

The s-block Elements : Group-I Alkali Metals

THE ELEMENTS OF GROUP I ARE:

Li - Lithium ,Na - Sodium ,K - Potassium ,Rb – Rubidium, Cs – Caesium, Fr – Francium

These elements are known as alkali metals because their oxides and hydroxides are alkaline in nature. Lithium is known as a bridge element. These do not occur in the native state.

GENERAL CHARACTERISTICS:

(i) **Electronic configuration** :- These are s-block elements and have one electron in the valence shell in s-orbital. In general their electronic configuration may be represented as [noble gas] ns^1 where 'n' represents the valence shell

Element	Atomic no.	Electronic configuration	Valence shell configuration
Li	3	[He] $2s^1$	$2s^1$
Na	11	[Ne] $3s^1$	$3s^1$
K	19	[Ar] $4s^1$	$4s^1$
Rb	37	[Kr] $5s^1$	$5s^1$
Cs	55	[Xe] $6s^1$	$6s^1$
Fr	87	[Rn] $7s^1$	$7s^1$

(ii) **Size of the atoms - Atomic radii**: The alkali metal atoms have the largest sizes in a particular period of the periodic table. With increase in atomic number, the atom becomes larger. The atomic and ionic radii of alkali metals increase on moving down the group i.e., they increase in size while going from Li to Cs.

(iii) **Density** –

- (a) These are light metals having low densities. Lithium is the lightest known metal.
- (b) On moving down the group, both the atomic size and atomic mass increases and since the increase in latter is not compensated by increase in former, consequently density increases from Li to Cs.
- (c) The density of potassium is lesser than that of sodium because of the abnormal increase in size on moving from Na to K.

(iv) **Melting and Boiling points** :-

- (a) The melting and boiling points of alkali metals are quite low and decreases down the group due to weakening of metallic bond.
- (b) Fr is a liquid at room temperature.

(v) **Softness** - These are soft, malleable and ductile solids which can be cut with knife. They possess metallic lustre when freshly cut due to oscillation of electrons.

(vi) **Ionisation energy**- The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

(vii) **Hydration Enthalpy**: The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes. $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$.

(viii) **Crystal structure** :- All alkali metals possess body centred cubic structures with co-ordination number 8

(ix) **Oxidation state** :- (a) The alkali metal atoms show only +1 oxidation state, because their unipositive ions have the stable gas electronic configuration (ns^2 or $ns^2 p^6$) in the valence shell. (b) Since the alkali metal ions have noble gas configuration with no unpaired electrons, they are diamagnetic and colourless but their permanganates and dichromates compounds are coloured.

(x) **Flame colouration** :-

(a) All alkali metals and their salts impart characteristic colours to the flame because of the bonding of the outermost electron. The outer electrons of these atoms are excited to higher energy levels. On returning to the original state they give out visible light of characteristic wavelength. This gives a characteristic colour to the flame.

(b) On moving down the group, the ionisation energy goes on decreasing and hence the energy or the frequency of emitted light goes on increasing in the order $Li < Na < K < Rb < Cs$. As a result, the colour shows following trend:

Li	Na	K	Rb	Cs
crimson red	golden yellow	pale violet	purple (violet)	sky blue

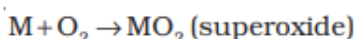
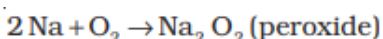
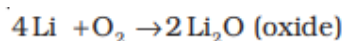
Due to low I.E., alkali metals especially K and Cs show photoelectric effect (i.e. eject electrons when exposed to light of high frequency) and hence are used in photoelectric cells.

(xii) **Electrical conductivity** :- Due to the presence of loosely held valence electrons which are free to move throughout the metal structure, the alkali metals are good conductors of heat and electricity. Electrical conductivity increases from top to bottom in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. However reverse trend is followed in aqueous medium due to hydration of ions.

Chemical Properties :

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

(i) **Reactivity towards air**: The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O_2^- ion is stable only in the presence of large cations such as K^+ , Rb^+ , Cs^+ due to stabilisation of larger anions by larger cations through lattice energy.

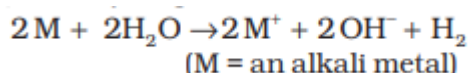


(M = K, Rb, Cs)

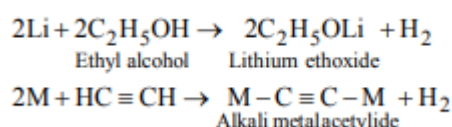
In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N as well. Because of their high reactivity towards air and water, alkali metals are normally kept in kerosene oil, but lithium is kept wrapped in paraffin wax because it floats on the surface of kerosene oil due to its very low density. Superoxides are coloured and paramagnetic as these possess three electron bond where one unpaired electron is present.

(ii) Reactivity towards water:

The alkali metals react with water to form hydroxide and dihydrogen.



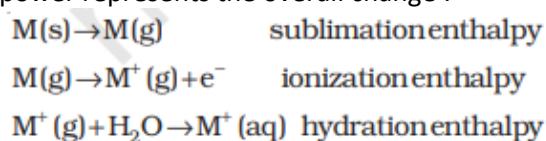
It may be noted that although lithium has most negative E^0 value, its reaction with water is less vigorous than that of sodium which has the least negative E^0 value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water. They also react with proton donors such as alcohol, gaseous ammonia and alkynes.



(iii) Reactivity towards dihydrogen: The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.

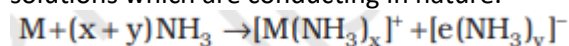
(iv) Reactivity towards halogens : The alkali metals readily react vigorously with halogens to form ionic halides, $M^+ X^-$. However, lithium halides are somewhat covalent because of the high polarisation capability of lithium ion. The reactivity of alkali metals towards a particular halogen increases in the order : $Li < Na < K < Rb < Cs$.

(v) Reducing nature: The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The standard electrode potential (E^0) which measures the reducing power represents the overall change :

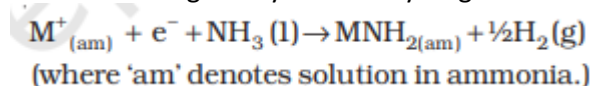


With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative E^0 value and its highest reducing power in aqueous solution.

(vi) Solutions in liquid ammonia: The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.



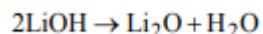
The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.



In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic due to the association of ammoniated electrons. - Due to the presence of ammoniated electrons, solution is a very powerful reducing agent and used in organic chemistry under the name Birch reduction.

(vii) Complex formation :- Alkali metals have a weak tendency to form complexes but polydentate ligands such as crown ethers and **cryptands** form highly stable complexes collectively called as **Wrap Around Complexes**. Cryptands are macrocyclic molecules with N and O atoms and their complexes are called **cryptates**. The name cryptate came from the fact that metal ion is hidden in the structure.

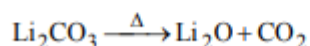
(viii) Nature of hydroxides :- Alkali metals hydroxides are very strong bases, highly soluble in water and are not decomposed on heating. However, LiOH decomposes on heating to give Li_2O because latter is more stable than former.



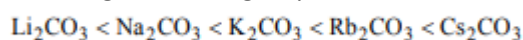
Their basic strength increases from LiOH to CsOH due to a corresponding decrease in the I.E. of the metal in a group, i.e., the order:- $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$.

(ix) Nature of carbonates and bicarbonates :-

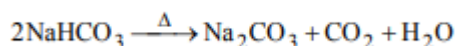
(a) Li_2CO_3 is unstable towards heat and decomposes to give Li_2O and CO_2 .



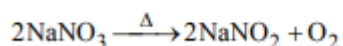
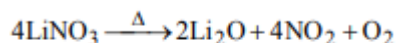
The thermal stability of carbonates increases with the increasing basic strength of metal hydroxides on moving down the group. Thus the order is



(b) The bicarbonates of all the alkali metals are known. All the bicarbonates (except LiHCO_3 which exists in solution) exist as solids and on heating form carbonates.



(x) Nature of Nitrates:- LiNO_3 on heating decomposes to give NO_2 and O_2 while the nitrates of the other alkali metals decompose on heating to form nitrites and O_2 .



All nitrates are soluble in water.

ANOMALOUS BEHAVIOUR OF LITHIUM :

Lithium, the first member of the alkali metal family shows an anomalous behaviour because of the following main reasons:- (a) It has the smallest size in the group (b) It has very high ionization energy and highest electronegativity in the group. (c) It has no vacant d-orbital in the valence shell.

As a result, it differs from the other member of the alkali metal family in following respects:

- (i) Lithium is harder than other alkali metals, due to strong metallic bond.
- (ii) Lithium combines with O_2 to form lithium monoxide, Li_2O , whereas other alkali metals form Peroxides, M_2O_2 and superoxides MO_2 .
- (iii) Lithium, unlike the other alkali metals, reacts with nitrogen to form the nitride etc.

DIAGONAL RELATIONSHIP : Lithium shows diagonal relationship with magnesium, the element of group 2 and this resemblance is due to polarising power. For example,

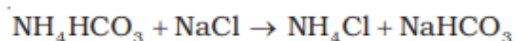
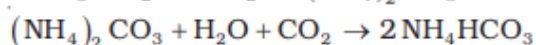
- i. Both combine with O_2 to form monoxides, e.g., Li_2O and MgO .
- ii. Both LiCl and MgCl_2 are predominantly covalent.
- iii. Both Li and Mg combine with N_2 to form their respective nitrides, Li_3N and Mg_3N_2 etc.

SOME IMPORTANT COMPOUNDS OF SODIUM :

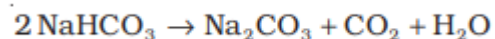
Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below:

I. Sodium Carbonate (Washing Soda), $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

In this process, NaCl (brine), ammonia and CO_2 are taken as raw materials. The involving reactions are:

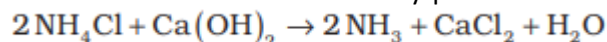


Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.



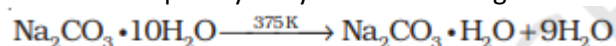
In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $\text{Ca}(\text{OH})_2$.

Calcium chloride is obtained as a by-product.



It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

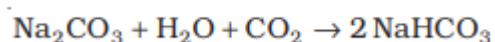
Properties : Sodium carbonate is a white crystalline solid which exists as a decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called **soda ash**.



Uses: (i) It is used in water softening, laundering and cleaning. (ii) It is used in the manufacture of glass, soap, borax and caustic soda. (iii) It is used in paper, paints and textile industries.

SODIUM BICARBONATE, BAKING SODA, NaHCO_3 :- Preparation :- It is obtained as an intermediate product in Solvay ammonia process.

Sodium hydrogencarbonate is also made by saturating a solution of sodium carbonate with carbon dioxide.



Sodium hydrogencarbonate is a mild antiseptic for skin infections. It is used in fire extinguishers.

Sodium Chloride, NaCl : The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, CaCl_2 , and magnesium chloride, MgCl_2 are impurities because they are deliquescent (absorb moisture easily from the atmosphere).

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 gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

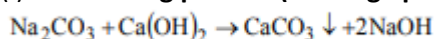
Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses : It is used as a common salt or table salt for domestic purpose.

SODIUM HYDROXIDE, CAUSTIC SODA, NaOH :

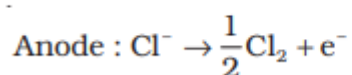
Preparation:-

(i) **Causticizing process (Gossage process):**

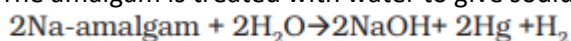


(ii) **Electrolytic process** : Mercury cathode process (Castner - Kellner cell):

A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.



The amalgam is treated with water to give sodium hydroxide and hydrogen gas.



Uses: It is used in (i) the manufacture of soap, paper, artificial silk and a number of chemicals, (ii) in petroleum refining, etc.

BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM :

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 mmolL^{-1} , whereas the potassium level is only 5 mmolL^{-1} within the red blood cells. These concentrations change to 10 mmolL^{-1} (Na^+) and 105 mmolL^{-1} (K^+). These ionic gradients demonstrate that a discriminatory mechanism, called the **sodium-potassium pump**, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The elements of group 2 are:

Be – Beryllium, Mg - Magnesium, Ca – Calcium, Sr – Strontium, Ba - Barium ,Ra - Radium

These metals are known as alkaline earth metals as their oxides are alkaline and occur in earth crust.

Radium was discovered from the ore Pitch blende by Madam Curie. It is used in the treatment of cancer. These metals do not occur in the native form (i.e., do not occur in free state).

GENERAL CHARACTERISTICS OF ALKALINE EARTH METALS:

(i) Electronic configuration: Like alkali metals, these are s-block elements, and have two electrons in the valence shell in s-orbital. Hence their electronic configuration may be represented as [noble gas] ns^2 where 'n' represents the valence shell.

<i>Element</i>	<i>Atomic No.</i>	<i>Electronic Configuration</i>	<i>Valence Shell configuration</i>
Be	4	[He] $2s^2$	$2s^2$
Mg	12	[Ne] $3s^2$	$3s^2$
Ca	20	[Ar] $4s^2$	$4s^2$
Sr	38	[Kr] $5s^2$	$5s^2$
Ba	56	[Xe] $6s^2$	$6s^2$
Ra	88	[Rn] $7s^2$	$7s^2$

(ii) Size of the atoms and ions (Atomic radii and ionic radii):

The atomic radii of these elements are quite large but smaller than those of the corresponding elements of group 1, due to increased nuclear charge of these elements which tends to draw the orbital electrons inwards.

The atomic as well as ionic radii go on increasing down the group due to the gradual addition of extra energy level and also because of the screening effect.

(iii) Density:

(a) These are much denser than alkali metals because of their smaller size and greater nuclear charge.

(b) The density, however, first decreases from Be to Ca and then steadily increases from Ca to Ra due to difference in crystal structure.

(iv) Melting and Boiling points:

These have higher melting and boiling points than those of alkali metals because the number of bonding electrons in alkaline earth metals is two.

The melting and boiling points decrease down the group with the exception of magnesium

(v) Ionization Energy:

The first I.E. of alkaline earth metals are higher than those of the corresponding alkali metals due to smaller size and higher nuclear charge.

The second I.E. values are higher than their first I.E. values but much lower than the second I.E. values of alkali metals.

On moving down the group due to increase in atomic size the magnitude of I.E. decreases.

(vi) Oxidation state:

Alkaline earth metals uniformly show an oxidation state of +2 despite the presence of high ionisation energy because in the solid state, the divalent ions M^{2+} form strong lattices due to their small size

and high charge (i.e., high lattice energy). In the aqueous solution, the M^{2+} cations are strongly hydrated due to their small size and high charge. The hydration energy released by the M^{2+} cation is very large. The divalent ions are diamagnetic and colourless due to the absence of unpaired electron.

(vii) Hydration Enthalpies :

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group. $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ while $NaCl$ and KCl do not form such hydrates.

(viii) Flame colouration:

Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration. As we move down the group from Ca to Ba, the ionisation energy decreases, hence the energy or the frequency of the emitted light increases. Thus,

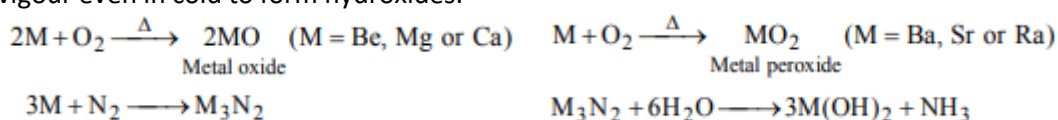
Ca	Sr	Ba	Ra
Brick red	Crimson red	Apple green	Crimson

Be and Mg because of their high ionization energies, however, do not impart any characteristic colour to the bunsen flame.

Chemical Properties :

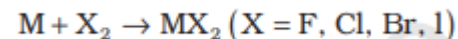
The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) Reactivity towards air and water: Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2 . Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2 . Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold to form hydroxides.

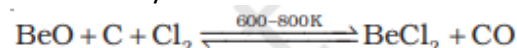


(ii) Reactivity towards the halogens (Halides):

All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.

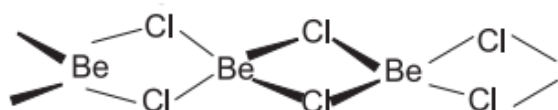


Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2 , and $BeCl_2$ is conveniently made from the oxide.



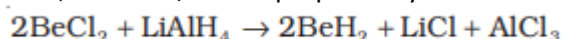
Beryllium halides (BeF_2 , $BeCl_2$ etc.) are covalent, hygroscopic and fume in air due to hydrolysis. The halides of other alkaline earth metals are fairly ionic and this character increases as the size of the metal increases.

$BeCl_2$ has a polymeric structure in the solid state but exists as a dimer in the vapour state and as a monomer at 1200 K



(iii) Reactivity towards hydrogen:

All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2 . BeH_2 , however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.



BeH_2 and MgH_2 are covalent and polymeric whereas the hydrides of Ca, Sr and Ba are ionic and monomeric in nature.

CaH_2 is also called **hydrolith**.

All the hydrides react with water to evolve H_2 and thus behave as strong reducing agents.

(iv) Reactivity towards acids:

Alkaline earth metals except Be, displace H_2 from acids



Reactivity, however, increases down the group from Mg to Ba.

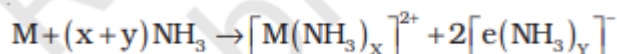
Only Mg displaces H_2 from a very dilute HNO_3

(v) Reducing nature:

Like alkali metals, the alkaline earth metals are strong reducing agents. However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be^{2+} ion and relatively large value of the atomization enthalpy of the metal. As we move down the group from Be to Ra, the reducing character increases due to decreasing I.E. from Be to Ra.

(vi) Solutions in liquid ammonia:

Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.



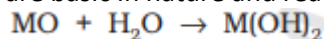
The tendency to form ammoniates decreases with increase in size of the metal.

GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS:

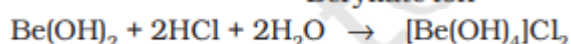
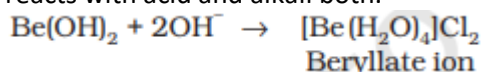
(i) Oxides and Hydroxides:

The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO , have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat.

BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

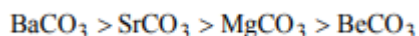


The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

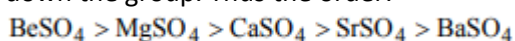


(ii) Salts of Oxoacids: The alkaline earth metals also form salts of oxoacids. Some of these are :

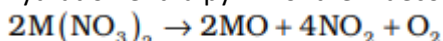
Carbonates: Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO₂. The thermal stability increases with increasing cationic size, i.e.



Sulphates: The sulphates of the alkaline earth metals are all white solids and stable to heat. BeSO₄, and MgSO₄ are readily soluble in water; : The solubility of sulphates of alkaline earth metals decreases as we move down the group from Be to Ba due to the reason that ionic size increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic sizes do not make any difference, but hydration enthalpy of cations decreases down the group. Thus the order:



Nitrates: The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.



(M = Be, Mg, Ca, Sr, Ba)

ANOMALOUS BEHAVIOUR OF BERYLLIUM : Beryllium, the first member of group 2 differs from the rest of the members of its group due to the following reasons:

- (i) It has a small atomic size as well as small ionic size.
- (ii) It has no vacant d-orbitals in valence shell.
- (iii) It has high electronegativity value.
- (iv) It has a high charge density.
- (v) Its hydration energy is high.

Some points of difference are:

- (i) Be is harder and denser than other members of the group.
- (ii) Be forms nitride Be₃N₂ with nitrogen which is volatile while nitrides of others are non-volatile
- (iii) Be does not react with water even at higher temperature where as other metals do.
- (iv) BeO and Be(OH)₂ are amphoteric in character whereas oxides and hydroxides of the group 2 metals are basic.

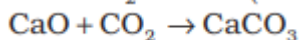
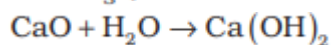
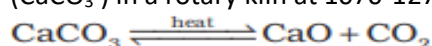
DIAGONAL RELATIONSHIP OR RESEMBLANCE BETWEEN Be AND Al : The first member of group-2, Beryllium, shows similarities in the properties with its diagonally opposite member aluminium of the next group 13 of the next higher period, due to the similar polarizing power of Be and Al.

e.g.

- i. Both have a strong tendency to form covalent compounds.
- ii. With conc. HNO₃, both are rendered passive due to the formation of a thin film of their respective oxides on the metal surface
- iii. Oxides and hydroxides of both are amphoteric in nature
- iv. Anhydrous chlorides of both i.e., BeCl₂ and AlCl₃ act as Lewis acids and dissolve in organic solvents.

SOME IMPORTANT COMPOUNDS OF CALCIUM:

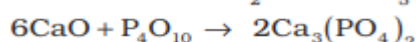
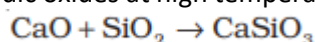
Calcium Oxide or Quick Lime, CaO : It is prepared on a commercial scale by heating limestone (CaCO_3) in a rotary kiln at 1070-1270 K.



The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

The addition of limited amount of water breaks the lump of lime. This process is called **slaking of lime**. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.



Uses: It is an important primary material for manufacturing cement and is the cheapest form of alkali. It is used in the manufacture of sodium carbonate from caustic soda.

Calcium Hydroxide (Slaked lime), Ca(OH)_2 :

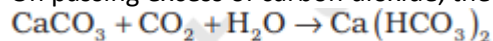
Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.

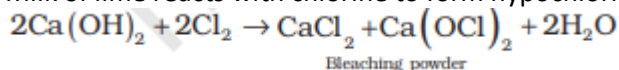
When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.



On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate



Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.



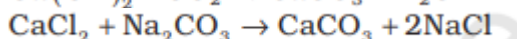
Uses:

It is used in the preparation of mortar, a building material

It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

Calcium Carbonate, CaCO_3 :

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

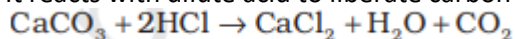


Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.



It reacts with dilute acid to liberate carbon dioxide.



Uses:

It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated CaCO_3 is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

Calcium Sulphate (Plaster of Paris), $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$:

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is heated to 393 K.

$$2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) \rightarrow 2(\text{CaSO}_4) \cdot \frac{1}{2} \text{H}_2\text{O} + 3\text{H}_2\text{O}$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, CaSO_4 is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immobilising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

CEMENT :

Cement is essentially a mixture of complex silicates and aluminates of Ca containing less than 1.0% free lime and some gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) Composition : An approximate composition is as follows :

1.	Lime	CaO	60-69%	62%
2.	Silica	SiO_2	17-25%	22%
3.	Alumina	Al_2O_3	3-8%	7.5%
4.	Magnesia	MgO	1-5%	2.5%
5.	Iron oxide	Fe_2O_3	0.5-5%	2.5%
6.	Sulphur trioxide	SO_3	1-3%	1.5%
7.	Sodium oxide	Na_2O	0.3-1.5%	1.0%
8.	Potassium oxide	K_2O	0.3-1.5%	1.0%

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form '**cement clinker**'. This clinker is mixed with 2-3% by weight of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to form cement. Thus important ingredients present in **Portland cement** are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) 11%.

Setting of Cement : When mixed with water, the cement forms a gelatinous mass sets to hard mass when three dimensional cross links are formed between ... Si-O-Si---and ---Si-O-Al--- chains. The reactions involved in the setting of cement are :

(i) Hydration : Hydration of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $2\text{CaO} \cdot \text{SiO}_2$ forming colloidal gel.

(ii) Hydrolysis : Hydrolysis of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{SiO}_2$ forming precipitates of $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$

Uses:

Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM :

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg.

All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL^{-1} . It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma