkaline earth metals like alkali metals dissolve in liquid ammonia and give dark blue coloured solutions by forming ammoniated ion.

$$M_{(s)} + (x + y) NH_{3(l)} \rightarrow [M(NH_3)_x]^{2+}_{(am)} + 2 [e(NH_3)_y]^{-}_{(am)}$$
  
The ammoniated ion  $[M(NH_3)_x]^{2+}_{(am)}$  can be obtained from solution.

Uses: Beryllium is used in production of alloys. Copper-beryllium alloy is used in the formation of springs having more strength. Beryllium metal is used in windows of X-ray tubes. Magnesium and aluminium form alloys with zinc, manganese and tin. Magnesium-aluminium alloy being light in weight is used in making aeroplanes. Magnesium powder and ribbons are used in flash powder, bulbs incidary bombs and signals. Mg metal is used in preparation of Grignard reagent. The suspension

of magnesium sulphate in water is known as milk of magnesia. It is used as antacid in medicines. Magnesium carbonate is one of the components in tooth paste. The use of calcium is made in the reduction of oxides which cannot be reduced by carbon to obtain metals. Calcium and barium metals, having reactivity with oxygen and nitrogen at higher temperatures, are used to remove air from vacuum tubes. Salts of radium are used in radiotherapy. e.g. in treatment of cancer.

# 6.17 Production, Properties and Uses of Some Compounds of Sodium: Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaHCO<sub>3</sub>

The useful compounds of sodium are NaOH, Na<sub>2</sub>CO<sub>3</sub>, 10H<sub>2</sub>O and NaHCO<sub>3</sub>. Their production, properties and uses will be studied here.

Production of Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub> • 10H<sub>2</sub>O): Sodium carbonate is also known as washing soda and soda ash. Generally, its industrial production is carried out by Solvay method (Solvay ammonia soda method) or process.

In this process advantage of less solubility of sodium hydrogen carbonate (Sodium bicarbonate) -NaHCO<sub>3</sub> is taken. It is precipitated by reaction of ammonium hydrogen carbonate (ammonium bicarbonate) with sodium chloride. Ammonium hydrogen carbonate is prepared by passing carbon dioxide from a solution of sodium chloride saturated with ammonia. Ammonium carbonate obtained is later on converted to ammonium bicarbonate. The reaction equations for the whole process are as follows:

$$\begin{split} 2\text{NH}_{3(g)} + & \text{H}_2\text{O}_{(l)} + \text{CO}_{2(g)} \rightarrow (\text{NH}_4)_2\text{CO}_{3(s)} \\ (\text{NH}_4)_2\text{CO}_{3(s)} + & \text{H}_2\text{O}_{(l)} + \text{CO}_{2(g)} \rightarrow 2\text{NH}_4\text{HCO}_{3(s)} \\ \text{NH}_4 & \text{HCO}_{3(s)} + \text{NaCl}_{(s)} \rightarrow \text{NaHCO}_{3(s)} + \text{NH}_4\text{Cl} \end{split}$$

Sodium hydrogen carbonate being sparingly soluble, its crystals are formed. They are separated and then heated so that sodium carbonate is formed.

$$2 \text{NaHCO}_{3(s)} \xrightarrow{\quad \Delta \quad} \text{Na}_2 \text{CO}_{3(s)} + \text{H}_2 \text{O}_{(g)} + \text{CO}_{2(g)}$$

Ammonia can be obtained back in this process. By reaction of Ca(OH)<sub>2</sub> with the solution containing NH<sub>4</sub>Cl, ammonia can be obtained as by product.

$$2NH_4Cl_{(s)} + Ca(OH)_{2(aq)} \rightarrow 2NH_{3(g)} + CaCl_{2(aq)} + H_2O_{(l)}$$

It is necessary here to remember that Solvay process cannot be used for production of potassium carbonate. The reason for this is that potassium hydrogen carbonate (bicarbonate)

is very highly soluble that by addition of ammonium hydrogen carbonate to potassium chloride, does not get precipitated.

### Properties:

Sodium carbonate is a crystalline white solid substance which possesses existence as decahydrate (ten molecules of water of crystallistion Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O). It is known as washing soda. When decahydrate is heated, it loses water of crystallisation and forms monohydrate (One molecule of water of crystallisation and forms monohydrate). On heating at temperature higher than 373K, it becomes completely anhydrous and changes to white powder form which is known as soda ash Na<sub>2</sub>CO<sub>3</sub>.

$$Na_2CO_3 \cdot 10H_2O_{(s)} \xrightarrow{373 \text{ K}} Na_2CO_3 \cdot H_2O_{(s)} + 9H_2O_{(g)}$$
  
 $Na_2CO_3 \cdot H_2O_{(s)} \xrightarrow{>373 \text{ K}} Na_2CO_{3(s)} + H_2O_{(g)}$ 

It produces cabton dioxide by reacting with acid.

$$Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

The carbonate ion of sodium carbonate reacts with water and forms alkaline solution by hydrolysis.

$$CO_3^{2-}_{(aq)} + H_2O_{(l)} \rightarrow HCO_3^{-}_{(aq)} + OH_{(aq)}^{-}$$

Sodium hydrogen carbonate is formed when carbon dioxide gas is passed through a solution of sodium carbonate.

$$\mathrm{Na_2CO_{3(aq)}} + \mathrm{H_2O_{(l)}} + \mathrm{CO_{2(g)}} \rightarrow \mathrm{2NaHCO_{3(aq)}}$$

**Uses:** It is used in (i) softening hard water (ii) washing and cleansing (iii) manufacturing of compounds like glass, soap, borax and caustic soda (iv) paper, dye and textile industries and (v) as laboratory reagent in chemical analysis.

# Sodium hydroxide (Caustic soda) (NaOH):

production: The industrial production of sodium hydroxide is carried out by electrolysis of a solution of sodium chloride in Castner Kellner cell. Electrolysis of brine solution (Solution containing sodium chloride) is carried out using mercury cathode and carbon anode. Sodium metal that is liberated at the cathode combines with mercury and forms sodium amalgam (Na-Hg) and chlorine is produced at the anode

Cathode: 
$$Na^+_{(l)} + e^- \xrightarrow{Hg} NaHg_{(l)}$$

Anode: 
$$Cl_{(l)}^- \rightarrow \frac{1}{2} Cl_{2(g)} + e^-$$

Sodium hydroxide and dihydrogen gas are produced by reacting amalgam with water.

$$2\text{Na-Hg(amalgam)}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{NaOH}_{(aq)} + \text{H}_{2(g)}$$

**Properties:** Sodium hydroxide is white translucent solid substance. It melts at 591 K temperature. It reacts with water and dissolves in it and produces heat because of its exothermic reaction and gives strong alkaline solution. Its crystals are highly hygroscopic. The solution of sodium hydroxide absorbs  $CO_2$  from the atmosphere above its surface and reacts, so that  $Na_2CO_3$  is formed.

Uses: Sodium hydroxide is used in (i) preparation of soap, paper, artificial silk and number of chemicals (ii) refining of petroleum (iii) purification of bauxite the mineral of aluminium (iv) textile industry for mercerization of cotton cloth (v) to prepare pure fat and oil and (vi) as reagent in laboratory.

# Sodium hydrogen carbonate (Sodium bicarbonate) (NaHCO<sub>3</sub>):

Sodium bicarbonate is called sodium hydrogen carbonate in modern nomenclature. It is also known as baking soda (baking powder). On heating it decomposes and produces bubbles of liberated carbon dioxide. Because of this holes are produced fluffy in edible substance like pastry etc. Due to this they become soft.

Sodium carbonate solution is saturated with carbon dioxide to prepare sodium hydrogen carbonate. It can also be obtained by Solvay ammonia soda process.

$$\text{Na}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}_{(l)} + \text{CO}_{2(\text{g})} \rightarrow 2\text{NaHCO}_{3(\text{aq})}$$

Its separates out as it is less soluble in water.

**Properties:** Sodium hydrogencarbonate is a white crystalline solid substance. It is less soluble than Na<sub>2</sub>CO<sub>3</sub>. It gives alkaline solution on reaction with water.

Uses: Sodium hydrogencarbonate is a mild antiseptic for the infection of skin diseases. Hence, (1) used as antiseptic, (2) it is used as fire extinguisher in extinguisher - cylinders, in the cylinder the acid kept with it reacts and produces carbon dioxide gas (3) As an antacid for the acid in the stomach and (4) as reagent in laboratory.

### 6.18 Biological Importance of Na<sup>+</sup> and K<sup>+</sup> Ions

Anybody having weight of 70 kg possesses 90 gram Na and 170 gram K. In its comparison only 5 gram Fe and 0.06 gram Cu are possessed.

Primarily sodium ions are present on the cells being located in blood plasma and the interstitial fluid which surrounds the cells. These ions play an important role in nerve signal transmission control of flow of water between cell membrane, for transport of sugar and amino acids. It seems that sodium and potassium possess many similarities from chemistry point of view but differentiate quantitatively in penetration through cell wall, their flow mechanism and efficiency in activating the enzyme. Thus potassium ions are cation in abundance where they activate the enzyme and become responsible for producing ATP by oxidation of glucose and transport of nerve signal with sodium. On the opposite sides of the cell membranae there is a noticeable variation in the concentration of sodium and potassium ions.

If we take a typical example, the level of sodium in the red blood cells in blood plasma is about 143 mmollit<sup>-1</sup> while that of potassium is only 5 mmollit<sup>-1</sup>. These concentrations change to 10 mmollit<sup>-1</sup> (Na<sup>+</sup>) and 105 mmollit<sup>-1</sup> (K<sup>+</sup>). This concentration degradation is the indication of a discriminative mechanism which is called sodium potassium pump. This pump utilities more than one third part of ATP when the animal is taking rest and in human being 15 kg per 24 hours. If this sodium-potassium pump does not work properly it creates many problems regarding blood pressure in human beings. For example, if concentration of Na<sup>+</sup> increases doctors advise to stop taking more sodium chloride. The high concentration of sodium ion increases blood pressure.

# 6.19 Production, Properties and Uses of Some Compounds of Calcium: CaO, CaCO, Plaster of Paris and Cement

Amongst the important compounds of calcium are quick lime (calcium oxide), slaked lime (calcium hydroxide), lime stone (calcium carbonate) and cement. These are important compounds from industrial point of view. We shall study production on large scale, properties and uses of these compounds

### (1) Quick lime (Calcium oxide) (CaO):

Calcium oxide is obtained on commercial scales by heating lime stone (CaCO<sub>3</sub>) at 1070-1270 K temperature in rotary kiln

$$CaCO_{3(s)} \xrightarrow{\text{Heat}} CaO_{(s)} + CO_{2(g)}$$

As soon as carbon dioxide is produced it is removed, so that the reaction goes towards

completion (Forward direction) and reverse reaction is stopped.

## Properties:

- (i) It is a pure white solid substance whose melting point is 2870 K.
- (ii) When heated in oxyhydrogen flame it emits bright white luminous flame.
- (iii) It absorbs carbon dioxide and moisture when kept open in air.

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$$
  
 $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}$ 

On adding limited amount of water, lumps of limestone break into pieces. This process is known as slaking of lime.

- (iv) Quick lime gives soda lime on mixing with caustic soda.
- (v) Being basic it combines with acidic oxides at high temperature.

$$\begin{split} &\text{CaO}_{(s)} + \text{SiO}_{2(s)} \rightarrow \text{CaSiO}_{3(s)} \\ &\text{6 CaO}_{(s)} + \text{P}_{4}\text{O}_{10(s)} \rightarrow 2\text{Ca}_{3}(\text{PO}_{4})_{2(s)} \end{split}$$

(vi) It forms calcium carbide with carbon at 2273 K.

$$CaO_{(s)} + 3C_{(s)} \xrightarrow{2273 \text{ K}} CaC_{2(s)} + CO_{(g)}$$

**Uses**: Calcium oxide is used in (1) preparation of slaked lime (2) preparation of bleaching powder, dyes and distemper, (3) in preparation of calcium carbide, cement, mortar etc. (4) in purification of sugar, coal gas and softening of hard water (5) as layers on the inner sides of electric furnaces (6) preparation of ammonia gas in the laboratory.

(2) Calcium hydroxide (Slaked lime (Ca(OH)<sub>2</sub>) -Preparation: When water is added to lumps of quick lime, large amount of heat is produced and the lumps break to give powder which makes the solution containing calcium hydroxide.

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + Heat$$

### Properties:

- (i) Calcium hydroxide is a white powder form solid.
- (ii) It is sparingly soluble in water.
- (iii) Its aqueous solution is called lime water which is alkaline.
- (iv) The suspension of slaked lime is known as milk of lime which is alkaline.
- (v) When carbon dioxide is passed through its solution it becomes turbid because sparingly soluble CaCO<sub>3</sub> is formed.

$$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$

If carbon dioxide gas is passed for a longer time from this solution, the precipitates of calcium carbonate dissolve in water and the solution of calcium hydrogen carbonate (calcium bicarbonate) Ca(HCO<sub>2</sub>) is obtained.

$$CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \rightarrow Ca(HCO_3)_{2(aq)}$$

- (vi) Milk of lime forms hypochloride by reaction with chlorine which is component of bleaching powder.
- (vii) Being alkaline it reacts with acid or acidic oxide to give salt and water

$$\begin{split} \operatorname{Ca(OH)}_{2(\operatorname{aq})} + \operatorname{2HCl}_{(\operatorname{aq})} &\to \operatorname{CaCl}_{2(\operatorname{aq})} + \operatorname{2H_2O}_{(\mathit{I})} \\ \operatorname{Ca(OH)}_{2(\operatorname{aq})} + \operatorname{CO}_{2(\operatorname{g})} &\to \operatorname{CaCO}_{3(\operatorname{s})} + \operatorname{H_2O}_{(\mathit{I})} \end{split}$$

Uses: Calcium hydroxide is used in (i) preparation of mortar which is one of the components of building materials (ii) white washing of walls because of its insecticide nature (iii) absorption of acidic gases and to get ammonia from ammonium chloride (iv) glass and leather industry, purification of sugar, preparation of bleaching powder (v) as antiseptic and in softening of hard water as well as in the laboratory for the test of carbon dioxide.

# Calcium carbonate (lime stone) (CaCO<sub>3</sub>):

**Preparation:** The chemical name of lime stone is calcium carbonate. It is obtained from nature in different forms such as chalk, marble, corals, shells. It is obtained in two crystalline forms Calcite and Aergonite.

It can be prepared by passing carbon dioxide through slaked lime or adding sodium carbonate to a solution of calcium chloride.

$$\begin{split} &\operatorname{Ca(OH)}_{2(\operatorname{aq})} + \operatorname{CO}_{2(\operatorname{g})} \ \to \operatorname{CaCO}_{3(\operatorname{s})} + \operatorname{H}_2\operatorname{O}_{(\mathit{l})} \\ &\operatorname{CaCl}_{2(\operatorname{aq})} + \operatorname{Na}_2\operatorname{CO}_{3(\operatorname{s})} \to \operatorname{CaCO}_{3(\operatorname{s})} + \operatorname{2NaCl}_{(\operatorname{aq})} \end{split}$$

Large amount of carbon dioxide should not be passed, otherwise calcium hydrogen carbonate will be obtained which is soluble in water

**Properties:** Calcium carbonate is (i) white fluffy powder (ii) It is almost insoluble in water (iii) On heating at 1200 K temperature it decomposes to give calcium oxide and carbon dioxide gas.

$$CaCO_{3(s)} \xrightarrow{1200K} CaO_{(s)} + CO_{2(g)}$$

(iv) On reaction with dilute acids it forms the corresponding calcium salts and carbon dioxide.

$$\begin{split} \operatorname{CaCO}_{3(s)} + 2\operatorname{HCl}_{(aq)} &\to \operatorname{CaCl}_{2(aq)} + \operatorname{H}_2\operatorname{O}_{(l)} + \operatorname{CO}_{2(g)} \\ \operatorname{CaCO}_{3(s)} + \operatorname{H}_2\operatorname{SO}_{4(aq)} &\to \operatorname{CaSO}_{4(aq)} + \operatorname{H}_2\operatorname{O}_{(l)} + \operatorname{CO}_{2(g)} \end{split}$$

Uses: (i) In the form of marble as construction material (ii) It is used in production of quick lime (iii) The mixture of calcium carbonate and magnesium carbonate is used as flux in the extraction of metal like iron (iv) Specially precipitated calcium carbonate is used for manufacture of high quality paper (v) It is used as antacid in medicines as abrasive in tooth paste as one component in chewingum and as filler in cosmetic materials.

Plaster of Paris : 
$$(CaSO_4, \frac{1}{2}H_2O)$$
 OR  $(2CaSO_4, H_2O)$  :

Plaster of Paris is hemihydrate or semihydrate of calcium sulphate.

When gypsum is heated at 393K plaster of Paris is obtained

$$2CaSO_4 \cdot 2H_2O_{(s)} \xrightarrow{393 \text{ K}} 2(CaSO_4) \cdot H_2O_{(l)} + 3H_2O_{(g)}$$

There is no water of crystallisation. When heated at temperature more than 393 K it becomes anhydrous CaSO<sub>4</sub>. This is known as dead burnt plaster. With every two Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions one molecule of water is combined.

### Properties:

(i) Plaster of Paris is white powder form solid substance. (ii) When it is soaked in water by one third portion of its weight, it becomes hard expanded substance by intercombination of gypsum crystals. This property of its setting with water is noticeable. It becomes very hard solid substance by setting in 5 to 15 minutes. (iii) Its setting velocity can be increased by addition of common salt. The setting velocity can be decreased by addition of borax or alum. (iv) When heated at temperature higher than 473K anhydrous CaSO<sub>4</sub> is formed and is unable to set. (v) The mixture of alum and plaster of Paris which becomes very hard on setting is called keen cement.

Uses: The maximum use of plaster of Paris is in (i) construction industry and in plastering (ii) plastering of fractured bones after operation, in muscles having sprain, in dentistry

for preparation of casts for dentures, casts for ornaments, preparation of statues (iii) in laboratory its plaster is applied on the vessels to make them airtight (iv) in chalks for writing on board.

**Cement:** Cement is one of the important substances for construction. It was first introduced by Joseph Aspidin in England in 1824. It is also called Portland because it is similar to natural lime stone available in the mines of stone in the 'Isle of Portland'.

Cement is such a product which can be obtained by reaction of quick lime rich in CaO with silica (SiO<sub>2</sub>). It is reacted with oxides of aluminium, magnesium and iron. The average composition of cement is CaO : 50-60%, SiO<sub>2</sub> : 20-25%, Al<sub>2</sub>O<sub>3</sub> : 5-10%, MgO : 2-3%, Fe<sub>2</sub>O<sub>3</sub> : 1-2% and SO<sub>3</sub> : 1.3%

For a good quality of cement, the ratio of silica  $(SiO_2)$  and alumina  $(Al_2O_3)$  must be between 2.5 to 4 and the ratio of lime (CaO) and total oxide [oxide of silicon  $(SiO_2)$  to oxide of aluminium  $(Al_2O_3)$  + oxide of iron  $(Fe_2O_3)$ ] should be as near as possible to 2.

The raw materials for production of cement are lime stone and clay. When clay and lime are heated very strongly, they melt and give a hard brick like substance which is known as cement clinker. To this cement clinker, 2-3% by weight gypsum (CaSO $_4$  • 2H $_2$ O) is added and heated at 1773 K temperature in rotary furnace. The substance obtained is passed through 325 mesh (measure of pores of sieve) sieve and 2-5% gypsum is added.

The important ingredients of portland cement are dicalcium silicate  $(Ca_2SiO_4)$  26%, tricalcium silicate  $(Ca_3SiO_5)$  51% and tricalcium aluminate  $(Ca_3Al_2O_6)$  11%

#### Properties:

(i) The quality of portland cement is known by

(A) Silica module : 
$$\eta = \frac{\% SiO_2}{\% Al_2O_3 + \% Fe_2O_3}$$

(B) Alumina module 
$$p = \frac{\%A1_2O_3}{\%Fe_2O_3}$$

(ii) If brought in contact with water it starts gaining strength and becomes hard.

- (iii) It appears like ash colour due to presence of iron.
- (iv) The constructions with this cement get affected by acid.
- (v) The water containing dissolved carbon dioxide and water containing calcium and magnesium salts have effect on its strength.

Setting of cement: When cement is mixed with water, it sets down and a hard substance is formed. This is called setting of cement. The reason for this is the hydration of component molecules and their rearrangement. The reason for addition of gypsum is to slow down the time of setting of cement so that it can become sufficiently hard. Its primary strength is seven days. The setting times of dicalcium and tricalcium silicates are 28 days and one year respectively.

Uses: After iron and steel, the selection of national requirement of any country is cement. It is used in

- (i) Construction of roads and buildings.
- (ii) Around the iron bars the concrete containing portland cement is allowed to set so that very hard reinforce cement concrete is formed and it is used in construction of slabs, bridges, dams etc.

# 6.20 Biological Importance of Mg<sup>2+</sup> and Ca<sup>2+</sup>

The body of an adult contains about 25 gram Mg and 1200 gram Ca as well as 5 gram Fe and 0.06 gram Cu. Its daily requirement in human body is estimated to be 200-300 milligram.

All the enzymes which use ATP in the transfer of phosphate; they require magnesium as a cofactor. The chief pigment of absorption of light in the plants is chlorophyll which contains magnesium (It is a complex of magnesium). About 99% of calcium present in the body is in bones and teeth.

In addition, it also plays an important role in neuromuscular function, interneuronal transmission cell membrane integrity and coagulation of blood. About 100 milligram liter<sup>-1</sup> concentration of calcium is regulated in plasma. It is carried out by two hormones calcitonin and dissolving and redepositing substance. Its proportion in human being is 400 milligram per day. All this calcium passes across the plasma.

#### **SUMMARY**

Group-1 (alkali metals) and group-2 (alkaline earth metals) are included in the s-block elements of the periodic table. They are known like this because their oxides and hydroxides are alkaline in nature. Alkali metals possess one and alkaline earth metals possess two s-electrons. They are highly electropositive metals and form monovalent cations (M<sup>+</sup>) and divalent cations (M<sup>2+</sup>) respectively.

With the increase in atomic number, the physical and chemical properties of alkali metals show regular trend. The atomic and ionic sizes increase on going down in the group and ionization enthalpies decrease in alkali metals. The same type of trend is observed in alkaline earth metals.

The first element of each of these two groups, namely, lithium in group-1 and beryllium in group-2 show similarities with the element of the next group viz. Li-Mg and Be-Al. This is called diagonal relationship. In fact, the first element of each group shows difference with other elements in the same group i.e their behaviour is anomalous.

Alkali elements are bright white, soft metals melting at low temperatures. Li and Na are obtained by electrolysis. They are very active and their compounds are ionic. Their oxides and hydroxides are soluble in water and give strong alkaline solution.

Amongst important compounds of sodium are sodium carbonate, sodium hydroxide, NaOH is produced by Castner Kellner process and sodium carbonate by Solvay ammonia soda process.

The chemistry of alkaline earth metals is similar to that of alkali metals. Even then some differences are there, because the atomic and ionic sizes of alkaline earth metals decrease and the charge of the cation increases. Their oxides are less basic than those of alkali metals.

Amongst the industrially important compounds of sodium are caustic soda, washing soda and those of calcium are calcium oxide, calcium hydroxide, plaster of Paris, calcium carbonate and Portland cement. The production of cement can be carried out by grinding the mixture of lime stone and clay and heating it in rotary kiln. The clinker obtained is mixed with gypsum (2-3%) which gives fine powder of cement. All these substances have many uses.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in larger proportion in biological fluid in a human being. These ions carry out important biological functions like maintenance of ionic equilibrium and nerve impulse conduction which is known as sodium-potassium pump.

# **EXERCISE**

# 1. Select the proper choice from the given multiple choices:

(1) Sodium metal is kept in

(A) Water

(B) Kerosene

(C) Alcohol

(D) Open in air

(2) The formula of washing soda is

(A) Na<sub>2</sub>CO<sub>3</sub>

(B) Na,CO, H,O

(C) Na<sub>2</sub>CO<sub>3</sub> •10H<sub>2</sub>O

(D) NaHCO,

(3) The formula of baking powder is

(A) Na<sub>2</sub>CO<sub>3</sub>

(B) NaHCO<sub>3</sub>

(C) NaOH

(D) NaCl

(4)	Which of the following pairs of elements possess diagonal relationship				
	(A) Li and Mg	(B) Li and Al			
	(C) Na and Mg	(D) Cs and Ba			
(5)	In which of the following solvents	s, the alkli metal gives coloured solutions?			
	(A) Water	(B) Alcohol			
	(C) Acetone	(D) Liquid ammonia			
(6)	Alkali metals can be obtained for	rom			
	(A) Aqueous solutions	(B) Ammoniated solutions			
	(C) Melted salts	(D) Nature			
(7)	Which metal from the following a	alkali metals has the lowest melting point?			
	(A) Na	(B) K			
	(C) Rb	(D) Cs			
(8)	Which of the following alkali me	stals gives hydrated salts?			
	(A) Li	(B) Na			
	(C) K	(D) Cs.			
(9)	Which of the following alkaline	earth carbonates is thermally stable?			
	(A) MgCO <sub>3</sub>	(B) CaCO <sub>3</sub>			
	(C) SrCO <sub>3</sub>	(D) BaCO <sub>3</sub>			
(10)	Which of the following alkali met	als is used in the street lights on the road?			
	(A) Li	(B) Na			
	(C) K	(D) Cs			
(11)	Which of the following elements give light green colour in flame test?				
	(A) K	(B) Rb			
	(C) Ca	(D) Ba			
(12)	Which metal is used in photoelectric cell?				
	(A) Na	(B) K			
	(C) Rb	(D) Cs			
(13)	Which salt cannot be obtained by	y Solvay ammonia soda process ?			
	(A) Na <sub>2</sub> CO <sub>3</sub>	(B) NaHCO <sub>3</sub>			
	(C) KHCO <sub>3</sub>	(D) NH <sub>4</sub> HCO <sub>3</sub>			
(14)	Which pump is important in biological reaction in human body?				
	(A) Ca-Mg pump	(B) Na - K pump			
	(C) Fe - Ca pump	(D) Ca- Fe pump			
(15)	Which is more basic - Na <sub>2</sub> CO <sub>3</sub>	or NaHCO <sub>3</sub> ?			
	(A) Na <sub>2</sub> CO <sub>3</sub>	(B) NaHCO <sub>3</sub>			
	(C) Both	(D) Neither of the two			

### 2. Write balanced chemical equations for the following reactions:

- (1) Sodium metal and liquid ammonia
- (2) Calcium hydroxide and ammonium chloride
- (3) Sodium pexoride and water
- (4) Beryllium hydroxide and sodium hydroxide
- (5) Lithium nitride and water
- (6) Heating calcium oxide with phosphorus pentoxide at high temperature
- (7) Passing more carbon dioxide from a solution of calcium carbonate
- (8) Passing chlorine gas from calcium hydroxide solution
- (9) Reaction of aluminium oxide with con. NaOH

# 3. Write answers of the following questions:

- (1) Explain the diagonal relationship of Li of first group and Mg of second group.
- (2) How beryllium differs from other elements of its group?
- (3) Describe Castner-Kellner process of obtaining sodium metal.
- (4) Describe Solvay ammonia soda method (process) for obtaining sodium carbonate.
- (5) Describe biological importance of Na<sup>+</sup> and K<sup>+</sup> ions.
- (6) Write preparation and uses of cement.
- (7) Describe biological importance of Mg<sup>2+</sup> and Ca<sup>2+</sup> ions.
- (8) Explain the solubility and stability of oxo salts of alkaline earth metals.

# 4. Give scientific reasons for the following:

- (1) Sodium gives yellow colour in flame test.
- (2) Potassium hydrogen carbonate can not be obtained by Solvay soda process.
- (3) Alkali and alkaline earth metals are not available free in nature.
- (4) Discuss the oxidation number of oxygen in oxide, dioxide and superoxide.
- (5) Sodium is found to be more useful than potassium.