16

CHAPTER

s-block elements

ALKALI METALS

Selected data on group I alkali metals

Chemical symbol, name	At. No.	Electron arrangement	Melting point	Boiling point	Atomic radii (pm)
Li, Lithium	3	$1s^2, 2s^1$	181°C, 454 K	1347°C, 1620 K	152
Na, Sodium	11	$1s^2, 2s^2\ 2p^6, 3s^1$	98°C, 371 K	883°C, 1156 K	186
K, Potassium	19	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6, 4\mathrm{s}^1$	64°C, 337 K	774°C, 1047 K	231
Rb, Rubidium	37	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6, 5s^1$	39°C, 312 K	688°C, 961 K	244
Cs, Caesium	55	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^2\ 5p^6, 6s^1$	29°C, 302 K	679°C, 952 K	262
Fr, Francium	87	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5\mathrm{s}^2\ 5p^6, 6s^2\ 6p^6, 7s^1$	27°C, 300 K	677°C, 950 K	270

- These elements are collectively called as alkali metals and group I is known as alkali group as the hydroxides of these metals are soluble in water and these solutions are highly alkaline in nature.
- Alkali metals are highly reactive and hence do not occur in the free state but are widely distributed in nature in combined state in the form of halides, oxides, silicates, borates and nitrates. Off all the alkali metals, only sodium and potassium are found in abundance in nature, i.e. they are seventh and eighth most abundant elements by weight in earth's crust. The last member, francium, occurs only in traces as a radioactive decay product because its half life period is very small, i.e. 21 minutes.
- Alkali metals are *s*-block elements, because last electron in them enters the *s*-orbital.

- These metals have only one electron in their outer shell. Therefore they are ready to lose that one electron in ionic bonding with other elements.
- Alkali metals form the first element of the period, with one outer electron, in any period from period 2 onwards. This outer electron similarity makes them behave in a chemically similar way. Some of their physical properties are typical of metals and some are not so typical of metals. Although they all have one outer electron and so similar physical and chemical properties, a characteristic of a periodic table group, but always watch out for trends down a group too.
- As with all metals, the alkali metals are malleable, ductile, and are good conductor of heat and electricity.
- All the group-I elements are silvery-coloured metals. They are soft and can be easily cut with a knife to expose a shiny surface which dulls on oxidation.
- These elements are highly reactive metals. The reactivity increases on descending the group from lithium to caesium.
- There is a closer similarity between the elements of this group than in any other group of the periodic table.
- Caesium and francium are the most reactive elements in this group.
- All alkali metals dissolve in mercury and forming amalgams. This reaction is highly exothermic.
- Fire caused by burning of alkali metals is extinguished by sprinking CCl_4.
- Alkali metals are paramagnetic due to the presence of unpaired electrons. On the other hand, alkali metal ions are diamagnetic and colourless due to their noble gas configuration with no unpaired electrons.
- **Typical metallic properties :** Good conductors of heat and electricity, high boiling points, silvery grey surface (but rapidly tarnished by air oxidation).

  When an alkali metal atom reacts, it loses an electron (oxidation) to form a singly positively charged ion.

  e.g. $Na \rightarrow Na^+ + e^-$.

  In terms of electrons, 2, 8, 1 → 2, 8 and so forming a stable ion with a noble gas electron arrangement. They tend to react mainly with non-metals to form ionic compounds which are usually soluble in white solids.
- **Non-typical metallic properties :** Low melting points, low density (first three float on water), very soft (easily squashed, extremely malleable) and so they have little material strength.
- Important trends down the group with increase in atomic number.

  The melting point and boiling point generally decrease.
  - The element gets more reactive.
  - The atoms get bigger (as more electron shells are added).
  - Generally the density increases (although the atom gets bigger, there is greater proportional increase in the atomic mass).
  - Generally the hardness decreases.

Interesting facts about alkali metals

- Potassium is never found as a pure metal.

  0.07% of the ocean is made up of potassium chloride.
- The National Institute of Standards and Technology has created a caesium fountain atomic clock. It is the Nation's primary time and frequency standard.
- There is atmost one ounce of francium in the whole earth at any given time as a result of the decay of other radioactive elements.

- On moving down in the group from Li to Cs, electropositivity, atomic radii, atomic volume, reactivity, reducing power, conductivity, solubility of salts having small anion and density show an increasing trend. On the other hand, m.p. and b.p., hardness, ionization energy, electronegativity and solubility of salts having large anions (such as SO_4^{2-}, ClO_4^-, etc.) show a decreasing trend.
- The stability and solubility of carbonates, nitrates and bicarbonates increase in the order :

  $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$,

  $LiNO_3 < NaNO_3 < KNO_3 < RbNO_3 < CsNO_3$ and

  $LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$
- The stability of peroxides and superoxides increase in the order :

  $Na_2O_2 < K_2O_2 < Rb_2O_2 < Cs_2O_2$ and $NaO_2 < KO_2 < RbO_2 < CsO_2$
- The solubility, stability and basic strength of hydroxides increase in the order:

  $LiOH < NaOH < KOH < RbOH < CsOH$
- The solubility and basic strength of oxides increase in the order :

  $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$
- The peroxides of alkaline metals are colourless and diamagnetic while the superoxides are paramagnetic and coloured.
- Most metallic elements in the periodic table are Cs and Fr.
- KOH is better absorber of CO_2 than NaOH because potassium carbonate thus formed is more soluble and does not separate out.
- Li^+ is poor conductor of electricity than Cs^+ because hydrated Li^+ ion is larger in size than hydrated Cs^+ ion.
- Although lithium has the highest ionization enthalpy, yet it is the strongest reducing agent because of its large heat of hydration which is sufficient to overcome its ionization enthalpy.
- Lithium is the lightest metal, least fusible, least dense and least soft of all the alkali metals.
- Degree of hydration of alkali metal ions decreases in the order : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The relative ionic radii in water also decrease in the same order.
- Alkali metals are *paramagnetic* due to the presence of unpaired ns^1 electrons. On the other hand, alkali metal ions are *diamagnetic* and *colourless* due to their noble gas configuration with no unpaired electrons.

- In biological fluids, many cells tend to accumulate K^+ ions at the expense of Na^+ ions. These concentration gradients can be explained by different mechanisms such as *sodium pump* and *potassium pump.* Development and functioning of nerve cells are controlled by these cation gradients.
- $Na_2SO_4 \cdot 10H_2O$ is called *Glauber's salt*, anhydrous Na_2SO_4 is called *salt cake,* $NaNO_3$ is called *chile salt-petre,* $NaHSO_4$ is called *nitre cake* and KNO_3 is called *Indian salt-petre or nitre.*
- When common salt is fused with a little Na_2CO_3, 5-10% Na_2SO_4 and some sugar, it acquires a dark purple colour and has a characteristic saline taste. It is used in medicine to improve digestion. It is called *Kala namak or black salt or sulemani namak.*
- Although both NaCN and KCN are poisonous but KCN is more poisonous that NaCN.
- An alloy of Na and K is a liquid at room temperature. It is used in special thermometers for recording temperature above the b.p. of mercury (357°C).
- Sodium sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, which is neither deliquescent nor efflorescent,is used for wool washing.
- A mixture of Na_2O_2 and dil. HCl is commercially called oxone and is used for bleaching delicate fibres.
- Potassium superoxide (KO_2) is used as a source of oxygen in submarines, space shuttles and in emergency breathing apparatus. The moisture of the breath reacts with superoxide to liberate the apparatus (*oxygen mask*) to be continuously regenerated.

  $$KO_2 + 2H_2O \rightarrow 4KOH + 3O_2\ ;\ KOH + CO_2 \rightarrow KHCO_3$$
- Alkali metals combine with mercury to form compounds (alloys) known as *amalgams.* This reaction is highly exothermic.
- Li^+ ion does not form alums because it is too small to have a coordination number of six.
- Potassium salts of fatty acids are used to make *soft soaps* because they are more soluble than those of sodium salts.
- 28% NaCl solution is called *brine.*
- Sodium hydroxide breaks down the proteins of the skin flesh to a pasty mass and hence it is commonly known as *caustic soda.*
- Lithium is used as a scavenger in metallurgy to remove last traces of oxygen and nitrogen from copper and nickel.
- Fire caused by burning of alkali metals is extinguished by sprinkling CCl_4.
- Francium was discovered by Perey in 1939 in France during nuclear disintegration of actinium-227.

  $${}_{89}Ac^{227} \rightarrow {}_{87}Fr^{223} + {}_{2}He^{4}$$
- Because of the small size of Li^+ ion, lithium salts usually crystallise from their aqueous solutions in the form of hydrates.
- Only lithium combines directly with carbon to form lithium carbide, Li_2C_2. While other alkali metals react with ethyne to form the corresponding metal carbides.
- All alkali metals dissolve in mercury forming amalgams.

- Lithium sulphate does not form alums and is also not amorphous with other sulphates.
- Only $LiHCO_3$ exists in solution while all other alkali metal bicarbonates are solids.
- Lithium cannot be stored in kerosene oil since it floats over the surface due to its very low density. Therefore, lithium is usually kept wrapped in paraffin wax.
- **Solubility in liquid ammonia :** All the alkali metals dissolve in liquid ammonia giving deep blue solution when dilute due to the presence of ammoniated (solvated) electrons in the solution but the colour changes to bronze with increasing concentration. If ammonia is evaporated we get back the metal.

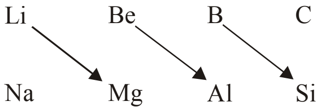
$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

- The solution of alkali metals in liquid ammonia :
  (i) is strongly reducing due to the presence of ammoniated electrons so it is used in Birch reduction as a reducing agent.
  (ii) is conducting due to ammoniated electrons and ammoniated cations, on cooling the conductivity increases.
  (iii) shows paramagnetism due to presence of ammoniated electrons. On increasing the concentration association of ammoniated electrons occur to yield diamagnetic species because of which the colour changes to copper bronze acquiring metallic lusture due to the formation of metal ion clusters.

$$2e^- (NH_3)_y \rightarrow [e^-(NH_3)_y]_2$$

Diagonal relationship between lithium and magnesium

- Lithium shows diagonal relationship with magnesium since they have the same charge/size ratio i.e. polarising power.
- The first element of group often shows resemblance to the second element of the neighbouring group on the right. This type of behaviour is known as Diagonal Relationship.

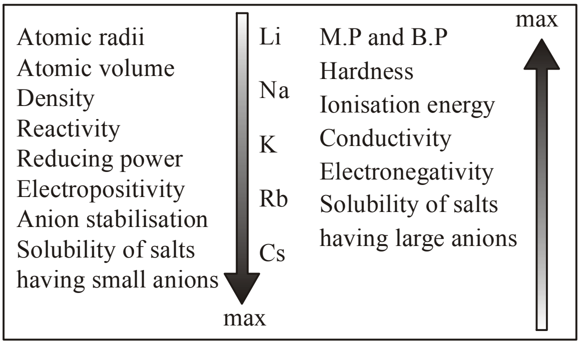


- This similarity between Li and Mg is particularly striking and arises because of their similar ionic sizes (Li^+ = 76 pm; Mg^{2+} = 72 pm)
- Li and Mg show close resemblance in the following :

Nitrides	Li and Mg both form nitrides. Other alkali metals do not. $6Li + N_2 \xrightarrow{\Delta} 2Li_3N$, $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$
Carbonates	Like $MgCO_3$, Li_2CO_3 is decomposed by heat (the other alkali carbonates are thermally stable). Both carbonates are insoluble while Na_2CO_3, K_2CO_3... are soluble. $MgCO_3 \xrightarrow{\Delta} MgO + CO_2$, $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$
Nitrates	$LiNO_3$ decomposes to give Li_2O like $Mg(NO_3)_2$, but other alkali metal nitrates give nitrite. $Mg(NO_3)_2 \xrightarrow{\Delta} MgO + 2NO_2 + 1/2O_2$ $2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + 1/2O_2$

Oxides	Both give their normal oxides, Li_2O, MgO when they burn in oxygen. Na forms peroxide, Na_2O_2, while *K* forms superoxide, KO_2.
Hydration	Both Li^+ and Mg^{2+} are heavily hydrated.

- **Gradation properties of alkali metals**



- **Anomalous behaviour of lithium**

Reason for the anomalous behaviour of lithium is mainly due to its small size and hence it has highest polarizing power. The main points of difference :

(i) Li is harder than any other alkali metal.
(ii) Li combines with O_2 to form monoxide whereas other alkali metals form peroxides and superoxides.
(iii) Li is the only alkali metal which directly reacts with N_2 to form Li_3N.
(iv) Li(OH) decomposes at red heat, however hydroxides of other alkali metals do not decompose.
(v) The bicarbonate of Li is not known in solid state while the bicarbonates of other alkali metals are known in solid state.
(vi) In presence of NH_3, lithium forms imide Li_2NH while other alkali metals form amides, MNH_2.

- **Fajan's rule**

The partial covalent character in ionic compounds results through polarisation of the anion by the cation so that the electron density between the two nuclei increases. The covalent character is favoured by the following factors which are collectively known as Fajan's rules.

(i) **Small cation** : Smaller the cation larger is the covalent character. For example, LiCl is more covalent than KCl.
(ii) **Large anion** : Bigger the anion, larger is the covalent character. For example, amongst KF, KCl, KBr and KI, KI is most covalent.
(iii) **Large charge on the cation or anion** : With increase in the magnitude of charge on the cation or the anion, the covalent character increases. For example, covalent character increases in the order : NaCl, $MgCl_2$, $AlCl_3$, $SiCl_4$ etc.
(iv) **Pseudo inert gas configuration** : For two ions of the same size and charge, one with a pseudo inert gas configuration (transition elements) will be more polarising than a cation with noble gas configuration. For example, AgCl (Ag^+ = 1.26 Å) is more covalent than KCl (K^+ = 1.33 Å).

MICROCOSMIC SALT, $Na(NH_4)HPO_4.4H_2O$

- It is prepared by dissolving molecular proportions of Na_2HPO_4 and NH_4Cl in hot water and crystallising the contents.

$$Na_2HPO_4 + NH_4Cl \rightarrow Na(NH_4)HPO_4 + NaCl$$

Disod. hydrogen phosphate

It is used for performing 'bead test' for detecting coloured ions (e.g. Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}) in qualitative inorganic analysis. The bead test is based on the fact that on heating it forms a transparent glassy bead of metaphosphate. The metaphosphate so formed gives coloured beads of orthophosphates when heated with coloured salts (*microcosmic bead test*).

$$Na(NH_4)HPO_4 \rightarrow NH_3 + H_2O + NaPO_3$$

Sod. metaphosphate

$$CuSO_4 \rightarrow CuO + SO_3,\ CuO + NaPO_3 \rightarrow CuNaPO_{4}\text{(blue bead)}$$

It is especially used for detecting silica which, being insoluble in $NaPO_3$, gives a cloudy bead.

POINTS TO REMEMBER

- **Monoxides, peroxides and superoxides of alkali metals**. All the five alkali metals can be induced to form normal oxides (*i.e.* monoxides), peroxides and superoxides by dissolving the metal in liquid ammonia and bubbling in the appropriate amount of oxygen.
- **Crystal structures of monoxides of alkali metals**. Except Cs_2O which has anti-$CdCl_2$ layer structure, all other monoxides, *i.e.* Li_2O, Na_2O, K_2O and Rb_2O have anti-fluorite structures.
- **Potassium superoxide (KO_2)** is used as a source of oxygen in submarines, space shuttles and in emergency breathing apparatus such as oxygen masks. Such masks are used in rescue work in mines and in other areas where the air is so deficient in oxygen that an artificial atmosphere must be generated.
- **Lithium hydroxide (LiOH)** is used to remove CO_2 from exhaled air in confined quarters like submarines and space vehicles.
- The alkali metals react with halogens and interhalogen compounds forming ionic polyhalide compounds.
- The solution of alkali metals such as Li, Na, or K in liquid ammonia is used for reduction of ethylenic double bonds, acetylenic triple bonds to double bonds and aromatic compounds under the name Birch reduction.
- Lithium is the highest known metal, having density = 0.534 g/cc. Therefore, it cannot be stored in kerosene oil because it floats on the surface. It is kept wrapped in paraffin wax.
- Cs is the most electropositive element due to its lowest ionization energy.
- Lithium cannot be used in making photoelectric cells because out of all the alkali metals, it has highest ionization energy and cannot emit electrons when exposed to light.
- The compounds of alkali metals are colourless (unless the anion is coloured like permanganate or dichromate) and diamagnetic. This is because they have noble gas configuration with no unpaired electron.
- All alkali metals exist as body-centred cubic lattice with a coordination number of 8.
- Due to small size, lithium does not form alums.

ALKALINE EARTH METALS

- The group II of the periodic table consists of six elements - beryllium, magnesium, calcium, strontium, barium and radium. These elements are known as alkaline earth metals and group II is known as alkaline earth group. Although early chemists gave the name “earths” to a group of naturally occurring substances that were unaffected by heat and insoluble in water, the alkaline earth metals are also usually found in the continental crust. Alkaline earth metals always form divalent cations.

Electronic configuration of alkaline earth metals

Element	At. No.	Electronic configuration	Configuration of the valence shell
Be	4	$1s^2, 2s^2$	[He] $2s^2$
Mg	12	$1s^2, 2s^2$, $2p^6$ $3s^2$	[Ne] $3s^2$
Ca	20	$1s^2, 2s^2$ $2p^6$, $3s^2$ $3p^6$, $4s^2$	[Ar] $4s^2$
Sr	38	$1s^2, 2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^{10}$, $4s^2$ $4p^6$, $5s^2$	[Kr] $5s^2$
Ba	56	$1s^2, 2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^{10}$, $4s^2$ $4p^6$ $4d^{10}$, $5s^2$ $5p^6$, $6s^2$	[Xe] $6s^2$
Ra	88	$1s^2, 2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^{10}$, $4s^2$ $4p^6$ $4d^{10}$, $5s^2$ $5p^6$, $6s^2$ $6p^6$, $7s^2$	[Rn] $7s^2$

Factors responsible for divalent oxidation states

(i) The lattice energy increases as the charge on the ion increases. The increase in the lattice energy on account of the second electron from ns^2 is much more than the energy required (second ionisation energy) to remove it. Hence, the stability of +2 oxidation state is due to high lattice energy.

(ii) The second factor responsible for +2 oxidation state is the hydration energy which is high for M^{2+} ions. On account of the availability of energy, the process does not stop to M^+ state but reach to M^{2+} state readily.

Since the bivalent ions, M^{2+} have an inert gas configuration, it is very difficult to remove the third electron and hence oxidation state higher than +2 is not possible.

- Calcium is present in the soil, plants, bones as $Ca_3(PO_4)_2$ and egg shells etc.
- Gypsum $CaSO_4 \cdot 2H_2O$ is also known as *alabaster.*
- Calcium ions play an important role in *muscle contraction.*
- Magnesium ions are present in *chlorophyll-a* green colouring pigment in plants which absorbs light and is essential for *photosynthesis.*
- The ionization enthalpy or radium is higher than that of barium.
- Melting points of halides decrease as the size of the halogen increases. The correct order is : $MF_2 > MCl_2 > MBr_2 > MI_2$
- Thermal stability of carbonates and sulphates increases down the group from Be to Ba. The correct order is :

$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$ and

$BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$

- Basic character of oxides and hydroxides increases in the order :

  $BeO < MgO < CaO < SrO < BaO$ and

  $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- Solubility of sulphates and carbonates decreases in the order:

  $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ and

  $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

  Whereas the solubility of hydroxides increases in the order:

  $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- Solubility of chlorides, bromides and iodides decreases in the order :

  $MgX_2 > CaX_2 > SrX_2 > BaX_2$ (where X = Cl, Br or I)
- BeF_2 is soluble whereas fluorides of Mg, Ca, Sr and Ba are insoluble in water. Solubility decreases in the order :

  $BeF_2 > MgF_2 > CaF_2 > SrF_2 > BaF_2$
- Anhydrous $CaCl_2$ is a good desiccant but it cannot be used to dry alcohol and ammonia as it forms addition products with them.
- Aqueous $Ba(OH)_2$ is known as *baryta water.*
- Only Mg displaces hydrogen from a very dilute HNO_3.
- Like alkali metals, alkaline earth metals also dissolve in liquid ammonia giving coloured solutions which are good conductors of electricity.
- The hydride of Be can be prepared indirectly by reducing $BeCl_2$ with lithium aluminium hydride

  $$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$
- Since the alkaline earth divalent ions have no unpaired electrons, these are diamagnetic and colourless.
- Density of calcium is less than that of magnesium due to the presence of vacant 3*d*-orbitals leading to much increase in atomic volume.
- In alkaline earth metals the properties such as metallic nature, reducing nature, reactivity, electropositive character and ionic nature of compounds increases from Be to Ba whereas the complex formation tendency decreases.
- Fly ash, a waste product from steel industry has properties similar to cement. It can be added to cement to reduce the cost without affecting its quality.
- $BaSO_4$ being insoluble in H_2O and opaque to X-rays is used under the name *barium meal* to scan the X-rays of the human digestive system.
- Bicarbonates of alkaline earth metals do not exist in the solid state but are known in soution only.

- Most of the kidney stones consist of calcium oxalate, $CaC_2O_4{\cdot}H_2O$ which dissolves in dilute strong acids but remains insoluble in bases.
- Magnesium perchlorate, $Mg(ClO_4)_2$ is used as a drying agent under the name anhydrone.
- Mg in powder form is used in *flash bulbs* used in photography and Ca is used as *deoxidiser* as well as *desulphuriser* of metals.
- The anhydrous form of $CaSO_4$ (called *anhydrite*) is called *dead burnt plaster* because it does not set like plaster of paris when moistened with water.
- Mortar used in making buildings is a mixture of lime (CaO) and sand in the ratio 1 : 3 with enough water to make a thick paste. When the mortar is placed between bricks, it slowly absorbs CO_2 from the air and the slaked lime reverts to $CaCO_3$.

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

  Although the sand in the mortar is chemically inert, the grains are bound together by the particles of calcium carbonate and a hard material results.
- The ions Na^+, K^+, Mg^{2+} and Ca^{2+} are the most abundant metal ions in biochemical systems. Ca^{2+}, for example, is important in the process of muscle contraction and blood coagulation, Mg^{2+} is the metal ion present in chlorophyll, the green colouring pigment of the plants.
- Hydroxyapatite, $Ca_5(PO_4)_3OH$ is the main component of tooth enamel. Cavities in your teeth are formed when acids decompose the weakly basic apatite coating.

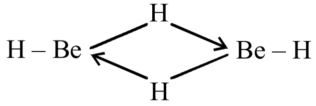
  $$Ca_5(PO_4)_3OH_{\,(s)} + 4H^+_{\,(aq)} \rightarrow 5Ca^{2+}_{\,(aq)} + 3HPO_4^{2-}{}_{(aq)} + H_2O_{\,(l)}$$

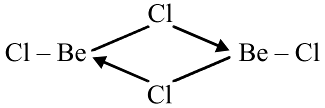
  This can be prevented, however, by converting hydroxyapatite to a much more-resistant coating, fluorapatite

  $$Ca_5(PO_4)_3(OH)_{\,(s)} + F^-_{\,(aq)} \rightarrow Ca_5(PO_4)_3F_{\,(s)} + OH^-_{\,(aq)}$$

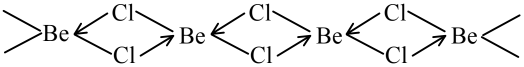
  The source of fluoride ion can be stannous fluoride, sodium fluoride or sodium monofluorophosphate commonly known as MFP in your tooth paste or a soluble fluoride such as NaF in your water supply.
- $CaCl_2{\cdot}6H_2O$ is widely used for melting ice on roads, particularly in very cold countries, because a 30% eutectic mixture of $CaCl_2/H_2O$ freezes at –55°C as compared with $NaCl/H_2O$ at –18°C.
- Anhydrous $CaCl_2$ is a good drying agent (desiccant) due to its hygroscopic nature ($CaCl_2{\cdot}6H_2O$). However it cannot be used to dry alcohols or ammonia/amines since it forms addition products ($CaCl_2{\cdot}6C_2H_5OH$, $CaCl_2{\cdot}6NH_3$ etc.)
- On heating MgC_2 changes into Mg_2C_3 which upon treatment with water gives propyne or allylene.

  $$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3C \equiv CH$$
- BeH_2 like $BeCl_2$ is polymeric with the only difference that BeH_2 has three-centre Be.....H.....Be bonds while $BeCl_2$ has halogen bridges in which a halogen atom bonded to one Be atom uses its lone pair of electrons to form a coordinate bond with other Be atom.





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



- Magnesium burns with dazzling light even in CO_2 and N_2.
- Except beryllium, all other alkaline earth metals directly combine with hydrogen to form metal hydrides (MH_2).
- Beryllium does not form a peroxide.
- The most abundant alkaline earth metal in the earth's crust is Ca (5th most abundant element) and least abundant is Ra.
- Amongst alkaline earth metals, m.p. of Mg is lowest while density of Ca is the lowest.
- Be and Mg crystallize in *hcp*, Ca and Sr in *ccp* and Ba in *bcc* structures.
- ***Flame colouration :*** Alkaline earth metals impart characteristic flame colour like alkali metals. As we move down the group from Ca to Ba, the ionisation energy decreases hence the flame shows a gradual shift from red to violet. Thus,
  Ca - brick red ; Sr - crimson red ; Ba - apple green ; Ra - crimson
  Be and Mg, due to their high ionisation energies, however, donot impart any characteristic colour to Bunsen flame.

Industrial importance of alkaline earth metals

- **Beryllium** - Used in corrosion resistant alloys.
- **Magnesium** - When alloyed with Al, Mg is widely used as structural material because of its high strength, low density and ease in machining.
- **Calcium** - As an alloying agent to harden aluminium, calcium is the primary constituent of teeth and bones.
- **Strontium** - $SrCO_3$ is used for the manufacture of glass for colour TV picture tubes.
- **Barium** - $BaSO_4$ is used in medicine as a contrast medium for stomach and intestinal X-rays.
- **Radium** - Used in cancer-radiotherapy

Anomalous behaviour of beryllium

- Beryllium, the first member of alkaline earth metals differs from rest of the metals and shows an anomalous behaviour. The main reasons for this difference are as follows.

– Because of high (IE) and small atomic size it forms compounds which are largely covalent and its salts are easily hydrolysed.

– Beryllium ($1s^2 2s^2 2p^0$) can use only $2s$ and three $2p$ orbitals in coordination thus maximum co-ordination number (C.N.) of Be is 4 while other elements can show C.N. of 6 in their compounds by use of *d*-orbitals in addition to *s* and *p* orbitals.

– BeO and $Be(OH)_2$ are amphoteric while other oxides are basic.

Some important properties in which beryllium differs from the rest of the members of its group are as follows:

(i) Beryllium is harder than other members of its group. This is due to the fact that maximum metallic bonding is present on account of smallest size amongst alkaline earth metals.

(ii) It has higher melting and boiling points than the other members due to maximum metallic bonding.

(iii) Be is least reactive as its ionization potential is high. However, it does react with oxygen and nitrogen at high temperature.

(iv) Beryllium forms covalent compounds because of high charge density and hence greater polarising power, whereas other members form ionic compounds.

(v) It dissolves in alkalies with evolution of hydrogen.

$$Be + 2NaOH + 2H_2O \rightarrow \underset{\text{sodium beryllate}}{Na_2BeO_2 \cdot 2H_2O} + H_2$$

Other alkaline earth metals donot react with alkalies.

(vi) Hydroxide of beryllium is amphoteric in nature. The hydroxide is insoluble in water. It is covalent in nature. The hydroxides of other alkaline earth metals are basic, ionic and their solubility increases on moving from $Mg(OH)_2$ to $Ba(OH)_2$.

(vii) Its salts can never have more than four molecules of water of crystallisation as it has only four available orbitals in its valency shell. Other alkaline earth metals can extend their coordination number to 6 by using *d*-orbitals.

- **Diagonal relationship between beryllium and aluminium**

$$\begin{tikzcd} & \text{Group IIA} & \text{Group IIIA} \\ \text{Second period} & \text{Be} \arrow[dr] & \text{B} \\ \text{Third period} & \text{Mg} & \text{Al} \end{tikzcd}$$

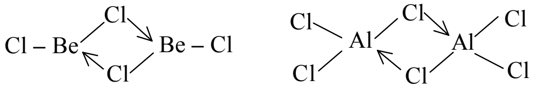
Beryllium shows some similarities in properties with aluminium, the second typical element of group IIIA of the next higher period. This type of relationship between diagonally placed elements is called diagonal relationship. This is due to the reason that these two elements have the same electronegativity (Be = 1.5, Al = 1.5) and the polarising power *i.e.* charge/radius ratio ($Be^{2+} = 2/31 = 0.064$ and $Al^{3+} = 3/50 = 0.060$) of their ions are very similar.

Some points of similarity are given below.

(i) Both metals have a tendency to form covalent compounds, e.g. the chlorides of both (*i.e.* $BeCl_2$ and $AlCl_3$) being covalent are soluble in organic solvents.

(ii) Both $BeCl_2$ and $AlCl_3$ act as strong Lewis acids.

(iii) Both $BeCl_2$ and $AlCl_3$ have bridged chloride structures in the vapour phase.



(iv) Both the metals dissolve in strong alkalies to form soluble complexes : beryllates $[Be(OH)_4]^{2-}$ and aluminates $[Al(OH)_4]$.

(v) The oxides of both beryllium (BeO) and aluminium (Al_2O_3) are hard high melting insoluble solids.

(vi) Salts of both these elements form hydrated ions, e.g. $[Be(OH_2)_4]^{2+}$ and $[Al(OH_2)_6]^{3+}$ in aqueous solutions.

(vii) Because of similar polarising power both beryllium and aluminium forms complexes. For example, beryllium forms tetrahedral complexes such as $[BeF_4]^{2-}$ and $[Be(C_2O_4]^{2-}$ and aluminium forms octahedral complexes like $[AlF_6]^{3-}$ and $[Al(C_2O_4)_3]^{3-}$.

POINTS TO REMEMBER

- Amongst alkaline earth metals, melting point of Mg is lowest while density of Ca is the lowest.
- The most abundant alkaline earth metal in the earth's crust is Ca (5th most abundant element) and least abundant is Ra.
- Beryllium does not form a peroxide.
- Except beryllium, all other alkaline earth metals directly combine with hydrogen to form metal hydrides (MH_2).
- Magnesium burns with dazzling light even in CO_2 and N_2.
- $CaCl_2{\cdot}6H_2O$ is widely used for melting ice on roads, particularly in very cold countries, because a 30% eutectic mixture of $CaCl_2/H_2O$ freezes at –55°C as compared with $NaCl/H_2O$ at –18°C.
- Mortar used in making buildings is a mixture of lime (CaO) and sand in the ratio 1 : 3 with enough water to make a thick paste. When the mortar is placed between bricks, it slowly absorbs CO_2 from the air and the slaked lime reverts to $CaCO_3$.

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

  Although the sand in the mortar is chemically inert, the grains are bound together by the particles of calcium carbonate and a hard material results.
- The anhydrous form of $CaSO_4$ (called anhydrite) is called **dead burnt plaster** because it does not set like plaster of Paris when moistened with water.
- Mg in powder form is used in flash bulbs used in photography and Ca is used as deoxidiser as well as desulphuriser of metals.
- Most of the kidney stones consists of calcium oxalate, $CaC_2O_4{\cdot}H_2O$ which dissolves in dilute strong acids but remains insoluble in bases.

- Bicarbonates of alkaline earth metals do not exist in the solid state but are known in solution only.
- $BaSO_4$ being insoluble in H_2O and opaque to X-rays is used under the name barium meal to scan the X-ray of the human digestive system.
- Fly ash, a waste product from steel industry has properties similar to cement. It can be added to cement to reduce the cost without affecting its quality.
- Since the alkaline earth divalent ions have no unpaired electrons, these are diamagnetic and colourless.
- Only Mg displaces hydrogen from a very dilute HNO_3.
- The ionization enthalpy of radium is higher than that of barium.
- Magnesium ions are present in chlorophyll - a green colouring pigment in plants which absorbs light and is essential for photosynthesis.
- Calcium ions play an important role in muscle contraction.
- Gypsum $CaSO_4\cdot 2H_2O$ is also known as alabaster.
- Calcium is present in the soil, plants, bones as $Ca_3(PO_4)_2$ and egg shells etc.

End