

16

Group IIA (Group 2)*. Beryllium, Magnesium and the Alkaline Earths

Beryllium, magnesium, strontium, barium and radium are members of group IIA (group 2). Their relative per cent abundances in the earth's crust are :

Be(0.006%); Mg(2.0%); Ca(3.4%); Sr(0.02%); Ba(0.04%).

As with the alkali group the first member beryllium is present in very small quantity. This is due to the transmutation of the beryllium atoms under natural bombardment by protons. Presence of considerable amount of helium in beryllium minerals lends support to this hypothesis. With increasing atomic number the abundance again falls.

Very early in the development of chemical science chemists were familiar with a group of substances such as lime, strontia and baryta which were alkaline in nature and were much resistant to thermal decomposition. The three elements—calcium, strontium and barium are therefore collectively called as *alkaline earths*.

16.1. COMPARATIVE STUDY OF THE GROUP IIA (GROUP 2) ELEMENTS

16.1.1. General Considerations : All the elements possess an s^2 configuration (Table 16.1) over a noble gas core. This s^2 configuration has led to their inclusion in group IIA (group 2) of the Periodic Table. The s^2 electrons are lost to give dipositive oxidation states. The first ionisation potentials are rather low but the second potentials are rather high. In keeping with general expectation the potential values gradually decrease with increasing atomic number. This is a pointer that the basic properties increase down the group. It might be argued that the elements may show both the + 1(I) and the + 2 (II) oxidation states since the two ionisation potentials vary rather widely. Overwhelming amount of experimental facts points to a consistent dipositive state in the group. There is only one or two minor reports which claim that electrolysis of acidulated water with beryllium or magnesium electrodes is not in conformity with Faraday's law. The amount of hydrogen liberated at the cathode and the amount of beryllium (or magnesium) dissolved at the anode points to the metals passing into solution not entirely as + 2(II) ions but to some extent as + 1(I) ion. A study of the

* IUPAC recommendation

following ionisation potentials will convince us that in no case a + 3(III) state can be realised :

Element / Ion	Ca	Ca ⁺	Ca ²⁺	Ar
Ionisation potential			51.21	15.75
eV/atom	6.11	11.87	4940	1520
kJ/mole	590	1145		

The third stage ionisation potentials (i.e for further ionisation of M²⁺ ions of beryllium and magnesium) are 14847 and 7731 kJ/mole respectively.

The charge on the cations is + 2 and the sizes of the ion are considerably smaller than the preceding alkali metals. Fajans' rules will predict that in the small-sized beryllium and to some extent magnesium there will be a considerable degree of covalence and complexation. Be²⁺ ion neither occurs in solid state nor in solution. Beryllium chemistry is dominated by covalence and complexation. Covalent character of magnesium is indicated by its diagonal relationship to lithium of group IA (group 1). In the alkaline earths, however, the sizes of the cations have increased substantially to counter the effect of the charge. *The chemistry of the alkaline earths is therefore largely the chemistry of their ions.*

Table 16.1 : Electronic Configurations and some Properties of Group IIA (Group 2) Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential eV/atom (kJ/mole)	Electro-negativity
Be	4	[He]2s ²	9.32, 18.20 (899, 1756)	1.5
Mg	12	[Ne]3s ²	7.64, 15.03 (737.5, 1450)	1.2
Ca	20	[Ar]4s ²	6.11, 11.67 (590, 1126)	1.0
Sr	38	[Kr]5s ²	5.69, 11.02 (549, 1063)	1.0
Ba	56	[Xe]6s ²	5.21, 10.00 (502.5, 964.8)	0.9
Ra	88	[Rn]7s ²	5.27, 10.14 (508.4, 978)	0.9

The electronegativities (Table 16.1) fall from beryllium to radium. For the alkaline earths the electronegativities are close to those for the alkalis but that of beryllium is comparatively

high. In the formation of halides the electronegativity difference between the alkaline earths and the halogens is large enough to give ionic compounds. For beryllium substantial covalent character is predicted for the halides.

As expected the standard potentials of the elements become more negative down the group (Table 16.2). The increasing electropositive character with increasing atomic number is thus indicated. Low reduction potential of beryllium indicates its poor electropositive character. But the reduction potentials of the alkaline earths are close to those of the alkalis.

Table 16.2 : Some more Properties of Group IIA (Group 2) Elements

Element	Atomic Radius (A)(pm)	Ionic Radius (M ²⁺)(A)(pm)	M.P. (°C)	B.P. (°C)	Density (g/ml)	E° (volt) (M ²⁺ + 2e ⇌ M)
Be	1.11 (111)	0.31 (31)	1284	2507	1.84	-1.85
Mg	1.60 (160)	0.65 (65)	651	1103	1.74	-2.37
Ca	1.97 (197)	0.99 (99)	851	1440	1.54	-2.87
Sr	2.15 (215)	1.10 (110)	770	1320	2.60	-2.89
Ba	2.17 (217)	1.29 (129)	710	1500	3.50	-2.90
Ra	—	1.50 (150)	960	1140	~5	-2.92

The atomic and ionic radii (Table 16.2) are smaller than the preceding alkalis due to increase in nuclear charge. The metals have higher melting points, boiling points, densities and heats of vapourisation than the alkalis. The two valence electrons of the group IIA (group 2) make far stronger binding in the metallic state. Compared to the alkalis these elements have much higher densities since they have much smaller-sized atoms.

16.1.2. Chemical Behaviour. In keeping with Fajans' rules the alkaline earth compounds are predominantly ionic. Beryllium compounds are covalent and magnesium assumes an intermediate role. The tendency towards complexation is the highest in the smallest beryllium and gradually falls off in the series.

Hydrides : By virtue of their greater electropositive character the alkaline earths form ionic hydrides : CaH₂, SrH₂ and BaH₂. These are high melting, conducting in fused state and on electrolysis liberate hydrogen at the anode. These are obtained by the direct combination of hydrogen with the metals at ~200°—400°C. Beryllium hydride is covalent and polymerised and magnesium hydride has properties intermediate between those of ionic and covalent hydrides. Thermal stability of the alkaline earth hydrides follows the order : Ca > Sr > Ba. Like the alkali metal hydrides chemical reactivity increases from calcium to barium. Reaction of CaH₂ with water provides a ready source of hydrogen.

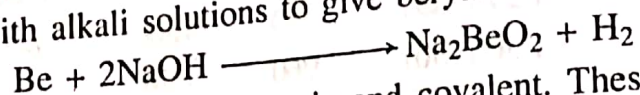
Oxides : Beryllium oxide is polymeric and covalent. All the other oxides are ionic and have high melting points (Table 16.3). In general, the tendency to form peroxides and superoxides increases along the group. Thus beryllium does not form any peroxide, magnesium only a peroxidated oxide MgO₂.3MgO and the alkaline earths form monoxides, MO and

peroxides MO_2 . Calcium superoxide has been reported in about 8% yield as an admixture with calcium peroxide by reaction at 100°C between calcium peroxide and 30% H_2O_2 .

Table 16.3 : Melting Points of some Compounds of Group IIA (Group 2) Elements

Compound	M.P. ($^\circ\text{C}$)	Compounds	M.P. ($^\circ\text{C}$)
BeO	2570	BeCl_2	405
MgO	2800	MgCl_2	715
CaO	2572	SrCl_2	870
SrO	2430	BaCl_2	955

The oxides react in water to form hydroxides. The basic properties of the hydroxide increase, as expected, from beryllium to barium. Beryllium hydroxide is amphoteric and all the others are only basic. As expected from their high negative standard potentials calcium, strontium and barium readily react with cold water to form hydroxides with liberation of H_2 . Magnesium reacts only on heating. Metallic beryllium, unlike the other members of group IIA (group 2), reacts with alkali solutions to give beryllate and hydrogen :



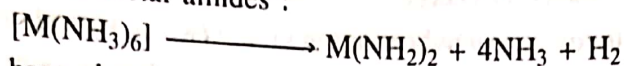
Halides : Beryllium halides are polymeric and covalent. These are non-conductors in fused state. The other halides are ionic in nature. In fused state they conduct electricity and they possess ionic crystal structure. Melting points of the chlorides appear in Table 16.3. CaF_2 is a high melting (M.P. 1418°C) water-insoluble solid while the chlorides are lower melting ($715\text{--}955^\circ\text{C}$) and deliquescent. The bromides and the iodides have still lower melting points and have higher solubilities in water and alcohol.

Nature of the Aqueous Solution : Since the complexing tendency decreases down the group from beryllium to radium it will only be logical to expect that the degree of hydration will fall in the same direction. Indeed the hydration energies fall from beryllium to barium and the ionic mobilities, for the same reason, increase from beryllium to barium. It is also interesting to observe that the hydration energies of group IIA (group 2) metal ions, M^{2+} , are roughly four times larger than those of the preceding alkalis. This is due to a greater charge/surface ratio *i.e.* charge density of these elements (Chapter 5).

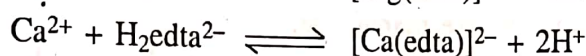
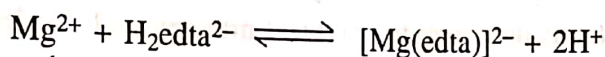
Table 16.4 : Hydration Energies and Ionic Mobilities of Group IIA (Group 2) Elements

Property	Be	Mg	Ca	Sr	Ba	Ra
Ionic Radius $\text{M}^{2+}(\text{A})(\text{pm})$	0.31(31)	0.65(65)	0.99(99)	1.10(110)	1.29(129)	1.50(150)
Hydration Energy of M^{2+}						
kcal/mole	-570	-459	-395	-355	-325	-
(kJ/mole)	(-2385)	(-1920)	(-1653)	(-1485)	(-1360)	-
Ionic mobility $\times 10^5$						
(cm/sec/volt)	30	55.5	59.8	59.8	64.2	67

Nature of the Solution in Liquid Ammonia : The alkaline earths dissolve in liquid ammonia to give ammoniated cations and ammoniated electrons. The molar extinction coefficient of the calcium solution is nearly double that of a sodium solution. In general, the behaviours of these solutions are like those of the alkalis. Copper coloured metal ammoniates $[M(NH_3)_6]$ ($M = Ca, Sr, Ba$) have been recovered on evaporation. They are, however, unstable and decompose to metal amides :



Complexes : We have already seen that beryllium is the most complexing in this group and that the complexing tendency decreases down the group. By virtue of a double charge on the cations the overall complexing ability of the alkaline earths is far greater than that of the monovalent alkalis. This is easily seen by these elements forming quite a number of complexes with strong polydentate ligands. For example, with 8-hydroxyquinoline (Hoxin) magnesium readily forms an insoluble $[Mg(\text{oxin})_2]$. This forms a basis for the gravimetric estimation of magnesium. Besides, both magnesium and calcium form soluble and stable complexes with edta (Chapter 10), which is the basis of the complexometric determination of water hardness.



Among all Mg(II) complexes the most celebrated one is Nature's chlorophyll—a square planar MgN_4 with porphyrin N_4 macrocycle. Chlorophyll is the key figure in photosynthesis by plants (see Chapter 13 for details).

The alkaline earths form some poorly known acetylacetonate complexes. Their ammine complexes, such as $[Mg(NH_3)_6]Cl_2$, are weak and are easily dissociated into ammonia and the metal halide. The tendency of complexation dies down the group.

Recent studies with polycyclic ethers (called *crown ethers*) and poly macrocyclic ethers with nitrogen bridge heads (called *cryptands*) reveal that they are good complexing ligands for heavy alkaline earths like Sr^{2+} and Ba^{2+} . Such a tricyclic cryptand is $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N (=L)$. Complexes of the type $[Sr/Ba(L)]SO_4$ have been characterised. The metal ion is trapped inside the macrocyclic hole (cf. 15-III).

16.2. BERYLLIUM

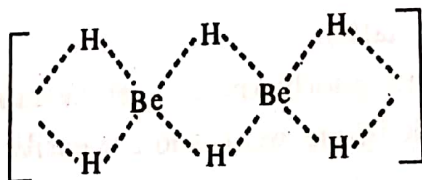
16.2.1. General Considerations : Beryllium is the first member of group IIA (group 2). It has $[He]2s^2$ electronic configuration, has the highest ionisation potential in the group (9.32, 18.20 eV), has the highest electronegativity (1.5) in the group and has the smallest atomic (1.11 Å) (111 pm) and ionic radii (Be^{2+} , 0.31 Å) (31 pm). These properties of elementary beryllium make it a most suitable element for exhibiting covalent properties. Its complexing ability consequently is the highest in the group.

Beryllium chemistry is dominated by a tetrahedral geometry and to a lesser extent by a linear coordination. Beryllium is a member of the second period and hence can have no more

than four orbitals (one s and three p 's) in the $n = 2$ quantum shell. This quantum shell does not have a d -orbital. Thus beryllium can have a maximum of four coordination and thus can attain the next noble gas configuration by complex formation. However four coordination can be attained either through a tetrahedral (sp^3 hybridisation) or a square planar (dsp^2) geometry. Since with beryllium the only d -orbital possible is the much higher energy $3d$, square planar dsp^2 geometry is energetically unfavourable. For the linear coordination in beryllium we have to invoke an sp hybridisation giving two sp hybrid orbitals at 180° to each other (Chapter 5). Such a coordination provides a valence shell of only $4 = (2 + 2)$ electrons around the metal. Hence beryllium tends to raise its coordination number to four allowing itself a noble gas configuration. Because of this tendency we find that the compounds with an apparent coordination number 2 (say $BeCl_2$) are really polymeric with a coordination number 4. The desire to attain noble gas configuration also makes beryllium a good electron pair acceptor (Lewis acid). For example $BeCl_2$ readily forms addition compounds with neutral donors, giving compounds such as $BeCl_2 \cdot (OR)_2$.

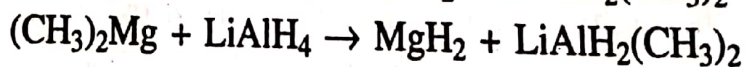
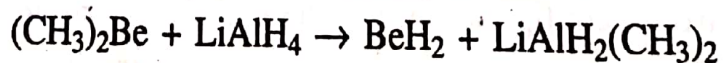
It should be noted that the arguments advanced in favour of four-coordinate tetrahedral geometry in beryllium compounds are equally valid for other elements of the same period. Thus trivalent boron, tetravalent carbon, trivalent nitrogen and divalent oxygen also prefer a tetrahedral geometry to a square planar one.

16.2.2. Chemical Behaviour : Hydrides : The hydride of beryllium (BeH_2) and of magnesium (MgH_2) are intermediate between the ionic hydrides of lithium and sodium, and



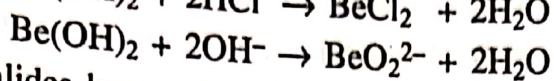
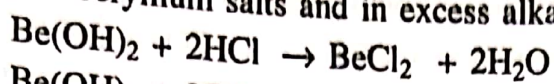
(16-1)

the covalent hydrides of the remaining elements in these periods. These hydrides are solid polymerised molecules held together by three-centred two-electron ($3c-2e$) hydrogen bridge bond comparable to that in diborane, B_2H_6 . These hydrides are therefore not ionic and cannot conduct electric current. BeH_2 (16-1) appears to be more covalent than MgH_2 due to its smaller size and its electronegativity (1.5) being closer to that (2.1) of hydrogen. BeH_2 and MgH_2 are synthesised by the reaction of dimethyl beryllium / magnesium with lithium aluminium hydride (lithium tetrahydridoaluminate) in ether :

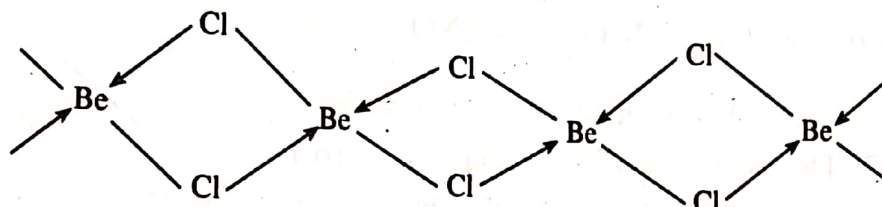


Oxide and Hydroxide : Due to the small size and comparatively large charge of the beryllium ion BeO is covalent. Yet the compound has a high melting point ($2570^\circ C$). This is due to the compound having a polymeric lattice rather than discrete covalent molecules. Each beryllium atom is tetrahedrally coordinated by oxygen. Beryllium does not form any

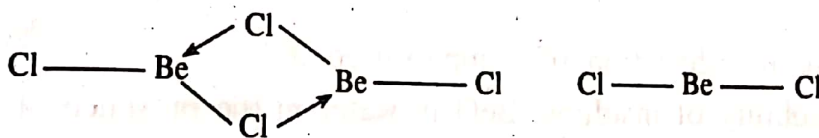
peroxide or superoxide. Beryllium hydroxide is precipitated on the addition of OH^- ions to an aqueous solution of a beryllium compound. The hydroxide and the oxide are amphoteric. These dissolve in acids to give beryllium salts and in excess alkali to give beryllate ions :



Halides : Beryllium halides have rather low melting points (Table 16.3) and are non-conductors in fused state. The conductivity of fused beryllium chloride is about a thousandth of that of a fully ionised salt (say NaCl). These halides are polymeric and four-covalent, polymerisation occurring through halogen bridging. Ordinary crystalline BeCl_2 has a polymeric chloro-bridged structure (16-II). Beryllium is approximately sp^3 hybridised (tetrahedral). In vapour phase it assumes a three-coordinate planar dimeric structure (16-III) and finally a linear monomer sp hybridised. In the dimer beryllium is sp^2 hybridised and in the monomer sp hybridised. The polymeric structure (16-II) can be broken down even by weak ligands such as Et_2O to give monomeric $[\text{BeCl}_2(\text{OEt}_2)_2]$ where beryllium still remains sp^3 hybridised.



(16-II)



(16-III)



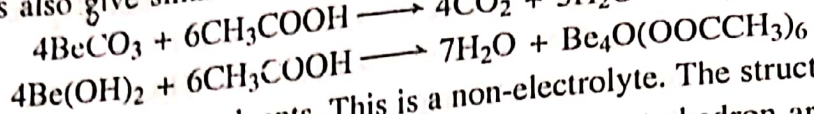
(16-IV)

The anhydrous beryllium chloride dissolves very readily in water with large evolution of heat to form the tetrahydrate $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$. This water is not lost over P_4O_{10} even over months, suggesting the tetraqua structure $[\text{Be}(\text{H}_2\text{O})_4]\text{Cl}_2$.

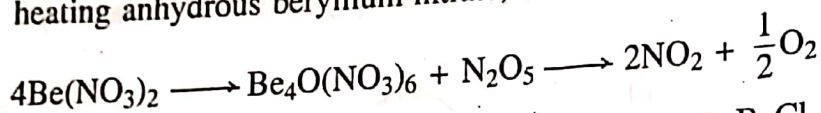
Beryllium fluoride cannot be obtained by neutralising beryllium hydroxide with HF since the fluoride hydrolyses on evaporation. It is obtained by igniting BeO in a stream of gaseous HF or better by heating fluoroberyllates. The chloride and the bromide are obtained by the action of halogens on a mixture of BeO and C or by the action of halogens on beryllium carbide. The iodide is best made by the action of HI on BeC_2 .

Complexes : Complexing tendency of beryllium is reflected in the formation of polymeric species, in the strong hydration of its salts, in adduct formation of their halides and in the formation of a variety of neutral, cationic and anionic complexes. The class 'a' character of beryllium (Chapter 8) is exhibited by its readily forming complexes with nitrogen donors like ethylenediamine or with oxygen donors like water, acetylacetonone etc. The coordination number in such complexes is always four and the stereochemistry of beryllium is tetrahedral.

A very interesting complex of beryllium is basic beryllium acetate $\text{Be}_4\text{O}(\text{OOCCH}_3)_6$. This is obtained by refluxing beryllium carbonate or hydroxide with acetic acid. Other carboxylic acids also give similar complexes. The basic acetate is a crystalline but volatile substance, soluble in non-polar solvents. The structure is now well-established (Fig 16.2). The four beryllium atoms complete a tetrahedron around the central and unique oxygen. The six carboxylate groups span the six edges of the tetrahedron. The compound has interlocking six-membered rings satisfying the tetrahedral bond angles of the four beryllium atoms. Note that each of the four beryllium atoms is also tetrahedrally coordinated to four oxygen. Three of these four oxygens come from the carboxylate groups and the fourth oxygen is the central, unique oxygen.



Basic beryllium nitrate, $\text{Be}_4\text{O}(\text{NO}_3)_6$, is obtained by heating anhydrous beryllium nitrate, $\text{Be}(\text{NO}_3)_2$, to 125°C :



The anhydrous $\text{Be}(\text{NO}_3)_2$ is made by reacting BeCl_2 and NO_2 at 50°C . The basic beryllium nitrate (Fig. 16.1) has a unique oxygen tetrahedrally surrounded by four Be atoms. The six edges of the tetrahedron are bridged by didentate NO_3 ions.

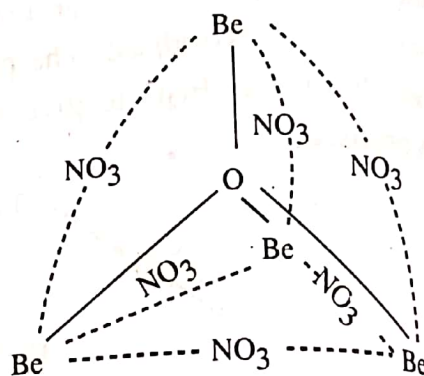


Fig. 16.1 : Basic beryllium nitrate.

Another interesting manifestation of complexation is the increase in the solubility of insoluble BeO in water in the presence of BeSO_4 . This is

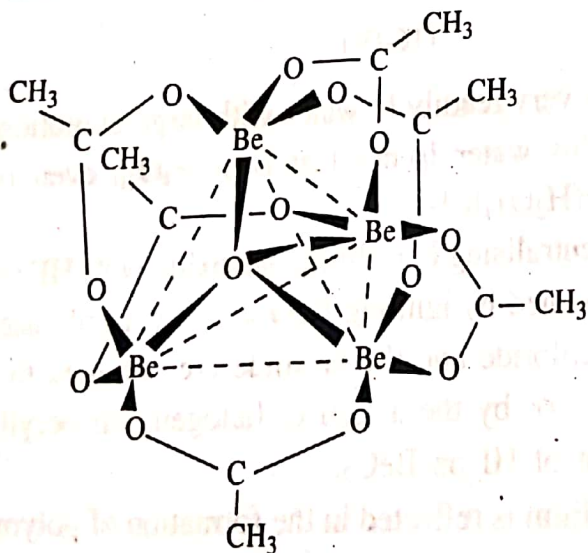


Fig. 16.2 : Basic beryllium acetate

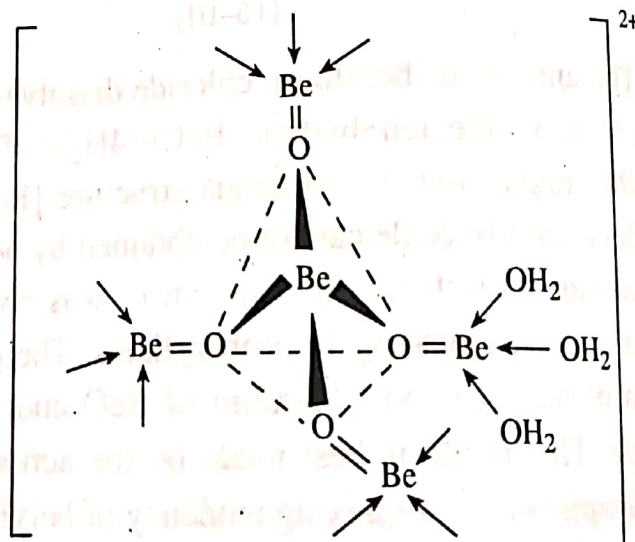
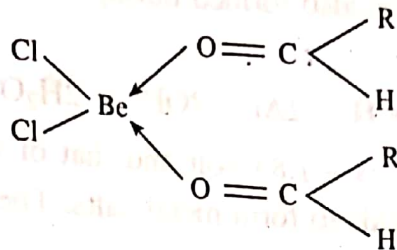


Fig. 16.3 : The $[\text{Be}(\text{OBe}(\text{H}_2\text{O})_3)_4]^{2+}$ ion

due to the replacement of the tetrahedrally disposed aqua molecules of $[\text{Be}(\text{H}_2\text{O})_4]\text{SO}_4$ by four BeO units, the oxide oxygen forming a bond to the central beryllium (Fig 16.3) The

coordination around the BeO units is completed by three water molecules. The ultimate species in solution is $[\text{Be}(\text{OBe}(\text{H}_2\text{O})_3)_4]^{2+}$.

Beryllium halides act as Lewis acids giving adducts with Lewis bases such as aldehydes (16-V), ketones and ethers :



Complexes such as $[\text{BeCl}_2(\text{bpy})]$, $[\text{BeCl}_2(\text{o-phen})]$, $[\text{Be}(\text{acac})_2]$ are also known. In general, oxygen donor complexes are more stable than nitrogen donor complexes.

Of the halocomplexes the fluoroberyllates, $[\text{BeF}_4]^{2-}$ are well-known. The complex $[\text{BeCl}_4]^{2-}$ is rather unstable. The fluoroberyllates can be made by dissolving BeO in concentrated solutions of ammonium hydrogenfluoride. The size of the $[\text{BeF}_4]^{2-}$ is comparable to that of $[\text{SO}_4]^{2-}$ and both the ions are tetrahedral. The two ions are therefore isomorphous. Just like the sulphate ion the fluoroberyllate ion also forms Schönite type double fluoroberyllates : $\text{M}^I_2\text{M}^{II}(\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$.

16.3. COMPARISON OF BERYLLIUM AND ALUMINIUM : DIAGONAL RELATIONSHIP

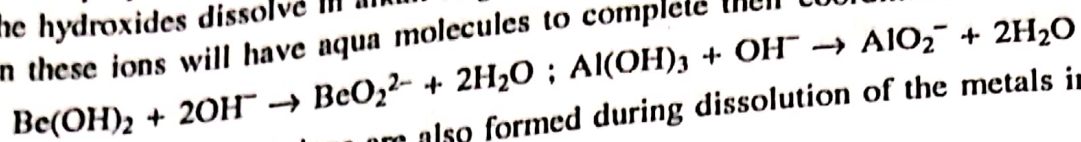
Compared to beryllium, aluminium has a higher charge on its ion and also a higher size. The charge / radius ratio (Chapter 5) is almost the same for the two elements, and therefore they are of similar deforming power. Note that the charge / radius ratios of these two elements are far closer to each other than the lithium-magnesium pair. As a result the properties of beryllium / aluminium are much more similar than those of lithium / magnesium. Indeed beryllium / aluminium pair is hailed as the best diagonal pair in the Periodic Table.

Element	Be	Al
Charge on the ion	+2	+3
Ionic radius (A)	0.31	0.51
Charge/radius ratio	6.4	6.0

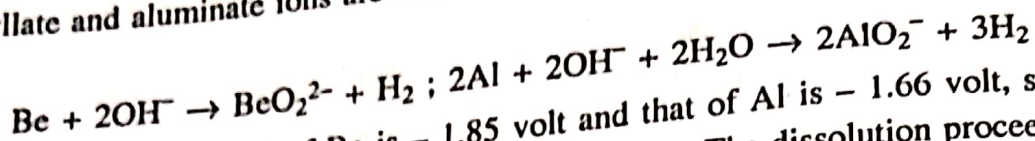
The points of similarities are :

- Both the elements show strong tendency to covalence and complex formation. Aluminium halides are dimeric and covalent. Beryllium halides are polymeric and covalent. In aqueous solutions the aqua ions are formed : $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.
- Both beryllium hydroxide and aluminium hydroxide have amphoteric properties. Both

betray basic properties in the presence of acids-forming compounds like BeSO_4 or $\text{Al}_2(\text{SO}_4)_3$. Both the hydroxides dissolve in alkali to give beryllate and aluminate, although in aqueous solution these ions will have aqua molecules to complete their coordination zone.



The beryllate and aluminate ions are also formed during dissolution of the metals in strong bases :

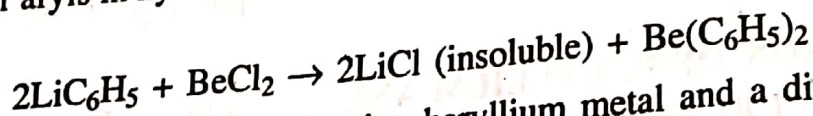


3. The standard potential of Be is -1.85 volt and that of Al is -1.66 volt, so that the metals should readily dissolve in acids to form metal salts. The dissolution proceeds best in HCl and H_2SO_4 and least in HNO_3 .

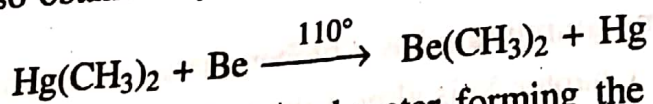
4. Beryllium and aluminium occur together in nature in beryl $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Both Be and Al are isolated by electrolysis, the former from fused BeCl_2 and the latter from Al_2O_3 . BeCl_2 is mixed with NaCl to bring it to the conducting (but unstable) form $[\text{BeCl}_4]^{2-}$. Al_2O_3 is dissolved in fused cryolite and then electrolysed.

16.4. ORGANOBERYLLIUM AND ORGANOMAGNESIUM COMPOUNDS

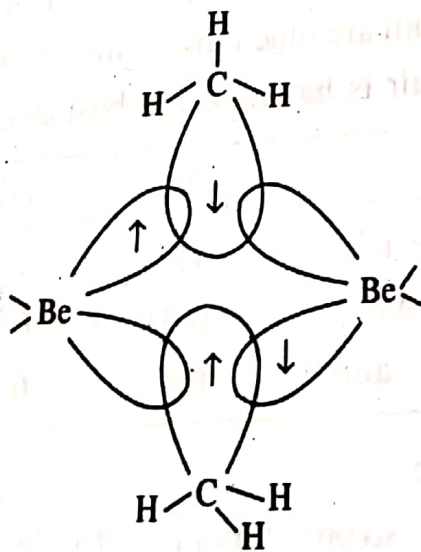
Organoberyllium compounds (with beryllium-carbon σ bond) are obtained via reaction of lithium alkyls or aryls in hydrocarbon solvents with beryllium chloride in ether when LiCl is precipitated :



Beryllium alkyls are also obtained by heating beryllium metal and a dialkylmercury :



Beryllium alkyls are very sensitive to air and water forming the oxide or the hydroxide. $\text{Be}(\text{CH}_3)_2$ is monomeric in ether as also in the vapour state but in the solid state is polymeric



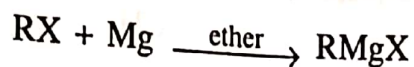
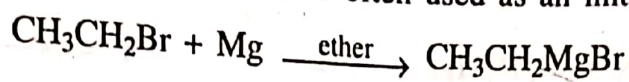
(16-VI)

with bridging methyl groups (3 centred 2 electron bond). The carbon of the bridging methyl

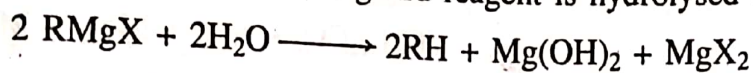
group contributes one electron while one of the two bridging Be atoms contributes one (16-VI) towards the three-centred bond.

Note that polymeric BeCl_2 has usual $2c-2e$ bonds between the bridging chlorines and beryllium. Compare $3c-2e$ bonds in B_2H_6 (Section 14.6).

Of all the organomagnesium compounds the Grignard reagents, RMgX ($\text{R} = \text{alkyl/aryl}$; $\text{X} = \text{halogen}$), are the most famous. They are of immense importance in a variety of organic syntheses. Grignard reagents are prepared by the reactions of alkyl/aryl halide with metallic magnesium in ether solvent or tetrahydrofuran, preferably in the absence of air and moisture. To begin with the reaction is slow—iodine is often used as an initiator.



Moisture and water are avoided as the Grignard reagent is hydrolysed :

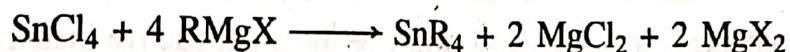


For synthetic purposes the Grignard reagents are utilised in ether solvent as prepared.

In several cases the Grignard reagents have been isolated as crystalline dietherate *eg.* $\text{C}_6\text{H}_5\text{MgBr} \cdot 2(\text{Et}_2\text{O})$; $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{Et}_2\text{O})$. Crystal structure reveals that $\text{Mg}(\text{II})$ is tetrahedral, the four vertices of the tetrahedron being occupied by C, Br and the two ether O.

Grignard reagents are of varied utility in organic syntheses :

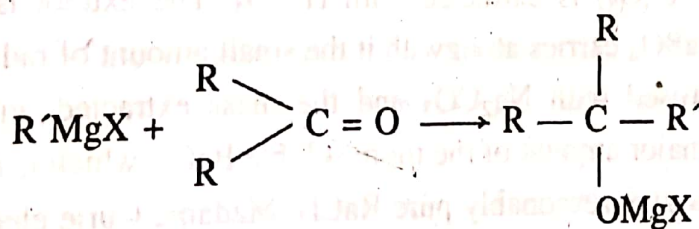
1. Alkyl/Aryl groups are introduced in exchange of halogens :



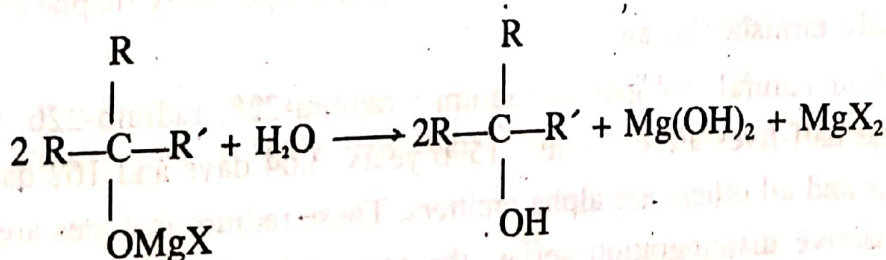
2. Alkyl halides react with RMgX to give saturated hydrocarbons :



3. Grignard reagents react with carbonyl compounds in the following way :

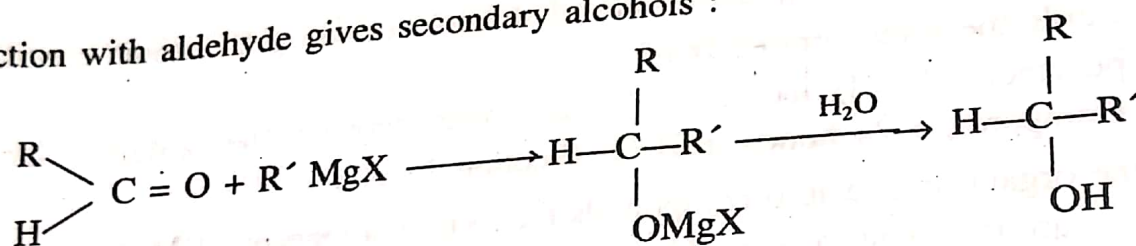


Addition of water hydrolyses the product to an alcohol :



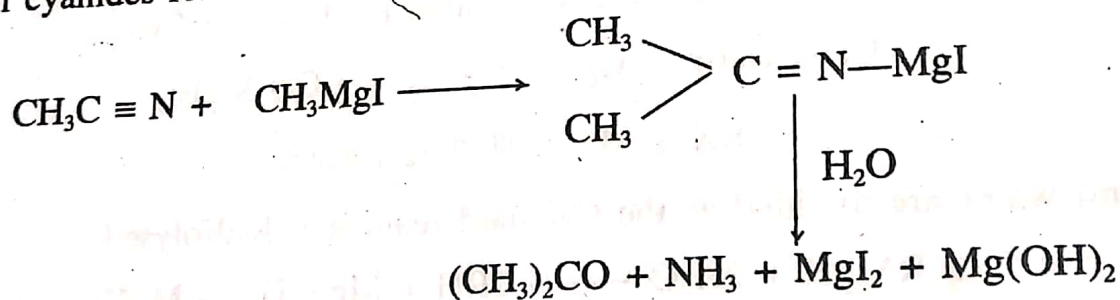
Thus reaction of a Grignard reagent with a ketone gives a tertiary alcohol.

Reaction with aldehyde gives secondary alcohols :



(see also Chapter 4).

4. Alkyl cyanides react with Grignard reagents to give ketones :



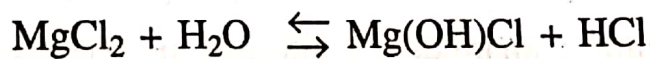
There are indeed vast amount of literature on Grignard reagents—for more informations the reader need to consult Texts on Organic Chemistry. Grignard was awarded the Nobel Prize in 1912.

16.7. COMPOUNDS OF MAGNESIUM AND THE ALKALINE EARTHS

16.7.1. Magnesium Sulphate : This occurs in nature as the heptahydrate called *Epsom salt* or *episomite* and as the monohydrate *kieserite*, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. Most of the commercial heptahydrate salt is obtained from magnesite, MgCO_3 , by treating with dilute sulphuric acid and crystallising. The heptahydrate has its six water molecules coordinated to Mg^{2+} and the seventh water molecule being hydrogen bonded to the sulphate radical.

When a solution of magnesium sulphate (or any other soluble magnesium salt) is treated with alkali carbonate solution, a precipitate of magnesium carbonate and hydroxide is obtained. This light but voluminous precipitate is mixed with ~ 15% asbestos fibre and the mixture is widely used as an insulating material for boilers and steam pipes. Magnesium sulphate is also used as a mild purgative.

16.7.2. Magnesium Chloride : This is extracted from carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ with a hot 20% solution of MgCl_2 . On concentrating and cooling KCl first crystallises. The mother liquor on further concentration gives crystals of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The chloride may also be obtained from the carbonate by HCl treatment. Anhydrous magnesium chloride cannot be obtained by simply heating the hexahydrate since hydrolysis occurs :



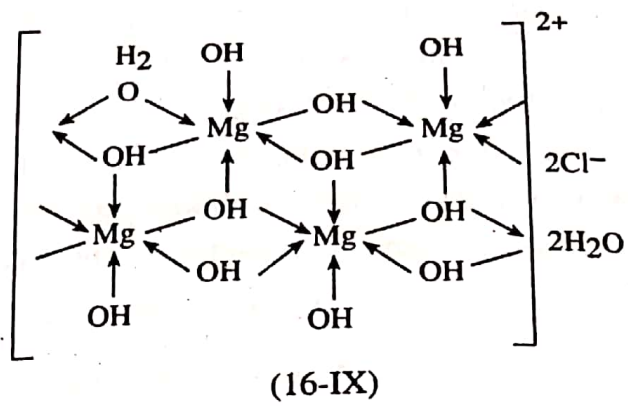
Heating in an atmosphere of HCl gas provides the anhydrous salt. Presence of HCl gas suppresses the above possible hydrolysis.

16.7.3. Sorel's Cement or Zyolith : Magnesium carbonate decomposes at ~ 700°C to MgO and CO_2 . The resulting fluffy powder consisting of MgO and little MgCO_3 is known as 'light-burnt magnesia'. When a concentrated solution of magnesium chloride is mixed with light-burnt magnesia the paste sets to a hard marble-like mass called *Sorel's cement* or *Zyolith*.

Sorel's cement is considered as a basic chloride of the type $\text{MgCl}_2 \cdot 3\text{Mg(OH)}_2 \cdot 8\text{H}_2\text{O}$.

is believed to have a tetrameric structure (16-IX) containing bridging H₂O and OH groups. Charge balancing chloride ions and some H₂O are outside the tetrameric unit.

Fillers such as saw dust, asbestos, powdered fireclay are mixed with MgO and concentrated aqueous magnesium chloride and suitable dyes to make *floor materials*, *artificial marble* and *artificial ivory* (buttons etc.). These materials are used only for interior decoration as these are not resistant to water.

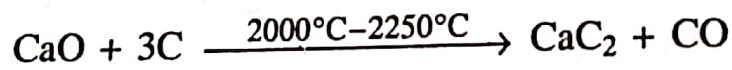


16.7.4. Magnesium Perchlorate : This

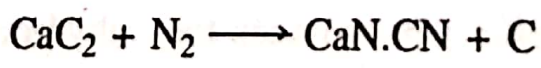
is obtained by the action of HClO₄ on magnesium carbonate. The anhydrous perchlorate is a very efficient drying agent, and is known as *anhydrone*.

16.7.5. Plaster of Paris : This is calcium sulphate hemihydrate, CaSO₄ · ½ H₂O or (CaSO₄)₂ · H₂O. This is obtained commercially by careful heating of gypsum CaSO₄ · 2H₂O to 120-130°C. The heating is generally done in large steel pots provided with mechanical stirrers or in rotary kilns. When Plaster of Paris is mixed with water to a paste it sets in a few minutes to a solid mass owing to rehydration. It is used in preparation of moulds for casting metals and for making casts for statues and also in surgical settings.

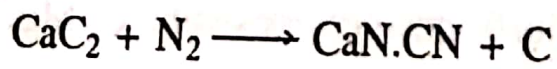
16.7.6. Calcium Carbide : This is an ionic carbide. This is manufactured by heating a mixture of quicklime (CaO) and coke to a high temperature in an electric furnace :



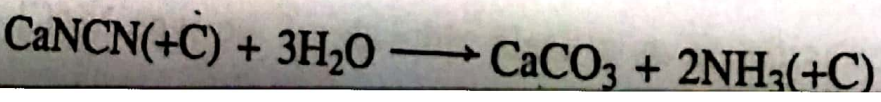
From time to time fresh mixture of quicklime and coke is introduced into the furnace from the top. Electric arc is set in the lower part of the furnace and above the arc region there are air inlets to burn the CO. The heat produced during the burning of CO in air helps in preheating the incoming charge of CaO and C. The calcium carbide collects at the bottom of the furnace and is tapped off from time to time. Calcium carbide is used in the preparation of acetylene (CaC₂ + 2HCl → CaCl₂ + C₂H₂), in oxyacetylene flame, as an illuminant and in the manufacture of calcium cyanamide—a nitrogenous fertiliser :



16.7.7. Calcium Cyanamide : This is manufactured by heating finely divided calcium carbide at ~ 1000°C in an atmosphere of nitrogen :



The resulting black mixture of calcium cyanamide and carbon is known as *nitrolim*. This is used in the synthesis of ammonia. On treating nitrolim with steam under pressure, calcium carbonate and ammonia are produced :



Metallic barium is produced by procedures analogous to those used for calcium.

16.9. USES OF THE GROUP IIA (GROUP 2) ELEMENTS

Beryllium has important uses in alloys. A copper-beryllium alloy with ~ 6% Be is as hard as steel and has a high chemical and mechanical resistivity. Beryllium-copper alloys containing ~ 2% Be and ~ 0.5% Ni is also very hard and has a high elasticity. This alloy is used in the manufacture of high grade springs. Metallic beryllium is used in making windows for X-ray tubes since it absorbs X-rays only to the extent of one-seventeenth of that by aluminium.

Due to its low neutron absorption cross section (section 12.20) elemental beryllium is widely used as a construction material for nuclear reactors. It is also used as a moderator of neutrons and as a source of neutrons (section 12.12).

Magnesium alloys are light and are used in aircraft and automobile parts. *Magnalium* is a magnesium aluminium alloy with 10-30% Mg. Other elements with which alloys have been made are Zn, Mn, Sn, Zr. Magnesium is a good and useful reducing agent. Magnesium turnings are used to reduce UF_4 in graphite-lined steel reactors to produce uranium metal.

The metal is used as a reducing agent in the production of metals Be, Ti, Zr, Hf from their chlorides. It is extensively used in organic syntheses as a component of Grignard reagents.

Magnesium is an essential element in biological functions. It is bound to ATP and the Mg-ATP complex serves as the energy supplier in all biological reactions (section 13.8.1). It is also a part of the chlorophyll of green plants, which is responsible for the synthesis of carbohydrates (glucose $C_6H_{12}O_6$). Chlorophyll is a magnesium (II) complex of an N_4 macrocycle porphyrin. The magnesium is seated ~ 0.4Å (40 pm) above the centre of the plane of N_4 atoms of the macrocyclic ligand. For details see section 13.10.

Calcium is a powerful reducing agent. It is often used in the preparation of metals whose oxides are resistant to reduction. Metallic calcium is used in the production of certain lead alloys. A lead alloy containing 0.7% Ca, 0.6% Na and 0.04% Li is used as a bearing metal.