8. ALKALINE EARTH METALS (IIA)

SYNOPSIS

Electronic configuration of alkaline earth metals, occurrence and relative abundance:

* Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra) are IIA elements

* The alkali earth metals have general electronic configuration

$_{4}Be$: $[He]2s^2$ $_{12}Mg$: $[Ne]3s^2$

$_{20}Ca$: $[Ar]4s^2$ $_{38}Sr$: $[Kr]5s^2$

$_{56}Ba$: $[Xe]6s^2$ $_{88}Ra$: $[Rn]7s^2$

* The oxides of these elements [Ex.: CaO (Lime), SrO(strontia), BaO (Baryta)] are thermally very stable and basic in nature & hence, they are called alkaline earths.

* Radium is a radioactive element.

* Like alkali metals, these are reactive but less reactive than alkali metals.

* The outer electronic configuration of these metals is ns^2.

* As atomic number increases, the physical properties show a gradation down the group.

* Due to similar outer electronic configuration, they show similar chemical properties.

* Some important minerals of alkaline earth metals.

Elements	Minerals
Beryllium (Be)	Beryl – $3BeO.Al_2O_3.6SiO_2$ (or) $Be_3Al_2Si_6O_{18}$ Chrysoberyl – $BeO.Al_2O_3$ Phenacite – $2BeO.SiO_2$ (or) Be_2SiO_4
Magnesium (Mg)	Magnesite – $MgCO_3$
Calcium (Ca)	Lime stone, Chalk, Marble, Calcite (or) Aragonite – $CaCO_3$ Fluorapatite – $[3Ca_3(PO_4)_2.CaF_2]$ Gypsum – $CaSO_4.2H_2O$ Anhydrite – $CaSO_4$ Dolomite – $CaCO_3.MgCO_3$
Strontium (Sr)	Celestite – $SrSO_4$ Strontianite – $SrCO_3$
Barium (Ba)	Barytes or Heavy spar – $BaSO_4$ Witherite – $BaCO_3$
Radium (Ra)	Pitchblende (or) uranite - U_3O_8 Carnotite $K_2O.U_2O_3(VO_4)_2.3H_2O$

Relative Abundance:

* Abundance (% by weight) Ca > Mg > Ba > Sr > Be
* Mg and Ca are the most abundant of alkaline earth metals.

Physical Properties

* **Atomic volume, atomic and ionic radii**

  Because of the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume increases from Be to Ra.

* The atoms of these elements although fairly large, are smaller than those of the corresponding elements of the group IA.
* This is due to higher nuclear charge of these atoms which tends to draw the orbital electrons towards the nucleus. The ions are also large but smaller than those of the elements of group 1. This is again due to the fact that removal of the two valence electrons to from M^{2+} ions increases the effective nuclear charge which pulls the electrons inwards and thus reduces the size of the ion. Atomic as well as ionic radii increase on moving down the group on account of presence of an extra shell at each step.

Ionisation energy

* Since the alkaline earth metals possess smaller size and greater nuclear charge than the alkali metals, the electrons are more tightly held and hence the first ionisation energy is greater than that of the alkali metals.
* The first ionisation energy represents the energy required to remove an electron from a neutral atom (M) while the second ionisation energy represents the energy required to remove an electron from

  positive ion (M^+) which, of course, is difficult than the former case.
* After the removal of one electron, the effective nuclear charge increases and hence the remaining electron is held even more tightly leading to very high ionisation energy.
* However, the second ionization energy of the second group elements is less than the second
* ionization energy of the 1st group element.
* On the basis of the fact that the M^{2+} ions are extensively hydrated and a large amount of energy, known as hydration energy is released in the process which counterbalances the higher value of IE_2 which is responsible for the formation of M^{2+} ions in solutions. Higher value of hydration energy, in turn, is due to their much larger charge to size ratio leading to a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.

Oxidation state

* Due to the presence of two s-electrons in the outermost orbit, high heat of hydration of the dipositive ion and comparatively low values of IE_2, the alkaline earth metals are bivalent. Moreover, since the bivalent ions have an inert gas configuration, it is very difficult to remove the third electron from the element and hence oxidation state higher than 2 are not encountered. Further, the bivalent ion has no unpaired electron hence their compounds are diamagnetic and colourless provided their anions are also colourless.

Electropositive character

* Due to their large size and comparatively low ionisation energies, the alkaline earth metals are strongly electropositive elements. However, these are not as strongly electropositive as the alkali metals because they have smaller size and higher ionization energies than the alkali metals, and hence, unlike alkali metals, these elements do not emit electrons on exposure to light. On moving down the group, the electropositive character increases.

Metallic character

* The alkaline earth elements are metals and their metallic character increases down the group. Metallic nature is again due to low ionization energy and since the ionization energy decreases down the group, their metallic character increases. Further due to larger number of valence electrons and HCP or CCP type of metallic packing, they are less soft, less malleable and more hard than their corresponding alkali metal.

* This packing leads to high melting points than those of alkali metals: This is because these metals possess two valence electrons and are much strongly bonded in the solid state than the alkali metals.

Heat and electrical conductivity

* Due to the presence of two loosely held valence electrons per atom which are free to move throughout the crystal structure, the alkaline earth metal, are good conductors of heat and electricity.

Flame colouration

* Salts of alkaline earth metals, except that of Be and Mg, produce characteristic colour to the flame due to easy excitation of electrons to higher energy levels. Beryllium and magnesium atoms due to their small size, bind their electrons more strongly. Hence they possess high excitation energy and are not excited by the energy of the flame to higher energy state. No colour is produced to the flame.

Reducing properties

* Alkaline earth metals have two electrons outside the noble gas configuration. Due to their large size and low ionisation energy, they can easily lose outermost electrons and hence undergo oxidation (loss) of electrons easily.

* $M \longrightarrow M^{2+} + 2e^-$ They are, therefore strong reducing agents. Further since the ionisation energy decreases (Le. electropositive character increases) from Be to Ba, the reducing character of the alkaline earth elements increases from Be to Ba, which is evident from the value of their oxidation potential which increases from Be to Ba (recall that higher the value of oxidation potential or higher the negative value of reduction potential, greater is the electropositive character and reducing property of the element).

* Hence governing factor for oxidation potential to increase down the group is ionisation energy.

* Berrillium, being very small in size has a very large I.P. which is not comm balanced by the H.E.

* Hence beryllium, on account of its relatively lower oxidation potential, liberates hydrogen from acids slowly; on the other hand, other elements having high values of oxi~ion potential react vigorously even with water.

CHEMICAL PROPERTIES

* The chemical properties of the alkaline earth metals are comparable to those of alkali metals. But due to smaller size, greater charge and high ionisation energy, these are much less reactive than the corresponding alkali metals. Further since their ionisation energies decrease with increase in atomic number, their reactivity increases from Be to Ba. Lastly, beryllium being extremely small in size has unique chemical behaviour.

Action of air

* Their less reactivity than the alkali metals is evident by the fact that they are only slowly oxidised on exposure to air. When burnt in air they form ionic oxides of the type MO, however the higher members (Sr to Ra) form peroxides.

* Thus the tendency of the metals to form higher oxides like peroxide increases on moving down the group.

$2M + O_2 \longrightarrow 2MO$ (when M = Be, Mg or Ca)

$M + O_2 \longrightarrow MO_2$ (when M = Sr, Ba or Ra) Metal peroxide

Action of water

* These metals react slowly with water liberating hydrogen and forming metal hydroxides.

$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

Action of hydrogen

* All elements except beryllium, combine with hydrogen to form hydrides, MH_2. Magnesium hydride (like BeH_2) is covalent while other hydrides are ionic.

Action of halogens

* All these elements combine with halogens at elevated temperature forming halides, MX_2. Beryllium halides are covalent while the rest are ionic and thus dissolve in water and conduct electricity in aqueous solution and in molten state.

* The case of formation of nitrides decreases on moving down the group.

* They readily liberate hydrogen from dilute acids.

With Dil Acids

$M + H_2SO_4 \longrightarrow MSO_4 + H_2$

$M + 2HCl \longrightarrow MCl_2 + H_2$

* The reactivity of alkaline earths increases on moving down the group. This could be related to the increase in electropositive character from Be to Ba. Thus beryllium reacts very slowly, Mg react very rapidly while Ca, Sr and Ba react explosively.

Formation of amalgam and alloys

* They form amalgam with mercury and alloys with other metals.

Complex formation

* As described earlier. complex formation is favoured by small size, highly charged ion and suitable empty orbitals, alkaline earth metal ions, not having these characteristics, do not have a

significant tendency (although it is more than in the alkali metals by virtue of their double charge) to form complexes. e.g., $[BeF_3]^-$, $[BeF_4]^{2-}$, $[Be(H_2O_4)]^{2+}$, etc.

Compounds of Alkaline Earths

Oxides and Hydroxides

* The alkaline earth metal oxides, MO are prepared either by heating the metals in oxygen or better by calcination (heating at high temperature) of carbonates.

$2Ca + O_2 \rightarrow 2CaO$

$CaCO_3 \rightarrow CaO + CO_2$

ANOMOLOUS PROPERTIES OF BERYLLIUM:

* Be^{2+} is extremely small and has a high polarizing power.
* Thus, compounds of beryllium are more covalent and readily hydrolyse in water.
* Be is not readily affected by dry air.
* Be can not decompose water at room temperature.
* Be is amphoteric (i.e) it can react with both acids and alkalies.
* Be dissolves in alkalies forming beryllates.
* $BeSO_4$ is soluble in water while sulphates of all others are insoluble in water.
* Be and its salts do not show any flame colouration while Ca shows brick red, Sr shows crimson red and Ba shows apple green colours.
* Due to small size and high charge density, Be forms many complexes while others do not have such a tendency.
* Be shows a maximum covalency of 4.

DIAGONAL RELATIONSHIP OF Be & TRENDS IN ATOMIC & IONIC RADII

Diagonal relationship of Be

* Be shows diagonal relationship with Al
* Be & Al show same electronegativity of 1.50.
* Be forms covalent halides. Aluminium halides (except AlF_3) are covalent in the solid state.
* Due to covalent nature, compounds of Be are soluble in organic solvents and they have low melting points.
* Compounds of Be like those of Al undergo hydrolysis.

$$BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$$

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

* Be forms complex anions (beryllates) like aluminium forms aluminates, while other alkaline earth metals do not form complex anions.

$$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

* Both Be and Al are rendered passive by conc. HNO_3
* Passivity is the loss of original chemical reactivity of a metal when immersed in con. HNO_3. The passivity is due to formation thin protective layer of oxide coating on the metal.
* Carbides of Be and Al are called methanides since on hydrolysis they give methane.

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

* On the other hand carbide of Ca is called acetyllide since it gives acetylene on hydrolysis.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

CaO, $CaCO_3$, $CaSO_4$ AND PLASTER OF PARIS - PREPARATION AND USES

* CaO is known as quick lime.
* On calcination of lime stone ($CaCO_3$), CaO is formed $CaCO_3 \xrightleftharpoons{\Delta 10701c} CaO + CO_2$
* Reverse reaction is suppressed by removing CO_2 in lime kilns by calcining lime stone in an open vessel.
* Since lime stone contains clay as impurity it reacts at high temperature with CaO to form a fusible slag ($CaSiO_3$).
* Calcium carbonate is available in nature in different forms like chalk, marble, pumice stone etc.
* Calcium sulphate is formed when lime stone ($CaCO_3$) is treated with dilute H_2SO_4

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2\uparrow$$

* On concentrating and crystallising calcium sulphate dihydrate ($CaSO_4.2H_2O$) separates out.
* $CaSO_4.2H_2O$ is called as gypsum.
* In nature $CaSO_4$ occurs as (i) gypsum $CaSO_4.2H_2O$. (ii) anhydrite $CaSO_4$ (iii) Alabaster $CaSO_4.H_2O$.
* Alabaster is finely divided naturally available calcium sulphate.
* Plaster paris is $CaSO_4.\frac{1}{2}H_2O$ (or) $2CaSO_4.H_2O$
* Plaster paris is thus hemihydrate (or) semihydrate of calcium sulphate.
* It is prepared by heating gypsum at 120 - 130^{0}C
* It sets with water in two stages.

Stage I: (Setting stage):

$$CaSO_4.\frac{1}{2}H_2O + 3/2\ H_2O \rightarrow CaSO_4.2H_2O$$

(orthorhombic dihydrate gypsum)

* Stage II: (Hardning stage)

Orthorhombic gypsum changes into monoclinic form which is hard.

$$CaSO_4.\ 2H_2O \rightarrow CaSO_4.2H_2O$$

(Orthorhombic dihydrate) (monoclinic dihydrate)

* CaO is used in the manufacture of (i) Mortar (ii) Cement (iii) Glass (iv) $CaCl_2$

* Lime mortar is a mixture of 1 part slaked lime, 3 parts of sand and water. Sand present in mortar makes it porous and also harder. Sand prevents cracks on contraction. Water evaporates during hardening of mortar. The hardening is due to formation of calcium silicate.

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 + H_2O$$

Thus mortar sets into a hard mass due to several reactions occurring at the centre of mass.

* Cement mortar is mortar mixed with cement. This is stronger than mortar.

* Hydraulic mortar is formed when lime stone and

clay(10% Alluminium Silicate) are heated together. This also sets into a hard mass on addition of water. It is also used for bleaching purpose and as an antiseptic.

* Lime stone ($CaCO_3$) is used as a flux in metallurgy of Fe. Marble is used for building purposes. Lime stone is also used in the manufacture of cement, washing soda & glass.

* Gypsum is used in (i) the manufacture of cement & plaster of paris (ii) in agriculture (iii) in impregnating filter papers.

* Plaster of Paris is used (i) in the manufacture of crucibles, models and toys (ii) in medicine, for setting the fractured bones and in dentistry

Cement::

Cement is a dirty greyish heavy powder containg calcium aluminates and silicates.

The composition of the portland cement :

CaO 61.5%,

SiO_2 22.5%

Al_2O_3 7.5%

MgO 2.5%

Fe_2O_3 2.0%

K_2O 1.5%

SO_3 1.0%

Na_2O 1.5%

The essential constituents are lime, silica and alumina. these are generally kept in the following ratio:

$$\frac{\%SiO_2}{\%Al_2O_3} = 2.5 - 4.0$$

$$\frac{\%CaO}{\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3} = 1.9 - 2.1$$

USES OF ALKALINE EARTH METALS

* Be is used in making electrodes of neon sign lamps. It is also used in preparation of alloys with Cu etc.
* Mg is used in the manufacture of alloys like magnalium and electron. It is also used as a reducing agent in the preparation of B and Si
* It is used as a deoxidiser in metallurgy
* Ca is used in the preparation of Be, Cr and Th etc. It is also used to remove sulphur from petroleum and last traces of oxygen.

BIOLOGICAL IMPORTANCE OF Mg AND Ca, Mg^{2+} in biology:

* Mg^{2+} ions get concentrated in animal cells.
* Enzymes like phosphohydrolase and phosphotransferase contain Mg^{2+} ions. These enzymes participate in ATP reactions and release energy. Mg^{2+} is complexed with ATP.
* Mg^{2+} is a constituent of chlorophyll, the green pigment is plants.

Ca^{2+} in biology:

* Bones and teeth contain Ca^{2+} as apatite $[Ca_3(PO_4)_2]$.
* Enamel on teeth contains fluorapatite, $[3Ca_3(PO_4)_2.CaF_2]$.
* Ca^{2+} ions are necessary for blood clotting.
* Ca^{2+} ions are necessary to maintain heart beating.
* Ca^{2+} ions are necessary for muscles contraction.