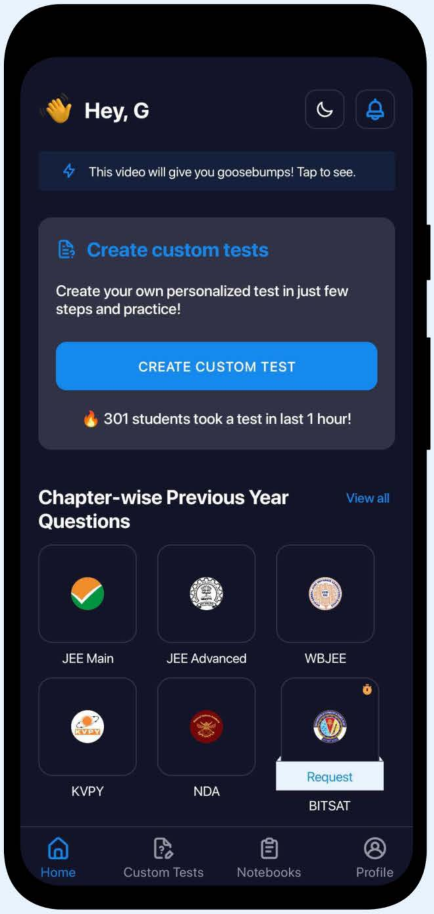


S-BLOCK ELEMENTS

S-BLOCK ELEMENTS

Introduction

Shells upto (n – 1) are completely filled and differentiating (last) electron enters into ns sub-orbit. Elements under this class are called S-Block elements

- Alkali metals forms compounds with + 1 oxidation state and those of alkaline earth metals + 2 oxidation state, ions having nearest noble gas configuration
- General electronic configurations is

  [Inert gas] ns^1 - Alkali metals,

  [Invert gas] ns^2 - Alkaline earth metals;

ALKALI METAS

Physical Properties

(a) All the alkali elements are silvery white solids. These are soft in nature and can be cut with the help of knife except lithium. When freshly cut, they have a bright lustre which quickly fades due to surface oxidation. These are highly malleable and ductile.

The silvery lustre of alkali metals is due to the presence of highly mobile electrons of the metallic lattice. There being only a single electron per atom, the metallic bonding is not so strong. As a result of this, these metals are soft in nature. However, the softness increases with increase of atomic number because there is continuous decrease of metallic bond strength on account of an increase in atomic size. Bibber is the size of metal kernel weaker is the metallic bonding.

(b) Atomic and ionic radii : Group IA atoms are the largest in their horizontal periods in the periodic table. When the outermost electron is removed to give a positive ion, the size decreases considerably. There are two reason for this :

(i) The outermost shell of electrons has been completely removed.

(ii) The positive charge on the nucleus is now acting on lesser number of electrons, i.e., attraction increases which bring contraction in size.

Atomic as well as ionic size increases for Li to Fr due to the presence of one extra shell of electrons.

	Li	Na	K	Rb	Cs
At. radii (A)	1.23	1.57	2.03	2.16	2.35
Ionic radii (A)	0.60	0.95	1.33	1.48	1.67

Atomic volume also increases as the atomic number increases.

	Li	Na	K	Rb	Cs
At. volume (mL)	13.0	23.7	44.4	55.8	69.3

(c) Density : All are light metals. The densities are low. Lithium, sodium and potassium are lighter than water. Density gradually increases in moving down from Li to Cs. Potassium is, however, lighter than sodium.

	Li	Na	K	Rb	Cs
Density (g/mL)	0.54	0.97	0.86	1.53	1.87

The reason for the low values is that these metals have high atomic volumes. The abnormal value of potassium is due to unusual increase in atomic size. i.e., atomic volume.

(d) Melting and boiling points : The energy binding the atoms in the crystal lattices of these metals is relatively low on account of a single electron in the valency shell. Consequently, the metals have low melting and boiling points. These decrease in moving down from Li to Cs as the metallic bond strength decreases or cohesive force decreases.

	Li	Na	K	Rb	Cs
Melting point (°C)	181	98	63	39	28.5
Boiling point (°C)	1347	880	766	688	705

(e) Ionisation energies and electropositive character : Due to their large size, the outermost electron is far from the nucleus and can easily be removed. Their ionisation energies or ionisation potentials are relatively low. Thus, the metals have a great tendency to loss the ns^1 electron to change into M^+ ions. These metals are highly electropositive in nature. As the ionisation potential decreases from Li to Cs, the electropositive character increases, i.e., metallic character increases. The reactivity of the these metals increases from Li to Cs.

	Li	Na	K	Rb	Cs
Ionisation potential (eV)	5.4	5.1	4.3	4.2	3.9
	$\xrightarrow[\text{Decreases}]{}$				
Electropositive or metallic nature	$\xrightarrow[\text{Increases}]{}$				
Reactivity	$\xrightarrow[\text{Increases}]{}$				

The ns^1 electron is so loosely held that even the low energy photons (light) can eject this electron from the metal surface. This property is termed as photoelectric effect. K and Cs are used in photoelectric cells which are sensitive to blue light.

(f) Oxidation states : The alkali metals can lose their ns^1 electron quite easily to form univalent positive ion, M^+. The ion has a stable configuration of an inert gas.

Li^+	He-configuration
Na^+	Ne-configuration
K^+	Ar-configuration
Rb^+	Kr-configuration
Cs^+	Xe-configuration

The energy required to pull out another electron from M^+ ion is very high, i.e. the second ionisation potential values are high

	Li	Na	K	Rb	Cs
I_2 (eV)	75.6	47.4	32.0	28.0	25.0

Consequently, it is not possible for alkali metals to form M^{2+} ions under ordinary conditions. These metals, thus show only one oxidation state, i.e., +1 oxidation state. These metals are univalent in nature and show electrovalency, i.e., form electrovalent compounds.

Since the electronic configuration of M^+ ions are similar to those of inert gases, these ions have no unpaired electrons and consequently are colourless and diamagnetic in nature.

(g) Hydration of ions, hydrated radii hydration energy : The salts of alkali metals are ionic and soluble in water. The solubility is due to the fact cations get hydrated by water molecules.

$$M^+ + aq. \longrightarrow \underset{\text{(Hydrated cation)}}{[M(aq.)]^+}$$

The smaller the cation, the greater is the degree of its hydration. Thus, the degree of hydration of M^+ ions decreases from Li^+ to Cs^+. Consequently the radii of the hydrated ion decreases from Li^+ to Cs^+.

	$[Li(aq.)]^+$	$[Na(aq.)]^+$	$[K(aq.)]^+$	$[Rb(aq.)]^+$	$[Cs(aq.)]^+$
Hydrated radii (A)	3.40	2.76	2.32	2.28	2.27

The ionic conductance of these hydrated ions increases from $[Li(aq.)]^+$ to $[Cs(aq.)]^+$

Hydration of ions is an exothermic process. The energy released when one gram mole of an ion is dissolved in water to get it hydrated is called hydration energy. Since the degree of hydration decreases from Li^+ to Cs^+, the hydration energy of alkali metal ion also decreases from Li^+ to Cs^+.

(h) Electronegativity : The tendency to attract electrons is low as the alkali metals are electropositive. The electronegativity, thus, decreases from Li to Cs as the electropositive character increases.

(i) Conductivity : The alkali metals are good conductors of heat and electricity. This is due to the presence of loosely held valency electrons which are free to move throughout the metal structure.

(j) Specific heats : The specific heat values decrease from Li to Cs.

	Li	Na	K	Rb	Cs
Specific heat at 0°C	0.94	0.29	0.17	0.08	0.05

(k) Heat of atomisation : Heat of atomisation decreases from Li to Cs.

	Li	Na	K	Rb	Cs
Heat of atomisation (kJ mol^{-1})	163.6	104.2	83.2	79.5	75.7

This is due to the decrease in the metallic bond strength from Li to Cs.

(l) Flame colouration : The alkali metals and their salts impart a characteristic colour to flame.

The reason for flame colouration is that the energy of the flame causes an excitation of the outermost electrons which on return to their original position give out the energy so absorbed in the visible region. The energy released in minimum in the case of Li^+ and increases in order Li^+, Na^+, K^+, Rb^+, Cs^+. Thus, the frequency of the light emitted increases in accordance with the formula E = hv. The frequency of light in lithium is minimum which corresponds to red region of the spectra.

(m) Reducing nature : An element, which acts as a reducing agent, must have low ionisation energy. Alkali metals act as strong reducing agents as their ionisation energy values are low. Since ionisation energy decreases on moving down from Li to Cs, the reducing property increase in the same order. This, Li is weakest reducing agent while Cs is the strongest reducing agent amongst alkali metals in free state.

The tendency of an element to lose an electron in solution is measure by its standard oxidation potential value (E^{o}_{ox}). Since alkali metals have high E^{o}_{ox} values, these are strong reducing agents. However, it is observed that Li is the strongest reducing agent amongst alkali metals in solution as E^{o}_{ox} value of Li is maximum.

	Li	Na	K	Rb	Cs
Oxidation potential (V)	+3.05	+2.71	+2.93	+2.99	+2.99

It looks surprising at first sight that lithium having high value of ionisation energy amongst alkali metals acts as strongest reducing agent in solution. This can be explained if we understand the fact that ionisation energy is the property of an isolated atom in gaseous state while oxidation potential is concerned when the metal atom goes into the solution.

The ionisation energy involves the change to gaseous atom to gaseous ion,

$$M(g) \longrightarrow M^{+}(g) + e$$

while oxidation potential involves the following change :

$$M(s) \longrightarrow M^{+}(aq.) + e$$

The above change occurs in three steps :

(i) $M(s) \longrightarrow M(g) -$ sublimation energy

(ii) $M(g) \longrightarrow M^+(g) +$ e–ionisation energy

(iii) $M^+(g) + H_2O \longrightarrow M^+(aq.) +$ hydration energy

Sublimation energy is nearly same for all the alkali metals.

The energy required in (ii) step is the ionisation energy which is highest for lithium. Li^+ ion is smallest in size, hence it has maximum degree of hydration. Thus, in (iii) step, maximum hydration energy is released in lithium.

	Li	Na	K
Step (i)	+122 kJ	+78 kJ	+61 kJ
Step (ii)	+520 kJ	+496 kJ	+419 kJ
Step (iii)	– 480 kJ	–371 kJ	– 299 kJ
overall	162 kJ	203 kJ	181 kJ

Thus, with great ease the following overall change occurs in lithium and it acts as a strongest reducing agent :

$$M(s) \longrightarrow M^+(aq.) + e$$

It is, therefore, concluded that highest reducing power of lithium in solution is due to its large heat of hydration.

Chemical Properties of Alkali Metals

The alkali metals are highly reactive metals and the reactivity increases down the group. The reactivity is due to

(a) low value of first ionization energy

(b) large size

(c) low heat of atomization.

(1) Reaction with air : All alkali metals except lithium tarnish in air due to formation of an oxide or hydroxide on the surface. These are, therefore, always kept under kerosene oil to protect them from air.

$$4M + O_2 \longrightarrow 2M_2O$$

(where M = Li, Na, K, Rb, Cs)

$4Li + O_2$ (excess) $\longrightarrow 2Li_2O$ (Lithium oxide)

$2Na + O_2$ (excess) $\longrightarrow Na_2O_2$ (Sodium peroxide)

$K + O_2$ (excess) $\longrightarrow$ KO_2 (potassium superoxide)

This difference is due to small size, Li^+ has a strong positive field around it which attracts the negative charge so strongly that is does not permit the oxide onion O^{2-} to combine with another oxygen to form peroxide ion, O_2^{2-}. On the other hand, Na^+ ion because of its large size that Li^+ ion has comparatively weaker positive field around it. which cannot prevent O^2 ion to combine with another oxygen to form peroxide ion O_2^{2-}. The larger K^+, Rb^+ and Cs^+ ions have still weaker positive field around then which cannot prevent even peroxide ion, O_2^{2-} to combine with another oxygen aton to form superoxide O_2^-.

(2) Reaction with water : Alkali method decompose water with the evolution of hydrogen

$$2M + 2H_2O \longrightarrow 2MOH + H_2 (\uparrow)$$

Lithium decomposes water slowly. Sodium reacts with water quickly, K, Rb and Cs react with water vigorously. The decomposition is highly exothermic and the evolved hydrogen sometimes inflames. Thus, reactivity towards water increases from Li to Cs. This is due to electropositive character in same order.

Alkali metals react with other compounds containing acidic hydrogen.

$$2Na + 2HCl \longrightarrow 2NaCl + H_2 (\uparrow)$$

$$2Na + 2CH \equiv CH \longrightarrow 2NaC \equiv CH + H_2 (\uparrow)$$

(3) Affinity for non-metals : Alkali methods have great affinity for non-metals.

(i) Action with hydrogen

$2M + H_2 \longrightarrow 2MH$

$MH + H_2O \longrightarrow MOH + H_2 (\uparrow)$

(ii) Action with halogens :

$2M + X_2 \longrightarrow 2MX$

With the exception of certain Lithium halides, the alkali metal halides are ionic compounds ($M^+ X^-$)

Halides of potassium, rubidium and caesium have as property of combining with extra halogen atoms forming poly halides.

$$KI + I_2 \longrightarrow KI_3$$

Note : The insolubility of LiF in water can be explained in the following manner. The lithium ion has the highest energy of hydration as it is small in size in comparison to other alkali metal ions and thus it should have high solubility. However, the small Li^+ and F^- ion interact very strongly resulting in high lattice energy of LiF which is responsible for its insolubility (the ionic compounds, which posses low value of lattice energy, are freely soluble in water)

(iii) Action with sulphur and phosphorus : Alkali metals react with sulphur and phosphorus on heating to form sulphides and phosphides

$$16Na + S_8 \xrightarrow{\Delta} \underset{\text{Sodium sulphide}}{8\ Na_2S}$$

$$12Na + P_4 \xrightarrow{\Delta} \underset{\text{Sodium phosphide}}{4Na_3P}$$

(4) Solubility in liquid ammonia : All alkali metal dissolve in liquid ammonia giving deep blue solutions which are conducting in nature. These solutions contain ammoniated cations and ammoniated electrons as shown below :

$$M + (x + y)\ NH_3 \longrightarrow M^+ + e^{-1}(NH_3)_y$$

The blue colour of the solution is considered to be due to ammoniated electrons which absorb energy corresponding to red region of the visible light for the their excitation to higher energy levels. The transmitted light is blue which imparts blue colour to the solutions. The electrical conductivity of the solution is due to both ammoniated cations and ammoniated electrons. The blue solution on standing slowly liberates hydrogen resulting in formation of amide :

$$2M + 2NH_3 \longrightarrow \underset{\text{(Metal amide)}}{2MNH_2} + H_2$$

At concentration above 3M, the solutions of alkali metals in liquid ammonia are copper-bronze coloured. These solutions contains clusters of metal ions and hence possess metallic lusture. The blue coloured solutions are paramagnetic due to presence of large number of unpaired electrons, but bronze solutions are diamagnetic due to formation of electron clusters in which ammoniated electrons with opposite spin group together

These solutions are stronger reducing agents than hydrogen and hence will react with water to liberate hydrogen.

General Characteristic of the Compounds of the Alkali Metals

(i) Oxide and Hydroxides

All the alkali metals, their oxides, peroxides and superoxides readily dissolve in water to produce corresponding hydroxides with are strong alkalies eg

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$Na_2O + 2H_2O \longrightarrow 2NaOH$$

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

Thus peroxides and superoxides also act as oxidizing agents since they react with H_2O forming H_2O_2 and O_2 respectively.

The hydroxides of all the alkali metals are white crystalline solids. They are strongest of all base and readily dissolve in water with the evolution of much heat.

(a) Basic Strength : The Basic strength of these hydroxides increases as we move down the group Li to Cs. The hydroxides of alkali metals behave as strong bases due to their low ionization energies which decrease down the group. The decrease in ionization energies leads to weakening of the bond between metal and hydroxide ion and M – O bond in M – O – H can easily break giving M^+ and OH^-. This results in the increased concentration of hydroxyl ions in the solution i.e., increased basic characters.

(b) Solubility and stability : All these hydroxides are highly soluble in water and thermally stable except lithium hydroxide.

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

(ii) Nitrates (MNO_3)

The nitrates do not undergo hydrolysis. With the exception of $LiNO_3$, other nitrates decompose to nitrites and oxygen.

$$2MNO_3 \longrightarrow 2MNO_2 + O_2$$

$$\text{But, } 2LiNO_3 \longrightarrow Li_2O + 2NO_2 + I_2O_2$$

(iii) Halides

The alkali metals combine directly with halogens under appropriate conditions forming halides of general formula MX. These halides can also be prepared by the action of aqueous halogen acides (HX) on metals oxides, hydroxides or carbonate.

$M_2O + 2HX \longrightarrow 2MX + H_2O$

$MOH + HX \longrightarrow MX + H_2O$

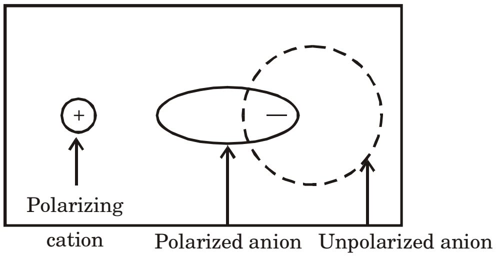
$M_2CO_3 + 2HX \longrightarrow 2MX + CO_2 + H_2O$ (M = Li, Na, K, Rb or Cs) and (X = F, Cl, Br or I)

The fluorides are the most stable while iodides are the least stable.

The trends in meting points, boiling points and solubility of alkali metals halides can be understood in terms of polarization effects, lattice energy and hydration of ions.

(A) Polarization effects

Comparison of ionic and covalent character of alkali metal halides.



When a cation approaches and anion, the electron cloud of the anion is attracted towards the cation and hence gets distorted. This effect is called polarization. The power of the cation of polarize the anion is called its polarizing power and the tendency of the anion to get polarized is called its polarizability. The greater the polarization produced more is the concentration of the electrons between the two atoms thereby decreasing the ionic character of increasing the covalent character. The covalent character of any compound in general depends upon the following factors.

(a) Size of the cations

Smaller the cation greater is its polarizing power and hence larger is the covalent character. The covalent character decreases as size of cation increases.

$LiCl > NaCl > KCl > RbCl > CsCl$

Thus LiCl is more covalent than KCl.

(b) Size of the anion

Larger the anion, greater is its polarizability. This explains the covalent character of lithium halides is in order

$LI > LiBr > LiCl > LiF$

(c) Charge of the ion

Greater the charge on the cation greater is its polarizing power and hence larger is the covalent character. The covalent character of some halides increase in the order

$Na^+Cl^- < Mg^{+2}\ Cl_2 < Al^{+3}\ Cl_3$

Similarly greater the charge on the anion, more easily it gets polarized thereby imparting more covalent character to the compound formed eg covalent character increase in the order : $NaCl < Na_2SO_4 < Na_3PO_4$

Thus the covalent character decreases as the charge of the anion decrease.

(d) Electronic configuration of the cation

It two cations have the same charge and size, the one with pseudo noble gas configuration i.e having 18 electrons in the outermost shell has greater polarizing power than a cation with noble gas configuration i.e having 8 electrons. For example CuCl is more covalent than NaCl.

(B) Lattice Energies

Lattice energy is defined as the amount of energy required to separate one mole of solid ionic compound into its gaseous ions. Evidently greater the lattice energy, higher is the melting point of the alkali metals halide and lower its solubility in water

(C) Hydration Energy

It is the amount of energy released when one mole of gaseous ions combine with water to form hydrated ions.

$$M^+ (g) + aq \longrightarrow M^+ (aq) + \text{hydration energy}$$

$$X^- (g) + aq\ X^- (aq) + \text{hydration energy}$$

Higher the hydration energy of the ions greater is the solubility of the compound in water.

Further the extent of hydration depends upon the size of the ions. Smaller the size of the ion, more highly it is hydrated and hence greater is its hydrated ionic radius and less is its ionic mobility (Conductance).

From above arguments, the melting point and solubility in water or organic solvent of alkali metal halides can be explained

(a) A delicate balance between lattice enthalpy and hydration enthalpy determines the ultimate solubility of a compound in water. For eg. Low solubility of LiF (0.27 g/100 g H_2O) is due to its high lattice energy (–1005KJmol^{-1}) whereas the low solubility of CsI (44g/100gH_2O) is due to smaller hydration energy of the two ions (–670 KJ/mol)

(b) The solubility of the most of alkali metal halides except those of fluorides decreases on descending the group since the decrease in hydration energy is more than the corresponding decrease in the lattice energy.

(c) Due to small size and high electronegativity, lithium halides except LiF are predominantly covalent and hence are soluble in covalent solvents such as alcohol, acetone, ethyl acetate, LiCl is also soluble in pyridine. In contrast NaCl being ionic is insoluble in organic solvents.

(d) Due to high hydration energy of Li^+ ion, Lithium halides are soluble in water except LiF which is sparingly soluble due to its high lattice energy.

(e) For the same alkali metal the melting point decreases in the order :

fluoride > chloride > bromide > iodide

because for the same alkali metal ion, the lattice energies decreases as the size of the halide ion increases.

(f) for the same halide ion, the melting point of lithium halides are lower than those of the corresponding sodium halides and thereafter they decrease as we move down the group for Na to Cs.

The low melting point of LiCl (887 K) as compared to NaCl is probably because LiCl is covalent in nature and NaCl is ionic.

Salts of oxoacids

Since the alkali metals are highly electropositive, therefore their hydroxides are very strong bases and hence they form salts with all oxoacids (H_2CO_3, H_3PO_4, H_2SO_4, HNO_3, HNO_2 etc). They are generally soluble in water and stable towards heat. The carbonates (M_2CO_3) of alkali metals are remarkably stable upto 1273 K, above which they first melt and then eventually decompose to form oxides Li_2CO_3, however is considerably less stable and decomposes readily.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

This is presumably due to large size difference between Li^+ and CO_3^{2-} which makes the crystal lattice unstable.

Being strongly basic, alkali metals also form solid bicarbonates. No other metals forms solid bicarbonates though NH_4CO_3 also exists as a solid. Lithium, however does not form solid bicarbonate though it does exist is solution. All the bicarbonate on gentle heating undergo decomposition to form carbonates with the evolution of CO_2.

$$2MHCO_3 \xrightarrow{\Delta} M_2CO_3 + CO_2 + H_2O$$

All the carbonates and bicarbonates are soluble in water and their solubilities increase rapidly on descending the group. This is due to the reason that lattice energies decrease more rapidly than their hydration energies on moving down the group.

Anomalous Behaviour of Lithium and its Diagonal Relationship with Magnesium

The properties of lithium are quite from the properties of other alkali metals. On the other hand, it shows greater resemblance with magnesium, which is diagonally opposite elements of it. The main reasons for the anomalous behaviour of lithium as compared to other alkali metals are

(i) The extremely small size of lithium atom and its ion.

(ii) Greater polarizing power of lithium ion (Li^+), due to its small size which result in the covalent character in its compounds.

(iii) Least electropositive character and highest ionization energy as compared to other alkali metals.

(iv) Non availability of vacant d-orbitals in the valance shell.

The reason for resemblance of properties of lithium with magnesium is that these two elements have almost same polarizing power.

The following points illustrate the anomalous properties of lithium and its diagonal relationship with magnesium

(a) The melting point and boiling point of lithium are comparatively high.

(b) Lithium is much harder than the other alkali metals. Magnesium is also hard metal.

(c) Lithium reacts with oxygen least readily to form normal oxide whereas other alkali metals form peroxides and superoxides.

(d) LiOH like $Mg(OH)_2$ is weak base. Hydroxides of other alkali metals are strong bases.

(e) Due to their appreciable covalent nature, the halides and alkyls of lithium and magnesium are soluble in organic solvents.

(f) Unlike elements of group 1 but like magnesium. Lithium forms nitride with nitrogen.

$$6Li + N_2 \longrightarrow 2Li_3N$$

(g) LiCl is deliquescent and crystallizes as a hydrate, $LiCl.2H_2O$. Other alkali metals do not form hydrates. $MgCl_2$ also forms hydrate, $MgCl_2.8H_2O$.

(h) Unlike other alkali metals lithium reacts directly with carbon to form an ionic carbide. Magnesium also forms a similar carbide.

(i) The carbonates, hydroxides and nitrates of lithium as well as magnesium decompose on heating.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

$$MgCO_3 \longrightarrow MgO + CO_2$$

$$2LiOH \longrightarrow Li_2O + H_2O$$

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

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \longrightarrow 2Mg + 4NO_2 + O_2$$

The corresponding salts of other alkali metals are stable towards heat.

(j) Lithium nitrate, on heating, decomposes to give lithium oxide, Li_2O whereas other alkali metals nitrates decomposes to give the corresponding nitrite.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

(k) Li_2CO_3, LiOH, LiF and Li_3PO_4 are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.

(l) Hydrogen carbonates of both lithium and magnesium can not be isolated in solid state. Hydrogen carbonates of other alkali metals can be isolated in solid state.

Illustration :

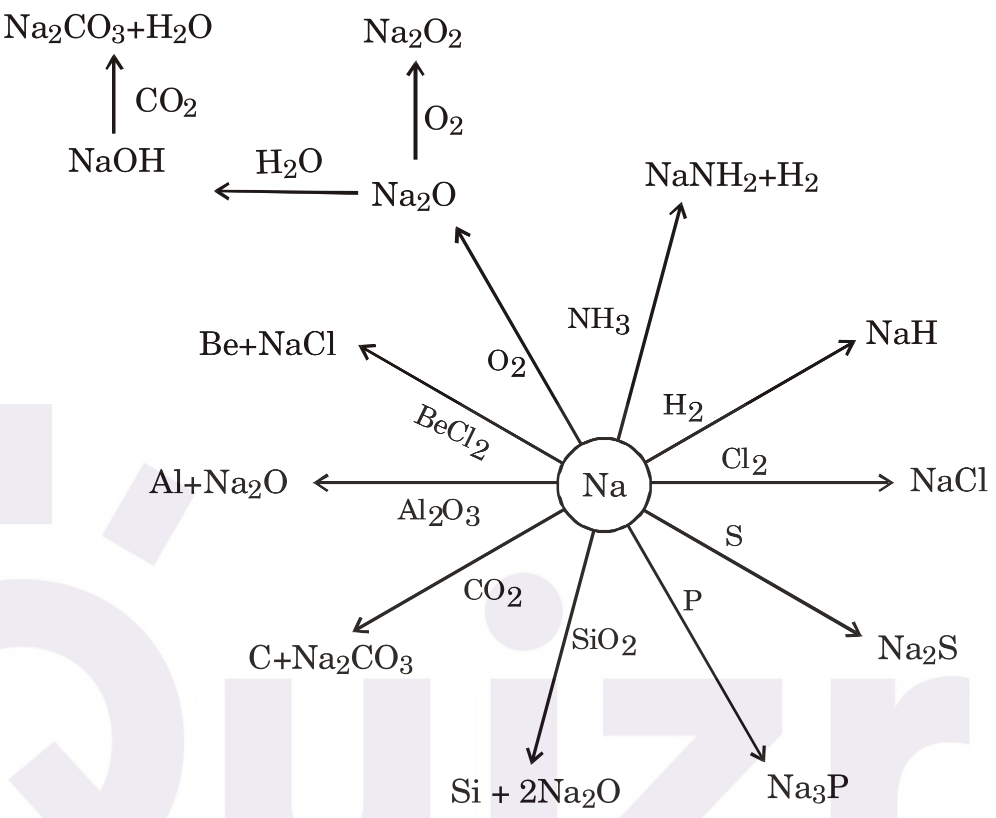
The chemistry of Lithium is very much similar to that of magnesium even though they are placed in different groups-Explain.

Solution : The ratio of their charge to size is nearly same by which they show the diagonal relationship.

COMPOUNDS OF ALKALI METALS

1. Sodium :

Some basic reactions are :



Compounds of sodium

1. Sodium oxide, Na_2O

$Na_2O + H_2O \longrightarrow 2NaOH$

2. Sodium peroxide (Na_2O_2)

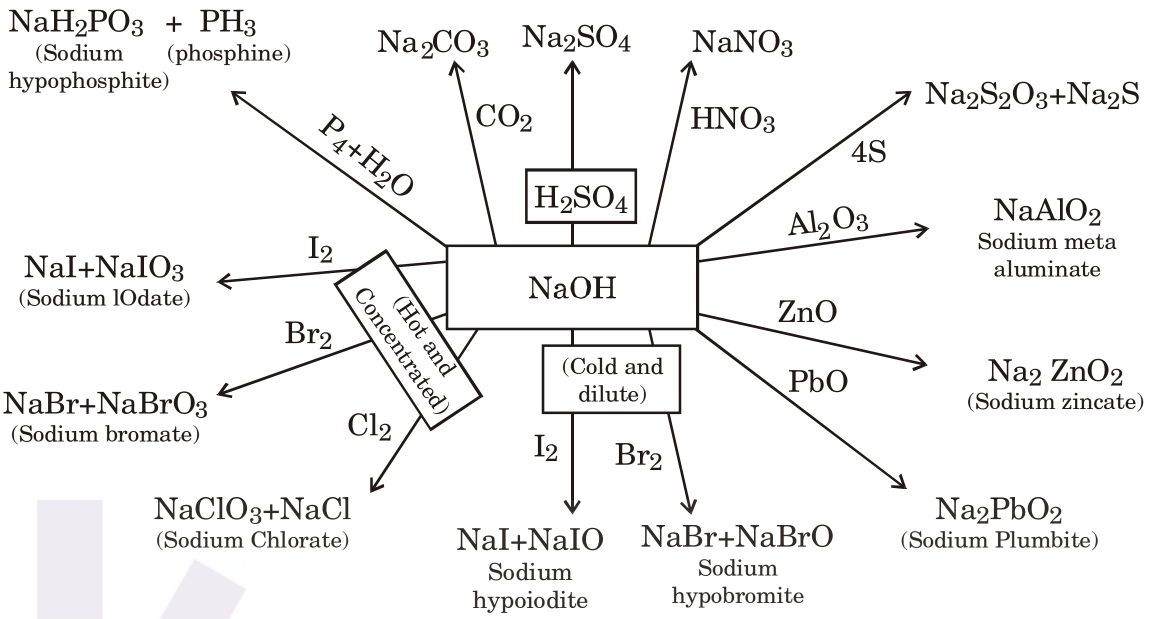
It is a pale yellow powder. It is used as an oxidizing agent

$Na_2O_2 + 2H_2O \xrightarrow{\text{ice-cold water}} 2NaOH + H_2O_2$

$Na_2O_2 + 2H_2O \xrightarrow{25°C} 2NaOH + O_2$

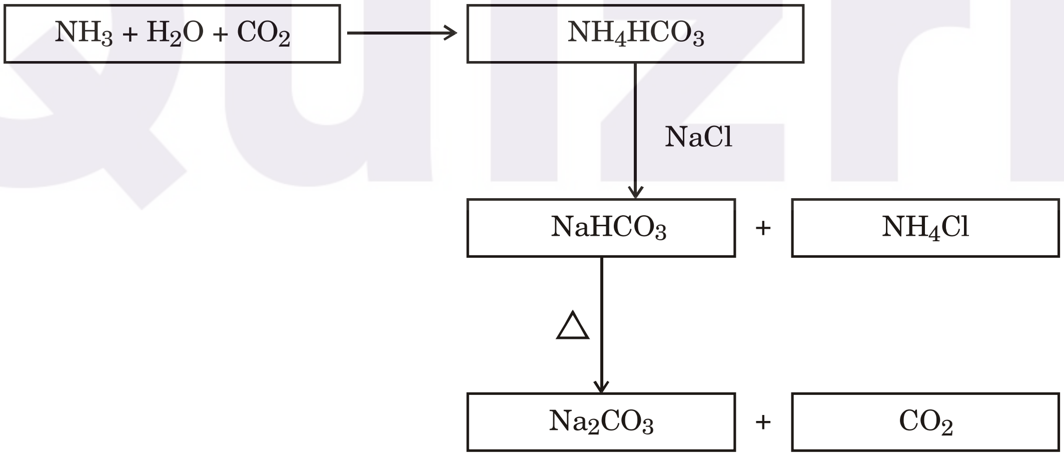
$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

3. Sodium Hydroxide (Caustic soda), NaOH



4. Sodium Carbonate

Preparation : (By solvays process)



$Na_2CO_3 \cdot 10H_2O \longrightarrow$ Washing soda

$Na_2CO_3 \longrightarrow$ Soda ash or light ash

Properties :

$Na_2CO_3 + SiO_2 \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + CO_2\ (\uparrow)$

Sodium silicate is called soluble glass or water glass as its is soluble in water.

$$Na_2\ CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

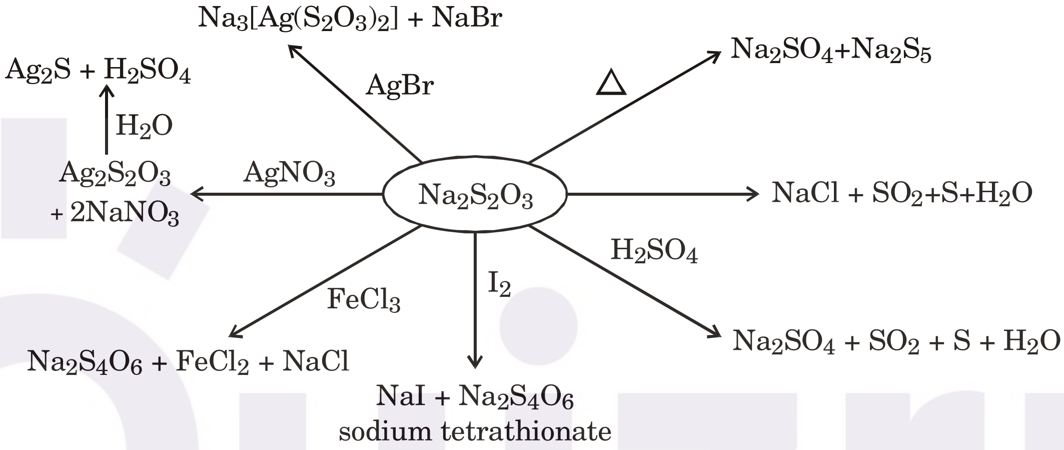
5. Sodium Bicarbonate (Baking soda)

It is used as a medicine to neutralize the acidity in stomach. It is also used in fire extinguishers.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2\ CO_3 + H_2O + CO_2$$

6. Sodium thiosulphate, $Na_2S_2O_3 .\ 5H_2O$

It is also know as Hypo.



Action on copper sulphate : Cuprous thio sulphate is formed which dissolves in excess of sodium thio sulphate to form a complex.

$$CuSO_4 + Na_2\ S_2O_3 \longrightarrow CuS_2O_3 + Na_2\ SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_2O_6$$

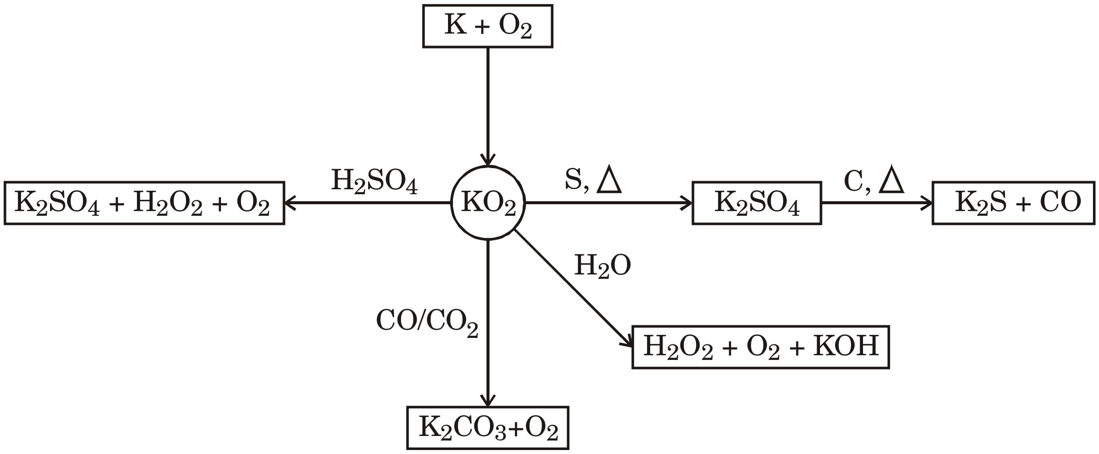
$$3CuS_2O_3 + 2Na_2S_2O_3 \longrightarrow \underset{\text{Sodium cuprothiosulphate}}{Na_4[Cu_6(S_2O_3)_5]}$$

Some more compounds of sodium

1. Glauber's salt , $Na_2SO_4 .\ 10H_2O$
2. Cryolite, Na_3AlF_6
3. Soda Felspar, $NaAlSi_3O_8$

2. Potassium

1) Potassium superoxide



2) Potassium carbonate, K_2 CO_3

It is also called potash or pearl ash.

$K_2CO_3 + 2H_2O \longrightarrow 2KOH + H_2CO_3$

3) Potassium sulphate

$K_2SO_4 + Al_2(SO_4)_3 + H_2O \longrightarrow \underset{\text{(potash alum)}}{K_2SO_4 .\ Al_2\ (SO_4)_3 .\ 24H_2O}$

$K_2SO_4 + 4C \xrightarrow{\Delta} K_2S + 4CO\ (\uparrow)$

4) Potassium iodide, KI

$AgNO_3 + KI \longrightarrow \underset{\text{(yellow)}}{AgI} + KNO_3$

$Pb(CH_3COO)_2 + 2KI \longrightarrow \underset{\text{(yellow)}}{PbI_2} + 2CH_2\ COO$

$HgCl_2 + 2KI \longrightarrow \underset{\text{(red ppt.)}}{HgI_2} + 2KCl$

$HgI_2 + \underset{\text{(excess)}}{2KI} \longrightarrow \underset{\text{(nessler's regent)}}{K_2HgI_4}$

ALKALINE EARTH METALS

Physical Properties

(a) Physical state : 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 IA elements due to possession of 2 valency electrons. However, hardness decreases with increase in atomic number. These elements are malleable and ductile but less than alkali metals.

(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 than 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+}.

	Be	Mg	Ca	Sr	Ba	Ra
Atomic radii Å	1.12	1.60	1.97	2.15	2.22	—
Ionic radii (M^{2+}) Å	0.31	0.65	0.99	1.13	1.35	1.40

Atomic volume also increases as the atomic number increases.

	Be	Mg	Ca	Sr	Ba	Ra
At. vol. (ml)	4.90	13.97	25.9	35.54	36.7	38.0

(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 upto calcium and then increases considerably upto radium. Irregular trend is due to the difference in the crystal structure of these elements.

	Be	Mg	Ca	Sr	Ba	Ra
Density (g ml^{-1})	1.84	1.74	1.55	2.63	3.62	5.5

(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.

	Be	Mg	Ca	Sr	Ba	Ra
m. pt. (°C)	1277	650	838	763	714	700
b. pt. (°C)	2770	1107	1440	1380	1640	1140

(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.

	Be	Mg	Ca	Sr	Ba	Ra
First I.E. (eV)	9.32	7.64	6.11	5.70	5.2	5.3
Second I.E. (eV)	18.21	15.03	11.87	11.0	10.0	10.1

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

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 electrons 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, i.e., with electropositive nature. Thus, these characters increase gradually from Be to Ba.

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

Electropositive nature increase
Metallic character increases
Reactivity of the metals Increases

(f) Oxidation states : All show a stable oxidation state +2 in their compounds. The second ionisation energy is nearly double the first ionisation energy for all elements. This should cause these elements of exhibit a stable +1 oxidation state and form compounds like BaCl, SrBr, CaI, etc., instead of $BaCl_2$, $SrBr_2$, CaI_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 of 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+} ions 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.

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

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

	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Heats of hydration (kcal mol^{-1})	570	460	395	355	305

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.

	Be	Mg	Ca	Sr	Ba	Ra
Electronegativity	1.47	1.23	1.04	1.0	0.97	0.97

(i) Conductivity : On account of the presence of two loosely bond valency electrons per atom which can move freely through 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 electron and change into bivalent cation :

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

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

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

	Be	Mg	Ca	Sr	Ba
Oxid. potential (volt)	1.85	2.37	2.87	2.89	2.90

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.

(l) 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.

Mg^{2+} = 2, 8

= $1s^2$, $2s^2$ $2p^6$

= $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \ \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

Chemical Properties of Alkaline Earth Elements

Table summarizes reactions of Group 2(IIA). From this, it is evident that as we go down the group, reactivity increases.

Reactions of Group 2 (IIA)

Reaction	Comment
$M + 2H_2O \longrightarrow M(OH)_2 + H_2$	Be probably reacts with stream, Mg with hot water, and Ca, Sr and Ba react rapidly with cold water.
$M + 2HCl \longrightarrow MCl_2 + H_2$	All the metals react with acids liberating H_2. With HNO_3, Be becomes passive due to formation of oxide layer.
$3M + N_2 \longrightarrow M_3N_2$	All form nitrides at high temperatures. Stability Be > Mg > Ca (hydrolysis to NH_3)
$M + X_2 \longrightarrow MX_2$ ($X_2 = F_2, Cl_2, Br_2, I_2$)	All the metals form MX_2. No polyhalides are formed.
$M + 2NH_3 \longrightarrow M(NH_2)_2 + H_2$	All the metals dissolve in liquid NH_3 to give deep blue black solutions from which ammoniates $[M(NH_3)_6]^{2+}$ can be recovered and form amides at high temperatures.
$2M + O_2 \longrightarrow 2MO$	All the metals form normal oxide. Ba also forms peroxide (BaO_2).
$Ba + O_2 \longrightarrow BaO_2$	
$M + H_2 \longrightarrow MH_2$	Ionic salt-like hydrides formed at high temperatures by Ca, Sr and Ba.
$Be + 2H_2O + 2OH^- \longrightarrow [Be(OH)_4]^{2-} + H_2(g)$	Not with other alkaline earth metals.
$M(s)\ 2C(s) \longrightarrow MC_2(s)$	At high temperature Be forms Be_2C, ionic compounds
$M + S \longrightarrow MS(s)$	The sulphides are insoluble, but hydrolyse if heated in water.

Some points to note :

1. Be is amphoteric, as it reacts with acid as well as with base

$$\text{Be} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow \underset{\text{Sodium beryllate}}{\text{Na}_2[\text{Be(OH)}_4]} + \text{H}_2$$

Mg, Ca, Sr and Ba do not react with NaOH and thus are purely basic.

2. Except beryllium, all combine with hydrogen directly to form hydrides of the type MH_2 when heated with hydrogen

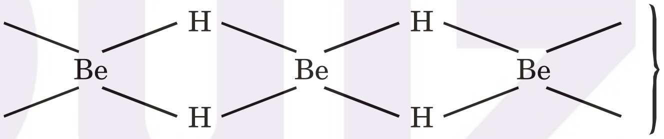
$$\text{M} + \text{H}_2 \longrightarrow \text{MH}_2$$

BeH_2 and MgH_2 are covalent in nature while other hydrides are ionic in nature.

BeH_2 is formed by reacting beryllium chloride with lithium aluminium hydride

$$2\text{BeCl}_2 + \text{LiAlH}_4 \longrightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$$

It is polymeric. $(BeH_2)_n$ process 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 a tons lie in the plane perpendicular to the plane of molecule containing beryllium atoms



3. Alkaline earth metals dissolve in liquid ammonia to form coloured solutions.

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

$$2\text{NH}_3 + 2e^- \longrightarrow 2\text{NH}_2^- + \text{H}_2$$

$$\text{M}^{2+} + 2\text{NH}_2^- \longrightarrow \text{M(NH}_2)_2$$

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

$$\text{M(NH}_3)_6 \longrightarrow \text{M(NH}_2)_2 + 4\text{NH}_2\ (\uparrow) + \text{H}_2\ (\uparrow)$$

4. Carbides : The carbides are ionic in nature and have NaCl type of structure with M^{2+} replacing Na^+ and $C\equiv C^{2-}$ replacing Cl^-. Beryllium forms methanide, Be_2C, with carbon and acetylide, BeC_2, with acetylene. Magnesium on heating with carbon forms $Mg_2\ C_3$ also, which is an allylide since with water it liberates allylene

$$\underset{\text{carbide}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{acetylene}}{C_2H_2}$$

$$Be_2C + 4H_2O \longrightarrow 2\ Be(OH)_2 + \underset{\text{methane}}{CH_4}$$

$$\underset{\text{allylide}}{Mg_2C_3} + 4H_2O \longrightarrow 2\ Mg(OH)_2 + \underset{\text{allylene}}{CH_3 - C \equiv CH}$$

5. 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 $[Be(H_2O)_4]^{2+}$

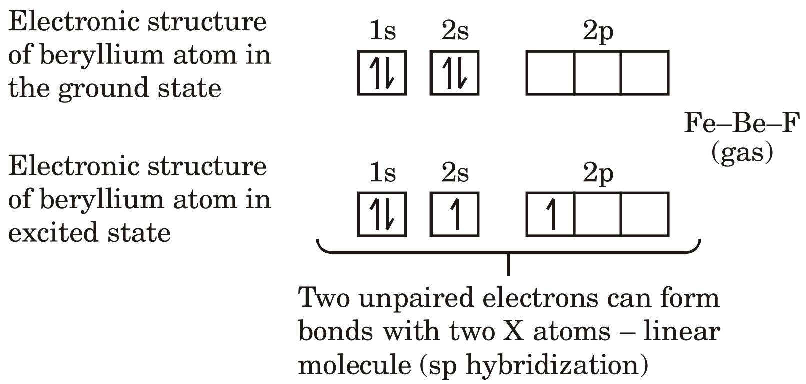
   The most important complex formed by magnesium is chlorophyll in which magnesium is bonded to the four heterocyclic nitrogen atoms. The rest of the elements from calcium to barium form complexes only with strong complexation agents such as acetylacetone, ethylene diamine teraacetic acid (EDTA), etc.

Anomalous Behaviour of Beryllium

Be differs form the rest of the group for three reasons.

1. It is extremely small and Fajan's rule state that small highly charged ions tend to form covalent compounds.
2. Be has a comparatively high electronegativity. Thus when beryllium reacts with another atom, the difference in electronegativity is seldom large, which again favours the formation of covalent compounds. Even BeF_2 (electronegativity difference 2.5) and BeO (electronegativity difference 2.0) show evidence of covalent character.
3. Be is in the second row of the periodic table and the outer shell can hold a maximum of eight electrons. (The orbitals available for bonding are one 2s and three 2p orbitals. Thus Be can form a maximum of four conventional electron pair bonds and in many compounds the maximum coordination number of Be is 4. The later elements can have more than eight outer electrons and may attain a coordination number of 6 using one 's', three 'p' and two 'd' orbitals for bonding. Exceptions occur if multi-centre bonding occurs, as for example in basic beryllium acetate, when higher coordination numbers are obtained.

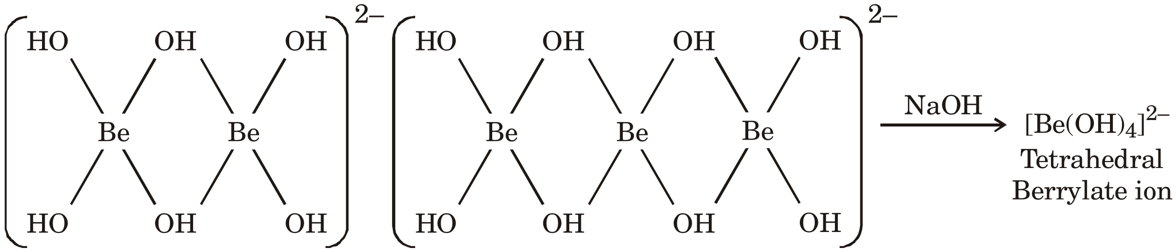
   Thus, we should expect Be to form mainly covalent compounds and commonly have a coordination number 4. Anhydrous compounds of Be are predominantly two-covalent and BeX_2 molecules should be linear.



In fact linear molecules exist only in the gas phase, as this electronic arrangement has not filed the outer shell of electrons. In the solid state four fold coordination is always achieved. There are several ways by which this can be achieved.

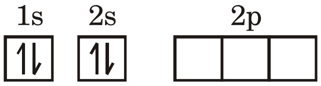
1. Two ligands that have a lone pair of electrons may form coordinate bonds using the two unfilled orbitals in the valence shell of Be. Thus two F^- ions might coordinate of BeF_2, forming $[BeF_4]^{2-}$. Similarly diethyl ether can coordinate to Be(+II) in $BeCl_2$, forming $[BeCl_2(OEt)_2]$.
2. The BeX_2 molecules may polymerise to form chains, containing bridging halogen groups, for example $(BeF_2)_n$, $(BeCl_2)_n$. Each halogen forms one normal covalent bond and uses a lone pair to form a coordinate bond.
3. $(BeMe_2)_n$ has essentially the same structure as $(BeCl_2)_n$, but the bonding in the methyl compound is best regarded as three-centre two electron bonds covering one Me and two Be atoms.
4. A covalent lattice may be formed with a zinc blende or wurtzite structure (coordination number 4), for example by BeO and BeS.

In water beryllium salts are extensively hydrolysed to give a series of hydroxo complexes of unknown structure. They may be polymeric and of the type:

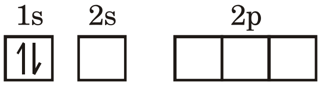


If alkali is added to these solutions, the polymers break down to give the simple mononuclear berrylate ion $[Be(OH)_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[Be(H_2O)_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[Be(H_2O)_4]^{2+}$, rather than Be^{2+} and the hydrated ion too is a tetrahedral complex ion. Note that the coordination number is 4. Forming a hydrated complex increases the effective size of the beryllium ion, thus spreading the charge over a larger area. Stable ionic salts such as $[Be(H_2O)_4]SO_4$, $[Be(H_2O)_4](NO_3)_2$ and $[Be(H_2O)_4]Cl_2$, are known.

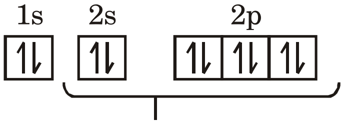
Electronic structure of beryllium atom in the ground state



Electronic structure of Be^{2+} ion



Electronic structure of Be^{2+} ion having gained four electron pairs from four oxygen atoms in water molecules



Four electron pairs tetrahedral (sp^3 hybridization)

Beryllium salts are acidic when dissolved in pure water because the hydrated ion hydrolyses producing H_3O^+. This happens because the Be–O bond is very strong and so in the hydrated ion this weakens the O–H bonds and hence there is a tendency to lose protons. The initial reaction is

$$H_2O + [Be(H_2O)_4]^{2+} \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H_3O^+$$

but this may be followed by further polymerization, involving hydroxobridged structures. In alkaline solutions $[Be(OH)_4]^{2-}$ is formed. The outer group II salts do not interact so strongly with water and do not hydrolyse appreciably.

Beryllium salts rarely have more than four molecules of water of crystallization associated with the metal ion, because there are only four orbitals available in the second shell of electrons, whereas magnesium can have a coordination number of 6 by using some 3d orbitals as well as 3s and 3p orbitals.

COMPOUNDS OF ALKALI EARTH METALS

1. Oxides and Hydroxides

Preparation :

1. $2\ Be + O_2 \longrightarrow 2\ BeO$

$2Ca + O_2 \longrightarrow 2CaO$

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$

2. $MgO + H_2O \longrightarrow Mg\ (OH)_2$

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

Note : Basic strength of hydroxides increase going down the group.

$$Be\ (OH)_2 < Mg\ (OH)_2 < Ca\ (OH)_2 < Sr\ (OH)_2 < Ba\ (OH)_2$$

Properties :

(1) BeO is insoluble in H_2O but dissolves in acid and alkali

$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$

$BeO + NaOH \longrightarrow \underset{\text{Sodium Beryllate}}{Na_2BeO_2} + H_2O$

CaO combines with solid acidic oxides at high temperature

$CaO + SiO_2 \longrightarrow CaSiO_3$

$6\ CaO + P_4O_{10} \longrightarrow 2\ Ca_3\ (PO_4)_2$

(2) $Ca(OH)_2$ is called lime water or slaked lime and $Ba(OH)_2$ is called baryta water, Lime water or baryta turns milky by CO_2

$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$

$Ba(OH)_2 + CO_2 \longrightarrow \underset{\text{milky}}{BaCO_3} + H_2O$

Milkyness disappears when excess of CO_2 is passed, due to formation of soluble bicarbonates

$CaCO_3 + H_2O + \underset{\text{excess}}{CO_2} \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$

$2\ Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + \underset{\text{Calcium hypochlorite}}{Ca(ClO)_2} + 2H_2O$

Bicarbonates and Carbonates

- The carbonates are all ionic, but due to excessive hydration of Be^{2+}, $BeCO_3$ is unusual because it contains the hydrated ion $[Be(H_2O)_4]^{2+}$
- $BeCO_3$ decomposes at low temperature and is placed in the atmosphere of CO_2

$$BeCO_3 \longrightarrow BeO + CO_2$$

Thermal stability increases with increase in atomic weight down the group or with increasing cationic size

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

- $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ exist in water causing temporary hardness which can be removed as insoluble carbonates by boiling

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\ (\downarrow) + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3\ (\downarrow) + H_2O + CO_2$$

- $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are amphoteric thus neutralized by acid as well as base :

$$Ca(HCO_3)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O + 2W_2$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3\ (\downarrow) + 2H_2O$$

Sulphates

- The solubility of the sulphates in water decreases down the group.

$$\underbrace{BeSO_4 > MgSO_4}_{\text{Soluble}} > \underbrace{CaSO_4}_{\text{Sparingly soluble}} > \underbrace{SrSO_4 > BeSO_4}_{\text{insoluble}}$$

High solubilities of $BeSO_4$ and $MgSO_4$ are due to the high enthalpy of hydration of the smaller Be^{2+} and Mg^{2+} ions, which over comes the lattice energy factors.

- The sulphates decompose into oxides and SO_3

$$MSO_4 \xrightarrow{\Delta} MO + SO_3$$

- $MgSO_4.\ 7H_2O$ is called Epsom Salt Although correct formulation is

$$[Mg\ (H_2O)_6]\ SO_4.H_2O$$

$$\begin{tikzcd}
MgSO_4 \cdot 7H_2O \arrow[r, "150^\circ C"] & MgSO_4 \cdot H_2O \arrow[d, "200^\circ C"] \\
\frac{1}{2}O_2 + SO_2 + MgO \arrow[r, "\text{strong heating}"] & MgSO_4
\end{tikzcd}$$

Note : The reason that it first changes to monohydrate lies in the above give formulation $[Mg(H_2O)_6]\ SO_4.H_2O$

- $CaSO_4 \cdot 2H_2O$ is called gypsum

$$\underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow{150°C} \underset{\text{plaster of paris}}{CaSO_4 \cdot \frac{1}{2}H_2O} \xrightarrow{200°C} \underset{\text{anhydrite}}{CaSO_4}$$

$$CaSO_4 \xrightarrow{1100°C} CaO + SO_3$$

$$CaSO_4 + 4C \longrightarrow CaS + 4CO$$