ALKALINE EARTH METALS

INTRODUCTION:

- * The metal oxides of these elements like $lime^{(CaO)}$, Strontia^(SrO), Baryta^(BaO) etc., are thermally stable and exhibit basic character. Therefore these elements are called Alkaline earth metals.
- * The alkaline earth metals are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and Radium (Ra).
- * The general outer electronic configuration of alkaline earth metals is ns^2 .
- * The typical elements among alkaline earth metals are Be and Mg.
- * Abundance: Ca is more abundant and is least abundant Ca > Mg > Ba > Sr > Ra.
- * Element Be Mg Ca Sr Ba Ra Density 1.84 1.74 1.55 3.75 6.00
- * In melting and boiling points no regular trend is observed
- * Be has highestm.p and b. p values.
- * Mg has lowest m. p and b. p values.
- * 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, due to inert gas configuration of unipositive alkalimetal ions $^{I.P_2}$ of $^{IA} < IIA$
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- * On moving down the group, the electro positive character increases due to increase in atomic radii.
- * Oxidation states
- * Alkaline earth metals uniformly show an oxidation state of +2 despite the presence of high ionization energy. Because
 - i) In the solid state, the dipositive ions M^{2+} form strong lattices due to their small size and high chage (i.e., high lattice energy)
 - ii) 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 and compensates ionisation potential values.
- * Hydration Energy: Hydration energy is higher than those of alkali metal ions.
 - $= \frac{ch \arg e \text{ of ion}}{size \text{ of ion}}$
- * It decreases for to with increase in size.
- * Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration.
- * As we move down the group from Ca to Ba, the ionization energy decreases, hence the energy of the frequency of the emitted light increases.

Ca Brick red
Sr Crimson red
Ba Apple green

- * Be and Mg because of their high ionization energies, however, do not impart any characteristic colour to the bunsen flame.
 - i) Like alkali metals, these dissolve in liquid ammonia giving coloured solutions.
 - ii) The tendency to form ammoniates decreases with increase in size of the metal atom from Be to Ba.
- * Reaction with water
- * Group 2 elements are less reactive with water as compared to alkali metals. They react with H_2O evolving H_2 gas.

$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$

where
$$M = Mg, Ca, Sr$$
 or Ba

- * Alkaline earth metals combine with Oxygen to form monoxides of the type MO and the peroxides of the type MO_2
- * The affinity for oxygen increases down the group.
- * Be, Mg and Ca when heated with O_2 form monoxides while Sr, Ba and Ra form peroxides.

$$2M + O_2 \xrightarrow{\Delta} 2MO$$

$$M + O_2 \xrightarrow{\Delta} MO_2$$
Metal peroxide

- * Be, Mg do not form peroxide.
- * The stability and ease of formation of peroxides increases from Be to Ba.
- * BeO and $Be(OH)_2$ are amphoteric while the oxides and hydroxides of other alkaline earth metals are basic.
- * The basic strength, however, increases from Be to Ba according as the ionization energy of metal decreases down the group thus the order

$$BeO < MgO < CaO < SrO < BaO$$
 and $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

- * Aq. $Ba(OH)_2$ is known as baryta water.
- * Reactivity, however, increases down the group from Mg to Ba i.e. Mg<Ca<Sr<Ba
- * BeH_2 and MgH_2 are covalent and polymeric whereas the hydrides of Ca, Sr and Ba are ionic and monomeric in nature.
- * Polymeric $(BeH_2)_n$ structure is with three centre bonds.
- * is also called hydrolith
- * The stability of hydrides decreases from Be to Ba.
- * All the elements of group IIA combine with halogens at high temperature, forming their halides (MX_2) $M + X_2 \xrightarrow{\Delta} MX_2$

$$Mg + Cl_2 \xrightarrow{\Delta} MgCl_2$$

* The solubility of halides decreases from Be to Ba

$$MgX_2 > CaX_2 > SrX_2 > BaX_2$$

- * Beryllium halides $(BeF_2, BaCl_2 etc.)$ are covalent, hygroscopic and fume in air due to hydrolysis $BeCl_2 + H_2O \rightarrow Be(OH)_2 + HCl$
- * Anhydrous CaCl_2 is a good drying agent due to hygroscopic nature $^{\left(CaCl_2.2H_2O\right)}$ and cannot be used to dry alcohol or ammonia as it forms addition products with them. Used as laboratory desiccant.
- * BeCl₂ has a polymeric structure in the solid state but exists as a dimer in the vapour state and as a monomer at 1200 K.

* Melting points of halides decrease as the size of the halogen increases.

$$MF_2 > MCl_2 > MBr_2 > MI_2$$

Nitrides:

* These metals burn in nitrogen to form nitrides of the types M_3N_2 which are hydrolysed with water of evolve NH_3

$$3M + N_2 \rightarrow M_3 N_2$$

 $M_3 N_2 + 6H_2 O \rightarrow 3M (OH)_2 + 2NH_3$

- * The ease of formation of nitrides increases from Be or Ba. (Be_3N_2) is volatile in nature.
- * When heated with carbon, these form their respective carbides of the general formula MC_2 (except Be) and are called acetylides containing the discrete ${}^{C_2^{2-}}$ anion.

$$[-C \equiv C -]^{-2}$$

$$M + 2C \xrightarrow{\Delta} MC_2$$
(Where M=Mg, Ca, Sr or B1)

* On heating MgC_2 gives Mg_2C_3 called allylide which the disrete ${}^{C_3^{-4}}$ anion and gives allylene (methyl acetylene) onhydrolysis.

$$Mg_2C_2 + 4H_2O \rightarrow 2Mg(OH)_2 + C_3H_4$$

- * The carbonates of alkaline earth metals can be regard as salts weak carbonic acid (H_2CO_3) and (H_2CO_3) and (H_2CO_3) hydroxide,
- * Bicarbonates of these metals do not exist in solid state. Bicarbonates exist only in solution while the bicarbonates of 1A group exist in solid state.
- * The thermal stability of carbonates increases BeCO_3 form to BaCO_3
- * Solubility of carbonates: The solubility of the carbonates in water decreases down the group dues to the decrease in the magnitude of hydration energy.
- * Be is harder and denser then other members of the group.
- * The m.p., b.p., and ionisation energy of Be are highest of all the alkaline earth metals.
- * BeO and Be(OH)₂ are amphoteric in character where as oxides and hydroxides of the group 2 metals are basic.
- * Be is least metallic of all the alkaline earth metals and forms covalent compounds.
- * Be forms Be_2C with carbon while the other members of the group from ionic carbide MC_2 .
- * Diagonal Relationship or Resemblance between Be and Al.
- * Both form fluoro complex anions $^{BeF_4^{2-}}$ and $^{AlF_6^{3-}}$ in solution.
- * Both react with conc. NaOH liberating H_2 $Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$ Sodium berylate
- * Carbides of both liberate methane on hydrolysis

$$2Al + 2NaOH + 2H_2O \rightarrow \underbrace{2NaAlO_2}_{\text{Sodium metaaluminate}} + 3H_2$$

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

- * Anhydrous chlorides of both i.e., BeCl_2 and AlCl_3 act as Lewis acids and dissolve in organic solvents.
- * Both do not impart any colour to the flame.

* Magnalium Al + Mg_(85-99%) + (1-15%)

Magnalium is light and hard alloy. It is used in the preparation of balance beams, aeroplane parts or motor parts. This alloy can take a high polish.

$$Mg + Zn + Cu$$

Elektron: (95%) (4.5%) 0.5%

Electron is used in the manufacture of Aeroplane parts.

It is used in ratio tubes to remove the last traces of O_2 .

Calcium Oxide:

- * It is also known as quick lime
- * Chemical formula is CaO
- * Reacts with acidic oxides to from salts, hence used as basic flux in metallurgy $CaO + SiO_2 \xrightarrow{high \ temperature} CaSiO_3$
- * With carbon

$$CaO + 3C \rightarrow CaC_2 + CO$$

Calcium carbide reacts with water to produce acetylene, and with nitrogen on heating gives calcium cyanamide (nitrolim)

$$CaC_2 + N_2 \rightarrow CaCN_2 + C_{(gr)}$$

- * Nitrolim is used as a fertiliser.
- * As a flux in metallurgy to remove silica and as a basic lining in furnaces
- * As a drying agent used in drying ammonia gas.
- * Action of water on quick lime

$$CaO + H_2O \rightarrow Ca(OH)_2$$

* Carbondioxide makes lime water milky due to precipitation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

* On passing excess carbondioxide, the precipitate first fromed dissolves due to the formation of soluble bicarbonate

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

- * Being a strong base stronger than ammonia, it libertes ammonia gas on heating it with ammonium salt, $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
- * Being a strong base stronger than ammonia, it liberates a ammonia gas on heating it with ammonium salt.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2H_2O + 2NH_3$$

* It forms hypochlorite in cold and chlorate salts when hot

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$$

$$6Ca(OH)_2 + 6Cl_2 \rightarrow 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

- * It is found in nature in huge quantities invarious forms such as limestone, marble, chalk, calcite, aragonite, etc.
- * It can be obtained by passing carbon dioxide through limewater

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

* Adding sodium carbonate solution to CaCl₂

- * Calcium sulphate dihydrate is called gypsum. Finely divided naturally available form of *CaSO_4* is called Alabaster.
- * Anhydrous ^{CaSO}₄ is called anhydrite.
- * The presence of Calcium Sulphate causes permanent hardness to water.
- * Gypsum is prepared by the action of dil. H_2SO_4 on CaO or CaCO_3 $^{CaO} + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O$ $^{CaCO_3} + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_3 \uparrow$
- * $CaSO_4$ is readily soluble in hot. Conc. Solution of ammonium sulphate due to the formation of double salt $CaSO_4(NH_4)_2SO_4.H_2O$

On heating gypsum to $200^{\circ}C$ gives "dead burnt" due to complete dehydration..

$$CaSO_4.2H_2O \xrightarrow{120-130^{\circ}C} CaSO_4.\frac{1}{2}H_2O \xrightarrow{200^{\circ}C} CaSO_4$$

Plaster of Paris

Caso_4.2H_2O \tag{200^{\choose Caso}} Caso_4

- * In the preparation of plaster of Paris, in agriculture, in the impregnation of filter paper.
- * Gyspum increases the setting time of cement. Therefore it is used for the manufacture of cement.
- * Anhydrous ^{CaSO}₄ is used as drying agent
- * Calcium sulphate hemihydrate or half hydrate is called Plaster of Paris.
- * When gypsum is heated to $^{120^{\circ}C}$, plaster of Paris is obtained.

$$CaSO_4.2H_2O \xrightarrow{120^0C} CaSO_4.\frac{1}{2}H_2O + \frac{3}{2}H_2O$$

- * Plaster of Paris combines with little water (half to it's weight) and sets to a hard mass.
- * Setting of plaster of Paris involves hydration and it is exothermic reaction.
- * Setting of plaster of paris is catalyzed by NaCl and retarded by borax or alum.
- * Setting of plaster of Paris

$$\begin{array}{cccc} 2CaSO_4.H_2O & \xrightarrow{Setting \ stage} & CaSO_4.2H_2O \\ Plaster \ of \ Paris & Ortho \ Rombic \ Hydride \\ \hline \\ CaSO_4.2H_2O & \xrightarrow{Hardning \ stage} & CaSO_4.2H_2O \\ Ortho \ Rombic \ Hydride & Monoclinic \ ditydrate \\ \hline \end{array}$$

- * Hardening of plaster of paris is due to conversion of orthorhombic form to monoclinic form.
- * Plaster of paris on heating to $200^{\circ}C$ gives anhydrous CaSO_4 . It is called dead plaster (or) dead burnt Calcium sulphate.
- * In denstistry
- * In making black board chalks.
- * IN making models, crucibles.
- * A mixture of 3 parts of sand, 1 part of slaked lime and water is called lime mortar.
- * A mixture of cement and mortar is called cement mortar. It is much harder than lime mortar.
- * Sand makes mortar not only porous but also harder. While hardening, sand prevents the cracks on contraction.
- * Lime stone and clay (containing 10% Aluminum silicate) when heated together, it gives hydraulic mortar.
- * Setting of mortar to hardness may be due to evaporation of water.
- * Mortar mixed with the cement is called cement mortar. This is stronger than mortar.
- * Mg^{2+} Ions get concentrated in animal cels.
- * In phosphate transfer Mg acts as cofactor.

- * Enzymes like phosphohydrylase and phosphotransferase contain Mg^{2+} ions. These enzymes participate in ATP reaction and release energy is complexed Mg^{2+} with ATP.
- * Mg^{2+} is constituent of chlorophyll, the green pigment is plants.
- * Bones and teeth contain Ca^{2+} as $\left[Ca_3(PO_4)_2\right]$ apatite.
- * Enamel on teeth contains fluorapatite, $\left[3Ca_3(PO_4)_2.CaF_2\right]$
- * In human body 99% of Ca is present in bones and teth.
- * Role of Ca in Human body
 - 1. Neuro muscular function 2. Inter reuronal transmission
 - 3. Cell membrane integrity 4. Blood coagulation