Inorganic chemistry II
Second stage / First semester
The Eighth lecture 2021/2022 Pro. Dr. Mohammed Hamid

Alkaline Earth Metals and their Compounds(Group IIA or 2, ns^2)

POSITION OF ALKALINE EARTH METALS IN PERIODIC TABLE

The group IIA of the periodic table consists of six elements-beryllium, magnesium, calcium, strontium, bariums and radium. These elements are collectively called as alkaline earth metals because their earths (the old name for oxide) are basic (alkaline) and group IIA is known as alkaline earth group. The oxides of three principal members calcium strontium and barium were known much earlier than the metals themselves. These oxides were alkaline in nature and existed in the earth and were named alkaline earths. The metals when discovered were also called alkaline earths. This term is now applied to all the six elements of group IIA.

Element	Symbol	The most important minerals
Beryllium	Be	$Be_3AL_2(SiO_3)_6$
Magnesium	Mg	$KCl.MgCl_2.6H_2O$
Calcium	Ca	$MgCO_3.CaCO_3$,$CaSO_4.2H_2O$
Strontium	Sr	$SrCO_3$
Barium	Ba	$BaSO_4$, $BaCO_3$
Radium	Ra	It is found in uranium ores

The first member beryllium is less active than other members and shows some abnormal properties like lithium in 1A group. However, it shows resemblance with aluminium (a member of Iird group). *i.e.* diagonal relationship. The last member, radium is radioactive in nature. Each member of this group occupies a place just after the members of IA group in various periods of periodic table except first period.

IA	Li 3	Na 11	K 19	Rb 37	Cs 55	Fr 87
IIA	Be 4	Mg 12	Ca 20	Sr. 38	Ba 36	Ra 88

The members of this group show a marked resemblance in their properties and possess same electronic configuration. There is gradual gradation in the properties with the increase of atomic number. This justifies their inclusion in the same group of periodic table. The main properties are discussed below for this justification.

Electronic Configuration

The valence electron configuration of the atoms of the group IIA elements is ns^2 , where n is the period number. The arrangement or the distribution of electron on various subshells in the atoms of alkaline earth metals is given below

Element	At. No.	Electronic Configuration	Configuration of the valency shell
Beryllium	4	$1s^2\ 2s^2$	$[He]2s^2$
Magnesium	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$	$[Ne]3s^2$
Calcium	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	$[Ar]4s^2$
Strontium	38	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10} 4s^2\ 4p^6\ 5s^2$	$[Kr]5s^2$
Barium	56	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10} 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2$	$[Xe]6s^2$
Radium	88	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2$	$[Rn]7s^2$

The outermost shell of these elements has two electrons and the penultimate shell contains 8 electrons except the first member which contains 2 electrons. Since, the last electron enters ns orbital, these are s-block elements. Beryllium shows somewhat abnormal properties as its electronic configuration is slightly different than the rest of the members. Because of their similarity in electronic configuration [noble gas] ns^2, they are included in the same group, i.e., IIA of the periodic table and closely resemble each other in the physical and chemical properties.

2. Physical Properties

(a) Physical state: All the group IIA elements are metals and too reactive, so that cannot occur in the uncombined state in nature. They are all silvery white metals. They have greyish white lustre when freshly cut, but tarnish soon after their exposure in air due to surface oxidation.

They are soft in nature but harder than alkali metals because metallic bonding is stronger than 1A elements due to possession of 2 valency electrons. However, hardness decreases with increase in atomic number.

(b) Atomic and ionic radii: The size of the atom increases gradually from Be to Ra, on account of the presence of an extra energy shell at each step. The atoms are large but smaller han corresponding IA elements since the extra charge on the nucleus attracts the electron cloud inwards. Their ions are also large and size of the ion increases from Be^{2+} to Ra^{2+}

Atomic volume also increases as the atomic number increases

(c) Density: These metals are denser than alkali metals in the same period because these can be packed more tightly due to their greater nuclear charge and smaller size. The density decreases slightly up to calcium and then increases considerably up to radium. Irregular trend is due to the difference in the crystal structure of these elements.

(d) Melting and boiling points: The melting and boiling points of these elements are higher than corresponding alkali metals. This is due to the presence of two electrons in the valency shell and thus, strongly bonded in the solid state. However, melting and boiling points do not show any regular trend because atoms adopt different crystal structures.

(e) Ionisation energies and electropositive character: The first and second ionisation energies of these metals decrease from Be to Ba. The second ionisation energy in each case is higher than the first, nearly double the first ionisation energy.

The ionisation energy of last member, radium, is slightly higher than that of barium and it is difficult to explain this anomalous behaviour.

Symbol	Abundance in earth's crust p.p.m	Atomic radius A^0	Ionic radius A^0	Density g/cc	Ionization potentials	
					1^{st}eV	2^{nd} eV
Be	6	0.89	0.31	1.8	9.3	18.2
Mg	20.9	1.36	0.65	1.7	7.6	15.0
Ca	36.3	1.74	0,99	1.6	6.1	11.9
Sr	300	1.91	1.13	2.6	5.7	11.0
Ba	250	1.98	1.35	3.5	5.2	10.0
Ra	$1.3\text{x}10^{-4}$	-	1.50	5.0	5.3	10.1

Although, the ionisation energies of these elements are higher than those of alkali metals, yet these are sufficiently low to make these atoms to lose two electron of their valency shell to form M^{2+} ions and achieve the inert gas configuration. These metals are thus, strongly electropositive in nature but less than corresponding alkali metals. The electropositive character increases from Be to Ba. Metallic character and reactivity are directly linked with the tendency to lose electron or electrons, te with electropositive nature. Thus, these characters increase gradually from Be to Ba.

$$\underrightarrow{\text{Be Mg Ca Sr Ba Ra}}$$

Electropositive nature increases Metallic

character increases Reactivity of the metals increases

(f) Oxidation states: The alkaline earth metals form a basic oxide with general formula RO. All show a stable oxidation state +2 in their compounds. The second ionisation energy is nearly double the first ionisation energy for all these elements. This should cause these elements to exhibit a stable +1 oxidation state and form compounds like BaCl , SrBr , Cal etc., instead of $BaCl_2$, $SrBr_2$, Cal_2, etc. However, 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. 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.

Amongst alkaline earth metals, beryllium has the highest ionisation energy, i.e., least electropositive in nature. Thus, beryllium has the minimum tendency to form Be^{2+} ion and hence a number of compounds of beryllium are covalent in nature.

(g) Hydration of ions and hydration energy: The M^{2+} jons of alkaline earth metals are extensively hydrated to form hydrated ions, $[M(H_2O)_x]^{2+}$ and during hydration a huge amount of energy, called hydration energy, is released.

$$M^{2}+ + xH_2O \rightarrow [M(H_2O)_X]^{2+} + \text{Energy}$$

The degree of hydration and the amount of hydration energy decreases as the size of the ion increases from Be^{2+} to Ba^{2+}

The hydration energies of alkaline earth metal ions are higher than those of alkali metal ions and thus the compounds of alkaline earth metals are more extensively hydrated than alkali metals. Magnesium chloride and calcium chloride exist as $MgCl_2$ $6H_2O$ and $CaCl_2$-$6H_2O$, respectively, while sodium chloride and potassium chloride exist as NaCl and KCl.

The ionic mobilities or ionic conductance of these ions increase from $[Be(H_2O)_x]^{2+}$ to $[Ba(H_2O)_x]^{2}+$ because $[Be(H_2O)_x]^{2+}$ becomes heavy due to high degree of hydration.

(h) Electronegativity : The tendency to attract electrons is low. The electronegativity values are thus small and decrease from Be to Ra.

Symbol	m.pt.(K)	b.pt.(K)	Oxid. Potential (Volt.)	Electronegativity
Be	1560	2745	1.97	1.5
Mg	924	1363	2.36	1.2
Ca	1124	1767	2.84	1.0
Sr	1062	1655	2.89	1.0
Ba	1002	2078	2.92	0.9
Ra	973	-	-	-

(i) Conductivity : On account of the presence of two loosely bond valency electrons per atom which can move freely throughout the crystal lattice, the alkaline earth metals are good conductors of heat and electricity.

(j) Flame colouration: In the case of Ca, Sr. Ba and Ra, the electrons can be excited by the supply of energy to higher energy levels. When the excited electrons return to the original level, the energy is released in the form of light. In beryllium and magnesium, the electrons are tightly held and hence excitation is rather difficult, thus do not show flame colouration. Ca, Sr, Ba and Ra impart a characteristic colour to the flame. Ca-brick red; Sr-crimson; Ba-green; Ra-crimson

(k) Reducing nature: The alkaline earth metals have the tendency to lose electrons and change into bivalent cation:

$$M \longrightarrow M^{2+} + 2e$$

Hence, they act as strong reducing agents. The reducing nature increases as the atomic number increases.

Strength of a reducing agent is linked with the value coxidation potential. The values of the oxidation potential increases from Be to Ba, hence the strength as a reducing agent increases in the same order.

The oxidation potentials are lower than those of the alkali metals, hence, the alkaline earth metals are weaker reducing agents than alkali metals. The reason for the lower values of oxidation potentials is due to high heats of atomisation (sublimation) and ionisation energies.

(1) Colour and magnetic property: Since, the divalent ions have noble gas configuration with no unpaired electrons, their compounds are diamagnetic and colourless unless the anion is coloured. The metals are also diamagnetic in nature as all the orbitals are fully filled with spin paired electrons, e.g.,

$$\begin{aligned} Mg^{2+} &= 2,\ 8 \\ &= 1s^2,\ 2s^2\ 2p^6 \\ &= \boxed{\uparrow\downarrow}\quad \boxed{\uparrow\downarrow}\quad \boxed{\uparrow\downarrow \mid \uparrow\downarrow \mid \uparrow\downarrow} \end{aligned}$$

Chemical Properties

(a) Occurrence: Alkaline earth metals are reactive elements and hence do not occur free in nature. Magnesium and calcium are found in abundance in nature. Beryllium is not very abundant. Strontium and barium are much less abundant. Radium is a rare element.Calcium and magnesium are the most common and commercially useful of the alkaline earth elements. We can see in the table given below, calcium is the fifth and magnesium is the eighth most abundant element in the earth's crust.

Ten most Abundant Elements in the Earths Crust

No.	Element	Mass percentage	No.	Element	Mass percentage
1	Oxygen	46.6	6	Sodium	2.8
2	Silicon	27.7	7	Potassium	2.6
3	Aluminum	8.3	8	Magnesium	2.1
4	Iron	5.1	9	Titanium	0.4
5	Calcium	3.6	10	Hydrogen	0.1

Like the alkali metals, the group IIA elements occur i nature as silicate rocks. They also occur as carbonates an sulphates, and many of these are commercial sources of alkalin earth metals and compounds.

These metals occur in nature largely as carbonates, sulphate and silicates.

(b) Extraction: The metals of this group are not easy to produce on account of following reasons: (i) The metals cannot be produced by chemical reduction because they are themselves strong reducing agents and they react with carbon and form carbides.

(ii) They are strongly electropositive and react with water and so aqueous solutions cannot be used for displacing them with another metal.

(iii) The electrolysis of aqueous solutions of their salts produces hydrogen at cathode rather than the metal as the metal reacts with water. Electrolysis of an aqueous solution can be carried out by using mercury as cathode, but recovery of the metal from amalgam is difficult.

These metals are best isolated by electrolysis of their fused metal halides containing NaCl. NaCl lowers the fusion temperature and makes the fused mass as good conductor of electricity.

(c) Reactivity towards water: Calcium, strontium, barium and radium decompose cold water readily with evolution of hydrogen.

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

Magnesium decomposes boiling water but beryllium does not react with water, even when red hot, its protective oxide film survives even at high temperature as its oxidation potential is lower than the other members.

Reactivity of alkaline earth metals increases as we move down the group as the oxidation potential increases. However, the reaction of alkaline earth metals is less vigorous than alkali metals.

(d) Reactivity towards atmosphere: Except beryllium, these metals are easily tarnished in air as a layer of oxide is formed on their surface. The effect of atmosphere increases as the atomic number increases. Barium in powdered form bursts into flame on exposure to air.

$$M + \text{air} \rightarrow MO + M3N2$$

(Ca, Sr or Ba)

(e) Reactivity towards acids: Like alkali metals, the alkaline earth metals freely react with acids and displace hydrogen.

$$M + H_2SO4 \rightarrow MSO4 + H_2$$

$$M+2HC1 \rightarrow MCl_2 + H_2$$

Beryllium behaves differently as it dissolves in caustic alkalies also with liberation of hydrogen. It is due to diagonal relationship with aluminium. Be is thus amphoteric in nature.

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

Sodium beryllate

(f) Affinity for non-metals: Alkaline earth metals have great affinity for non-metals. They directly react with non-metals at the appropriate temperature.

(i) Reaction with hydrogen: Except beryllium, all combine with hydrogen directly to form hydrides of the type MH_2 when heated with hydrogen.

$$M + H_2 \rightarrow MH_2$$

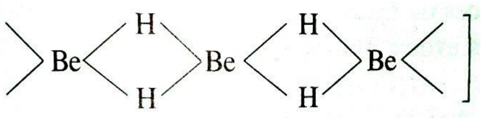
BeH_2 and MgH_2 are covalent in nature while other hydrides are ionic in nature. Calcium, strontium and barium hydrides liberate hydrogen at anode on electrolysis in the fused state. Ionic hydrides are violently decomposed by water evolving hydrogen, CaH_2 is technically called hydrolith and used on large scale for the production of hydrogen.

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

[BeH_2 is not obtained by direct combination of beryllium and hydrogen. It is formed by reacting beryllium chloride with lithium aluminium hydride.

$$2BeCl_2 + LiAIH_4 \rightarrow 2BeH_2 + LiCl + AlC13]$$

It is polymeric. (BeH_2), possesses hydrogen bridges. Three centre bonds are present in which a banana shaped molecular orbital covers three atoms Be---H---Be and contains two electrons. Hydrogen atoms lie in the plane perpendicular to the plane of molecule containing beryllium atoms.



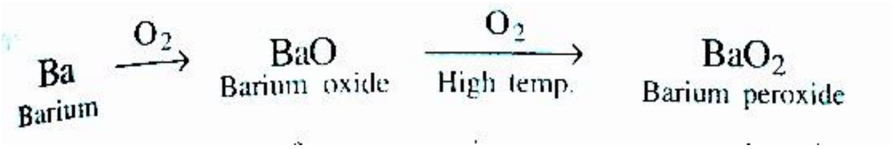
The stability of the hydrides decreases with increasing atomic number because the metallic nature of the elements increases.

(ii) Reaction with oxygen (Oxides and Hydroxides): Except Ba and Ra, these elements when burnt in oxygen form oxides of the type MO.

$$2M + O_2 \rightarrow 2MO$$

Beryllium metal is relatively unreactive and does not react below 600 ^{0}C. but the powder form is much more reactive and burns brilliant. The element. Mg burns with dazzling brilliance evolving a lot of heat.

Barium and radium, being highly electropositive, form peroxides.

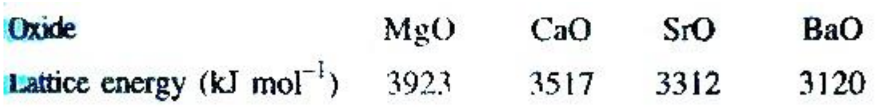


Thus, the affinity for oxygen increases on moving down the group.

BeO is usually formed by ignition of the metal, but the other metal oxides (*MO* type) are usually obtained by thermal decomposition of the carbonates, MCO_3.

$$MCO_3 \xrightarrow{Heat} MO + CO_2$$

The oxides are very stable compounds (BeO and MgO are used as refractory materials) and white crystalline solids. Except BeO (predominantly covalent), all the other oxides are ionic and possess NaCl structure (face centred cubic). The reason for high stability is due to high lattice energy values which, however, decrease as the size of the metal ion increases.



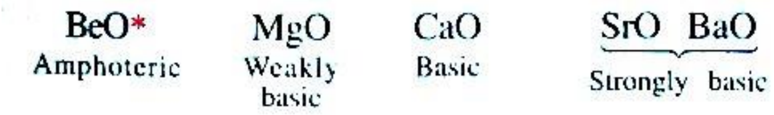
Oxide	MgO	CaO	SrO	BaO
Lattice energy (kJ mol^{-1})	3923	3517	3312	3120

Except BeO, which is amphoteric in nature, other *MO* oxides are basic in nature as they combine with water to form basic hydroxides. This reaction is highly exothermic.

$$MO + H_2O \rightarrow M(OH)_2 + \text{Heat}$$

(where, $M = Ca^{2}+$, Sr^{2+} or $Ba^{2}+$)

Basic nature of the oxides increases gradually from BeO to BaO.



$$\underset{\text{Amphoteric}}{BeO^*} \quad \underset{\text{Weakly basic}}{MgO} \quad \underset{\text{Basic}}{CaO} \quad \underbrace{SrO \quad BaO}_{\text{Strongly basic}}$$

(*The amphoteric nature is supported by its reaction with acids as well

$BeO + 2HCl \rightarrow BeCl_2 + H_2O$. $BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$.)

[BeO and MgO are insoluble in water as these are tightly held together in the solid state.]

$Be(OH)_2$ is amphoteric, but the hydroxides of other alkaline earth metals are basic. The basic strength increases gradually.

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

$$Be(OH)2 + 2NaOH \rightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2} + 2H_2O$$

$$Be(OH)_2 + 2OH^- \rightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4 1^{2-}}$$

The solubility of the hydroxides increases with increase of atomic number of the alkaline earth metals. This is due to the fact that decrease in lattice energy is more than decrease in hydration energy on moving down the group. The increasing solubility can also be explained on the basis of values of their solubility products which increase from $Be(OH)_2$ to $Ba(OH)_2$. $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in water.

Metal hydroxide	$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
Solubility product	$1.6\text{x}10^{-26}$	$8.9\text{x}10^{-12}$	$1.3\text{x}10^{-4}$	$3.2\text{x}10^{-4}$	$5.4\text{x}10^{-3}$ (K_{sp})

The hydroxides decompose on heating. The thermal stability increases from $Be(OH)_2$ to $Ba(OH)_2$.

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

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

(iii) Reaction with halogens (Halides): The alkaline earth metals directly combine with halogens, when heated with them.

$$M + X_2 \xrightarrow{\text{Heated}} MX_2$$

($X_2 = F_2, Cl_2, B_2$, or I_2)

The alkaline earth metal halides can be obtained by the action of halogen acids on metals, their oxides, hydroxides and carbonates.

$$M + 2HX \longrightarrow MX_2 + H_2$$

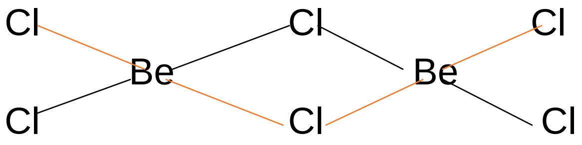
$$MO + 2HX \longrightarrow MX_2 + H_20$$

$$M(OH)_2 + 2HX \longrightarrow MX_2 + 2\ H_20$$

$$MCO_3 + 2HX \longrightarrow MX_2 + H_20 + CO_2$$

Beryllium halides are covalent in nature. This is due to small size and high charge of Be^{2+} ion, i.e., it has high polarising power. The glassy forms of halides are known to have chains of

---- X_2Be X_2Be----.



The halides of the type MX_2 (fluorides, chlorides, bromides and iodides) of other metals are ionic solids. The solubility of these halides decreases with increasing atomic number of the metal as there is decrease in hydration energy with the increase in the size of the metal ion. Solubility of BeF_2 will therefore be greater than BaF_2.

As the ionic character increases on moving down the group. the melting points and their conductivity increase from magnesium halides to barium halides. They are good conductors in molten state.

The halides are hygroscopic in nature and readily form hydrates, e.g., $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2\ 2H_2O$, etc. Calcium chloride has a strong affinity for water and is used as a dehydrating agent. However, $BeCl_2$ fumes in moist air due to its hydrolysis.

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

(iv) Reaction with nitrogen : All the alkaline earth metals burn in nitrogen to form nitrides of the type M_3N_2.

$$3M + N_2 \longrightarrow M_3N_2$$

The ease of formation of nitrides decreases from Be to Ba. This is in contrast to alkali metals where only $Li3N$ is formed. Because the N_2 molecule is very stable, it requires very high energy to form N^3 ions. The large amount of energy comes from the very large amount of lattice energy evolved when the crystalline solid is formed. The lattice energy is particularly high because of the high charges on the ions M^{2+} and N^{3-}

Be_3N_2 is volatile (covalent character) while other nitrides are not volatile as they are ionic crystalline solids. The nitrides are hydrolysed with water liberating ammonia.

$$M_3N_2 + 6H_2O \longrightarrow 3M(OH)_2 + 2NH_3$$

(v) Reaction with carbon (Carbides): With the exception of Be, other metals when heated with carbon in an electric furnace or when their oxides are heated with carbon form carbides of the type MC_2. These carbides are called acetylides as on hydrolysis they evolve acetylene.

$$M + 2C \longrightarrow MC_2$$

$$MO + 3C \longrightarrow MC_2 + CO$$

$$MC_2 + 2H_2O \longrightarrow M(OH)_2 + C_2H_2$$

MC_2 carbides, all have a distorted sodium chloride type of structure, M^{2+} replaces Na^+ and $[- C{\equiv}C-]^{2-}$ replaces Cl^-.

MgC_2, on heating, changes into Mg_2C_3. Mg_2C_3 on hydrolysis evolves propyne, CH_3-$C{\equiv}CH$ methyl acetylene).

$$Mg2C3 + 4H_2O \longrightarrow 2Mg(OH)_2 + C3H4$$

When BeO is heated with carbon at about 2000°C, a brick red coloured carbide of formula, Be_2C, is formed. This on hydrolysis evolves methane and is, thus, called methanide.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_2$$

It is also ionic but possesses an antifluorite structure.

(vi) Reaction with sulphur and phosphorus : Alkaline earth metals directly combine with sulphur and phosphorus when heated with them to form sulphides of the type MS and phosphides of the type M_3P_2, respectively.

$$M + S \longrightarrow MS$$

$$3M + 2P \longrightarrow M_3P_2$$

Sulphides on hydrolysis liberate H_2S, while phosphides on hydrolysis evolve phosphine.

$$MS + \text{dil.acid} \rightarrow H_2S$$

$$M_3P_2 + \text{dil.acid} \rightarrow PH_3$$

Sulphides are phosphorescent. They cannot be precipitated by passing H_2S through their salts solutions as they are decomposed by water.

$$2MS + 2H_2O \longleftrightarrow M(OH)_2 + M(HS)2$$

(g) Nature of oxy salts: (i) Bicarbonates an carbonates: Bicarbonates of alkaline earth metals do no exist in solid state but are known in solutions only. When such solutions are heated, bicarbonates are decomposed with evolution of carbon dioxide.

$$\underset{\text{(Solution)}}{M(HCO3)2} \xrightarrow{\text{Heated}} MCO3 + CO_2 + H_2O$$

Carbonates of alkaline earth metals (MCO3) are insoluble water. These dissolve in water in presence of carbon dioxide

$$MCO3 + H_2O + CO_2 \rightarrow M\ (HCO3)2$$

Solubility of carbonates decreases on moving down t group, while stability increases. This is evident from the values of decomposition temperatures of various carbonates which increase gradually.

$$MCO_3 \longrightarrow MO + CO_2$$

Decomposition	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	BaCO3
temp. (°C)	100	540	900	1290	1360

Increasing stability can be explained on the basis of polarisation and covalent character. Be^{2+} is smallest in size hence show high polarising power. $BeCO_3$ is least ionic and has least stability.

$$\xrightarrow[\text{Increasing ionic character and stability}]{\text{BeCO3 < MgCO3 < CaCO3 < SrCO3 < BaCO3}}$$

The instability of BeCO3 is due to small size of Be^{2+} ion which is unable to stabilise the bigger CO_3^{2-} ion. However, it can stabilise the smaller O^{2-} ion. The stability of other carbonates increases as the size of other cations increases gradually.

The carbonates are all ionic, but BeCO3 is unusual because it contains hydrated ion $[Be(H_2O)_4]^{2+}$ rather than $Be^{2}+$.

(ii) Sulphates: Alkaline earth metals form sulphates of the type MSO4. These are prepared by the action of sulphuric acid on oxides, hydroxides or carbonates.

$$MO + H_2SO_4 \rightarrow MSO_4 + H_2O$$
$$M(OH)_2 + H_2SO_4 \rightarrow MSO_4 + 2H_2O$$
$$MCO3 + H_2SO4 \rightarrow MSO_4 + H_2O + CO_2$$

The solubility of sulphates decreases on moving down the group. $CaSO_4$ is sparingly soluble, while $SrSO_4$, $BaSO_4$ and $RaSO_4$ are almost insoluble. The solubilities of $BeSO_4$ and $MgSO_4$ are due to high energy of solvation of smaller $Be^{2}+$ and $Mg^{2}+$ ions. The values of solubility products which decrease gradually also explain the decrease in solubility on moving down the group.

Metal sulphate	$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$	$BaSO_4$
Solubility product	very high	10	2.4×10^{-5}	$7.6x10^{-7}$	$1.5x10^{-9}$

The sulphates decompose on heating to give the corresponding oxide (MO).

$$2\ MSO_4 \xrightarrow{Heat} 2\ MO + 2SO_2 + O_2$$

The stability increases as the basic nature of the meta increases. This is evident from the decomposition temperatures

Metal sulphate	$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
Decomposition temp. (°C)	500	895	1149	1374

Sulphates are reduced into sulphides on heating wit carbon.

(iii) Nitrates: Alkaline earth metals form nitrates of the type $M(NO_3)_2$. These are prepared by the action of nitric acid with oxides, hydroxides and carbonates.

Nitrates of these metals are soluble in water. On heating they decompose into their corresponding oxides with evolution of a mixture of nitrogen dioxide and oxygen.

$$2M(NO3)_2 \longrightarrow 2MO + 4NO_2 + O_2$$

Beryllium also forms a basic nitrate in addition to the norm salt. Basic nitrate is a covalent compound.

$$Be(NO_3)_2 \xrightarrow{125°C} [Be\ O(NO_2).]$$

Basic beryllium nitrate

(h) Solutions of metals in liquid ammonia: Like alkali metals, alkaline earth metals also dissolve in liquid ammonia to for coloured solutions. Dilute solutions are bright blue in colour due to solvated electrons. These solutions decompose very slowly forming amides and evolving hydrogen.

$$M \longrightarrow M^{2+} + 2e$$

$$2NH3 + 2e \rightarrow 2NH_2^{1-} + H_2$$

$$M^{2+} + 2NH_2^{1-} \rightarrow M(NH_2)_2$$

When the solution is evaporated, hexammoniate, $M(NH_3)_6$ is formed. These slowly decompose to give amides.

$$M(NH_3)_6 \rightarrow M(NH_2)^2 + 4NH_3 \uparrow + H_2 \uparrow$$

Concentrated solutions of the metals in ammonia are bronze coloured.

(i) Formation of amalgams: Alkaline earth metals combine with mercury to form amalgams.

(j) Complex formation: Generally, the alkaline earth metals do not form complexes. However, the smaller ions have some tendency to form complexes. Beryllium forms stable complexes such as $[BeF_3]^-$, $[BeF_4]^{2-}$ and $[Be(H_2O)_4]^{2+}$Complexes of the type $BeCl_2R_2$ are formed where R is an ether, aldehyde or ketone with an oxygen as a donor atom. Beryllium is unique in forming a series of stable complexes of formula $[Be_4O(R)_6]$, where R may be NO_3^-, $HCOO^-$, CH_3COO^-, $C_6H_5COO^-$, etc.

The most important complex formed by magnesium is chlorophyll in which magnesium is bonded to the four heterocyclic nitrogen atoms. Calcium, strontium and barium form complexes only with strong complexing agents like acetylacetone, EDTA, etc.

(k) Organo-metallic compounds : Both Be and Mg form an appreciable number of compounds with M-C bonds but only a few are known for Ca, Sr and Ba. Grignard reagents are very important in organic chemistry which can be used to form a wide variety of organic compounds.

$$Mg + RBr \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagents}}{RMgBr} \quad (R = \text{alkyl or aryl})$$

$BeCl_2$ reacts with Grignard compounds forming reactive dialkyls and diaryls.

$$2RMgCl + BeCl_2 \xrightarrow{\text{Ether}} BeR_2 + 2MgCl_2$$

Dialkyls and diaryls of Mg, Ca, Sr and Ba can also be obtained by similar reactions.

SOLUBILITY OF COMPOUNDS OF ALKALINE EARTH METALS

In the case of the compounds of Ca, Sr and Ba the following facts are observed:

(i) The solubility of hydroxides, fluorides and oxalates increases from calcium to barium.

(ii) The solubility of carbonates, sulphates and chromates decreases from calcium to barium.

The solubility of an ionic compound depends on two factors: (i) lattice energy and (ii) hydration energy. These two factors oppose each other. If lattice energy is high, the ions will be tightly packed in the crystal and, therefore, solubility will be low. If hydration energy is high, the ions will have greater ten dency to be hydrated and, therefore, the solubility will be high.

In the case of hydroxides, fluorides and oxalates the lattice energies are different, i.e., lattice energy decreases as the size of the cation increases. This tends to increase the solubility as it overcomes the counter effect of decrease in hydration energy. Hence, the solubility of the hydroxides, fluorides and oxalates increases from Ca to Ba.

In the case of carbonates, sulphates and chromates the anions are large in size and small changes in cation size do not alter the lattice energies, i.e., lattice energies are about the same. However, the hydration energies decrease from Ca^{2+} to Ba^{2+}. Hence, the solubility of carbonates, sulphates and chromates decreases from calcium to barium.

DIFFERENCE BETWEEN ALKALINE EARTH METALS AND ALKALI METALS

Both alkaline earth metals and alkali metals are s-block elements as the last differentiating electron enters the *ns*-orbital. They resemble with each other in many respects but still there are certain dissimilarities in their properties on account of different number of electrons in the valency shell, smaller atomic radii, high ionisation potential, higher electronegativity, etc. The man points of difference between alkaline earth metals and alkali metals are given below:

Properties	Alkaline earth metals	Alkali metals
(i) Electronic configuration	**Two electrons are present in the valency shell. The con figurations is ns^2.**	**One electron is present in the valency shell. The configuration is ns^1.**
(ii) Valency	**Bivalent.**	**Monovalent.**
(iii) Electropositive nature	**Less electropositive.**	**More electropositive.**
(iv) Hydroxides	**Weak bases, less soluble and decompose on heating.**	**Strong bases, highly soluble and stable towards heat.**
(v) Bicarbonates	**These are not known in free state. Exist only in solution.**	**These are known in solid state.**
(vi) Carbonates	**Insoluble in water. Decompose on heating.**	**Soluble in water. Do not decompose on heating (Li_2CO3 is an exception).**
(vii) Action of nitrogen	**Directly combine with nitrogen and form nitrides.**	**Do not directly combine with nitrogen.**
(viii) Action of carbon	**Directly combine with carbon and form carbides.**	**Do not directly combine with carbon.**
(ix) Nitrates	**Decompose on heating evolving a mixture of NO_2 and oxygen.**	**Decompose on heating evolving only oxygen.**
(x) Solubility of salts	**Sulphates, phosphates, fluorides, chromates, oxalates, etc., are insoluble in water.**	**Sulphates, phosphates, fluorides, chromates, oxalates, etc., are soluble in water.**
(xi) Physical properties	**Are less reactive and comparatively harder metals. High melting points. Diamagnetic.**	**Soft, low melting points. Paramagnetic.**
(xii) Hydration of compounds	**The compounds are extensively hydrated. $MgCl_2$-$6H_2O$, CaCl2-$6H_20$ and $BaCl_2$ $2H_2O$ are hydrated chlorides.**	**The compounds are less hydrated. NaCl, KCl and RbCl form non-hydrated chlorides**
(xiii) Reducing power	**Weaker, as ionisation potential values are high and oxidation potential values are low.**	**Stronger, as ionisation potential values are low and oxidation potential values are high.**