

Radium is radioactive.

The oxides of these elements were known much earlier than the metals themselves.

These were named alkaline earths because :

- (i) these were alkaline in nature like alkali metal oxides.
- (ii) these were found in earth's surface.

ELECTRONIC CONFIGURATION

All these elements have two electrons in their *s*-orbital of the outer-most major shell *i.e.*, all alkaline earth metals have ns^2 configuration. The electronic configuration of the elements is given in table 3.3.

Table 3.3 Physical Properties of Alkaline Earth Metals

Property	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium	
Atomic number	4	12	20	38	56	88	
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$	
Atomic radii, Å°	1.05	1.62	1.97	2.13	2.17	—	
Ionic radii, $M^{++}, \text{Å}^\circ$	0.31	0.65	0.99	1.13	1.35	1.50	
Ionisation energies, g. (atom)^{-1}	1st	733.9	587	546.8	500	50.8	
	2nd	1747	1443	1139	1058.5	959	962
	3rd	14781	14781	9908	41229	3422.6	—
$E^\circ, M^{2+}/M \text{ (V)}$	-1.85	-2.34	-2.87	-1.89	-2.90	-2.92	
Electronegativity	1.50	1.2	1.1	1.0	0.9	0.9	
Heat of atomisation (at 298 K and 1 atm) kJ mol^{-1}	327	146.8	177	163	175.7	—	
Atomic weight	9.0	24.3	40.0	87.6	137.4	226	
Density of solid at 298 K, g/cc	1.86	1.75	1.55	2.6	3.39	5	
Melting point, K	3043	1380	1710	1639	1810	1413	
Colour of the flame	—	—	brick red	Crimson	Grassy green	—	
Enthalpy of hydrides, kJ/mol^{-1}	2385	1925	1653	1485	1276	—	
Atomic volume (c.c.)	4.90	13.97	25.91	34.54	36.72	38.00	

GENERAL TRENDS IN PHYSICAL PROPERTIES

All alkaline earth metals resemble closely in their physical and chemical properties because of their identical ns^2 configuration. The important physical properties are given in table 3.3. The general trend in the physical properties of these elements can be explained in terms of

- (i) loose binding of valence *s*-electrons and (ii) size of their atoms and ions

Following physical properties of alkaline earth metals can be explained on these concepts.

1. Atomic and ionic radii. Atoms of the alkaline earth metals have large size. Even the size of +2 ions formed by the loss of two *s*-electrons is quite large. However, the size of alkaline earth metals and their +2 ions is small as compared to the corresponding alkali metals and their +1 ions. This is because of the increased nuclear charge in case of alkaline earth metals and their +2 ions.

Within the group, the atomic as well as ionic radii of alkaline earth metals increase with the increase in the number of energy shells. For example, Mg atom (having 3 shells) is larger than the size of beryllium atom (having 2 shells).

2. Ionisation potential. On account of large atomic size, the outermost electron in an alkaline earth metal is loosely held. Consequently, alkaline earth metals have low ionisation potentials.

Alkaline earth metals have smaller size and greater value of nuclear charge as compared to the corresponding alkali metals. Therefore, the electrons in alkaline earth metals are more firmly held than in the

alkali metals. Hence, ionisation energy of alkaline earth metals is greater than the corresponding alkali metals.

The second ionisation energy of alkaline earth metals is much higher (almost double) than their first ionisation energy. This is because the second electron has to be removed from smaller sized $+1$ ion in which the second electron feels much greater attraction from the nucleus.

On moving down the group, the ionisation potential decreases. It is because the s-electrons of the outermost shell are getting away from the nucleus due to the addition of new shells. Therefore, the attractive pull exerted by the nucleus on outermost electron decreases. Hence, electron can be removed by expending less energy.

3. Electropositive or metallic character. The alkaline earth metals have a high tendency to lose electrons due to their low I.P. values. Consequently these are strongly electropositive or metallic in nature.

Since alkaline earth metals have higher ionisation energies as compared to alkali metals, the alkaline earth metals have less tendency to lose electrons. Hence, alkaline earth metals are less electropositive than alkali metals.

4. Electronegativity. Due to their strong electropositive character, alkaline earth metals have very little tendency to attract electrons. Therefore, they have very low electronegativity values. However, electronegativity of alkaline earth metals is higher than those of alkali metals. It is due to their small size and higher value of nuclear charge.

5. Electron affinity. Due to their stable configurations (fully filled s-orbitals), alkaline earth metals have very little tendency to gain electrons. Hence, these have very low electron affinity values.

6. Ionic compound formation. Since these elements are highly electropositive, they readily react with highly electronegative elements by the transfer of their valence electrons. Therefore, compounds formed are ionic in nature.

7. Nature of metallic bonding in alkaline earth metals. In case of alkaline earth metals, two electrons per atom are involved in metallic bonding as compared to only one in alkali metals. At the same time, alkaline earth metals have smaller size than the corresponding alkali metals. This results in more close packed structure in alkaline earth metals. Hence, alkaline earth metals are denser, harder and have higher melting points than alkali metals.

8. Crystal structure. (a) In elementary state, both beryllium and magnesium crystallise with a hexagonal crystal lattice. In this structure :

(i) there is hexagonal close packing of spheres. Hence the interstitial space between them is minimum.

(ii) each unit cell contains two atoms because each of the corners is common to 8 unit cells.

(b) In elementary state, both calcium and strontium crystallise with a face centred cubic structure.

In this structure :

(i) each Ca-atom has 12 neighbours at equal distance of $2\sqrt{\frac{a}{2}} = 3.34\text{\AA}$

Where a is the side of cube and is equal to 5.56\AA

(ii) each Sr atom has 12 neighbours at equal distance of $2\sqrt{\frac{a}{2}} = 3.48\text{\AA}$ where $a = 6.05\text{\AA}$

(c) In elementary state, barium crystallises with body centred cubic structure. In this structure :

(i) each Ba-atom has 8 neighbours at equal distance of $\frac{a}{2}\sqrt{3} = 4.34\text{\AA}$ where $a = 5.01\text{\AA}$.

(ii) The spheres occupy 68.02% space in the structure.

9. Formation of complex compounds. Due to their smaller size and higher charge than alkali metals, these metals have a greater tendency to form complexes. For example :

(i) Beryllium ions have the smallest size out of all the alkaline earth metals. These form complexes having coordination number four. For example, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, BeF_4^- etc.

(ii) Magnesium, calcium etc. ions form complexes having coordination number six. For example, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ etc. Large sized Mg^{2+} , Ca^{2+} ions etc. form complexes with chelating agents like EDTA.

10. Enthalpy of hydration of Mg^{2+} ions. Smaller the size of cation, greater will be its tendency to form hydrates. Hence, greater will be the evolution of enthalpy of hydration. As we go down the group, the size of cation increases. Hence enthalpy of hydration decreases.

The enthalpy of hydration of alkaline earth metal ions is much more than that of corresponding alkali metal ions. This difference can be explained in terms of increased charge on alkaline earth metal ions. For example, the enthalpy of hydration of Ca^{2+} ions is about four times than that of Na^+ ions although their sizes are nearly same. This can be explained on the generalisation: 'the enthalpy of hydration is proportional to the square of the charge on the ion'.

11. Formation of dipositive ions. The alkaline earth metals neither form +1 nor +3 ions but only +2 ions. The reason is as follows:

Although the energies required to vaporise and ionise these metal atoms to form M^{2+} ions is very high yet high lattice energies in their solid state and high hydration energies of M^{2+} (aq) ions compensate for it. Thus these metals form dipositive ions only in aqueous solutions.

Bipositive ions are diamagnetic. It is because, these ions have stable noble gas configuration and have no unpaired electron.

Bipositive ions are colourless. It is because, these ions have stable noble gas configuration and no electronic transition takes place in their visible region. If acid radical is coloured, then these ions form coloured salts. These metals do not form +3 ions.

Reason for not forming +3 ions

The reason is that bipositive alkaline earth metal ions have noble gas configuration due to loss of two s-valence electrons. In order to form +3 ions, the third electron has to be pulled out from the noble gas core. For this purpose, very high energy is needed which is not available in ordinary chemical reactions. Thus, these metals do not form +3 ions.

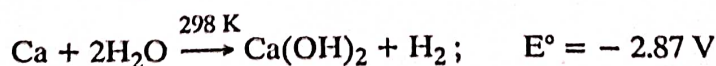
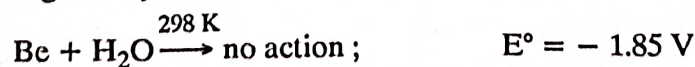
Trend down the group

As we go down the group from beryllium to barium, the size of the atoms increases regularly. Thus, the first and second ionisation energies of elements decrease and reactivity of elements increase regularly.

Radium has higher first and second ionisation energies than barium. It is also slightly less reactive than barium.

Reason. Radium comes after the lanthanide series of elements in the periodic table. The size of radium, thus, decreases because of lanthanide contraction. This decrease in size, results in the increase of ionisation potential and less reactivity of radium than barium.

12. Reducing agent. All the alkaline earth metals have high negative value of standard electrode reduction potential, E° (Table 3.3) in their aqueous solution. Greater the negative value of E° , stronger will be the reducing agent. Their high negative value of E° is responsible for their vigorous action with dilute acids, $[\text{H}^+(\text{aq})]$ to give hydrogen. Elements like calcium, strontium, barium and radium which have very high negative value of E° , react vigorously even with water to form hydrogen.



Trend down the group. As we go down the group, the negative value of their standard reduction potential, E° goes on increasing. Thus, their power to act as reducing agent and hence reactivity goes on increasing down the group.

13. Colouration to the flame. Except beryllium and magnesium, all these elements impart colour to the bunsen flame. When energy is supplied to these elements or their salts (specially chlorides because of their more volatile nature), their electrons get excited to higher energy states as alkali metals do under similar conditions. When such electrons fall back to their original energy level, the extra energy is emitted in the form of visible light.

For the same excitation energy (of bunsen flame), the energy level to which the electron in Ca (higher I.E.) rises, is lower than the level to which the electron in Sr (lower I.E.) rises and this in turn is lower than the level to which the electron in Ba rises and so on. As a result :

(i) When the electron returns to the ground state, the energy released is lowest in Ca and increases in the order, Ca \rightarrow Ra.

(ii) The frequency of light emitted in the bunsen flame will be minimum in case of calcium (and thus, it will impart brick red colour to the flame). It increases in the order Ca \rightarrow Ra. Thus the colour of flame is crimson red in Sr and grassy green in barium.

Beryllium and magnesium do not impart any colour to the flame because these have very small size and very high ionisation energies. The energy of the flame is not sufficient to excite their electrons to higher energy levels. Hence, these do not impart any colour to the flame.

CHEMICAL REACTIVITY AND TRENDS

The alkaline earth metal ions are smaller in size and have increased charge as compared to alkali metal ions. So their metal ions are better polarizers or distorters than the latter. Their size increases while polarising power decreases down the group. Thus, their compounds tend to become more and more ionic down the group.

Thus : (a) Beryllium tends to become covalent in its compounds.

(b) Magnesium tends to be partly ionic in some compounds and is covalent in others.

(c) Calcium, strontium, barium and radium show the following trends down the group in their physical and chemical properties.

(i) Since the ionisation energy of elements decreases down the group, their rate of reaction with hydrogen increases.

(ii) Thermal stability of their carbonates, nitrates and peroxides increases down the group.

(iii) The tendency of their crystalline salts to form hydrates increases.

(iv) Except fluorides, the solubility of their halides, nitrates and sulphates decreases.

(v) The solubility of their halides in ethyl alcohol decreases.

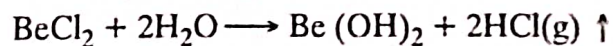
(vi) The solubility of the compounds of alkaline earth metals in water is less than those of alkali metals.

Reason. Due to smaller size and higher charge (+2) of alkaline earth metals than alkali metals (larger size and charge +1), the lattice energy of alkaline earth metal compounds is more than that of alkali metals. Greater the lattice energy, lesser the solubility of compounds in water. Hence alkaline earth metal compounds are less soluble in water than alkali metal compounds.

Reactivity. Due to their low ionisation energies and electronegativities, alkaline earth metals are highly reactive. However, these are less reactive than alkali metals.

(ii) Beryllium halides are covalent and soluble in organic solvents. The other halides are electrovalent and hence are readily soluble in water. Except BeF₂, the fluorides of other elements are insoluble. The solubility of BeF₂ is because of the large hydration energy of Be²⁺ ion which more than compensates the large value of lattice energy.

(iii) The anhydrous halides of alkaline earth metals are hygroscopic. Halides of beryllium fume in air due to the formation of HCl gas during its hydrolysis and form acidic solutions. On the other hand, halides of other group 2 elements dissolve in water producing neutral solutions.



Halides of alkaline earth metals combine with water to form hydrates such as MgCl₂·6H₂O, CaCl₂·6H₂O. Based on this property, anhydrous CaCl₂ is used as a dehydrating agent.

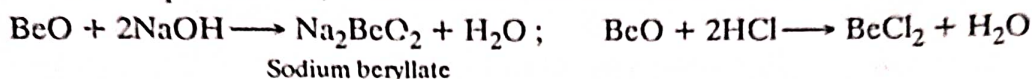
(iii) As already described, chlorides of alkaline earth metals (except Be and Mg) impart characteristic colour to the flame.

3. Reducing properties. These elements are strong reducing agents because of their negative reduction potential. The reduction potential becomes more negative as we go down the group from Be to Ba. Hence reducing character increases from Be to Ba.

COMPOUNDS OF ALKALINE EARTH METALS

Oxides. (i) State. These oxides are white crystalline solids.

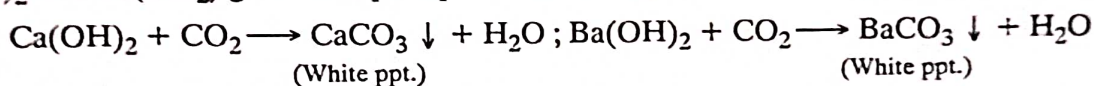
(ii) Basic nature. As we go down the group, the electronegativity and ionisation energy decreases down the group, but ionic radius increases. Due to their combined effect, the bond $M - O - H$ breaks between M and oxygen to give OH ions. Thus, the basic character of their oxides and hydroxides increases down the group. Beryllium oxide is amphoteric *i.e.*, it forms salts with acids as well as alkalis



(iii) Solubility in water. Due to small size of Be^{2+} and Mg^{2+} ions, the oxides of beryllium and magnesium are tightly held together in the solid state. So, these are insoluble in water. The oxides of higher metal oxides (Ca, Sr, Ba) are soluble in water and form hydroxides $[\text{M}(\text{OH})_2]$ which are strong bases.

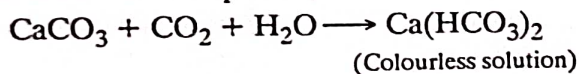
Alkaline earth metal hydroxides are less basic than alkali metal hydroxides. It is because of smaller ionic size, higher ionisation energy and higher charge (bipositive) in alkaline earth metals than alkali metals.

(iv) $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ give white precipitate when CO_2 is passed through them.



This reaction can be used to detect and estimate CO_2 .

If excess of carbon dioxide is passed, the insoluble carbonates change into soluble bicarbonates as



Anomalous behaviour of beryllium oxide. It is amphoteric in nature while hydroxides of other metals are basic.

(a) BeO is basic as it reacts with concentrated strong acids to form $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$.

(b) BeO is acidic as it reacts with strong bases to form $[\text{Be}(\text{OH})_4]^{2-}$.

$[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ is an acid. The reason is that small size and high charge on Be^{2+} ions causes very intense electric field around it. As a result, Be^{2+} ions withdraw the electrons from surrounding water molecules and polarize them. This facilitates the removal of protons (H^+ ions) from water molecules and helps to form $[\text{Be}(\text{OH})_4]^{2-}$. Thus, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ is an acid.

$[\text{Be}(\text{OH})_4]^{2-}$ ion is a base because it has a tendency to accept protons.

(iv) Structure. BeO has wurtzite (4 : 4) structure while the other normal oxides (MO) have sodium chloride (6 : 6) structure.

Relative basicity of metal oxides. As we go down a group, the size of an atom increases with the increase in atomic mass of the atom. Since the charge on the metal atom remains the same in the group, the *charge to size ratio decreases and basicity increases*.

Consider the oxides of group 2 elements (BaO, MgO, CaO, SrO and BaO). Their basicity increases down the group because their charge to size ratio decreases. Thus :

BeO is amphoteric, MgO is weakly basic while CaO, SrO and BaO are increasingly basic.

All hydrides act as reducing agents. The reducing character increases down the group. It is because as we go down the group, the size of central metal ion increases and $M - H$ bond length increases. Longer the

bond, weaker it is. So, the tendency of hydrides to lose H-atom increases down the group. So, reducing character increases down the group.

HALIDES

Solubility. Except BeF_2 , all alkaline earth metal fluorides are insoluble in water because of their large value of lattice energies.

Periodic trend. Except beryllium, the chlorides, bromides and iodides of alkaline earth metals are fairly ionic. Their ionic character increases with increase in size of cation down the group.

Melting and boiling point. Due to small size of Be^{2+} ion, BeCl_2 is covalent and hence has lower melting and boiling point than other alkaline earth metal chlorides. Being covalent, BeCl_2 is soluble in organic solvents like ether.

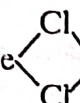
Structure. BeCl_2 has different structures in different states. For example :

(i) In vapour state, it exists as a dimer and has bridged structure. At about 1200 K, it dissociates to give triatomic molecules. In this state, the dipole moment of BeCl_2 is zero. It suggests that Be-atom in BeCl_2 is *sp* hybridised and has linear structure.

(ii) In solid state. In this state, BeCl_2 has following polymeric chain structure (fig. 3.4).

In this structure :

(i) ClBeCl bond angle is 98° instead of $109^\circ 28'$. So coordination about the beryllium atom is *irregular tetrahedron*.

(ii) Adjacent Be  Be planes are at 90° to each other.

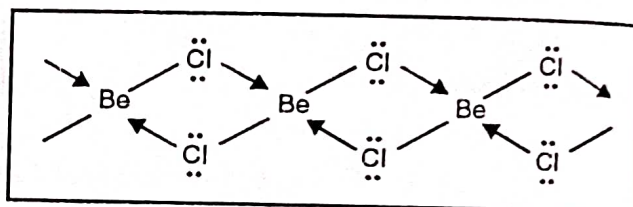


Fig. 3.4.

(iii) Most of the alkaline earth metal halides crystallise in the **fluorite type structure** in their anhydrous state.

Periodic trend. As we move along a period, the size of the element decreases. Thus, the covalent character of the halides of these elements increases while ionic character decreases. For sample, LiF is more ionic than BeF_2 .

As we move down the group, the size of the element increases. Thus, the covalent character of the halides of these elements decreases while ionic character increases. For example, KCl is more ionic than NaCl.

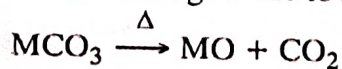
CARBONATES

As we go down the group 2, the size of the metal ion increases. Greater the ionic size, smaller is the hydration of positive ion.

Hence the **solubility of their carbonates decreases**. This behaviour is in opposition to that of hydroxides and fluorides.

Stability of carbonates. The size of carbonate ion (CO_3^{2-}) is so large ($= 3 \text{ \AA}$) that even the small sized cations do not affect their lattice energies to much extent. Thus, the carbonate lattices of alkaline earth metals become only slightly less stable with the increase in their cationic size.

On heating, the metal carbonates give rise to metal oxides.



[M = Alkaline earth metal]

Since the size of oxide ion and cation are quite comparable, the lattice energy of metal oxide is affected by the size of the cation. It is observed that *smaller the size of cation, greater is the stability of metal oxide*.

From this it is clear that

(i) the carbonates of smaller cations decompose to give oxides with low absorption of heat as compared to cations of larger size.

(ii) smaller the size of cation, greater is the stability of alkaline earth metal oxide and easier is the decomposition of its carbonates. Thus MgCO_3 decomposes at a lower temperature than CaCO_3 .

Their sulphates are stable to heat

8. **Complex formation.** Group-2 elements have a great tendency to form complexes because of their small size (of dipositive ion) and high charge. Chlorophyll which acts as a photosensitiser in the photosynthesis process is a complex compound of magnesium. The greater tendency of alkaline earth elements to form complexes is more than that of alkali metals. It is because the alkali metals as well as their monovalent ions are larger in size than alkaline earth metals and their ions.

ANOMALOUS BEHAVIOUR OF BERYLLIUM

(a) **Difference between beryllium and other members of the family**

Beryllium, the first member of the family, differs from other alkaline earth metals due to the following reasons:

- (i) It has extremely small size.
- (ii) It has high electronegativity and I.P. as compared to other family members.
- (iii) It has no vacant *d*-orbitals in its valence shell.

The main points of difference between Be and other members of the family are given in the following table by taking Mg as representative of other alkaline earth metals.

Difference Between Be And Mg

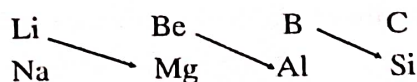
	Property	Beryllium	Magnesium
1.	Hardness	Hard	Soft
2.	M. pt. and B. pt.	High	Low
3.	Nature of compounds	Usually covalent due to much less electro-positive and metallic nature than Mg	Mainly ionic
4.	Action of H ₂ O	No action	Forms MgO and H ₂ with boiling water
5.	Action with N ₂	Forms volatile nitride	Forms non-volatile nitride
6.	Nature of hydroxides and oxides	Amphoteric	Basic
7.	Nature of carbides	Forms methane $\text{Be}_2\text{C} + 4\text{H}_2\text{O} \rightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$	Forms acetylene $(\text{C}_2\text{H}_2) : \text{MgC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{C}_2\text{H}_2$
8.	Action with acid	No action	Forms H ₂ with acids $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$
9.	Tendency to form complexes	Yes	No (except in chlorophyll)

DIAGONAL RELATIONSHIP

The elements of the second period which are diagonal to the elements of third period are called diagonal elements. For example, Li, Be, B, C... elements are diagonal to Mg, Al, Si... respectively. The similarity between lithium (the first member of alkali metals) and magnesium (the second member of group 2) is called diagonal relationship.

Second period elements

Third period elements



Reasons for diagonal relationship

1. **Size and charge effect-similar polarising power of ions.** (a) *When sizes of ions are close.* The diagonal relationship arises because of the effects of charge and size. As we move down a **group**, the size of the ion increases and charge on the ion decreases. This causes **decrease** in the **polarising power** of ions. As we move **along a period** from left to right, the charge on the ions increases but their size decreases. This causes an **increase in the polarising power of the ions**. This results in the similar polarising power and hence similar behaviour of diagonally opposite elements. For example, lithium is smaller in size than sodium (of the same group). Also, magnesium (of group 2, and period 3) is smaller in size than sodium (of group 1 and period, 3). Thus Li and Mg have similar size value. It is clear from the sizes of Li⁺ (76 pm) and Mg⁺² (72 pm) ions which are very close to each other. Thus in case where size is important, their behaviour should be similar.

(b) When sizes of ions are not so close but the charge per unit area is similar. Beryllium and aluminium also show diagonal relationship. In this case, the charge per unit area is similar (Be^{2+} , 2.36 and Al^{3+} , 2.50) but the sizes are not so close ($\text{Be}^{2+} = 45 \text{ pm}$ $\text{Al}^{3+} = 53.5 \text{ pm}$) because the charges are + 2 and + 3 respectively.

$$\text{Charge per unit area} = \frac{\text{Ionic charge}}{\frac{4}{3} \cdot \pi (\text{ionic radius})^2} \quad \dots(1)$$

After substituting the values of ionic charge and ionic radius in relation (1) for Be^{2+} and Al^{3+} ions, charge per unit area for Be^{2+} and Al^{3+} are found to be 1.18 and 2.08 respectively which are very close to each other.

2. **Electronegativity values.** It has also been suggested that diagonal relationship arises because of the diagonal similarity in electronegativity values. It appears true because ionic charge and electronegativity are closely related to each other.

(i) Elements of second period.	Li	Be	B	C
Electronegativity values	1.0	1.5	2.0	2.5
(ii) Elements of third period.	Na	Mg	Al	Si
Electronegativity values	0.9	1.2	1.5	1.8

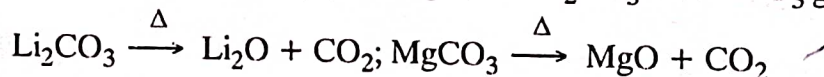
3. **Similar electropositive character.** As we go down a group, the electropositive character of elements increases while it decreases along a period. This results in the similar electropositive character of diagonally opposite elements. So, diagonally, opposite elements resemble in properties.

DIAGONAL RELATIONSHIP OF LITHIUM WITH MAGNESIUM

Lithium resembles more with diagonally opposite element magnesium than its congeners.

It is clear from the following characteristics :

- (i) Ionic radius of Li^+ ($= 0.60 \text{ \AA}$) is almost same as that of Mg^{2+} ($= 0.65 \text{ \AA}$)
- (ii) Electronegativity of Li ($= 1.00$) is almost similar to that of Mg ($= 1.20$)
- (iii) Boiling point of lithium ($= 1610 \text{ K}$) is comparable to that of Mg ($= 1375 \text{ K}$)
- (iv) Like magnesium, lithium is also a hard metal.
- (v) Atomic radius of Li (1.225 \AA) is comparable to that of Mg ($= 1.36 \text{ \AA}$)
- (vi) Polarising power [$= \text{Ionic charge}/(\text{ionic radius})^2$] of lithium and magnesium is similar.
- (vii) As MgCO_3 and $\text{Mg}(\text{NO}_3)_2$ on heating gives MgO, the Li_2CO_3 and LiNO_3 give Li_2O on heating



- (viii) Both elements combine with carbon to form carbides.
- (ix) Chlorides of both (LiCl , MgCl_2) are soluble in organic solvents like alcohol.
- (x) Covalent compounds of lithium (lithium aluminium hydride, LiAlH_4) and magnesium (RMgX) are soluble in ether.

(xi) Like $\text{Mg}(\text{OH})_2$, lithium hydroxide (LiOH) is sparingly soluble in water, less basic and decomposes on heating to give oxide (Li_2O).

(xii) Both burn in oxygen to form oxides (Li_2O , MgO).

(xiii) Both form ionic nitrides when heated in an atmosphere of nitrogen.



(xiv) Atomic volume of lithium ($= 12.97 \text{ ml}$) is similar to that of magnesium ($= 14.00 \text{ ml}$).

(xv) Enthalpies of vaporisation (ΔH_v) of both the elements are comparable.

(xvi) Li^+ ion being the smallest in size, gets heavily hydrated just like Mg^{2+}

(xvii) Fluorides, carbonates and phosphates of both elements are insoluble in water.

(xviii) Lithium perchlorate (LiClO_4) and magnesium perchlorate [$\text{Mg}(\text{ClO}_4)_2$] are soluble in water.

DIAGONAL RELATIONSHIP OF BERYLLIUM WITH ALUMINIUM

Following are some important points of similarity for beryllium and aluminium elements :

1. Similar deforming or polarising power. The charge/radius ratio for Be^{2+} and Al^{3+} ion is almost the same.

	Be	Al
(a) Charge on ion	+2	+3
(b) Ionic radius (Å°)	0.31	0.50
(c) Charge/radius	$\frac{2}{0.31} = 6.4$	$\frac{3}{0.50} = 6.0$

Since charge/radius ratio is a measure of deforming power, so deforming power of both Be^{2+} and Al^{3+} ions is the same.

Hence beryllium and aluminium resemble in properties.

2. Both elements have same enthalpy of vaporisation (= 292.9 kJ), electronegativity (= 1.5), reduction potential ($E^\circ \text{Be}^{2+}/\text{Be} = -1.78 \text{ V}$) ; $E^\circ \text{Al}^{3+}/\text{Al} = -1.67 \text{ V}$) and occurrence in nature as beryl ($3 \text{ BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$).

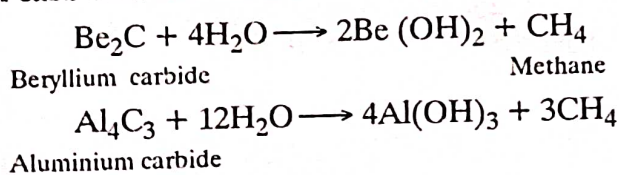
3. Beryllium dissolves in alkali (say NaOH) to form beryllate ion, $[\text{Be}(\text{OH})_4]^{2-}$ ion while Al gives $[\text{Al}(\text{OH})_6]^{3-}$ ion.

4. Be and Al both form fluoro-complex anions, BeF_4^{2-} and $[\text{AlF}_6]^{3-}$ in solution. The congeners of Be do not form such complexes.

5. BeCl_2 is covalent and possesses a bridged polymeric structure. Similarly aluminium trichloride is covalent and forms a bridged dimer, Al_2Cl_6 . Both chlorides are soluble in organic solvents, behave as strong Lewis acids and act as catalysts in Friedel and Craft reaction.

6. Action of Conc. HNO_3 . Both Be and Al are resistant to attack by concentrated nitric acid. It is because of the formation of inert and impervious oxide film on their surface. Other members of Be group react with conc. HNO_3 to give nitrates.

7. Hydrolysis of carbides. The carbides of beryllium and aluminium give methane gas on hydrolysis.



Other members of Be-family behave differently.

8. Out of the oxides of group 2 elements (alkaline earth elements), only beryllium oxide is extremely hard, has very high melting point, is amphoteric and non-volatile in nature. Aluminium behaves similarly.

DIAGONAL RELATIONSHIP OF BORON AND SILICON

Due to similar size, electropositive character and polarisation power, boron and silicon have the following common characters.

(i) Both occur in nature as oxo-compounds. For example, borates and silicates.

(ii) Their density is almost same. ($\text{B} = 2.34 \text{ gm/cc}$; $\text{Si} = 2.35 \text{ gm/cc}$).

(iii) Their electronegativity is almost same ($\text{B} = 2.0$; $\text{Si} = 1.8$).

(iv) B – O and Si – O bonds are of similar strength.

(v) Both exist in *amorphous and crystalline states*.

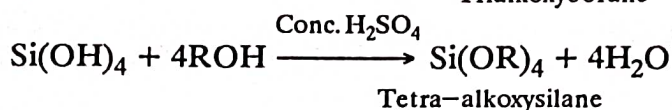
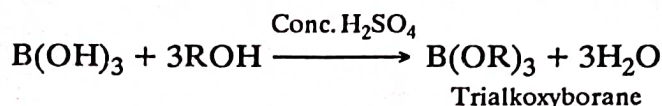
(vi) Both are *non-metals*.

(vii) *Boiling point* of both is almost same *i.e.* $\approx 2600^\circ\text{C}$.

(viii) Oxides of both have macromolecular structure and are soluble in alkaline solutions.



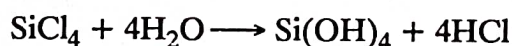
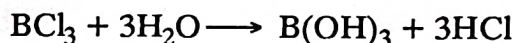
(ix) Acids of both when heated with alcohol (ROH) and conc. H_2SO_4 form *volatile ethers*.



(x) Acids of both are weak (K_a for

$$\text{H}_3\text{BO}_3 = 6.0 \times 10^{-10}; \text{H}_2\text{SiO}_3 \approx 10^{-10}$$

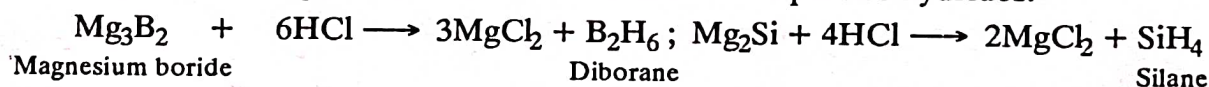
(xi) Halides of both undergo hydrolysis to form respective acids.



(xii) Both have similar but high charge/radius ratio. Thus their compounds have mainly covalent nature.

(xiii) Hydrides of both are gases and burn spontaneously in oxygen.

(xiv) Their magnesium compounds react with HCl to form respective hydrides.



COMPLEXES OF ALKALINE EARTH METAL (GROUP 2) IONS.

The major conditions for the formation of complexes are, small sized highly charged ions with suitable empty orbitals of low energy which can be used for bonding. Group 2 metals form divalent ions which are smaller in size than group 1 monovalent cations. So, group 2 ions form complexes more readily than group 1 ions. Out of group 2 elements, beryllium is appreciably smaller than other elements and hence form many complexes. The tendency to form complexes decreases down the groups.

1. **Complexes of beryllium.** (a) $[\text{BeF}_4]^{2-}$ *i.e.* tetrafluoroberyllate (II) ion. ${}_4\text{Be} = (\text{He})^2 2s^2$ has two unpaired electrons in its excited state $(\text{He})^2 2s^1 2p_x^1 2p_y^0 2p_z^0$. So it can form two covalent bonds.

For example, gaseous BeF_2 molecule is formed when two F-atoms share electrons with half-filled sp -hybrid orbitals of Be-atoms (fig. 3.5).

From the structure of BeF_2 , we see that two $2p$ -orbitals are vacant. So, Be-atom can undergo sp^3 hybridisation and can form $[\text{BeF}_4]^{2-}$ complex ion (tetrahedral). Here two F- ions, each donate an electron pair into an empty hybrid orbital forming two

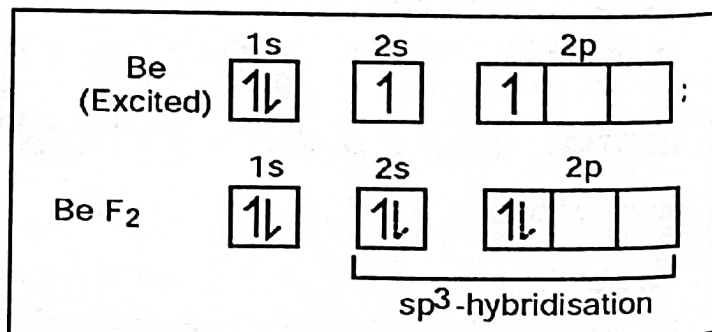


Fig. 3.5

coordinate bonds. Two F-atoms share electrons with half-filled sp^3 hybrid orbitals and form two covalent bonds (fig. 3.6).

(b) **Basic beryllium acetate, $[\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6]$.**

It is formed when $\text{Be}(\text{OH})_2$ is evaporated with acetic acid. Its structure consists of central O-atom surrounded tetrahedrally by four Be-atoms and with six $\text{CH}_3 - \text{COO}$ i.e., Ac groups spanning the edges of the tetrahedron (fig. 3.7). It lacks ionic properties, melts at 283°K, boils at 330°C without decomposition and dissolves in chloroform as the monomer.

Beryllium forms anionic complexes with chelating oxygen ligands. An alkaline solution of catechol dissolves $\text{Be}(\text{OH})_2$ to give a salt (fig. 3.8).

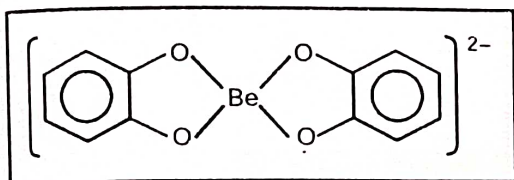


Fig. 3.8

Beryllium forms neutral chelate complexes with oxygen ligands. An example is bis (acetylacetonyl) beryllium i.e. (fig. 3.9). It is prepared by dissolving $\text{Be}(\text{OH})_2$ in dilute acetic acid and treating the solution with acetyl acetone.

(e) Linear chelate polymers such as (fig 3.10) can be prepared.

(f) Be also forms beryllium oxalate complex, $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ anion.

(g) **Beryllium phthalocyanine complex.** Phthalocyanines are one of the earliest classes of synthetic macrocyclic tetramines to be discovered.

Preparation. Beryllium phthalocyanine complex can be prepared with the help of following reaction (fig. 3.11).

In this reaction, the metal ion plays an essential role as a template*.

Characteristics. It has exceptional thermal stability. It undergoes sublimation in vacuum at temperature around 775 K. It is insoluble in polar solvents but its sulphonated derivative is soluble. It is an important pigment.

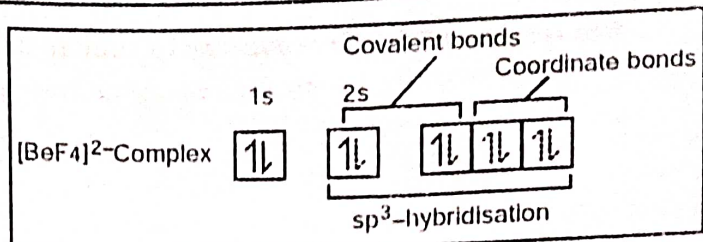
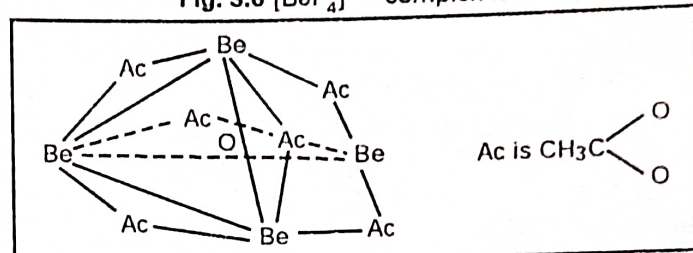

 Fig. 3.6 $[\text{BeF}_4]^{2-}$ complex ion.


Fig. 3.7 Basic beryllium acetate)

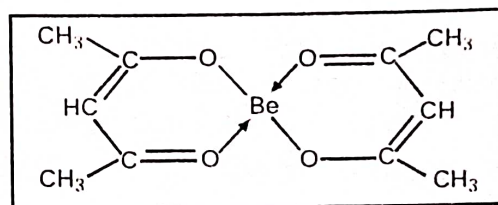


Fig. 3.9

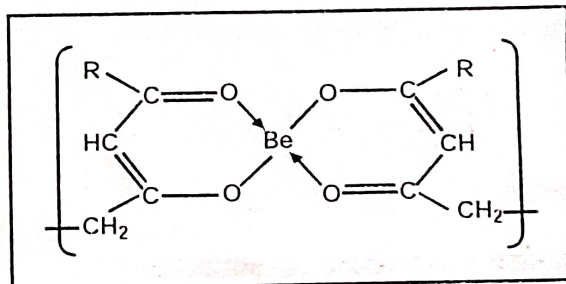


Fig. 3.10

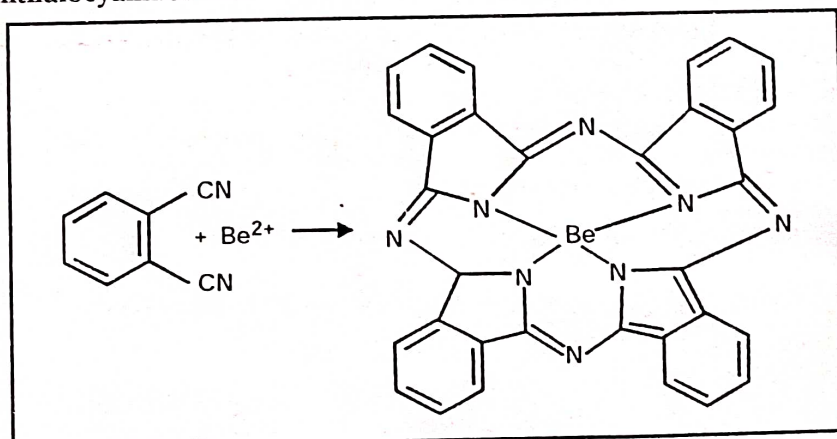


Fig. 3.11

Template means that the molecular structure of a compound that serves as a pattern for the production of the molecular structures of another specific compound in a reaction.

2. Complexes of Mg. The only nitrogen complexes of importance are the magnesium tetrapyrroles, the parent compound of which is porphyrin (fig. 3.12). These conjugated heterocycles provide a rigid planar environment for Mg^{2+} (and similar) ions. The most useful and important of such derivatives are the **chlorophylls** and related compounds which are of utmost importance in photosynthesis in plants.

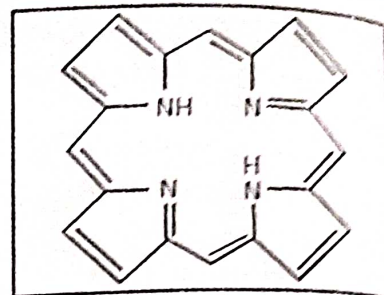
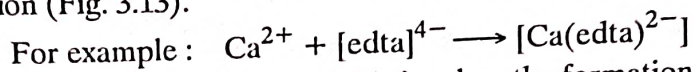


Fig. 3.12 Porphyrin

In such porphyrin compounds, the Mg-atom is formally four coordinated. It also appears that five-coordination is preferred to six coordination as in the case of **magnesium tetraphenylporphyrin hydrate** where the Mg-atom is out of the plane of the N-atoms and is approximately square pyramidal.

3. Oxo-complexes-Complexes of calcium. Oxygen chelate compounds such as ethylene diaminetetracetate (edta) type form complexes with Ca^{2+} ions easily in alkaline solution (Fig. 3.13).



The above complex probably involves the formation of a chelate complex whose stability is enhanced by the presence of 5-membered rings. The complexing of calcium by edta and also by polyphosphates is useful to remove Ca^{2+} ions from water and for the estimation of calcium volumetrically. In

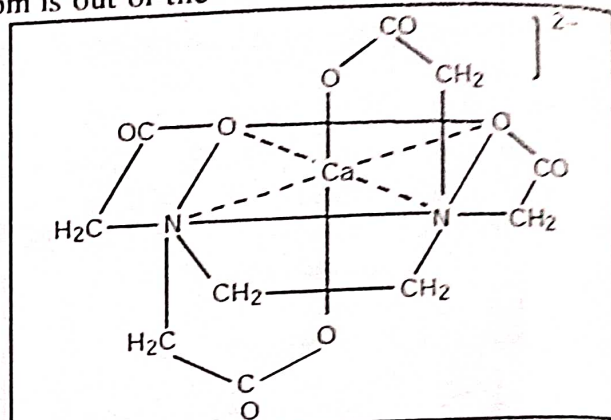
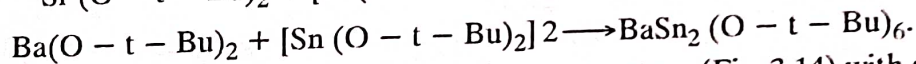
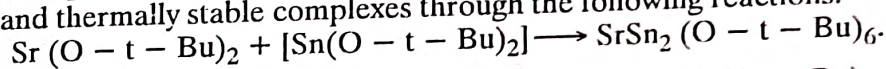


Fig. 3.13 Calcium EDTA complex (binategative ion)

$[Caedta]^{2-} \cdot 7H_2O$, the coordination in the anion is, 8.

4. Complexes of strontium and barium. Both Sr and Ba form petroleum soluble and thermally stable complexes through the following reactions.



The above complexes have a sandwich type structure (Fig. 3.14) with an MO_6 group and trigonal planar oxygen atoms.

Barium forms the green radical anion, $[Ba(NH_3)_2(\text{anthracene})_2]^-$ in liquid ammonia in presence of anthracene.

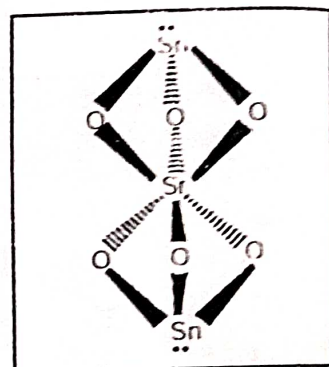


Fig. 3.14

Table 3.4 Some physical properties of group 13 or III A elements.

Property ↓	Elements, Boron, B →	Aluminium, Al	Gallium, Ga	Indium, In	Thallium, Tl
Atomic number	5	13	31	49	81
Electronic configuration	$[2He] 2s^2 2p^1$	$[10Ne] 3s^2 3p^1 + III$	$[18Ar] 3d^{10} 4s^2 4p^1$	$[36Kr] 4d^{10} 5s^2 5p^1$	$[54Xe] 4f^{14} 5d^{10} 6s^2 6p^1$
Oxidation states*	+III (covalent)	(covalent and ionic)	+ III (+1) (Ionic)	+ III (+1). (ionic)	+ III, + I
Ionisation energies (kcal/gm. atom)	1st 190.3 2nd 576.1 3rd 869.7	137.4 431.8 652.4	137.7 435.9 705.3	132.8 387.4 643.7	140.2 458.2 685.0
Total	1636.1	1221.6	1278.9	1163.9	1283.4
Heat of sublimation (kcal/gm atom)	135	77.9	65.3	77.7	42.8
Density (gm/ml)	2.34	2.70	5.90	7.31	11.83
Melting point (°C)	2227	660	29.8	156.2	303.6
Boiling point (°C)	2600	2447	2237	2047	1470
Electronegativity (Pauling scale)	2	1.5	1.6	1.7	1.8
Atomic radii (Å)	(0.80)	1.248	1.245	1.497	1.549
Ionic radii (Å) of M^{3+}	0.23	0.50	0.62	0.81	0.95
Atomic weight	10.81	26.98	69.7	114.82	204.37
Appearance	Black solid	Silvery white metal	Silvery white metal	Silvery white metal	Silvery white metal

*Uncommon oxidation states are given in brackets.

GENERAL CHARACTERISTICS

(a) **Physical properties.** Some physical properties of group III A or 13 elements are given in table 3.4. These properties are discussed below :

1. **Electronic configuration.** The electronic configuration of these elements (table 3.4) shows the presence of three electrons (ns^2np^1) in their valence shell. Thus all these elements are trivalent.

2. **Oxidation states.** (a) **Boron.** B^{3+} ion is not formed. It is because the ionisation energy required to produce B^{3+} ions is very high. It is neither available from the hydration of ions in aqueous solution nor from the lattice energies of its ionic compounds.

(b) **Aluminium.** (i) **In aqueous solution,** Al-compounds form Al^{3+} ions. It is because the hydration energy available from its aqueous solution is greater than its third ionisation energy.

(ii) **In solid state,** Al-compounds do not exist as Al^{3+} ions due to their high lattice energy.

(iii) **In gaseous state,** Al-compounds are covalent. It is because the small size and high charge of Al^{3+} ions give a high charge density to Al.

(c) **Gallium, indium and thallium show + 1 as well as + 3 oxidation states.** These elements have large size and greater screening effect than effective nuclear charge. Thus, these elements have low ionisation energy and lose np^1 valence electron easily and show + 1 oxidation state. The stability of + 1 oxidation states increases while that of + 3 oxidation state decreases down the group due to increase in **inert pair effect** down the group. Thus

(i) Decreasing order of stability of + 1 oxidation states is $Tl^+ > In^+ > Ga^+$

(ii) Decreasing order of stability of + 3 oxidation states is $Ga^{3+} > In^{3+} > Tl^{3+}$

The Tl^+ compounds are most stable and resemble alkali metals as described below :

(i) **Solubility in water.** $TlOH$ as well as $NaOH$, KOH etc. are soluble in water and give alkaline solution.

(ii) **Structure.** TlF has distorted $NaCl$ type structure while other halides have $CsCl$ type structure.

(iii) **Stability.** Salts (CO_3^{2-} , NO_3^- , SO_4^{2-} etc.) of Tl (1) and alkali metals are very stable and show isomorphism.

3. **Ionisation potential (or energy).** The ionisation energies of these elements do not show a regular trend down the group. The order of first ionisation energies in kcal/gm atom down the group are :

$$B(190.3) > Al(137.4) < Ga(137.7) > In(132.8) < Tl(140.2)$$

Reason. The I.E. of $B > Al$ as expected due to large size and greater screening effect than effective nuclear charge of Al than boron. In going from Al to Ga, there are ten first transition series elements. In these elements, the d -subshell is being filled. These intervening d -electrons do not screen the nuclear charge effectively. The effective nuclear charge becomes greater than screening effect in Ga than Al. Hence I.E. of Al is less than Ga. The further trend can be similarly explained on the basis of effective nuclear charge and screening effect.

4. **Atomic radius.** The atomic radii of these elements do not show a regular trend down the group. The order of atomic radii in Å, down the group are :

$$B(0.80) < Al(1.258) > Ga(1.245) < In(1.497) < Tl(1.549)$$

Reason is the same as explained under ionisation energies. *i.e.*, when the effective nuclear charge is greater than screening effect, the atomic radius decreases and *vice versa*.

5. **Ionic radius and electronegativity.** Ionic radii of M^{3+} ions show a regular increase down the group. It is due to regular increase in screening effect of intervening electrons as compared to corresponding effective nuclear charge.

The electronegativity decreases from boron to aluminium and then shows a regular increase upto thallium.

Reason. The effective nuclear charge of small sized B-atom is greater than the screening effect as compared to large sized Al-atom. Thus, B-atom attracts covalent electrons more strongly towards nucleus than Al-atom. Thus, electronegativity of B (2.0) is greater than Al (1.5). The regular increase in electronegativity from Al to Tl is explained on the basis of decrease in I.E. down the group and some structural changes.

6. Density. The density of an element depends upon its oxidation number, atomic weight, atomic volume and packing of atoms. Lesser the empty space between the packing of atoms or molecules in crystals, greater will be the density of the element. The density of IIIA group elements increases regularly down the group. It is indicative of regular decrease in the empty space between the packing of atoms (table 7.4).

7. Metallic nature. The metallic nature *i.e.*, electropositive character of elements increases from boron to aluminium and then decrease from aluminium to thallium.

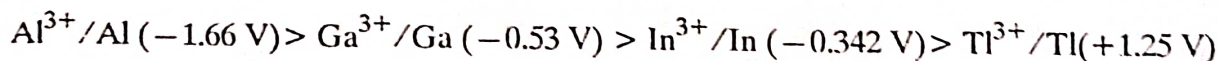
Metallic nature of B < Al. It is due to smaller size and higher ionisation potential of 'B' than Al.

Metallic nature of Al > Ga > In > Tl. Al-element follows after *s* block elements while Ga, In and Tl follow after *d*-block elements. The *s* electrons screen the nucleus more effectively, than *d*-electrons. Thus *d*-orbital electrons are more firmly held than *s*-orbital electrons and metallic character decreases from Al to Tl. The larger value of sum of first three ionisation energies of Ga (1278.9 K cal per gm. atom) than Al (1221.6 K cal/gm.atom) in spite of larger size of Ga confirms the above trend.

8. Melting point, boiling point and heat of sublimation. *The boiling points and heats of sublimation decrease regularly* from B to Tl. It can be explained on the basis of decreasing interatomic attractive forces as we go down the group.

The melting point decreases from B to Ga and increases from Ga to thallium. It can be explained on the basis of structural changes. Since gallium is less metallic than aluminium due to greater effective nuclear charge than screening effect, it exists as Ga₂ molecule. The forces among Ga molecules are weak van der Waal forces. Since less energy is required to separate these forces, Ga has low melting point. From Ga to Tl the atomic size increases regularly. Greater the size greater the surface area, greater the van der Waal forces and greater energy will be required to separate them. Hence melting point increases regularly.

9. Reducing agent. The reducing power of an element is determined by the magnitude of its reduction potential in its acidic or basic solution. Smaller the reduction potential of an element, greater is its reducing power. For example, the decreasing order of the reducing power of IIIA group elements is given below along with their reduction potentials.



DIFFERENCE OF BORON FROM OTHER MEMBERS OF THE FAMILY

Boron differs from other members of its family due to the following reasons.

(i) **Small Size.** Atomic radius (0.8 Å) of boron element is very large as compared to B³⁺ (0.23Å). Since the sum of first three ionisation potentials is extremely high, B³⁺ ions are not formed. The hypothetical B³⁺ ion will have small size and high charge density. Thus, all compounds of boron will be covalent.

(ii) **Trivalency.** ${}_5\text{B} (1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0)$ has one unpaired electron in its valence shell and should be monovalent but it is always trivalent. It is because the energy released in the formation of one B-X bond in BX₃ is high enough to unpair the 2s² electrons (${}_5\text{B} = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$) and cause sp² hybridisation.

(iii) **Maximum covalency is four.** It has no *d*-orbital. Thus, it exhibits maximum covalency of four (say in BF₄⁻). Other elements have *d*-orbitals and exhibit covalency six or more.

(iv) **Strong Lewis acid formation.** ${}_5\text{B} (\text{excited}) = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$ has one 2*p*-orbital vacant. It can thus accommodate one lone pair of electrons in its vacant orbital and attain inert gas configuration.

Thus, it acts as a strong Lewis acid. The Lewis acid character decreases in the order $B > Al > Ga > In$.
 (v) **Inert pair effect.** Boron does not exhibit inert pair effect. This effect increases down the group.

CHEMICAL PROPERTIES

1. Hydrides. The elements of group 13 do not react directly with hydrogen. However, hydrides are formed by indirect method.

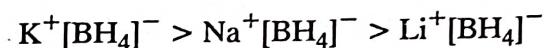
Diborane, B_2H_6 . For details see page 115.

(b) **Hydrides of aluminium.** Aluminium forms polymeric hydrides $(AlH_3)_x$ called alanes. In alanes, the Al-atoms are surrounded octahedrally by six H-atoms. The structure consists of a network of AlH_2Al bridges. The X-ray and neutron diffraction data has confirmed it. It decomposes into its elements on heating. Lithium aluminium hydride, $Li[AlH_4]$ is a useful organic reducing agent and cannot be used in aqueous solutions. It reduces aldehydes and ketones to alcohols and cyanides to amines.

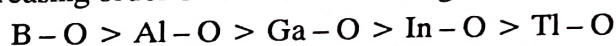
(c) **Gallium** forms GaH_3 called gallane. It is an unstable volatile oil. It also forms compounds analogous to the borohydrides, e.g., lithium gallium hydride, $Li[GaH_4]$.

(d) **Indium** forms polymeric hydride, $(InH_3)_n$ but the existence of thallium hydride, is doubtful.

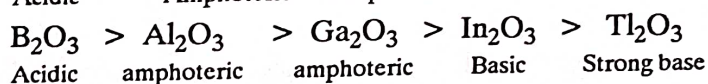
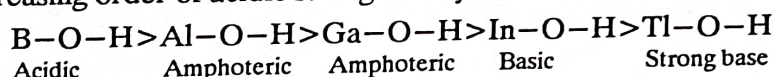
Stability of hydrides. It increases (i) with the increase in the polarising power of cation, and (ii) when extra electron is completely stabilised by the anion. For example, the decreasing order of stability of alkali metal borohydrides is as follows :



2. Oxides and hydroxides. Group 13 elements form trioxides, M_2O_3 . As we move down the group, there is a gradual change from acidic through amphoteric to basic nature of the oxides and hydroxides. It is because, as we go down the group, the atomic size goes on increasing and 'electronegativity and ionisation potential' of the elements go on decreasing. As a result, the bond between $M-O$ in $M-OH$ goes on weakening. Thus the decreasing order of $M-O$ bond strength is



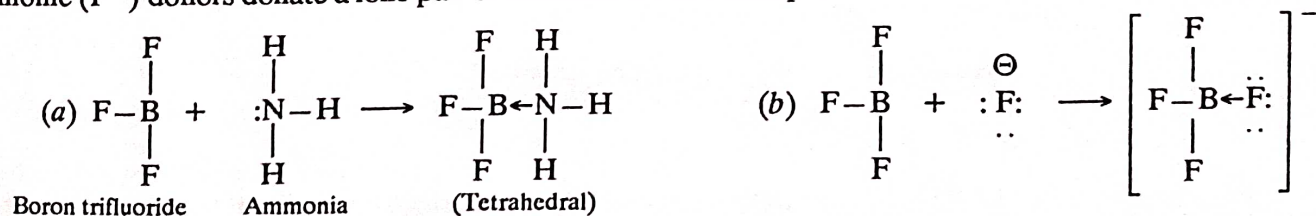
Hence decreasing order of acidic strength in hydroxides and oxides is as follows :



3. Halides. Elements of group 13 form trihalides, MX_3 . These are discussed below :

Halides of boron. Boron forms BF_3 , BCl_3 and BBr_3 . In all these compounds, B-atom is sp^2 - hybridised.

Thus, trihalides are **triangular planar molecules**. B-atom has one empty p -orbital. The neutral ($:NH_3$) or the anionic (F^-) donors donate a lone pair of electrons in this vacant p -orbital and form **tetrahedral complexes**.



It cannot extend its co-ordination number (i.e., number of groups/atoms bonded to central atom) beyond four due to nonavailability of d -orbitals.

Relative Lewis acid strength of BF_3 , BCl_3 , and BBr_3 . Boron halides are converted to their adducts with pyridine. Then, the heats of formation and dipolemoments of these adducts are measured. From the data, it

is observed that the relative electron pair acceptor strength of these halides is in the following order $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$.

On the basis of steric concept and electronegativity concept of F, Cl and Br, the relative electron pair acceptor strength of these halides should be in the order, $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$.

Explanation of anomalous behaviour. The above trend in the acidic strength of boron halides can be explained in terms of boron-halogen π -back bonding. F-atom has filled $2p$ -orbital while B-atom has vacant p orbital of same energy. The filled $2p$ -orbital of F-atom overlaps effectively with vacant $2p$ orbital of B-atom. As a result, $p\pi - p\pi$ dative or back bond is formed. This B-F bond has some double bond character. The various resonating structures of BF_3 are given below (fig. 3.15).

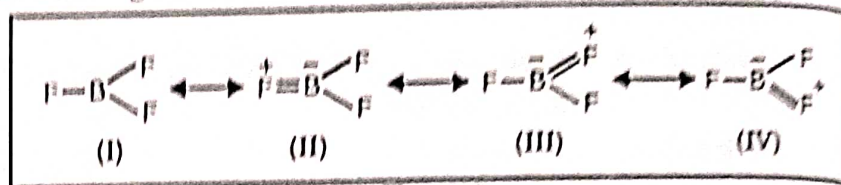


Fig. 3.15.

Due to back bonding (fig. 3.16) electron deficiency of B-atom is compensated to some extent. As a result, Lewis acidity of BF_3 gets decreased. The tendency of back bonding decreases in the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$. It is because the overlap of vacant $2p$ -orbital (lower energy) with filled $3p$ (of Cl-atom) and $4p$ -orbitals of Br-atom (of higher energy) does not take place effectively. Hence the relative Lewis acid strength of BF_3 , BCl_3 and BBr_3 is as follows $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$.

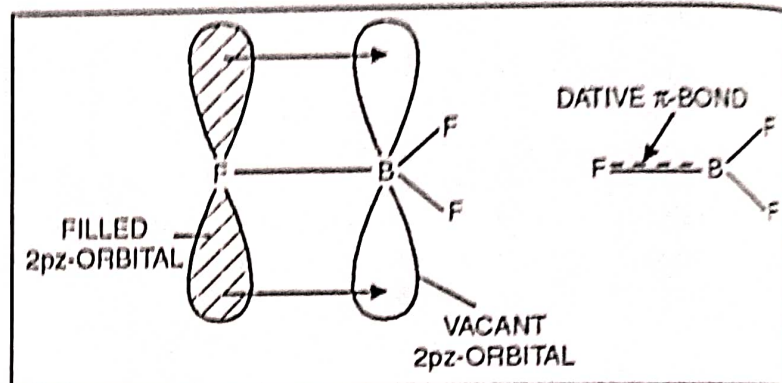


Fig. 3.16.

Relative Lewis acid strength of halides of IIIA group elements. As we go down the group, the size of atoms goes on increasing. As a result, their electron pair acceptor ability (or Lewis acidity) goes on decreasing in the order :

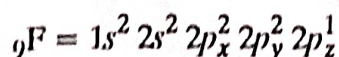
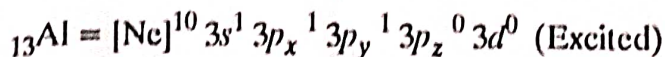
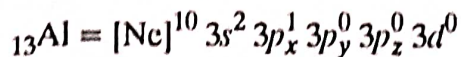


The trihalides of IIIA group elements (*i.e.*, BF_3 , AlCl_3) accept lone pair of electrons from groups containing donor atoms like S, O, N, P etc. These act as catalysts for Friedel-Crafts reactions like alkylation, acylation, polymerisation of olefines and esterification etc.

Boron forms BF_4^- but other elements of group III A form complexes of the type $[\text{AlF}_6]^{3-}$, $[\text{GaCl}_6]^{3-}$, $[\text{InCl}_6]^{3-}$ etc. It is because :

(i) B-atom has no d -orbital. Thus, it cannot extend its co-ordination number more than four.

(ii) Al, Ga, In etc. elements have vacant d -orbitals. Thus, these can extend their co-ordination number of six. For example, consider $[\text{AlF}_6]^{3-}$ formation.



In the formation of $[\text{AlF}_6]^{3-}$ ion, three F-atoms share one electron each with unpaired electrons of Al-atoms while each of F^- ion donates one lone pair of electrons to the vacant p and d -orbitals of Al-atom.

Boron halides exist as monomers but aluminum halides exist as dimers. It is explained as follows :

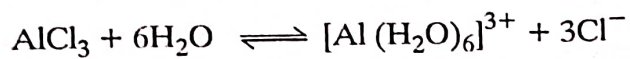
(a) Let BF_3 forms a dimer $\text{F}_3\text{B}-\text{BF}_3$. In this compound, a new B-B bond is formed. Thus energy will be released.

(b) In monomer BF_3 , there is $p\pi - p\pi$ back bonding between boron and fluorine. Due to this additional π - bond, energy is also released.

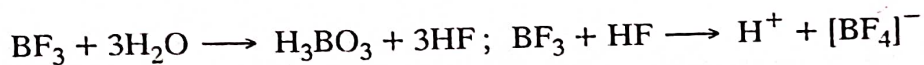
It has been observed that the energy released in the formation of dimer is less than that in monomer. Thus B_2F_6 has more energy and less stability. Hence B_2F_6 does not exist.

Aluminium chloride, aluminium bromide and indium iodides exist as dimers. It is because the big sized Al and In atoms use their vacant valence p -orbitals in vapour state and non-polar solvent in such a way that halogen atoms are arranged tetrahedrally around the central atom. As a result, a stable bridged structure is formed and an octet of electrons is attained (Fig. 3.17).

Nature of bonds. The fluorides of Al, Ga, In and Tl are ionic and possess high melting points. Chlorides, bromides and iodides of these elements are covalent when anhydrous. When dissolved in water, high heat of hydration is evolved. As a result, the dimer breaks to give $\text{M}(\text{H}_2\text{O})_6]^{3+}$ and 3X^- ions.



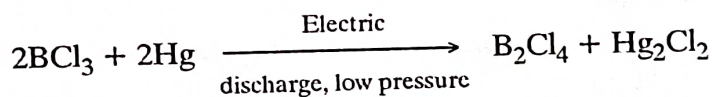
The boron halides also undergo hydrolysis. The fluorides form fluoroborates while other halides form boric acids.



BX_3 halides attain inert gas configuration *i.e.*, octet by back π -bonding. Elements other than boron are larger in size and are unable to have effective π -overlap.

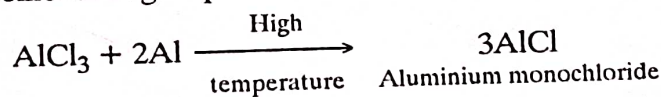
Thus, to attain octet, these undergo polymerisation.

Dihalides. Boron forms dihalides of the type B_2X_4 . B_2Cl_4 is formed by passing electric discharge through BCl_3 and Hg.



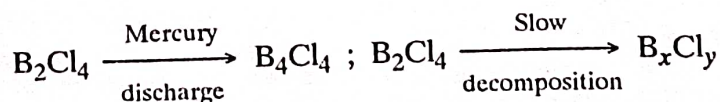
It is planar in solid state and non-eclipsed in liquid and gaseous state. Gallium forms dihalide (GaCl_2), which is written as $\text{Ga}^+[\text{GaCl}_4]^-$. It contains Ga(I) and Ga(III). Indium behaves similarly. Thallium forms univalent thallic halides which are more stable than trivalent thallic halides.

Monohalides. All elements of group IIIA form monohalides (MX) at high temperature.



MX compounds are covalent and are less stable. However, Tl^+F^- is ionic. Boron forms stable polymeric monohalides $(\text{BX})_n$.

For example :



where $x = y = 8, 9, 10, 11, 12$.

Complexes. Due to small size and increased charge, group IIIA elements form.

(i) Tetrahedral hydrides of the type $\text{Li}[\text{AlH}_4]$, $\text{H}[\text{BF}_4]$.

(ii) Octahedral complexes of the type $[\text{GaCl}_6]^{3-}$, $[\text{InCl}_6]^{3-}$ and $[\text{TlCl}_6]^{3-}$

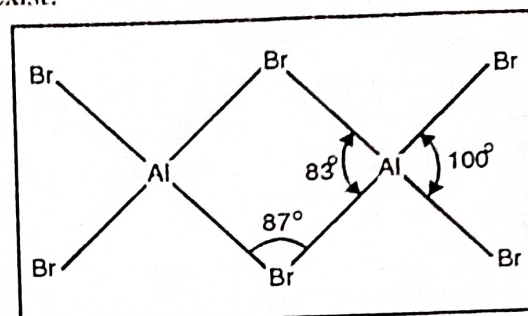


Fig. 3.17.