

10. The most stable complexes would be formed by the highly polarising cations. Li^+ being the most polarising cation of all the alkali metals, forms larger number of complexes than the other Group 1 metals.

UNIT 5 ALKALINE EARTH METALS

Structure

- 5.1 Introduction
 - Objectives
- 5.2 Occurrence, Extraction and Uses
- 5.3 General Characteristics
 - Physical Properties
 - Chemical Properties
 - Complexation Behaviour
- 5.4 Anomalous Nature of Beryllium
- 5.5 Summary
- 5.6 Terminal Questions
- 5.7 Answers

5.1 INTRODUCTION

In the previous unit, you studied the general characteristics of Group 1 elements, i.e., alkali metals and their compounds. Group 1 and Group 2 elements belong to the *s*-block of the periodic table, as they have ns^1 and ns^2 outer shell electronic configuration, respectively. *s*-Block elements are known to be very reactive metals and generally form ionic compounds. In this unit you will study the elements of Group 2 consisting of beryllium, magnesium, calcium, strontium, barium and radium. Elements Ca, Sr, Ba and Ra are called **alkaline earth metals** because their earths (earth is the old name for a mineral oxide) are alkaline in nature. However, beryllium is not counted as an alkaline earth metal since its earth is not alkaline. Like the Group 1 elements, they show a distinct group relationship in which similarities between the elements are more pronounced than the differences between them. The first member of the group is 'anomalous' (cf. lithium). In this unit, we will study the general characteristics and chemistry of this group of elements.

Objectives

After studying this unit you should be able to:

- describe the general trend in the properties of the Group 2 elements,
- explain chemistry of the Group 2 elements,
- correlate the complexation behaviour of these elements, and
- explain why and how beryllium differs from the rest of the members of the group.

5.2 OCCURRENCE, EXTRACTION AND USES

The alkaline earth metals, like alkali metals are very reactive, therefore, do not occur free in nature. All of them are found in the form of their salts. These metals are strong reducing agents and, therefore, it is very difficult to obtain them by chemical reduction methods. All of these find some or the other use in industry. Let us now study their occurrence, extraction and uses in this section.

Occurrence

Beryllium, the first member of the group is found in small quantities in the silicate mineral, phenacite, Be_2SiO_4 and beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Magnesium (2.76%) and calcium (4.66%) are among the eight most abundant elements in the earth's crust. Magnesium (0.13%) is the second most abundant metallic element next only to sodium (chloride) in sea water. It occurs as magnesite, MgCO_3 ; dolomite, $\text{MgCa}(\text{CO}_3)_2$; kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ and carnallite, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ in the earth's crust. Calcium occurs extensively as calcite and lime-stone (CaCO_3) in many mountain ranges. Calcium and magnesium are very important biologically too. Calcium is found in the bones of animals and human beings. Magnesium is found in the green pigment, viz., chlorophyll of the plants. Strontium (0.038%) and barium (0.039%) are much less abundant and occur as carbonates and sulphates. These metals are well known because they occur as concentrated ores and are easy to extract. Radium is extremely scarce ($10^{-10}\%$) and it is a radioactive element.

The gem stone, emerald, is beryl, the green colour being due to the presence of chromium.

Extraction

These metals are extracted by electrolysis of their fused chlorides, though magnesium has been manufactured by the carbon reduction of its oxide also. Thus, beryllium is obtained by the electrolysis of molten beryllium chloride. However, sodium chloride must be added to the melt as an electrolyte because BeCl_2 is covalent and, therefore, is a very poor electrical conductor. During the electrolysis, the less active metal, Be, is produced at the cathode and Cl_2 is evolved at the anode. Calcium is extracted from fused calcium chloride using anode of graphite and cathode of iron. Strontium chloride and barium chloride are used for the extraction of strontium and barium, respectively.

Uses

Beryllium is used for making atomic fuel containers because it absorbs very few neutrons and does not become radioactive. Being transparent to X-rays, it is used as a window material in X-ray apparatus. It has a number of uses as alloys, e.g., when mixed with Cu, Be increases the strength of Cu sixfold. Beryllium alloys are non-sparking, therefore, these are used in making hand tools for use in the petroleum industry. Magnesium, because of its lightness, is used as a construction alloy material, e.g., in aircrafts. For this purpose, it is alloyed with aluminium. Magnesium is used as a reducing agent in the extraction of some metals like titanium and uranium. It forms Grignard reagents, RMgX , which are important organic reagents. Calcium, strontium and barium as free metals do not find extensive uses because they are very reactive. Calcium oxide (quick lime) is a constituent of glass, mortar and portland cement. Thus, it finds extensive use in industry.



Mme. Marie Skłodowska Curie, 1867-1934. She got Nobel Prize in 1911 for discovering and isolating radium.

5.3 GENERAL CHARACTERISTICS

All the Group 2 elements have two electrons in their outermost orbital. Their outer orbital electronic structures may be written as $2s^2$, $3s^2$, $4s^2$, $5s^2$, $6s^2$ and $7s^2$ for Be, Mg, Ca, Sr, Ba and Ra, respectively. Because of their similar outermost electronic configuration, they show more or less similar properties. However, beryllium being the first element of the group, shows considerable differences from the rest of the elements of the group and exhibits diagonal relationship with aluminium in group 13. In this section we will discuss in brief the physical and chemical properties, solubility and complexation behaviour of these elements.

5.3.1 Physical Properties

The alkaline earth metals are quite soft metals, but are harder than the corresponding Group 1 elements. This is because of their two valence electrons which participate in metallic bonding. They are good conductors of electricity. In pure form they are silver coloured, but on exposure to atmosphere, the silvery lustre is lost, because of the formation of oxide layer on the surface of the metal. Their physical properties are given in Table 5.1.

Table 5.1: Properties of the Group 2 metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra	
Atomic Number	4	12	20	38	56	88	
Electronic configuration	$[\text{He}]2s^2$	$[\text{Ne}]3s^2$	$[\text{Ar}]4s^2$	$[\text{Kr}]5s^2$	$[\text{Xe}]6s^2$	$[\text{Rn}]7s^2$	
Atomic weight	9.012	24.312	40.08	87.62	137.34	226.02	
Ionic radius (pm)	31	65	99	113	135		
Covalent radius (pm)	89	136	174	191	198		
Boiling point (K)	3243	1380	1760	1607	1413	1700	
Melting point (K)	1553	934	1118	1062	998	700	
Enthalpy of hydration (kJ mol^{-1})	-2455	-1900	-1565	-1415	-1275		
Density ($10^3 \times \text{kg m}^{-3}$)	1.85	1.74	1.54	2.6	3.62	5.5	
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9	
Ionisation energy (kJ mol^{-1})	I	900	738	590	549	502	509
	II	1757	1450	1146	1064	965	975

The atoms of the alkaline earth metals are smaller than those of the corresponding Group 1 elements. This is because of the increase in effective nuclear charge with the increase in

atomic number. Due to increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the nucleus, thereby reducing the size of the atom. Similarly, their ionic radii are also smaller than those of Group 1 elements, because the removal of two orbital electrons increases the effective nuclear charge even further.

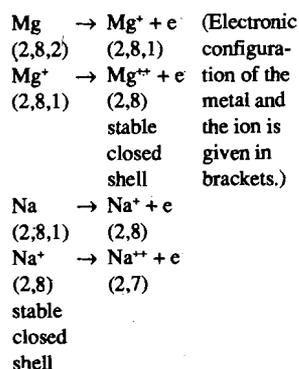
These elements are denser than Group 1 metals because they have two valence electrons per atom for bonding the atoms into a metallic lattice and as a result more mass can be packed into a smaller volume. The density decreases slightly on moving down the group from Be to Ca but increases considerably thereafter up to Ra.

The atomic and ionic radii increase from Be to Ra due to the effect of extra shells of electrons being added. This outweighs the effect of increased nuclear charge.

Group 2 metals have higher melting points when compared to the Group 1 metals. The reason being +2 charge on the cations in the metallic lattice, causing them to be more strongly attracted to the 'sea of electrons' and making it difficult to pull them apart.

The first ionisation energy (Table 5.1) of alkaline earth metals is more than that of corresponding alkali metals. This is because the alkaline earth metals have higher effective nuclear charge and are smaller in size, thereby the electrons are more tightly held to the nucleus. The second ionisation energy of these elements is almost twice their first ionisation energy. This is because once one electron has been removed, the effective nuclear charge felt by orbital electrons is increased, so that the remaining electrons are more tightly held and hence, much more energy is needed to remove the second electron. However, their second ionisation energy is less than that of the corresponding alkali metals because of stability of a closed shell configuration of the univalent cations that are formed in the latter cases. The ionisation energy of alkaline earth metals also decreases on moving down the group.

Lower second ionisation energies of the alkaline earth metals as compared to those of alkali metals can be exemplified as below:



The metals of this group (beryllium is an exception) form ionic compounds. This is because the assembly of positive and negative ions into a symmetrical crystal lattice results in the liberation of a large amount of energy. As a result of the exothermic process (refer to **Born Haber Cycle, Unit 3 of Atoms and Molecules** course), there is the overall formation of ionic compounds.

Electropositive character and the reducing property (tendency to lose electrons) increase on moving down the group.

As the alkaline earth metals may lose electrons quite easily, they form divalent cations which have a noble gas structure with no unpaired electrons. Therefore, their compounds are diamagnetic and colourless, unless the anion is coloured. Ca, Sr and Ba compounds give characteristic flame colourations which are used to identify them — Ca (brick red flame), Sr (crimson red flame) and Ba (apple green flame).

SAQ 1

Write answers for the following questions in short in the given space.

a) Why are Group 2 elements smaller in size than their counterparts of Group 1?

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b) Why are Group 2 metals harder and have higher melting points as compared to the Group 1 metals?

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Solubility, Lattice Energy and Hydration Energy

We observe some interesting trends in the solubility of alkaline earth metal compounds. The metal ions are easily hydrated, e.g., MgCl₂·6H₂O, CaCl₂·6H₂O, BaCl₂·2H₂O. The hydration energies of these ions are much greater than those of alkali metal ions (Table 5.2), because of their smaller size and increased cationic charge (see Unit 4, Sec. 4.3). The lattice energies

(Table 5.2) of alkaline earth metal salts are also much higher than those of alkali metal salts. Hydration and lattice energies decrease with increase in size of metal ions. Decreasing lattice energy favours increased solubility, whilst decreasing hydration energy favours decreased solubility. If on moving down a group the hydration energy decreases more rapidly than the lattice energy, the compound becomes less soluble. This occurs with most of the compounds except for fluorides and hydroxides, for example, solubility of sulphates decreases from BeSO_4 to BaSO_4 . Due to their small ionic radii, Be^{2+} and Mg^{2+} have high hydration energies. Thereby BeSO_4 and MgSO_4 are soluble in water. CaSO_4 is only slightly soluble in water, whereas SrSO_4 and BaSO_4 are almost insoluble in water. In case of fluorides and hydroxides, the lattice energy decreases more rapidly than their hydration energy. This causes a reverse trend, i.e., the fluorides and hydroxides increase in solubility on moving down the group.

For a substance to dissolve, the hydration energy must exceed the lattice energy

Table 5.2: Enthalpies of hydration, ΔH_{hyd} of alkaline earth metal ions, M^{2+} and lattice energies, ΔH_{latt} of their oxides, carbonates, fluorides and iodides in kJ mol^{-1}

	ΔH_{hyd}		ΔH_{latt}		
	M^{2+}	MO	MCO_3	MF_2	MI_2
Be	-2494	—	—	—	—
Mg	-1921	-3923	-3178	-2906	-2292
Ca	-1577	-3517	-2986	-2610	-2058
Sr	-1443	-3312	-2718	-2459	—
Ba	-1305	-3120	-2614	-2367	—

SAQ 2

On the basis of the data given in Table 5.2 predict the solubility behaviour of alkaline earth carbonates. Answer in about 60 words.

5.3.2 Chemical Properties

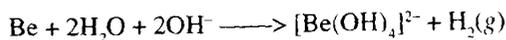
You studied in the earlier sections about some of the physical properties of Group 2 elements. Let us now see how they behave chemically.

A few of the chemical reactions shown by alkaline earth metals are given in Table 5.3. These metals are less reactive than alkali metals as they are less electropositive than the latter. However, the reactivity increases with increasing atomic number down the group.

Table 5.3: Reactions of the Group 2 metals

$2\text{M}(s) + \text{O}_2(g) \rightarrow 2\text{MO}(s)$	All burn if heated. Some MO_2 formed.
$\text{M}(s) + \text{S}(s) \rightarrow \text{MS}(s)$	The sulphides are insoluble, but hydrolyse if heated in water.
$\text{M}(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{M}(\text{OH})_2(s) + \text{H}_2(g)$	Be does not react even at red heat; Mg reacts with steam only; others react with water at room temperature.
$\text{M}(s) + 2\text{H}^+(aq) \rightarrow \text{M}^{2+}(aq) + \text{H}_2(g)$	Be only slowly; others more quickly.
$\text{M}(s) + \text{H}_2(g) \rightarrow \text{M}^{2+}2\text{H}^-(s)$	Not with Be. With others at high temperatures only. With Mg under pressure.
$\text{M}(s) + \text{X}_2(g) \rightarrow \text{MX}_2(s)$	X = halogen. No polyhalides are formed.
$3\text{M}(s) + \text{N}_2(g) \rightarrow \text{M}_3\text{N}_2(s)$	At red heat. Stability: $\text{Be} > \text{Mg} > \text{Ca}$ (hydrolyse to NH_3).
$3\text{M}(s) + 2\text{NH}_3(g) \rightarrow \text{M}_3\text{N}_2(s) + 3\text{H}_2(g)$	In liquid ammonia, Ca, Sr, Ba give blue solution because of solvated electrons (Unit 4, Section 4.4).
$\text{Be} + 2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow [\text{Be}(\text{OH})_4]^{2-} + \text{H}_2(g)$	Not with other alkaline earth metals.
$\text{M}(s) + 2\text{C}(s) \rightarrow \text{MC}_2(s)$	At high temperatures Be forms Be_2C . Ionic compounds.

- All the metals liberate hydrogen from acids, although beryllium reacts slowly. Beryllium also liberates hydrogen when treated with sodium hydroxide solution. The reaction can be given as:



This explains the anomalous behaviour of beryllium, in having amphoteric properties. All the alkaline earth metals burn in oxygen to form oxides, MO. The oxides are also formed by thermal decomposition of MCO_3 , $\text{M}(\text{OH})_2$, $\text{M}(\text{NO}_3)_2$ and MSO_4 . Beryllium oxide is covalent and all other oxides are ionic in nature. BeO has wurtzite (hexagonal ZnS) structure (Fig. 5.1), each ion has four nearest neighbours distributed tetrahedrally around it. Others have sodium chloride type of structure, i.e., each metal ion, M^{2+} , is surrounded by six O^{2-} ions and each O^{2-} is surrounded by six metal ions (Fig. 5.2). CaO is prepared on a large scale by heating calcium carbonate in lime kilns and is used in the manufacture of sodium carbonate, calcium carbide, bleaching powder, glass and cement.

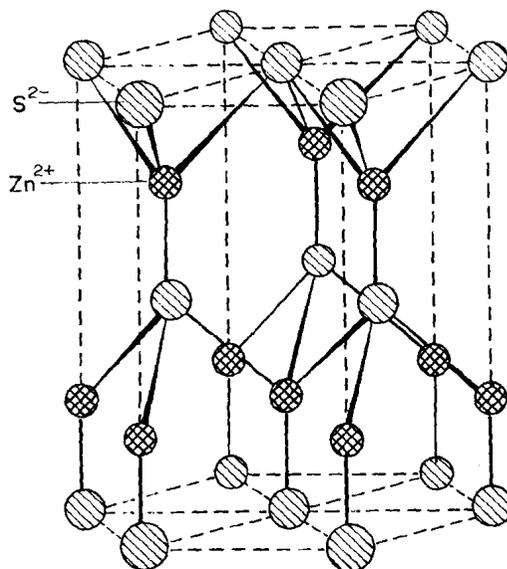


Fig. 5.1 : Wurtzite (ZnS) structure

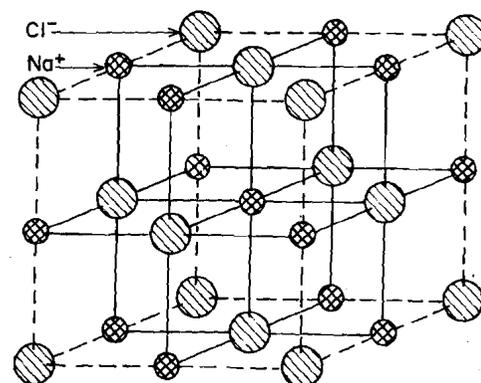
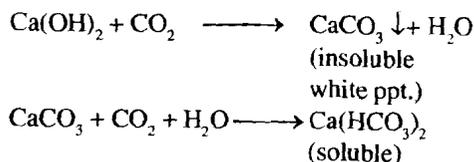


Fig. 5.2: Rock salt (NaCl) structure

Stalactite: The downward growth of CaCO_3 formed on the roof of a cave by the trickling of water containing calcium compounds.

Stalagmite: The upward growth from the floor of a cave; of the same nature and origin as a stalactite.

- Barium peroxide, BaO_2 , is formed by passing air over heated BaO , at $\sim 800\text{K}$, strontium peroxide, SrO_2 , is obtained in a similar way at high temperature and pressure. Calcium peroxide, CaO_2 , is obtained as a hydrate by treating $\text{Ca}(\text{OH})_2$ with hydrogen peroxide, H_2O_2 , and then dehydrating the product. Magnesium peroxide, MgO_2 , is obtained only in the crude form by using hydrogen peroxide, but no peroxide of beryllium is known. These peroxides are ionic solids having $(\text{O}-\text{O})^{2-}$ ion and can be considered as salts of very weak acid, H_2O_2 . The peroxides on treatment with dilute acids form H_2O_2 .
- Alkaline earth metals react with water less readily than alkali metals to give hydrogen and metal hydroxides. Beryllium does not react with water or steam even at red heat. Magnesium reacts with hot water and Ca, Sr and Ba react with cold water to form the corresponding hydroxides. Beryllium hydroxide, $\text{Be}(\text{OH})_2$, is amphoteric; the basic strength increases in the order Mg to Ba. Aqueous solutions of calcium and barium hydroxides are known as lime water and baryta water, respectively. $\text{Ca}(\text{OH})_2$ reacts with CO_2 to form first an insoluble CaCO_3 which further reacts with CO_2 to give soluble bicarbonate.



Calcium and barium bicarbonates are stable only in solution and decompose on removal of water to give carbonates. This property of bicarbonates is the reason for **stalactite** and **stalagmite** formation (Fig. 5.3).

- Metal halides, MX_2 , are obtained by direct combination with halogens as well as by the action of halogen acids on metals. Beryllium halides are covalent and other metal halides are ionic. Beryllium halides are hygroscopic and fume in air due to hydrolysis. They sublime and do not conduct electricity. Anhydrous beryllium halides are polymeric. Beryllium chloride vapours contain BeCl_2 and $(\text{BeCl}_2)_2$, but the solid is polymerised and can be represented as $(\text{BeCl}_2)_n$ (Fig. 5.4).

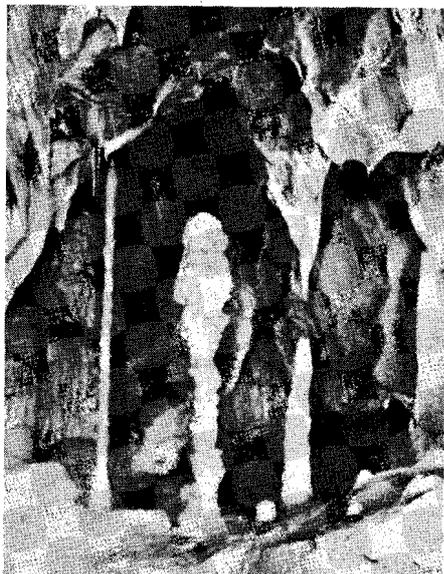


Fig. 5.3: The growth of stalactites and stalagmites (Cheddar Cave)

Sublimation is the conversion of a solid directly into vapour and subsequent condensation back to the solid. It occurs for a substance when at a particular pressure, its b.p. is lower than its m.p.

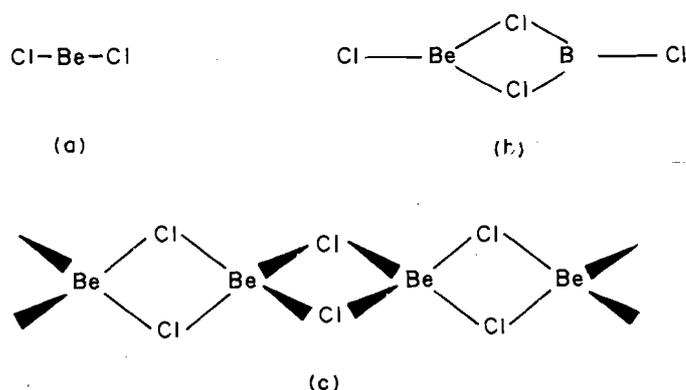


Fig. 5.4: Beryllium chloride. (a) monomer (b) dimer and (c) polymer

The halides are hygroscopic and form hydrates. CaCl_2 is a well known drying agent and anhydrous MgCl_2 is important in the electrolytic extraction of Mg.

- All the Group 2 elements except beryllium form hydrides, MH_2 , by direct combination with hydrogen. Beryllium hydride can be formed by reducing beryllium chloride with lithium aluminium hydride, LiAlH_4 . All these hydrides are reducing agents which react with water and liberate hydrogen. Calcium, strontium and barium hydrides are ionic and contain the hydride ion, H^- . Beryllium and magnesium hydrides are covalent and polymeric, $(\text{BeH}_2)_n$ has an interesting structure. The polymeric solid contains hydrogen bridges between beryllium atoms, (Fig. 5.5).

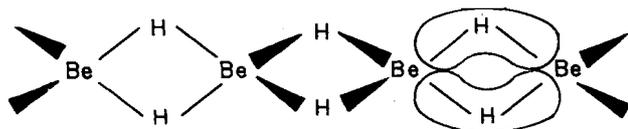
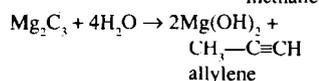
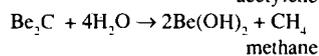
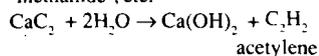


Fig. 5.5 : Beryllium hydride polymer

Each beryllium atom is bonded to four hydrogen atoms and each hydrogen atom forms two bonds as it is bridging two Be atoms. Since Be has two valence electrons and H only one, it is apparent that there are not enough electrons to form the usual electron pair bonds in which two electrons are shared between two atoms. Instead of this, three-centre bonds are formed in which a 'banana-shaped' molecular orbital covers three atoms $\text{Be}\dots\text{H}\dots\text{Be}$, and contains two electrons. The monomeric molecule BeH_2 , if formed with normal bonds, would have only four electrons in the outer shell of the beryllium atom and would be electron deficient.

The carbides are named depending upon the hydrocarbon they liberate on reaction with water. If it liberates acetylene, it will be named acetylide, and if methane is liberated, it will be called as 'methanide', etc.



This would make the molecule very unstable; that is why BeH_2 exists as a polymer. This is an example of a cluster compound in which each atom shares its electrons with several neighbours and receives a share in their electrons to acquire a stable configuration.

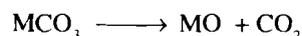
- All the metals in the Mg-Ba series or their oxides react directly with carbon to give the carbides (acetylides), MC_2 . These carbides are ionic in nature and have a NaCl type of structure (Fig. 5.2) with M^{2+} replacing Na^+ and $\text{C}\equiv\text{C}^{2-}$ replacing Cl^- . Beryllium forms methanide, Be_2C , with carbon and acetylide, BeC_2 , with acetylene. Magnesium on heating with carbon forms Mg_2C_3 also, which is an allylide since with water it liberates allylene (methylacetylene).
- The alkaline earth metals burn in nitrogen and form nitrides, M_3N_2 . It requires a lot of energy to convert the stable N_2 molecule into nitride ion, N^{3-} , and this is recovered from the very high lattice energies of the alkaline earth metal nitrides. The beryllium compound is rather volatile while others are not. They are all colourless crystalline solids which decompose on heating and react with water to liberate ammonia and form either the metal oxide or hydroxide, e.g.,

$$3\text{Mg}(s) + \text{N}_2(g) \longrightarrow \text{Mg}_3^{2+}\text{N}_2^{3-}(s)$$

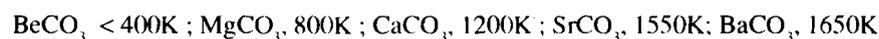
$$\text{Mg}_3^{2+}\text{N}_2^{3-}(s) + 6\text{H}_2\text{O}(l) \longrightarrow 3\text{Mg}^{2+}(\text{OH}^-)_2(s) + 2\text{NH}_3(g)$$

Thermal Stability of Oxysalts

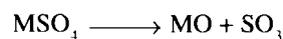
All the Group 2 elements form oxysalts. The thermal stability of the oxysalts increases with the increase in electropositivity of the metals. Thus, it increases down the group. The thermal stabilities of the salts of Group 2 are less than those of the Group 1 metals. The carbonates of alkaline earth metals are stable at room temperature. On heating, they decompose into the corresponding oxides and carbon dioxide:



The temperature at which the carbonates decompose are given as:



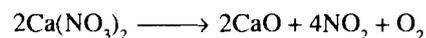
The sulphates are more stable than the carbonates. On heating, they decompose into oxides and sulphur trioxide.



The order of decomposition temperature of the sulphates is:



Alkali metal nitrates decompose into nitrites on heating whereas alkaline earth metal nitrates decompose on heating to metal oxide, nitrogen dioxide and oxygen, e.g.,



SAQ 3

Explain in brief why is the hydride bridge in $(\text{BeH}_2)_n$ considered to be electron deficient but not the halide bridge in $(\text{BeCl}_2)_n$.

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5.3.3 Complexation Behaviour

Let us discuss another interesting property of these elements, i.e., their complexation behaviour. Complex formation is favoured by small, highly charged cations with suitable empty orbitals of approximately the right energy with which the ligand orbitals can combine (see Unit 4, Section 4.6).

Alkaline earth metals form more complexes as compared to alkali metals. The tendency to form complexes (mostly with O & N donors) decreases with increasing atomic number. Thus, of the heavier ions only Ca^{2+} forms a complex with ethanol. Beryllium having the smallest ion in the group tends to form complexes most readily. It mostly forms complexes with tetrahedral arrangement because of the available orbitals as shown below:

	1s	2s	2p	
Be atom in ground state	↑↓	↑↓	□ □ □	No unpaired electrons so no covalent bonds Two unpaired electrons can form two covalent bonds
Be atom in excited state	↑↓	↑	↑ □ □	
Be in $[\text{BeF}_4]^{2-}$	↑↓	↑↓	↑↓ ↑↓ ↑↓	Two fluoride ions each donate an electron pair into an empty orbital forming a coordinate bond
		sp^3 hybridisation		

The well known tetrafluoroberyllates have a tetrahedral structure as shown in Fig. 5.6.

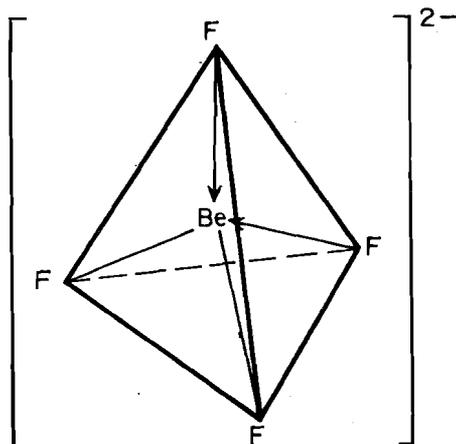


Fig. 5.6: Tetrafluoroberyllate complex ion, $[\text{BeF}_4]^{2-}$.

The arrows in the above figure indicate that two F^- ions form 'coordinate' bonds with BeF_2 . However, once these are formed, all the $\text{Be}-\text{F}$ bonds tend to become similar.

Beryllium forms white crystalline molecular oxide-carboxylates, of which **basic beryllium acetate**, viz., $[\text{OBe}_4(\text{CH}_3\text{COO})_6]$ is typical and important for the purification of Be because of its volatility and solubility in organic solvents. Beryllium forms a number of chelates also with ligands like oxalates, $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ (Fig. 5.7), and β -diketonate anions.

Chelates are the ring compounds formed as a result of coordination with ligands having more than one binding sites.

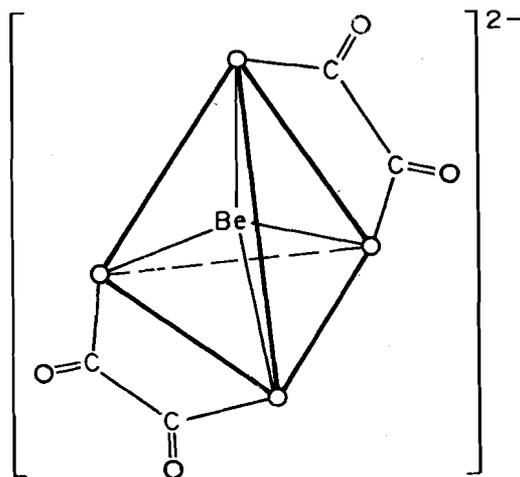
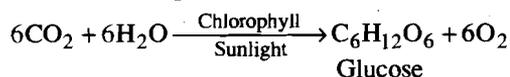


Fig. 5.7: Beryllium oxalate complex ion, $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$.

In the hydrated salts, e.g., $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$ and $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, beryllium ions exist in the form, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, where they show a coordination number of four.

Magnesium is known to form a very important complex occurring in nature, viz., chlorophyll; a green pigment of the plants which produces sugars for the plant in presence of sunlight, CO_2 and H_2O in a process called photosynthesis.



Magnesium, in chlorophyll, is coordinated by four nitrogen atoms in the heterocyclic porphyrin ring system (Fig. 5.8).

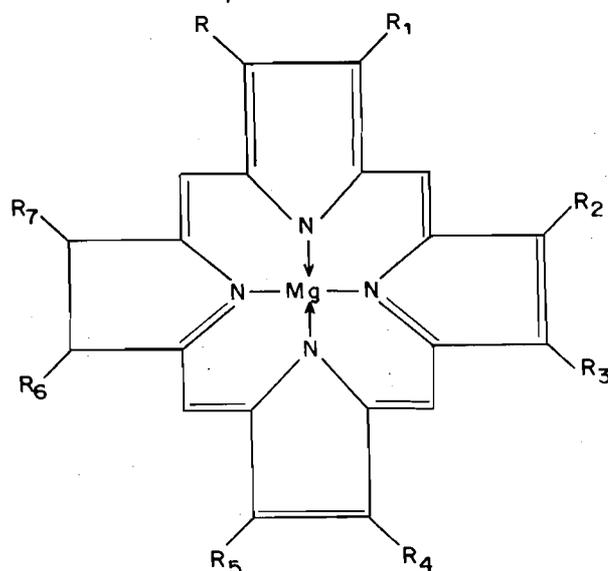


Fig. 5.8: Skeleton of chlorophyll molecule

When water does not form lather with soap, it is called as hard water. Hardness of water is due to the presence of heavy metal cations like Ca^{2+} , Mg^{2+} and Fe^{2+} etc.

The rest of the elements from calcium to barium form complexes only with strong complexation agents such as acetylacetonone, ethylenediaminetetraacetic acid (EDTA), etc. In fact, titrations are performed using EDTA in buffer solutions to estimate the amounts of Ca^{2+} and Mg^{2+} present in water, to determine the hardness of water.

SAQ 4

Why do alkaline earth metals form more complexes as compared to the alkali metals? Give only two reasons.

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5.4 ANOMALOUS NATURE OF BERYLLIUM

Beryllium, the first member of the group, appears to be quite different from the other members, in the same way as lithium differs from the other alkali metals and for the same reasons as discussed for lithium in the previous unit. Beryllium differs more from magnesium than lithium does from sodium, in fact, the anomalous nature of the first member of *s*- and *p*-block groups becomes more pronounced towards the middle of the table. Also beryllium shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium. Also the properties in which beryllium differs from magnesium, it shares with aluminium in general. Let us now consider all the factors one by one.

- a) The cohesive properties of beryllium are much greater than those of magnesium and other elements in the group. As a result it is much harder and has higher melting and boiling points.
- b) It has smaller atomic radii, higher electron affinity and higher ionisation energy.
- c) Its higher polarising power leads to all its compounds being largely covalent, with lower melting and boiling points and enthalpies of formation (e.g., BeF_2 , m.p. 1073K, for rest of the group about 1573K). All the compounds of Be are more soluble in organic solvents than the corresponding magnesium compounds. They hydrolyse in water, and in this respect they rather resemble aluminium.

5.5 SUMMARY

Let us now summarise the main points that we have discussed in this unit.

- The general properties of the Group 2 elements are similar due to the similarity in the outer shell electronic configuration, i.e., ns^2 .

- Like Group 1 elements, Group 2 elements also follow the group trends, i.e., increasing atomic size, density, electropositivity, reactivity, reducing power, hardness and conductivity. Their ionisation energy decreases down the group.
- The Group 2 metals are harder, have higher melting and boiling points, form hydroxides which are weaker alkalies and form carbonates which are less stable than those of corresponding Group 1 elements.
- The complexation behaviour in the group is mainly restricted to beryllium and very few complexes of the rest of the elements are known.
- Beryllium being the first member of the group exhibits anomalous properties and shows diagonal relationship with aluminium.

5.6 TERMINAL QUESTIONS

- 1 The first ionisation energy of beryllium is greater than that of lithium, but the position is reversed in the case of second ionisation energy. Why?
- 2 Why beryllium forms covalent compounds?
- 3 Describe the difference in the nature of bonding of BeH_2 and CaH_2 .
- 4 What are the usual coordination numbers for Be^{2+} and Mg^{2+} ? What is the reason for the difference?
- 5 Why do halides and hydrides of beryllium polymerise?
- 6 Which is more stable to heat, beryllium carbonate or barium carbonate, and why?

5.7 ANSWERS

Self Assessment Questions

- 1 a) Since the effective nuclear charge felt by the outer electrons in the atoms of Group 2 elements is comparatively higher, these elements are smaller in size than their counterparts of Group 1.
 - b) Since Group 2 elements have two valence electrons, they have stronger metallic bonding and show higher cohesive properties than their Group 1 neighbours. Thus they are harder and have higher melting points as compared to the Group 1 elements.
- 2 If you subtract the lattice energies from the hydration energies of MCO_3 , you will find the difference increasing from Mg to Ca, decreasing from Ca to Sr and again increasing from Sr to Ba showing a decrease in solubility from Mg to Ca, an increase from Ca to Sr and a decrease again from Sr to Ba. The maximum solubility is shown by MgCO_3 .
- 3 The hydrogen bridge in $(\text{BeH}_2)_n$ is held together by one electron pair only and is electron deficient in the sense that there is less than one electron pair for each pair of bonded atoms. But in $(\text{BeCl}_2)_n$, each pair of bonded pair of atoms has the normal electron pair and so, its bridge is not electron deficient.
- 4 As compared to the alkali metals, the alkaline earth metals form more complexes because they are smaller in size and have higher cationic charge.

Terminal Questions

- 1 Because of its smaller atomic size and higher effective nuclear charge, the first ionisation energy of Be is higher than that of Li. But the second ionisation energy of Be is smaller than that of Li because of the stability of a closed shell configuration of Li^+ .
- 2 According to Fajan's rule, small size and high charge density favours covalency and therefore, Be has a strong tendency for covalency.
- 3 According to Fajan's rule, calcium forms ionic hydride while beryllium forms covalent hydride.
- 4 The usual coordination numbers for Be^{2+} and Mg^{2+} are 4 and 6, respectively. The difference is due to the very small size of Be^{2+} and non-availability of *d* orbitals in it.
- 5 The monomeric molecules BeH_2 and BeCl_2 formed with normal bonds will result in only four electrons in the outer shell of the beryllium atom making it electron deficient. By polymerising, each atom shares its electrons with several neighbours and receives a

share in their electrons making the situation more favourable. Therefore, the halides and hydrides of Be polymerise.

- 6 BaCO_3 is more stable than BeCO_3 .
(Hint: Relate size of cation to size of anion.)

FURTHER READINGS

- 1 *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.
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- 3 *Advanced Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 9th reprint, 1986.
- 4 *Principles of Inorganic Chemistry*, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.