

CHAPTER 16

THE ALKALINE EARTH METALS

(Elements of Group II A)

The elements of group II are divided into two sub-groups, A and B. The elements of group IIA are known as *Alkaline Earth Metals*.

Group II A	Group II B
Be — Beryllium*	
Mg — Magnesium	
Ca — Calcium	Zn — Zinc
Sr — Strontium	Cd — Cadmium
Ba — Barium	Hg — Mercury
Ra — Radium	

The Electronic Structure

The metals of Group IIA, that is, Be, Mg, Ca, Sr, Ba and Ra have two electrons in the outermost energy level. These two electrons are very well screened by the nuclear charges which are similar to those of the alkali metals. The electronic configurations of IIA metals are given in Table 16.1. Each of the alkaline earth metals has two electrons in the valence shell which is just outside

Table 16.1. Electronic configuration of the alkaline earth metals.

At No. <i>Z</i>	Elements	Electronic structure	Valence electrons
4	Be	He core, $2s^2$	$2s^2$
12	Mg	Ne core, $3s^2$	$3s^2$
20	Ca	Ar core, $4s^2$	$4s^2$
38	Sr	Kr core, $5s^2$	$5s^2$
56	Ba	Xe core, $6s^2$	$6s^2$
88	Ra	Rn core, $7s^2$	$7s^2$

* Old name of Be is glucinum because all its salts have sweet taste.

an inert gas core. It is seen that alkaline earth metals are not the only elements with 2 electrons in the outermost energy level. It will be interesting to distinguish these elements here for the sake of an understanding of their chemical properties in relation to the alkaline earth metals.

<i>Elements</i>	<i>Outermost valence shell</i>
Helium—	s^2 (Stable state)
Alkaline earth metals—	s^2 (Valence electrons)
Transition elements—	s^2 (Part of valence electrons)
Zn, Cd, Hg (group II B)—	s^2 (Valence electrons)
Lanthanides and Actinides—	s^2 (Part of valence electrons)

Thus, the electron grouping of s^2 in the outermost energy level of the above group of elements occur in each case, but the chemistry is vastly different in certain cases. The electrons in the inner orbitals also play a very important part in determining the nature of an element or groups of elements.

Physical Properties

The two outermost s electrons of alkaline earth metals resonate and thus form covalent bond between each atom and its adjacent atoms in the crystal lattice. Like alkali metals these electrons move through metallic network under electrical potential. The metals are, therefore, good conductors of electricity and heat. The silvery appearance of a freshly cut surface is due to the presence of the s electrons reflecting light. Because there are two electrons instead of one, the bonds between the atoms are stronger and hence the alkaline earth metals are harder and heavier than the alkali metals. Beryllium is hard enough to scratch glass. The alkaline earth metals also have higher melting points for the same reason. Some of the physical properties of the alkaline earth metals are given in Table 16.2

As the radius of the atom of the alkaline earth metals increase, the ease of removing the outer electrons is also increased and hence the reactivity of the metals increase with the atomic number. The values of the ionization potentials

Table 16.2. Physical properties of alkaline earth metals.

Properties	Be	Mg	Ca
Atomic Number	4	12	20
Atomic radius (Å)	0.90	1.36	1.74
Ionic radius, M^{+2} ion (Å)	0.31	0.65	0.99
Ionization potential (ev)	9.30	7.60	6.10
Electronegativity	1.50	1.20	1.00
Density (g/cm ³)	1.86	1.75	1.55
Melting point (°C)	1280	651	851
Boiling point (°C)	1500	1100	1487
Electrode potential (v)	Be/Be ⁺² 1.7	Mg/Mg ⁺² 2.34	Ca/Ca ⁺² 2.87
Oxidation states	+2	+2	+2
Heat of hydration M^{+2} (aq.) (Kcal/g.ion) }	570	460	395
Properties	Sr	Ba	Ra
Atomic number	38	56	88
Atomic radius (Å)	1.91	1.98	2.20
Ionic radius, M^{+2} (Å)	1.13	1.35	1.52
Ionization potential (ev)	5.70	5.20	5.20
Electronegativity	1.00	0.90	0.97
Density (g/cm ³)	2.60	3.59	6.00
Melting point (°C)	770	710	960
Boiling point (°C)	1366	1537	1150
Electrode potential (v)	Sr/Sr ⁺² 2.89	Ba/Ba ⁺² 2.90	Ra/Ra ⁺² 2.92
Oxidation states	+2	+2	+2
Heat of hydration M^{+2} (aq.) (Kcal/g.ion) }	355	305	—

and the electrode potentials signify the same trend in the reactivity. Be, the first element in group IIA, is a bridge element and resembles Al in group IIIA. Magnesium is also somewhat different from Ca, Sr and Ba. Thus the hydroxides of Be and Mg are almost insoluble in water and Be(OH)₂ is amphoteric whereas the hydroxide of Ca, Sr and Ba are strongly basic and soluble in water. This is due to small size of Be and Mg which have tendency to form oxides and

hydroxides and other compounds which are more covalent than those of the heavier and large-sized Ca, Sr and Ba atoms, Complexes of Be are quite numerous and stable but others show less tendency to form stable complexes. The solubility of carbonates and sulphates of the alkaline earth metals decreases considerably with the increase in the ionic sizes from Be to Ra.

An interesting feature regarding the trend in the group is observed in the temperature of decomposition of their carbonates to MO and CO₂.

<i>Compounds</i>	<i>Temperature of decomposition</i>
	°C
BeCO ₃	90
MgCO ₃	540
CaCO ₃	900
SrCO ₃	1290
BaCO ₃	1360

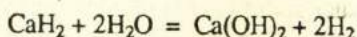
As in the case of alkali metal carbonates, the CO₃⁻² has a resonating structure and the metal is bonded to an oxygen of CO₃⁻² either by ionic bond or gradual increase of covalent bond as the charge on M increases. The most stable carbonates have purely ionic bond. Increase of charge and decrease of size of M produces polarization effect with oxygen of the carbonate resulting in the formation of M—O bond and release of CO₂.

The term 'alkaline earth' was formerly used to denote oxides of Ca, Sr and Ba because of their resemblance with Al₂O₃ which is a typical "earth" and due to the fact that they produce alkalis in water. The term 'alkaline earth' has now been extended to include Be and Mg. Radium has quite similar chemistry particularly to that of Ba but is radioactive.

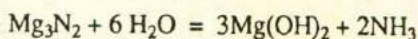
Chemical Properties

(a) *Reaction with air (O₂ and N₂)* : The alkaline earth metals react readily on heating with oxygen and nitrogen of the air to form oxides, MO, and nitrides, M₃N₂. Pure oxygen gives oxides. Be reacts less rapidly and requires high temperatures for the formation of BeO which is covalent and others are ionic. Ba forms peroxides, BaO₂, because of its greater reactivity. Be does not form peroxides.

(b) *Reaction with hydrogen* : Ca, Sr and Ba react with hydrogen when heated to produce crystalline ionic hydrides. These hydrides readily react with water to give hydrogen :



(c) *Reaction with nitrogen* : Alkaline earth metals form M_3N_2 on heating in presence of nitrogen. These are hydrolysed by water to give ammonia :



(d) *Reaction with water* : The Alkaline earth metals react readily with water giving off H_2 and forming M(OH)_2 . Mg and Be do not react with water readily. The electrode potential of Be is much lower than the other alkaline earth metals.

(e) *Reaction with acids* : They react vigorously with acids forming the corresponding salts.

(f) *Reaction with halogens* : The alkaline earth metals form halides, MX_2 , by direct reaction with halogens. Beryllium halides are covalent whereas other halides of the group are ionic. These halides are readily soluble in water except the fluorides of Mg, Ca, Sr and Ba. Alkaline earth metal halides form hydrates.

Comparison of the Alkali and the Alkaline Earth Metals

The alkali and alkaline earth metals have quite a good deal of resemblance in their properties. The reason for this is the same outermost energy level involved for the valence electrons shown below :

Z	Alkali metals			Z	Alkaline Earth metals		
3	Li	(2)	$2s^1$	4	Be	(2)	$2s^2$
11	Na	(10)	$3s^1$	12	Mg	(10)	$3s^2$
19	K	(18)	$4s^1$	20	Ca	(18)	$4s^2$
37	Rb	(36)	$5s^1$	38	Sr	(36)	$5s^2$
55	Cs	(54)	$6s^1$	56	Ba	(54)	$6s^2$
87	Fr	(86)	$7s^1$	88	Ra	(86)	$7s^2$

The points of similarity are :

(1) Like alkali metals, they are electropositive and have great chemical activity. They do not occur in the free state in nature.

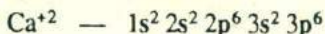
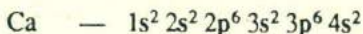
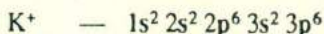
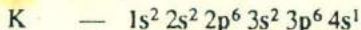
(2) Both are extracted by electrolytic methods from their stable salts such as chlorides.

(3) Both are soft, silvery white in untarnished conditions.

(4) React with water to give metal hydroxides and H_2 .

(5) The hydroxides give strong bases with water.

The points of the contrast between the alkali and alkaline earth metals arise mainly due to the presence of 2 valence electrons in the case of alkaline earth metals and 1 valence electron in the case of alkali metals. It is noted that M^{+2} and M^{+1} ions have the same electronic configurations as in the case of K^+ and Ca^{+2} as given below :—



But the excess positive charge of M^{+2} pulls the electron cloud closer to the nucleus than in M^{+1} . Hence there is greater decrease in size in M^{+2} than in M^{+1} . Moreover, the s^1 and s^2 electrons give rise to the differences in the physical characteristics of the two metals.

Some of the points of contrasts are :

(1) The alkaline earth metals are harder, heavier and have higher melting points than those of alkali metals.

(2) Increased charge and smaller size of M^{+2} give rise to greater polarizing capacity than the alkali metals. Hence the oxides and hydroxides of M^{+2} have more covalent character and are less basic as compared to the alkali metals. The covalent character is more pronounced in the case of Be and Mg compounds

because of their smaller ionic sizes which have stronger polarising effect on anions.

(3) Ca, Sr and Ba react less vigorously with water than alkali metals. Be and Mg can survive in contact with water for a long time.

(4) Carbonates and sulphates of alkaline earth metals are insoluble in water whereas those of alkali metals are soluble and undergo hydrolysis (except Li_2CO_3 which is insoluble).

(5) Phosphates of alkaline earth metals are insoluble whereas those of alkali metals are soluble (except Li_3PO_4 which is insoluble).

Occurrence of the Alkaline Earth Metals

Calcium is one of the most abundant elements and is widely distributed in nature in the form of limestone which is impure calcium carbonate. Calcium also occurs in the form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ known as *gypsum* and *fluorspar*, CaF_2 . Magnesium is found in carnallite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and in dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$. Beryllium occurs in *beryl*, an aluminosilicate, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$. Strontium is rare and the chief ore is *celestite*, SrSO_4 . Barium is more abundant and is found in *barite* or heavy spar, BaSO_4 , and also as BaCO_3 . Radium is found in *pitchblende* and *cleveite*.

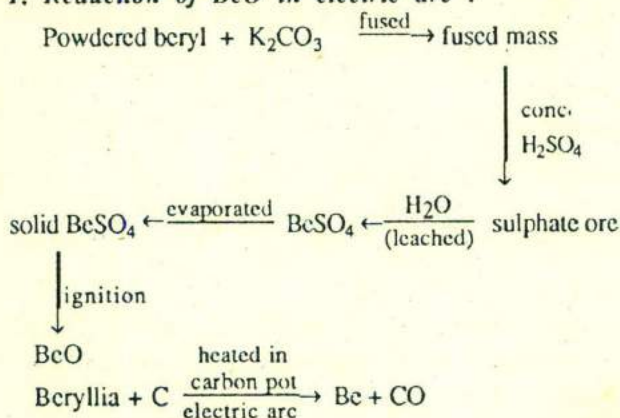
Metallurgy of Alkaline Earth Metals

Extraction of Beryllium :

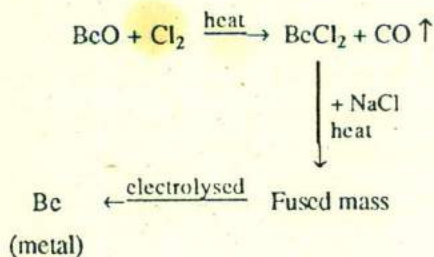
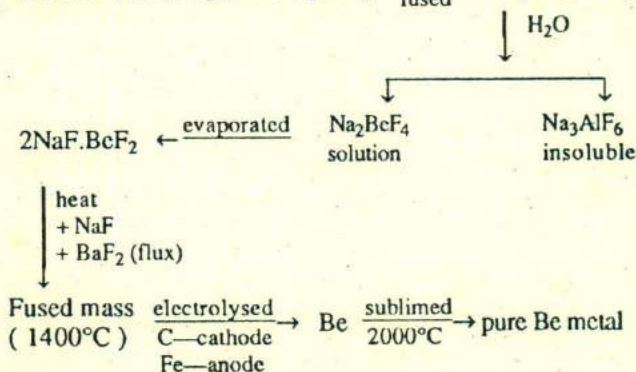
Sources : Beryl— $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$
 Chrysoberyl— BeAl_2O_4

Extraction Process : The ore beryl is first processed to get BeCl_2 , BeF_2 or BeO . The halides of Be are subjected to electrolysis in the fused state in presence of a conducting salt such as NaCl or NaF . BeO is reduced to Be in an electric arc furnace by means of carbon.

1. Reduction of BeO in electric arc :



2. Electrolytic method from BeO :

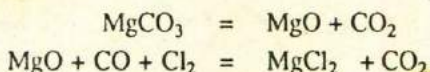
3. Ground ore (beryl) + Na₂SiF₆ $\xrightarrow[\text{fused}]{850^\circ\text{C}}$ Na₂BeF₄ + Na₃AlF₆

Extraction from Liquid NH_3 : Small quantities of Be is obtained in a very pure state by electrolysing BeCl_2 or $\text{Be}(\text{NO}_3)_2$ in liquid NH_3 .

Magnesium

Sources :	Magnesite	—	MgCO_3
	Dolomite	—	$\text{MgCO}_3 \cdot \text{CaCO}_3$
	Carnallite	—	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$
	Asbestos	—	$\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$

Extraction Process : Magnesium is extracted by the electrolysis of MgCl_2 or from MgO . Magnesium chloride used may be obtained from MgCO_3 . By thermal decomposition, MgCO_3 is converted to MgO which when heated with CO and Cl_2 gives anhydrous MgCl_2 :



MgCl_2 in the hydrated form, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, may be obtained from sea water or carnallite by precipitation of Mg^{+2} with slaked lime, $\text{Ca}(\text{OH})_2$. The precipitate of $\text{Mg}(\text{OH})_2$ is dissolved in HCl and the solution is evaporated to $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. This, on heating in presence of dry HCl gas, gives MgCl_2 .

The fused carnallite, $\text{MgCl}_2 \cdot \text{KCl}$, may also be used for the extraction of Mg by electrolysis process.

(1) The electrolytic vessel is a cast iron tank which is also made the cathode. A covered anode is made of graphite which dips in the fused MgCl_2 (containing NaCl or KCl to lower the fusion temperature and increase the conductivity) as shown in Fig. 16—1. The Cl_2 gas produced during the electrolysis escapes from the opening in the anode porcelain hood. The electrolysis is carried at a temperature of 700°C in an inert atmosphere (coal gas or H_2). The molten Mg metal formed at the cathode rises to the surface of the fused mixture and is collected. The purity of Mg is about 99.9% which is purified further by heating in a flux of MgCl_2 and NaCl .

(2) Mg can also be obtained directly from MgO by electrolytic method as in the case of Al from Al_2O_3 . MgO is dissolved in a fused mixture of BaF_2 , MgF_2 and NaF . The electrolysis is done with iron cathode and graphite anode in a steel

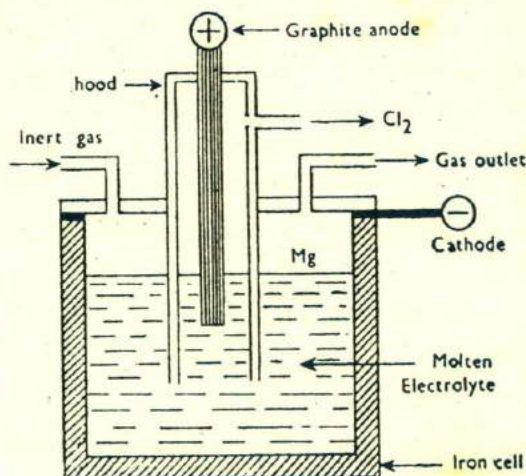
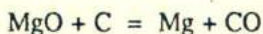


Fig. 16—1. Electrometallurgy of magnesium

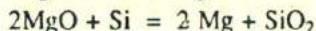
tank at a temperature of 950°C. Mg is liberated at the cathode and O₂ at the anode.

MgO can be directly converted to Mg by heating with C at a temperature of 2000°C :



Mg vaporises with CO and reoxidation of Mg is prevented by means of H₂ gas or coal gas in the reaction vessel and cooled rapidly to solidify Mg.

(3) Mg has been recently obtained by heating MgO with ferrosilicon under reduced pressure :



FeO forms a slag with SiO₂ giving FeSiO₃ which is easily removed.

Calcium, Strontium and Barium

Source of Ca :

Limestone, chalk, marble —	CaCO ₃
Gypsum —	CaSO ₄ ·2H ₂ O
Fluorspar—	CaF ₂
Phosphorite—	Ca ₃ (PO ₄) ₂

Extraction of Ca : The mineral CaCO_3 is converted to CaCl_2 which is subjected to electrolysis in the fused state mixed with an alkali metal halide or CaF_2 using iron cathode and graphite anode. The iron cathode is slowly raised as the liberated Ca collects at the tip of the cathode. The calcium is only 85% pure and is distilled in high vacuum to make it pure.

Strontium : This is obtained by electrolysis of fused SrCl_2 with KCl as in the case of Ca.

Barium : This may be obtained by the electrolytic method of fused BaCl_2 . Electrolysis of BaCl_2 solution using Hg cathode has also been in use. Ba amalgam formed is distilled to remove Hg.

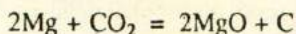
[N. B. Radium is treated separately in this book, see Chapter 27]

Uses of Alkaline Earth Metals

Uses of Be : 1. It is transparent to X-rays and the metal is used for window material in X-ray tubes.

2. Be is used in the manufacture of light alloys, such as Be—Cu and Be—Ni resistant to salt water corrosion.

Uses of Mg : 1. Mg has great reducing property and combines with oxygen and is used to separate non-metals, such as Si, B from their oxides. Burning Mg combines with O of CO_2 liberating C :



2. It is used in photoflash bulbs because it emits brilliant light and also used in military flares.

3. Light-weight alloys of Mg with special properties are made. These are :
Magnalium (Mg—90%, Al—9% and Cu—1%). It is hard, strong and light and is used in aeroplane engines, speed boats etc.

Electron (Mg—95% and Zn—5%). It is also a light alloy and has special properties.

Uses of Ca : 1. Ca is used as a dehydrating agent for organic solvents, such as alcohols.

2. As a scavenger to remove gases in fused metals.

3. As a reducing agent in the production of Cr, Th etc.

Uses of Ba : 1. Ba is used as a degassing agent in making vacuum tubes.

2. Ba—Ni alloys are used in vacuum tubes and spark plugs.

[N. B. Strontium has no significant use, its compounds are used in pyrotechniques.]

Compounds of Alkaline Earth Metals

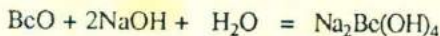
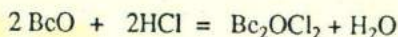
Some important compounds of alkaline earth metals are described with regard to their commercial uses and scientific studies.

Compounds of Be

Compounds of Be even with O and F have greater covalent character.

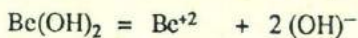
Beryllium oxide, BeO : This is formed by igniting BeCO_3 .

BeO is hard and insoluble in water. It dissolves both in acids and alkalis to show its amphoteric character :

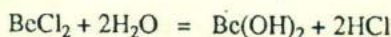


BeO is extremely poisonous and its use in fluorescent tube has been abandoned. BeO crystal consists of BeO_4 tetrahedra.

Beryllium hydroxide, Be(OH)₂ : This is formed as a precipitate by adding ammonia to a Be-salt solution. Caustic alkalis dissolve it forming clear solution. This is also soluble in acids and shows amphoteric character :

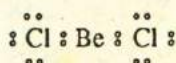


Beryllium halides, BeX₂ : When chlorine is passed over a heated mixture of BeO and C, BeCl_2 is obtained. This sublimes as white crystals. Beryllium halides are easily hydrolysed and in this respect it resembles Al^{+3} salts and forms an acid solution :

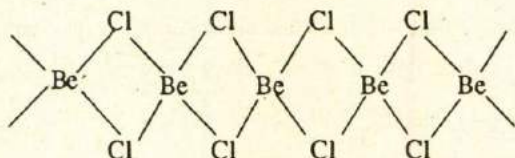


BeCl_2 is a linear molecule indicating the use of sp hybrid orbitals by Be to form two equivalent bonds at an angle of 180° . The properties of Be compounds indicate covalent bonding with Be. The electronic structure of Be is $1s^2 2s^2$. At

first sight it appears that Be may not form any compound and may behave like an inert gas. But by invoking the mechanism of promotion of electron to higher energy level as in the case of carbon, one of the 2s electrons of Be may be placed in a 2p orbital giving the excited state $1s^2 2s^1 2p_x^1$. The two unpaired electrons form two bonds but these two bonds of Be must be different from one another because one bond is formed by $2s^1$ electron and the other by $2p_x^1$ electron through sharing of electrons or overlap of orbitals with 2 other atoms such as those of Cl. But the two bonds of Be are completely identical in length and strength and are linear. It is, therefore, concluded that Be does not use the $2s^1$ and $2p_x^1$ electron orbitals separately but a combination of the two forming sp hybrid bond orbitals which are equivalent and collinear. Thus in BeCl_2 , the bonds between Be and 2Cl are formed by overlap of p orbitals of Cl atoms with sp hybrid orbitals of Be as given in Fig. 2—9 (page 78). The same structure for BeCl_2 is proved by the repulsion of two electron pairs which form the bonds. The gaseous BeCl_2 is a linear molecule.



But in most solid compounds Be occupies the tetrahedral positions indicating sp^3 hybrid bond formation. Thus, solid BeCl_2 is a polymer molecule in which each Be is surrounded by 4Cl :



Beryllium alkyls also show similar structures as in the case of $\text{Be}(\text{CH}_3)_2$, $\text{Be}(\text{C}_2\text{H}_5)_2$ etc.

Basic Beryllium acetate, $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$: This is obtained by the reaction of $\text{Be}(\text{OH})_2$ with CH_3COOH and evaporation. It is an interesting compound having the four beryllium atoms situated at the corners of a regular tetrahedron and oxygen at the centre. The six edges are occupied by the acetate

groups, Fig. 16—2 (a). [Compare from the structure of Be—oxalate Fig. 16—2. (b) in which Be is at the centre].

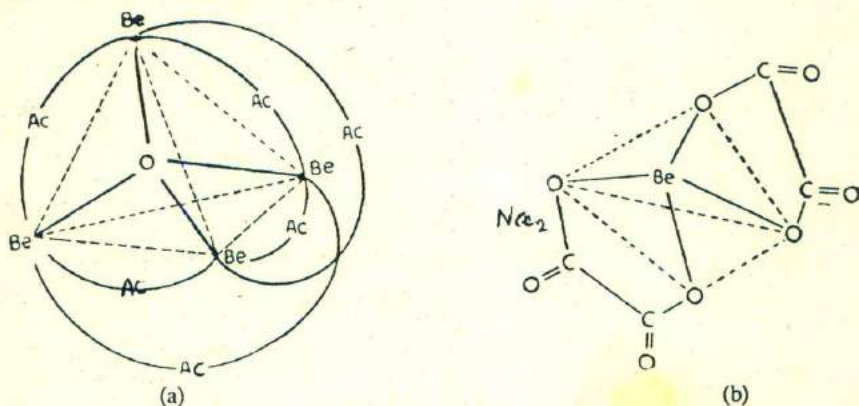


Fig. 16—2. (a) Structure of $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ (Ac = CH_3COO i.e. acetate group). Be atoms at the corners of a tetrahedron. (b) Beryllium oxalate structure. Be atom at the centre of the tetrahedron.

Anomaly of Beryllium : Many properties of beryllium are in contrast to those of the other alkaline earth metals. As in the case of lithium which is a bit different from the other alkali metals and resembles with magnesium, similarly, beryllium has similar relationship with aluminium. This is in accordance with the diagonal relationship in the Periodic Table. The small size of the beryllium ion is responsible for its anomalous behaviour. Beryllium hydroxide, like $\text{Al}(\text{OH})_3$, is amphoteric and, therefore, Be^{+2} salts are hydrolysed in water. This is not the case with other alkaline earth metal salts. Be forms quite a large number of complexes which the other alkaline earth metals do not. For instance, Na_2BeF_4 and oxalate complex, $\text{Na}_2\text{Be}(\text{C}_2\text{O}_4)_2$ etc. The interesting feature of these complexes is that beryllium is at the centre of tetrahedron and the four Be—O bonds are directed towards the corner as shown in Fig. 16—2 (b).

Be shows maximum bonds of 4 in most complexes, like Al as in $\text{Na}_2[\text{BeF}_4]$ and $\text{Al}[\text{NH}_3]_4\text{Cl}_3$ due to the availability of certain orbitals for bond formation. Like $\text{Al}(\text{OH})_3$, which gives NaAlO_2 , $\text{Be}(\text{OH})_2$ also gives Na_2BeO_2 .

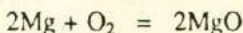
Normal carbonates of Be and Al are not formed because Be and Al are weakly basic elements. The carbonates of Be and Al are extensively hydrolysed

to give basic carbonates because of their small sizes and because BeO and Al₂O₃ are much more stable than their carbonates.

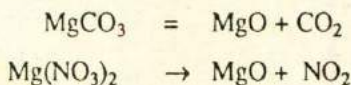
Compounds of Magnesium

Magnesium oxide, MgO : This is also known as magnesia. It is obtained as follows :

(1) By burning metallic Mg in air or oxygen :

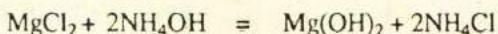


(2) By heating the hydroxide, nitrate, carbonate and even magnesite :



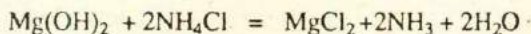
MgO is very light white powder and only sparingly soluble in water. It forms hydroxide very slowly. It fuses only at a very high temperature and is used for lining of furnace. MgO is used in medicine to neutralise hyperacidity. *Sorel's cement* is made by mixing fine powder of MgO with a solution of MgCl₂. This is a strong and durable cement and is said to be a basic salt, MgO.MgCl₂.

Magnesium hydroxide, Mg(OH)₂ : This occurs as the mineral brucite. It is prepared by adding ammonia or alkali to a soluble magnesium salt :



A large-scale manufacture of Mg(OH)₂ is done by adding milk of lime to MgCl₂ solution.

Mg(OH)₂ is insoluble in water, slightly soluble on boiling but completely insoluble in ammonium chloride. The solubility of Mg(OH)₂ is used in qualitative analysis :



A suspension of magnesium hydroxide is called "milk of magnesia" and is used in medicine for hyperacidity of the stomach.

Magnesium carbonate, MgCO₃ : It is found in nature as magnesite, MgCO₃. It is obtained as white precipitate by adding alkali carbonate solution to a solution of magnesium salt. The composition of the precipitate is

$3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, a basic carbonate. This is commercially known as *magnesia alba* and is used in toothpaste, cosmetic and silver polish.

MgCO_3 is easily decomposed by heat to MgO and CO_2 . It dissolves in aqueous CO_2 to form magnesium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$, which is soluble in water and is known as *fluid magnesia*. This is a constituent of hard water and the basic carbonate is precipitated from it on boiling.

Magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$: This is known as "Epsom salt". It is made by dissolving MgCO_3 in H_2SO_4 . It is less soluble in cold water but soluble on boiling. It is used in medicine as purgative.

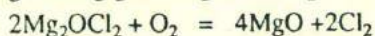
Magnesium chloride, MgCl_2 : This occurs in sea water and in the mineral carnallite. It is very soluble in water and crystallizes from aqueous solution as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The hexahydrate is a very hygroscopic substance. When heated $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ undergoes hydrolysis and forms MgO , HCl and H_2O .



On careful heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, the product of hydrolysis is Mg_2OCl_2 (Magnesium oxychloride) :

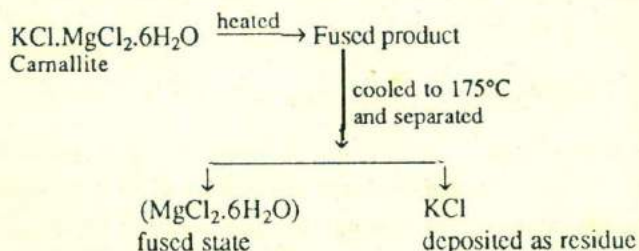


Mg_2OCl_2 on strong heating gives MgO and Cl_2 :



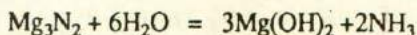
Anhydrous MgCl_2 : This is obtained by heating the hexahydrate in a current of hydrogen chloride or by burning magnesium in chlorine. The anhydrous MgCl_2 is also obtained by heating the double salt, $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$. Ammonium chloride prevents the hydrolysis of MgCl_2 during heating. The product is fused anhydrous MgCl_2 .

Separation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ from carnallite is accomplished as follows :

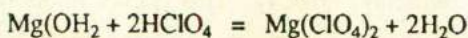


$MgCl_2$ in solution is used as a constituent of Sorel's cement with MgO .

Magnesium nitride, Mg_3N_2 : It is formed when magnesium is burnt in nitrogen. It is a colourless amorphous powder which is decomposed by water to $Mg(OH)_2$ and NH_3 . This is because Mg_3N_2 contains the true ionic species N^{3-} :



Magnesium perchlorate, $Mg(ClO_4)_2$: It is obtained by dissolving $Mg(OH)_2$ in $HClO_4$:

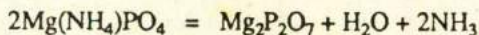


The solution on evaporation and drying gives $Mg(ClO_4)_2$. In the anhydrous state it is a highly efficient drying agent commercially known as "anhydron". It rapidly absorbs about 35% of its weight of water forming $Mg(ClO_4)_2 \cdot 6H_2O$. The drying efficiency is easily regenerated by heating the hydrate.

Magnesium phosphate : $Mg_3(PO_4)_2$ is formed when Na_3PO_4 is added to magnesium salt solution. With Na_2HPO_4 the precipitate is $MgHPO_4$.

When magnesium salt is added to a solution of phosphate in presence of ammonium chloride and ammonia, a crystalline precipitate is obtained on stirring or shaking. This is magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$:

Dilute NH_4OH is added to neutralize H^+ ion. This is almost insoluble in water. This white substance is used for both detection and determination of either magnesium or phosphate in analytical chemistry. The estimation of magnesium or phosphate was also used to be done by burning the crystalline precipitate to magnesium pyrophosphate, $Mg_2P_2O_7$:



Magnesium silicates : *Talc or soapstone* is a hydrated magnesium silicate, $Mg_3Si_4O_{11} \cdot H_2O$, which is greasy to touch and soft because of layer structures. It is of commercial importance for making face powders and for household furniture.

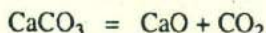
Asbestos is a hydrated magnesium silicate, $(\text{HO})_6\text{Mg}_6\text{Si}_4\text{O}_{11}\cdot\text{H}_2\text{O}$, with a fibrous structure because of chain structure of silicate. It is used in making incombustible fabrics, hardboard for flooring, roofing and sheets.

The Grignard reagents: This is an important group of compounds containing magnesium carbon bond. The general formula is R—Mg—X , where R is an organic group and X is a halogen. For example, $\text{CH}_3\text{—Mg—I}$ and $\text{C}_6\text{H}_5\text{—Mg—Br}$ etc. These are prepared from the reaction of magnesium metal with organic halogen compound in dry ether. This is extensively used in organic synthesis.

Compounds of Calcium

Calcium oxide, CaO: This is also known as quicklime or lime. This is manufactured from limestone, CaCO_3 , in a tall chimney-like furnace known as "limekiln", shown in Fig. 16—3.

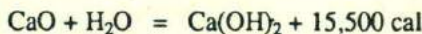
The limestone is fed at the top of the kiln and is decomposed by hot draft of gases from below obtained by burning fuels. Sometimes a rotary kiln is also used in which the burning is done by a jet of producer gas. The CO_2 is swept away by the hot gases and thereby permits the reaction to go to completion at a lower temperature.



Pure CaO is white amorphous powder and melts at a very high temperature, 2570°C . When strongly heated, it emits a bright light known as "limelight".

Lime is one of the most important compounds in chemical industry. It is used as a cheap alkali, for making slaked lime, bleaching powder, calcium carbide, calcium sulphite, mortar, cement and glass. It is also used in the purification of sugar and coal gas, in softening of water and tanning industries. Lime is used for liberating ammonia from ammonium salt. A mixture of CaO and NaOH is called "sodalime" and is used to remove both CO_2 and water vapour from gases.

Calcium hydroxide, Ca(OH)₂: When CaO reacts with water, Ca(OH)_2 is formed with the evolution of large amount of heat:



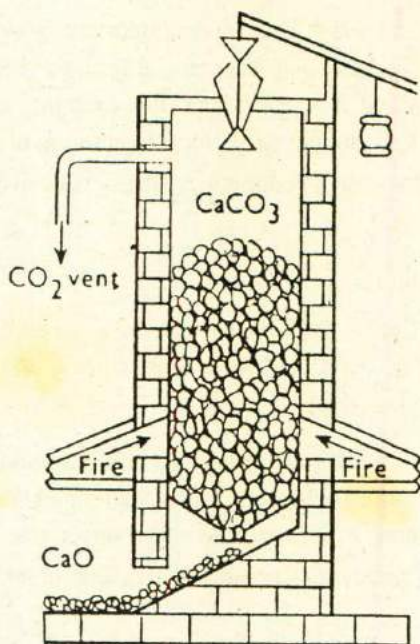


Fig. 16—3. A Lime-kiln.

Quicklime slowly exposed to the air takes up moisture and also CO_2 . Ca(OH)_2 first formed absorbs CO_2 forming CaCO_3 . This is the reason why lime crumbles on exposure to air.

Ca(OH)_2 is also known as slaked lime or hydrated lime. It is a dry white powder appreciably soluble in water. A saturated solution of Ca(OH)_2 is called *limewater*. A suspension of Ca(OH)_2 in water is known as *milk of lime*. This is used in making mortar and lime plaster for walls, ceilings and roofs because on long exposure it forms crystalline CaCO_3 which cements the binding materials. Ca(OH)_2 is used in many chemical industries mentioned in the case of lime.

Calcium carbonate, CaCO_3 : It occurs in nature and is widely distributed as minerals known by various names, such as limestone, marble,

chalk, Iceland spar, coral etc. Precipitated chalk is obtained by passing CO_2 gas to limewater or by adding Na_2CO_3 to a solution of CaCl_2 :



There are two forms of crystals of calcium carbonate : (i) Calcite and (ii) Aragonite, Calcite crystals (rhombohedral) are formed when precipitation occurs at below 33°C , while aragonite (rhombic prisms) is formed at above 30°C .

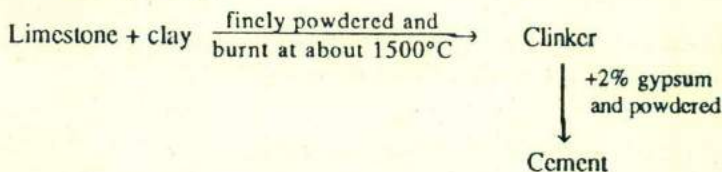
Calcite crystal is also known as "Iceland spar" and has the property of double refraction of light giving two images of the same thing. A pearl is made of CaCO_3 layers deposited upon a foreign particle, such as grain of sand, which has entered into the shell of an oyster.

CaCO_3 is not soluble in water but it dissolves in water when CO_2 is passed through the suspension forming calcium bicarbonate, $\text{Ca(HCO}_3)_2$, which is soluble in water. This solution on boiling deposits CaCO_3 .

Cement

Cement or Portland cement is essentially powdered calcium aluminosilicate. When treated with water it sets to a hard mass resembling stone which naturally occurs in Portland, England, and hence the name Portland cement.

The raw materials for the manufacture of cement are limestone and clay. Cement is made by pulverising a mixture of limestone and clay in the proper proportions, and roasting the powder in a rotary kiln heated by gas or powdered coal to a temperature of about 1500°C . The sintered lumps obtained is called "Clinker". The clinker is mixed with about 2% gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; and ground to a fine powder.



Setting of cement: The cement consists of the complex calcium aluminosilicate and it is believed that in contact with water hydrolysis occurs

forming $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$. These react with calcium silicate present forming interlocking crystals of calcium aluminosilicate and impart strengths and hardness to the mass.

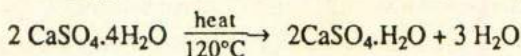
Concrete is made by mixing cement with broken pieces of bricks or aggregates or stone chips together with sand. Reinforced concrete contains steel bars or netting set in the concrete.

Calcium chloride, CaCl_2 : It is obtained as a by-product of the Solvay process for the manufacture of Na_2CO_3 . This can be obtained by dissolving oxide, hydroxide or carbonate of calcium with HCl . On crystallisation, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is obtained. On dehydration it gives CaCl_2 containing a little CaO .

CaCl_2 is very soluble in water and with ice it forms a freezing mixture having a temperature of -55°C . The anhydrous salt is used as a drying agent for gases and liquids.

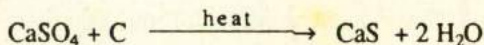
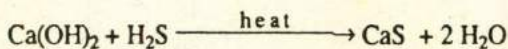
Calcium sulphate, CaSO_4 : This occurs in nature as anhydrous CaSO_4 (anhydrite), and as hydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum). The crystalline form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is called *alabaster*. Calcium sulphate is obtained in the form of precipitate when $\text{Ca}(\text{NO}_3)_2$ is treated with Na_2SO_4 or dil H_2SO_4 .

On heating gypsum, it loses water and forms $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$:

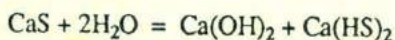


The hemihydrate, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, is known as "Plaster of Paris." When ground to fine powder and mixed with water to form a paste, it sets to a hard mass forming small interlocking crystals of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The anhydrous CaSO_4 does not possess the property of setting with water. Plaster of Paris is used in making plaster casts, moulds and for building purposes.

Calcium sulphide, CaS : It is made by several processes, such as when lime is heated in H_2S gas or when CaSO_4 is reduced with C :



It is a white powder and has a remarkable phosphorescence due to the presence of trace impurities, such as Bi, Mn, Cu etc. CaS is hydrolysed in H_2O to give $Ca(HS)_2$:



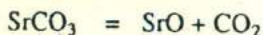
CaS and $Ca(HS)_2$ are used for removing hairs from skins and in tanning industries for removing hair from hides.

Calcium oxalate, CaC_2O_4 : When ammonium oxalate solution is added to a neutral Ca-salt solution in the hot condition, a white precipitate is obtained which is $CaC_2O_4 \cdot H_2O$, but insoluble in acetic acid and alkalis. The precipitation of CaC_2O_4 is used in the detection and estimation of Ca both gravimetrically by ignition to CaO and volumetrically by dissolving the precipitate in dil H_2SO_4 and titrating the liberated oxalic acid with $KMnO_4$ solution.

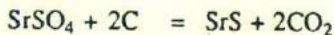
[For CaC_2 and $CaCN_2$ see Chapter 19 and for bleaching powder see Chapter 22]

Compounds of Strontium

Strontium oxide, SrO : This is obtained by a similar method as CaO, i.e. by heating of $SrCO_3$ or $Sr(NO_3)_2$:



$SrSO_4$ (celstine mineral) is converted to SrO by reducing $SrSO_4$ to SrS by C and treating with NaOH:



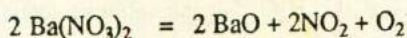
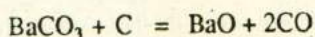
$Sr(OH)_2$ being less soluble is freed from Na_2S by water. $Sr(OH)_2$ on strong heating gives SrO .

SrO is slaked, like lime, with H_2O forming $Sr(OH)_2$ and has been used for the recovery of sugar from molasses by the process known as "Strontia method".

All other compounds of Sr are obtained by similar reactions as described in the case of Ca compounds.

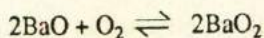
Compounds of Barium

Barium oxide, BaO : This is produced by heating BaCO_3 with finely divided carbon. The purpose of adding carbon is to reduce CO_2 to CO and thus to shift the equilibrium $\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$ to the right direction. The conversion of carbonate to BaO takes place at a much lower temperature than the decomposition temperature of BaCO_3 . BaO is also made from $\text{Ba}(\text{NO}_3)_2$ which easily decomposes when heated :

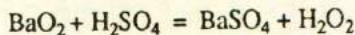


BaO is a white powder and is known as *Baryta*. It reacts with water to form $\text{Ba}(\text{OH})_2$. $\text{Ba}(\text{OH})_2$ is more soluble in water than $\text{Ca}(\text{OH})_2$ or $\text{Sr}(\text{OH})_2$ whereas $\text{Mg}(\text{OH})_2$ and $\text{Be}(\text{OH})_2$ are least soluble. The solution of $\text{Ba}(\text{OH})_2$ in water is known as *Baryta water*. It appears that the strength of the crystal forces decreases with increasing cation sizes. $\text{Be}(\text{OH})_2$ has the largest lattice energy and hence it is not easily soluble and so is the case with BeO . The lattice energies of the hydroxides and oxides of the alkaline earth metal decrease from Be to Ba .

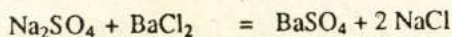
BaO is used for the preparation of BaO_2 . This is more easily formed than the preoxide of Ca or Sr . BaO_2 is obtained on heating BaO in air or oxygen at about 500°C :



On heating BaO_2 to about 700°C , it is decomposed giving BaO and oxygen. BaO_2 has been used for the production of H_2O_2 according to the reaction :



Barium sulphate, BaSO_4 : It occurs in mineral "Barytes", BaSO_4 . It is obtained by adding a soluble sulphate to a barium-salt solution :

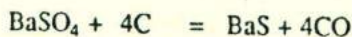


BaSO_4 is insoluble in water but slightly soluble in conc HCl and conc H_2SO_4 . The larger hydration energy of large SO_4^{-2} and Ba^{+2} ion makes BaSO_4 insoluble. smaller sizes of Be^{+2} and Mg^{+2} impart lower hydration energies for BeSO_4 and MgSO_4 which are soluble in water.

BaSO_4 is a starting material for all other barium compounds. BaSO_4 is converted into BaCO_3 by heating with Na_2CO_3 either in the solid state or in solution :



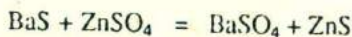
It is also converted into BaS by reduction with carbonate at high temperature :



BaS or BaCO_3 may then be dissolved in acids to produce the desired salts. The formation of insoluble BaSO_4 is used for identification and determination of both barium and sulphate.

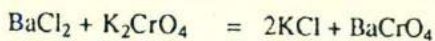
Barium sulphide, BaS : It is made as mentioned above. It is a white powder and is decomposed by water forming $\text{Ba}(\text{OH})_2$ and liberating H_2S .

It is used for removing hair from skins and hides. BaS is mixed with ZnSO_4 in aqueous solution to give a white precipitate consisting of a mixture of BaSO_4 and ZnS . This is isolated and dried in the powder form which is known as "*Lithopone*" :



Lithopone is not darkened by H_2S unlike white lead.

Barium chromate : This is obtained in the form of lemon-yellow insoluble precipitate when a soluble chromate is added to barium salt solution :



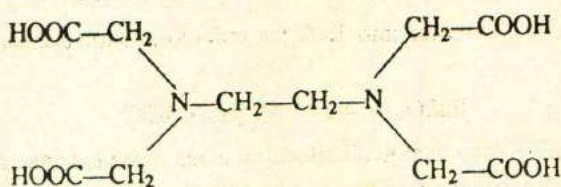
Ca and Sr do not form insoluble chromates and hence the precipitate of BaCrO_4 is used as a distinguishing test for Ba .

[N. B. The chemistry of radium which is almost similar to that of other alkaline earth metals, particularly to that of Ba has been described in chapter 27.]

Complex Compounds of Alkaline Earth Metals

Like the alkali metals, the alkaline earth metals are not very versatile in forming complex compounds. The complex forming ability decreases with the increase in atomic number in this group because of the increase in the size of the ions. But when an ion is encircled by a cyclic structure, it gives rise to a

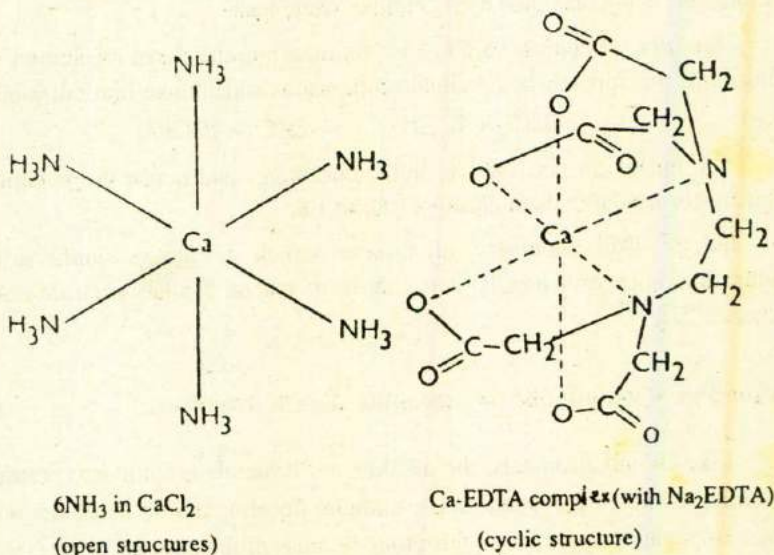
complex of great stability. Thus, $\text{CaCl}_2 \cdot 6\text{NH}_3$ is a very unstable complex and NH_3 is readily given off, but Ca^{+2} forms a stable complex with EDTA (ethylenediamine tetra-acetic acid), the anion of which completely envelops Ca^{+2} ion as shown in Fig. 16—4.



Ethylenediamine tetra-acetic acid

Mg^{+2} forms quite stable complexes of the cyclic structure types as the naturally occurring "chlorophyll" in which Mg is surrounded by four nitrogen forming part of a large organic ring called "porphyrin" group.

Be complexes have been mentioned earlier. Other alkaline earth metals are not important complex-forming elements.



6NH_3 in CaCl_2
(open structures)

Ca-EDTA complex (with Na_2EDTA)
(cyclic structure)

Fig. 16—4. Structures of $\text{Ca}(\text{NH}_3)_6^{+2}$ and $[\text{Ca-EDTA}]^{-2}$ complex

QUESTIONS AND PROBLEMS

1. Write short notes on alkaline earth metals and their compounds.
2. Describe the preparation and properties of the following and mention some of their uses :—
 - (a) Calcium cyanamide, (b) Lithopone.
3. How will you detect Ca and Ba in a solution ?
4. (a) what is carnallite ? How this can be used to obtain magnesia ?
(b) Described briefly the electrometallurgy of magnesium using magnesia as the raw materials.
(c) Mention some of the properties and uses of magnesium.
5. Describe the preparation and properties of calcium carbide
6. Discuss the anomalies in the chemistry of lithium and compare it with that of magnesium.
7. Write a note on the manufacture of Portland cement.
8. What is Portland cement? How does it differ from glass ? Describe briefly the manufacture of Portland cement from the raw-materials available in Bangladesh laying special emphasis on the chemical reactions occurring in the rotary kiln.
9. How will you justify the inclusion of alkaline earths in the same group of periodic chart ? How do they compare with Zn, Cd and Hg ?
10. Describe the preparation and properties of magnesium.
11. Describe the preparation and uses of anhydrous magnesium chloride.
12. Show the distribution of electrons in the atoms of Be (4), Mg (12) and Ca (20).
Explain the similarities in chemical properties of Be, Mg and Ca with reference to the arrangement of orbital electrons.
13. Write a short note on the gradation of properties in alkaline earth metals.
14. Discuss the anomalous position of Be with the alkaline earth metals. In what respects Be is different from other alkaline earth metals and why ?
15. Describe briefly the electrometallurgy of Mg.
16. Explain the dissolution of magnesium salts in NH_4Cl .
17. It is not possible to prepare anhydrous MgCl_2 by heating $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Why ?
18. What are the essential reactions involved in the setting of cement ?
19. Compare the chemistry of lithium and magnesium.
20. Write short notes on :
Alkaline earth metals and their compounds.

21. Discuss the two methods of preparation of beryllium from beryl. Compare the properties of beryllium with those of aluminium.
22. Write short note on "lithopone".
23. Give a description of the preparation and uses of quicklime.
24. Write the reactions of Ca^{+2} with the following : (a) HCO_3^- (b) Soap anion $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$ (c) Na_2Ze ($\text{Ze} = \text{Zeolite}$) (d) anion exchange resin ($\text{R}\cdot\text{SO}_3^-$).
25. What happens when CaC_2 and Mg react with atmospheric nitrogen when heated in air.
26. Write the chemical reaction for the preparation of magnesium from sea water. What are other elements which can be isolated from sea water.
27. What are the unique properties of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$ and $\text{Ca}(\text{HSO}_3)_2$?
28. Some solid CaO in a test tube picks up water vapour from air and completely changed to $\text{Ca}(\text{OH})_2$. The weight of the test tube with CaO was 10.860 g which increased to 11.149 g. What is the weight of the test tube ?

CHAPTER 17

ZINC, CADMIUM AND MERCURY

(Elements of Group IIB)

The metals of group IIB bear the same relation to the alkaline earth metals as those of group IB do to the alkali metals. Each of the metals Zn, Cd and Hg has two electrons in the outermost level immediately after the completed d^{10} level. The outer two valence electrons of these metals determine their chemistry.

The Electronic Structure : The electronic structures of Zn, Cd and Hg are given in Table 17.1.

Table 17.1. Electronic structures of Group IIB

At. No.	Elements	Electronic Configuration	Valence electrons
30	Zn	Ar core, $3d^{10} 4s^2$	$4s^2$
48	Cd	Kr core, $4d^{10} 5s^2$	$5s^2$
80	Hg	Xe core, $4f^{14} 5d^{10} 6s^2$	$6s^2$

Thus, it can be seen that there are two electrons (s^2) in each of the metals in the outermost orbitals.

Comparative Chemistry of Zn, Cd and Hg

It is expected that the two s electrons beyond the d^{10} sub-level will be lost giving the oxidation state of +2 in each case which is generally observed. But in the case of Hg it forms a univalent ion, Hg_2^{+2} , in some of its compounds although generally it is Hg^{+2} . Univalent Cd and Zn are not formed. Moreover, Hg is less reactive than the other two and occurs in the "free state" in nature indicating the $6s^2$ electrons to be not very active and thus resemble with its neighbour Au. The electron configuration of $5d^{10} 6s^2$ in Hg is an stable arrangement. The $6s^2$ electrons become almost inert. The formation of

monoatomic Hg in vapour state, small degree of ionization of HgCl_2 and formation of mercurous salt of Hg_2Cl_2 type indicate inertness of $6s^2$ electrons. This is not so well-marked in the case of Zn and Cd. The physical properties of Zn, Cd and Hg are given in Table 17.2.

Table 17.2 Physical properties of Zn, Cd and Hg.

Properties	Zn	Cd	Hg
At. No.	30	48	80
At. wt.	65.38	112.41	200.61
Outer electron orbitals	$3d^{10}4s^2$	$4d^{10}5s^2$	$5d^{10}6s^2$
Atomic radius (Å)	1.33	1.49	1.50
Ionic radius (Å)	0.74	0.97	1.10
Ionization potential (ev)	9.39	8.99	10.43
Electronegativity	1.66	1.46	1.44
Density at 20°C (g/cm^3)	7.14	8.6	13.55
Melting point (°C)	419	320	-39
Boiling point (°C)	907	767	357
Oxidation potential (v)	$\text{Zn}/\text{Zn}^{+2} + 0.76$	$\text{Cd}/\text{Cd}^{+2} + 0.40$	$\text{Hg}/\text{Hg}_2^{+2} - 0.79$ $\text{Hg}/\text{Hg}^{+2} - 0.85$
Oxidation states	+2	+2	+1, +2
Vaporization energy Kcal/mole at 25°C	31.2	27.0	14.5

It is seen that the melting points, boiling points and heats of vaporization of Zn, Cd and Hg are lower than any group of elements (except IA). The atoms of Zn, Cd and Hg, because of larger sizes, have small interatomic attractions. Hence they have low melting and boiling points. Hg has very weak interatomic forces and melts below room temperature. It is expected that these metals should have high oxidation potentials. The metals Zn and Cd are, therefore, easily oxidized but Hg is less susceptible to oxidation. The properties of these metals show the effect of the higher ionization potentials and the small size of the respective ions.

Some of the properties which are similar may be enumerated as follows :—

Similarities : 1. All the three metals form bivalent ions, M^{+2} .

2. They do not form any hydrides.

3. They are readily reduced to the metallic state from their ores and compounds. This is the reason that the metallic Zn and Hg are known from the earliest time.

4. Like coinage metals, these metals also form a large number of complexes and volatile organometallic compounds.

Dissimilarities : There are some irregularities in the gradation of properties within this group. These are :—

1. Zn and Cd are similar to each other and are different from mercury. Hg has very low melting point.

2. As the atomic number increases, the oxides (MO) become less stable towards heat. The chlorides (MCl_2) become less easily hydrolysed and the sulphides (MS) become more deeply coloured and less soluble in water.

ZnS is white and soluble in dil HCl. CdS is yellow-orange and soluble in conc HCl. HgS may be black and dissolves only in aqua regia.

3. HgO is the most basic and ZnO is amphoteric in the group Zn, Cd and Hg. This is in line with the increase in ionic radius from Zn to Hg.

4. $ZnCl_2$ is hygroscopic and dissolves readily to form Zn^{+2} . $CdCl_2$ gives ions of the type $CdCl^+$, $CdCl_3^-$ and $CdCl_4^{-2}$. $HgCl_2$ is practically non-ionised in aqueous solution. $HgBr_2$ and Hgl_2 are almost insoluble in water.

5. $Zn(OH)_2$, $Cd(OH)_2$ and $Hg(OH)_2$ are unstable, particularly $Hg(OH)_2$, which is not formed. The structure of the positive ions having non-inert gas structure are less stable.

6. Zn and Cd readily dissolve in acids giving hydrogen. Hg does not liberate hydrogen from acids. Hg, in fact, is a "noble metal." The electrophilic tendency of Zn due to the still less shielded 3d electrons and its ionic size makes it similar in properties to Be^{+2} and Al^{+3} .

Occurrence : Zn and Cd occur together in minerals, such as ZnS and $ZnCO_3$. Hg is found in the free state or as sulphide ore, HgS.

The Comparison of Group IIA and IIB Metals

Although Zn, Cd and Hg have been placed in group II along with the alkaline earth metals and have some well-marked similarities, as in the formation of divalent ions, there are many points of contrast. They are widely separated in the Periodic Table by the transition elements. These arise mainly because the electron configurations of IIA and IIB do not have the same penultimate orbitals. Thus the alkaline earth elements have s^2 electrons after an inert gas configuration whereas Zn, Cd, Hg have s^2 electrons after the completion of the transition series of d^{10} electrons.

1. Group IIA metals are light and have high atomic volume and atomic radii. Group IIB are heavier and have smaller size. The two s electrons in the two sub-groups in the outermost orbitals are not similar in arrangement.
2. Group IIA metals have high melting points whereas group IIB metals have low melting points. Hg is liquid at ordinary temperature (melting point -39°C).
3. Group IIA metals are reactive because the two s electrons occur just after the s^2p^6 orbitals of an inert gas electron arrangement. Group IIB metals are quite stable. The former are easily attacked by atmospheric action but IIB are not readily attacked.
4. Oxides of group IIA cannot be easily reduced to metals whereas group IIB metals can be easily reduced to the respective metals with carbon or by simple heating as in the case of HgO . The ionic character of group IIA compounds is more pronounced than that of the IIB compounds.
5. Group IIA generally forms colourless compounds, IIB forms quite a large number of coloured compounds, particularly Hg, because it is easy to excite electrons of the d orbitals by polarisation as in the case of HgI_2 .
6. Group IIA sulphates are insoluble in water whereas group IIB sulphates are soluble.
7. Group IIB metals form complex compounds with ammonia, IIA does not.

Metallurgy of Zn, Cd and Hg

Extraction of Zinc : Zinc is extracted from its ores by (i) carbon reduction process or (ii) electrolytic process.

Sources :

Zinc blende—ZnS

Zincite— ZnO

Calamine— ZnCO₃

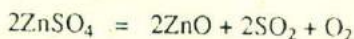
1. Carbon reduction process : The following metallurgical steps are involved in the extraction of Zn by carbon reduction process :—

(a) The ground ore is concentrated by froth floatation process.

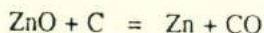
(b) The concentrated ore is roasted to convert it into oxide :



Some ZnSO₄ formed is also decomposed to ZnO :

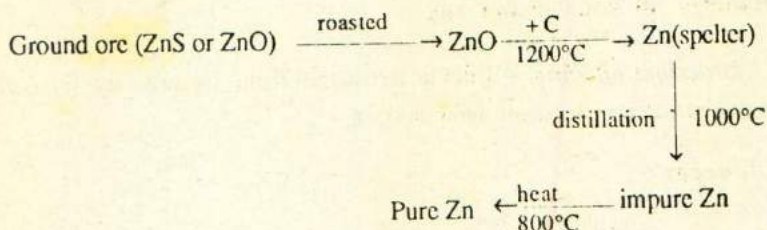


(c) The oxide is heated with carbon in retorts. ZnO is reduced to Zn and is distilled :

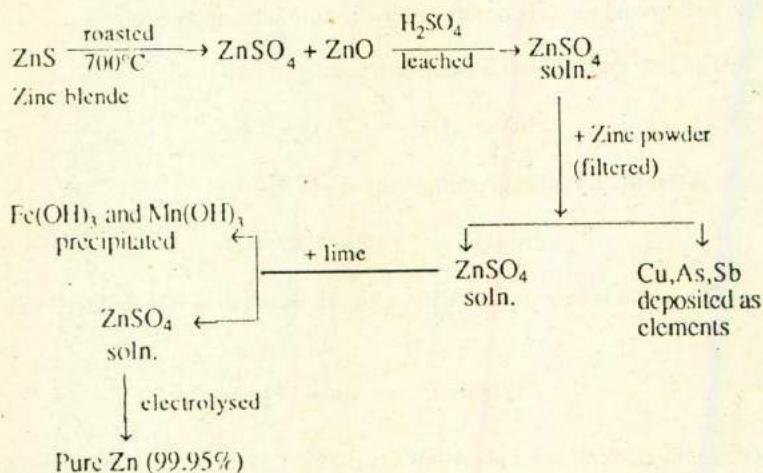


Zn obtained is impure and contains Cd. The reduction of ZnO is carried out in various types of furnaces, such as retort furnace, reverberatory furnace and vertical furnace which have different designs to collect the molten Zn in the form of condensate.

Purification of impure Zn : Zn obtained by the carbon reduction process is impure and is called "spelter". This is distilled at about 1000°C when only Zn and Cd are distilled over. Zn is made free from Cd by heating at about 800°C at which temperature only Cd is distilled over :



2. *Electrolytic process:* In this process the ore is roasted in a special furnace under controlled conditions to convert the sulphide to sulphate. The roasted ore is leached with dilute H_2SO_4 to dissolve ZnSO_4 and sulphates of other metals. The purified solution is electrolysed with aluminium cathode. Pure Zn deposits on the cathode and is scrapped off :



Extraction of Mercury :

Sources : Cinnabar — HgS

Extraction : The metallic mercury is produced by roasting cinnabar. Sulphur is removed as sulphurdioxide and mercury distils from the furnace and is condensed to the liquid :



The roasting of HgS in air gives some amount of HgO , but HgO is thermally unstable and decomposes readily at high temperature. The roasting of HgS is done in different types of furnaces, such as reverberatory furnace, muffle furnace or shaft furnace with arrangement of collecting distilled metallic mercury.

Metallic mercury is purified by filtering through chamois leather, washing it with nitric acid or by distillation in presence of oxygen.

Uses of Zn, Cd and Hg

Zn : Zn is used in the manufacture of dry cells and in the production of alloys, such as brass and bronze (see copper). Large quantity of Zn is used to protect iron and other metals from corrosion by air and water. The protective action of Zn is based upon the fact that a film of basic zinc carbonate is formed on the surface.

Zinc coating on iron is applied by various methods and the product is known as "galvanized iron". Galvanizing is done by various methods.

(a) *Hot galvanizing* : Iron or steel is first thoroughly cleaned by washing with caustic soda and by "pickling" in dilute H_2SO_4 . The cleaned iron is then dipped into molten zinc bath. The hot galvanized iron piece forms an alloy of iron and zinc on the surface with a layer of pure zinc outside.

(b) *Electro-galvanizing* : This is also known as cold galvanizing. This involves the continuous passage of iron strips of wires through a plating bath. Zn of high purity is deposited on the surface by this process.

(c) *Sherardizing* : In this process a layer of Zn is applied to small iron objects by placing them in a revolving drum with zinc dust, and heating to a high temperature to form zinc-iron alloy on the surface.

(d) *Metallizing process* : In this process the iron object is coated by spraying atomised zinc against the iron with great force. The layer of Zn adheres to the iron surface.

Cd : Cadmium metal is used as control rods for neutron captures in atomic reactors. It is used in Weston Standard Cell. Large number of alloys of cadmium are made for special use.

Hg : Mercury is used as an excellent thermometric and barometric substance. All metals (except Fe and Pt) dissolve in mercury or form *amalgams* which are used for various purposes, e. g., as reducing agent (Na—Hg), dentistry (Ag—Hg) etc. Mercury vapour lamps and fluorescent lamps are used for lighting highways because mercury in vapour condition is a good conductor of electricity and in doing so emits brilliant light.

Some Important Compounds of Zn, Cd and Hg

Compounds of Zinc

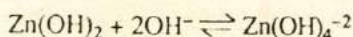
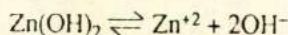
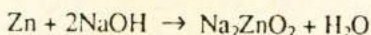
Zinc oxide, ZnO : This is obtained by burning zinc vapour in air. It is also prepared by precipitating basic zinc carbonate from zinc sulphate and then heating the precipitate to form ZnO.

It is a white powder which becomes yellow on heating. The white colour reappears on cooling. ZnO dissolves in acids producing zinc salt and in alkalis it gives zincates because of its amphoteric character:

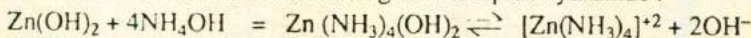


The white ZnO, commercially known as "zinc white", is used as pigment and also in the preparation of "*Rinman's Green*" which is also a pigment obtained by heating ZnO with a solution of $\text{Co}(\text{NO}_3)_2$ and has the composition CoZnO_2 (cobalt zincate). This is also formed during the blow-pipe test for zinc.

Zinc hydroxide, Zn(OH)₂ : It is obtained as a white flocculent precipitate on adding alkali to a solution of zinc salt. The precipitate is insoluble in water but readily dissolves in excess of alkali forming zincate in solution :

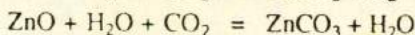
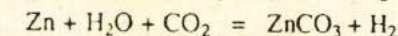


It is dissolved in excess of ammonia to give a complex hydroxide :

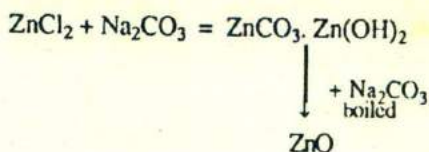


Zinc carbonate, ZnCO₃ : It is formed when :

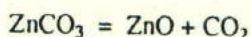
(1) Zn or ZnO dissolves in water in presence of CO₂ :



(2) Basic zinc carbonate is precipitate by adding sodium carbonate to a solution of zinc salt but on boiling it is converted to ZnO :

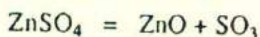


ZnCO₃ decomposes at about 160°C :



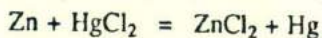
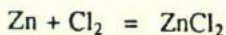
Zinc sulphate, ZnSO₄·7H₂O : It is known as *white vitriol* and is very soluble in water. It is obtained by dissolving Zn, ZnO or ZnCO₃ in dilute H₂SO₄, evaporating the solution and crystallising to give crystals of ZnSO₄·7H₂O.

On heating ZnSO₄·7H₂O at about 300°C it is converted to anhydrous ZnSO₄. At about 750°C it is decomposed to ZnO and SO₃ :



It is used for making a white paint known as "lithopone".

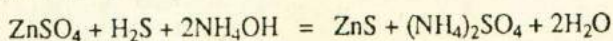
Zinc chloride, ZnCl₂ : Anhydrous ZnCl₂ is formed by passing Cl₂ gas over Zn or by distilling Zn with HgCl₂ because ZnCl₂ sublimes at a lower temperature than HgCl₂ :



It can be made from ZnO or ZnCO₃ by the action of conc HCl, evaporating the solution to dryness and fusing the residue to remove moisture. The white product melts at 262°C and is cast into sticks. Dilute HCl gives Zn(OH)Cl and Zn₂OCl₂.

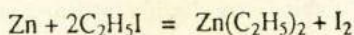
ZnCl₂ is very deliquescent and extremely soluble in water, alcohol, ether, acetone etc. Concentrated solution of ZnCl₂ dissolves cellulose which can be moulded like plastic. ZnCl₂ solution is used as wood preservative. Zn₂OCl₂ with water sets to a hard mass. These zinc compounds are very toxic and should be handled with care.

Zinc sulphide, ZnS : It occurs in nature as zinc blende, ZnS. When H_2S is passed into a Zn-salt solution in presence of NH_4OH and NH_4Cl , the white precipitate of ZnS is obtained. This is soluble in HCl but insoluble in acetic acid. ZnS can also be precipitated from $ZnSO_4$ solutions containing sodium acetate by passing H_2S :

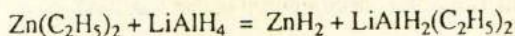
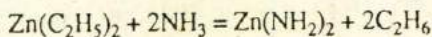


ZnS is used as a white pigment. ZnS containing traces of impurities such as Mn, Ca, Bi, Pb etc., is phosphorescent and can be used for luminous paints.

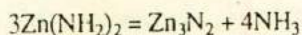
Zinc ethyl, $Zn(C_2H_5)_2$: This is made by heating Zn metal with ethyl iodide. This is an inflammable volatile liquid :



This is used for making zinc amide, $Zn(NH_2)_2$ and ZnH_2 which cannot be made directly :



$Zn(NH_2)_2$ on heating to redness gives Zn_3N_2 :



Compounds of Cadmium

Cadmium is isolated during the purification of zinc. Cadmium is more volatile than zinc and is distilled off.

The compounds of cadmium have similar properties as those of zinc. CdO and $Cd(OH)_2$ do not show amphoteric character as ZnO and $Zn(OH)_2$. $Cd(OH)_2$ is not soluble in NaOH.

Cadmium sulphide, CdS : It is formed when H_2S is passed through a solution of Cd-salt in neutral, alkaline or feebly acidic medium. It is generally yellow-orange in colour unlike ZnS which is white. CdS is not precipitated by H_2S if acid concentration is high. CdS is soluble in KI solution forming a complex K_2CdI_4 .

Cadmium sulphate, $CdSO_4 \cdot 8H_2O$: When CdO is dissolved in dilute H_2SO_4 it forms $CdSO_4$ in solution which on evaporation gives $CdSO_4 \cdot 8H_2O$. $CdSO_4$ is used in "Weston Standard Cell" which has Cd—Hg and Hg electrodes

containing CdSO_4 and mercurous sulphate. The E. M. F. is 1.019 volts at 20°C . The E. M. F. remains constant because the solubility of CdSO_4 does not vary with temperature.

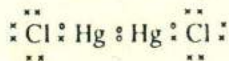
Cadmium chloride, CdCl_2 : It is not deliquescent nor hydrolysed with water like ZnCl_2 . The crystals lose water of crystallisation if any.

Cadmium cyanide, $\text{Cd}(\text{CN})_2$: It is formed when KCN is added to a solution of Cd-salts. The precipitate dissolves in excess KCN forming a complex $\text{K}_2\text{Cd}(\text{CN})_4$ which gives CdS on passing H_2S . Copper is not precipitated as CuS from $\text{K}_2\text{Cu}(\text{CN})_4$ solution and this fact is used for the separation of Cu from Cd.

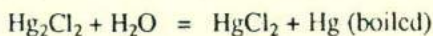
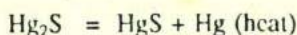
Compounds of Mercury

Mercury forms two types of compounds containing mercurous, Hg^+ and mercuric, Hg^{+2} . Some of the important compounds of both are described here.

Compounds of univalent mercury : The mercurous ion is a peculiar ion having $\text{Hg}-\text{Hg}$ bond. The univalent mercury has been proved to be a dimer by various methods. Thus, the determination of molecular weight by vapour density or cryoscopic methods, X-ray studies of mercurous chloride and spectral studies show the presence of Hg_2^{+2} rather than Hg^+ . The compounds of Hg_2^{+2} are diamagnetic and hence cannot contain the monomer Hg^{+2} ion. The ease with which metallic Hg is liberated from mercurous compounds also points to the formation of $\text{Hg} : \text{Hg}^{+2}$ ion. One valence electron of each Hg in mercurous compounds forms an electron-pair bond with the second Hg atom. Hg_2Cl_2 is thus :

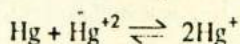


Metallic Hg is easily released from Hg^{+1} , i. e. Hg_2^{+2} compounds. Thus,



The study of the equilibrium between liquid Hg, Hg^{+2} ion and Hg_2^{+2} ion supports the formulation of Hg_2^{+2} ion for the mercurous mercury. Thus for

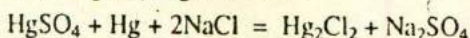
$\text{Hg} + \text{Hg}^{+2} \rightleftharpoons \text{Hg}_2^{+2}$, $K = [\text{Hg}_2^{+2}] / [\text{Hg}^{+2}]$ has been found to be valid since the value of K is constant. The other possibility :



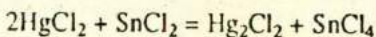
gives the constant, $K' = [\text{Hg}^+]^2 / [\text{Hg}^{+2}]$ which is not valid since K' does not give constant value indicating absence of Hg^+ ion.

Mercurous ions do not normally form any complex. Hg_2Cl_2 is not soluble in ammonia (compare from Ag^+).

Mercurous chloride (calomel), Hg_2Cl_2 : This is commercially made by heating a mixture of HgSO_4 , Hg and NaCl :

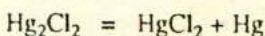


Also by the reaction :

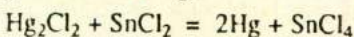


Hg_2Cl_2 is volatile and sublimes off in the form of white powder from the reaction mixture. It is insoluble in water and in dilute HCl which precipitates Hg_2^{+2} as Hg_2Cl_2 in group I of chemical analysis.

Hg_2Cl_2 decomposes to HgCl_2 and Hg on exposure to light and it is stored in brown bottles :

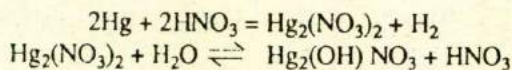


Hg_2Cl_2 with SnCl_2 is reduced to Hg :



Hg_2Cl_2 is generally known as *Calomel* and is used as medicine and in calomel electrode.

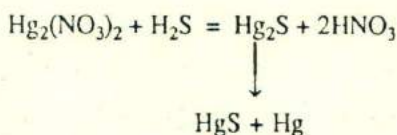
Mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$: When mercury is dissolved in dilute HNO_3 , the product is $\text{Hg}_2(\text{NO}_3)_2$ in presence of excess of Hg. It is the only readily soluble salt of mercurous Hg. The compound is hydrolysed in aqueous solution forming $\text{Hg}_2(\text{OH})\text{NO}_3$:



$\text{Hg}_2(\text{NO}_3)_2$ is readily oxidized to $\text{Hg}(\text{NO}_3)_2$.

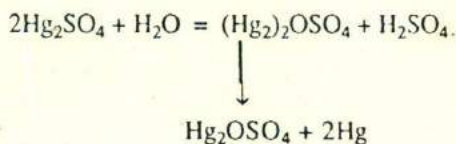
Mercurous oxide, Hg_2O : When NaOH solution is added to a solution of $Hg_2(NO_3)_2$, a dark brown powder is precipitated which is Hg_2O . This is decomposed in light to give $HgO + Hg$.

Mercurous sulphide, Hg_2S : When H_2S is passed into a solution of $Hg_2(NO_3)_2$, a precipitate of Hg_2S is formed which instantaneously changes into HgS :



Mercurous iodide, Hg_2I_2 : It is obtained by means of intimately mixing HgI_2 with I_2 forming a green powder and is changed to HgI_2 by simple heating.

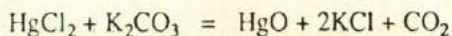
Mercurous sulphate, Hg_2SO_4 : On heating Hg with conc H_2SO_4 both Hg_2SO_4 and $HgSO_4$ are formed. When H_2SO_4 is added to $Hg_2(NO_3)_2$, white precipitate of Hg_2SO_4 is obtained. This is hydrolysed in hot water :



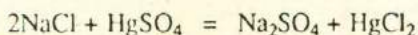
Compounds of divalent mercury (Hg^{+2}) : The mercuric ion forms mostly covalent compounds. The strong oxyacids, such as H_2SO_4 , HNO_3 and $HClO_4$, form ionic compounds with mercury which dissociate in aqueous solution. The bonds between Hg and S, C, Cl, Br or I etc. are covalent. The energies involved in the covalent bond formation with Hg are small but the bonds are stable towards air, water, acids and alkalis indicating strong covalent bond.

Mercuric oxide, HgO : When a strong alkali is added to a solution of Hg salts, HgO is precipitated. In the cold, the precipitate of HgO is yellow but from hot solution it is red. This difference is due to the fine state of sub-division of HgO . Both the varieties of HgO have the same crystal structures.

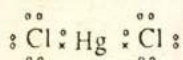
The formation of $\text{Hg}(\text{OH})_2$ does not take place since it is unstable and is decomposed to HgO and H_2O . The red HgO is also made by adding hot solutions of HgCl_2 and K_2CO_3 :



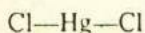
Mercuric chloride, HgCl_2 : It is obtained by heating Hg in an excess of chlorine or by dissolving HgO in HCl or in aqua regia. Commercially it is made from HgSO_4 and NaCl by heating :



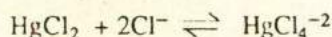
HgCl_2 is known as *corrosive sublimate* because of its corrosive properties and is a strong poison. It is soluble in many organic solvents and moderately soluble in water but only slightly ionized HgCl_2 has the formula,



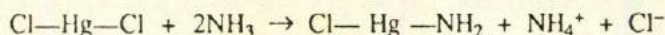
The structure of HgCl_2 uses sp hybrid orbitals of Hg as in the case of Be compounds and is a linear molecule :



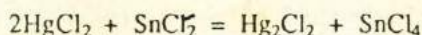
HgCl_2 dissolves in solution containing chloride ion to form stable complexes of the type HgCl_4^{-2} :



Mercuric chloride is ammonolysed to give ammonobasic mercuric chloride :

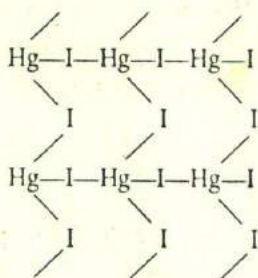


With SnCl_2 , Hg_2Cl_2 is precipitated :

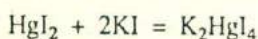


Mercuric iodide, HgI_2 : When potassium iodide is added to a solution of HgCl_2 , a red precipitate of HgI_2 is formed. This is soluble in excess of KI and also in excess of HgCl_2 forming complexes.

HgI_2 like other mercuric halides is linear in the solid state and is linked together in layer structure. HgI_2 has simple layer structure :

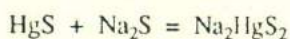
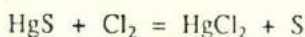


The formation of the complexes of HgI_2 is given by the equation :



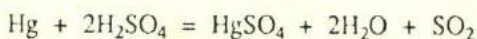
Mercuric sulphide, HgS : When H_2S is passed in a solution of mercuric salts, HgS is precipitated out. The precipitate is first white, then yellow, then red and finally black. It is insoluble even in conc HCl . When the black HgS is heated, red HgS is formed and this is used as a pigment under the name of *vermilion*.

HgS also occurs in nature as cinnabar. HgS is dissolved by aqua regia, KClO_3 and alkaline solution of Na_2S :



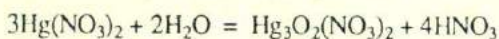
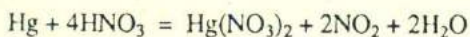
When heated, HgS is decomposed to mercury and sulphur or SO_2

Mercuric sulphate, HgSO_4 : HgSO_4 is obtained by heating Hg with conc H_2SO_4 :

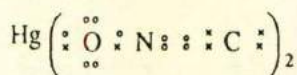


HgSO_4 is a white powder and on heating it is decomposed to Hg_2SO_4 .

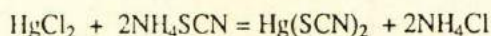
Mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$: This is obtained by heating Hg with excess of conc HNO_3 . It is a deliquescent substance and hydrolysed in water :



Mercuric fulminate, $Hg(ONC)_2$: It is formed by the action of HNO_3 on Hg in presence of alcohol. It is a highly explosive compound and is used as detonators. *Mercury fulminate* may be written as,



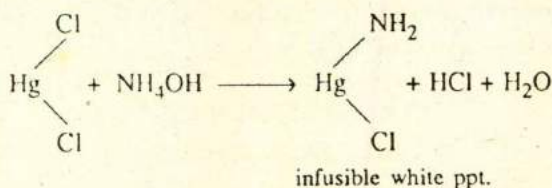
Mercuric Thiocyanate, $Hg(SCN)_2$: It is obtained by mixing mercuric chloride solution with NH_4CNS . It is a white precipitate and when dried and ignited, it evolves a voluminous serpent-like ash known as *Pharaoh's Serpent*.



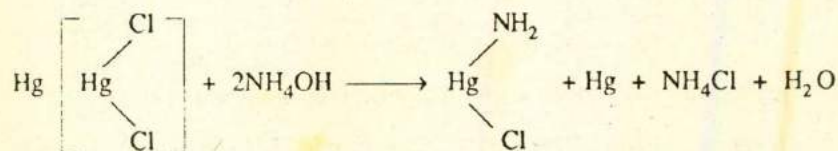
$Hg(SCN)_2$ is very slightly dissociated and mercuric ion in solution may be titrated with a solution of KSCN using ferric salt as an indicator.

Ammonobasic Compounds of Mercury

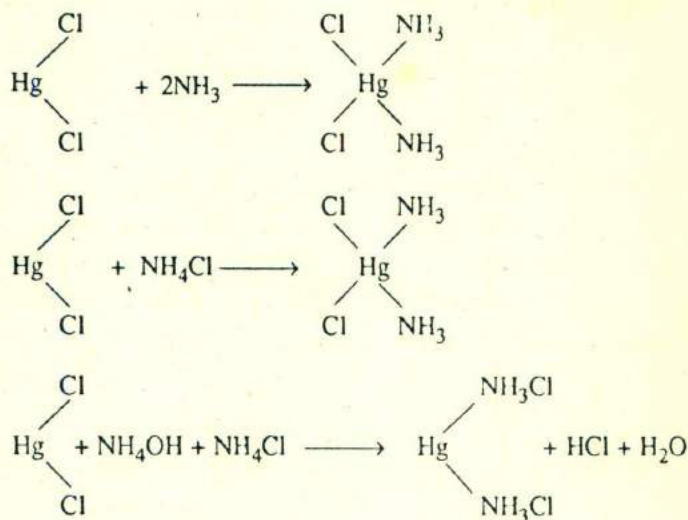
When NH_4OH is added to a solution of $HgCl_2$, a white precipitate is obtained, which is not $Hg(OH)_2$ or HgO , but contains N_2 and Cl_2 :



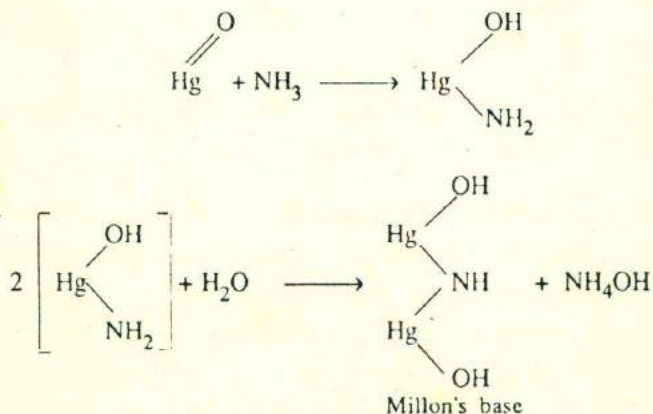
Hg_2Cl_2 gives grey precipitate due to the liberation of Hg along with $Hg(NH_2)Cl$:



The above two reactions are used to distinguish between Hg^{+2} and Hg_2^{+2} . When NH_3 gas is passed over $HgCl_2$, the product is a fusible white precipitate, also obtained in conc NH_4OH and NH_4Cl :

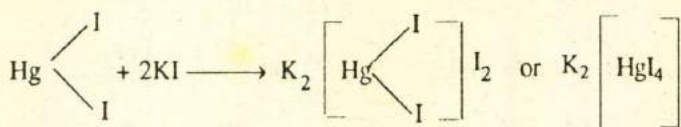


When precipitated HgO is suspended in NH₄OH solution, a pale yellow powder is formed which is called "Millon's base" 2HgO.NH₃. This is obtained by both ammonolysis and hydrolysis processes :

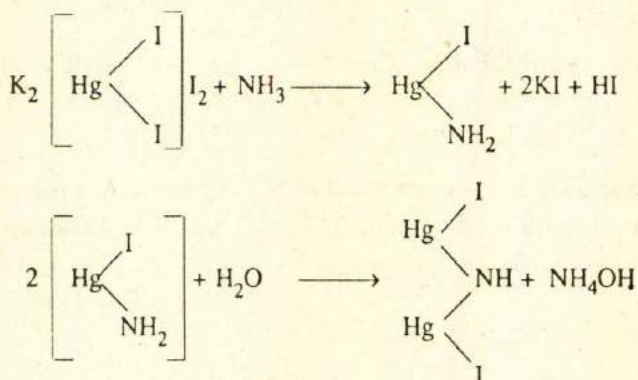


The hydrated form of Millon's base is Hg₂(OH)₂NH₂OH.

Nessler's Reagent : When KI is added to a solution of HgCl₂, a red precipitate of HgI₂ is first formed which dissolves on adding excess KI forming a colourless solution containing Hg⁺² ion in the complex form K₂HgI₄.



KOH solution is added to this colourless complex solution of $\text{K}_2[\text{HgI}_4]$ which is the Nessler's Reagent. This reagent provides a sensitive test for NH_3 . When NH_3 gas is passed through the solution or even when an ammonium salt is added to the reagent the liberated NH_3 gives brown precipitate or colouration which is the iodide of Millon's base :



The hydrated form is $\text{Hg}_2\text{I}_2 \cdot \text{NH}_2\text{OH}$. The reactions for Nessler's reagent is $2\text{K}_2\text{HgI}_4 + \text{NH}_3 + \text{KOH} \longrightarrow \text{NH}_2\text{Hg}_2\text{I}_3 + 5\text{KI} + \text{H}_2\text{O}$.

Complex compounds of Zn, Cd and Hg : Like the coinage metals (IB), the metals of zinc group (IIB) also form a large number of complex compounds. Some complexes have already been mentioned before. The most common complexes are formed by the halides, cyanide and ammonia groups. Most of the complexes possess the tetrahedral structures involving sp^3 bonds as in $\text{Zn}(\text{NH}_3)_4\text{Cl}_2$, $\text{K}_2\text{Zn}(\text{CN})_4$, K_2HgI_4 etc. Zn and Cd also form 6 coordinated complexes as in $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ which are considered as outer orbital complexes.

Amalgams : Amalgams are solutions of other metals in mercury. In some cases, such as with Na and K, distinct chemical compounds (Hg_2Na and Hg_2K) are formed with Hg. Iron has the least solubility in mercury, other metals

such as lead, zinc, silver etc. are highly soluble giving amalgams of invariant composition.

QUESTION AND PROBLEMS

1. Write a short note on Nessler's Reagent.
2. Give an account of occurrence, extraction and purification of mercury. Describe the reactions which occur when an aqueous solution of mercuric chloride is treated with an excess of (a) an aqueous solution of potassium iodide, (b) an aqueous solution of stannous chloride, (c) an aqueous solution of sodium hydroxide and (d) copper.
3. Write a brief note on the action of ammonia on salts of mercury and silver.
4. Write short notes on the following :-
(a) Calomel, (b) Lithopone, (c) Corrosive sublimate and (d) Zinc white.
5. Discuss the comparative chemistry of group IIA and group IIB elements with particular reference to the properties based on electronic configurations.
6. Discuss the principles involved in the extraction of zinc from zinc blende.
7. How can you extract pure zinc from zinc sulphide by the electrolytic process?
8. How will you separate and identify Cd and Cu in a mixture of their solution?
9. Write a note on the ammonolytic compounds of mercury.
10. What are the advantages of galvanizing iron sheets and pipes? Describe briefly the process of galvanizing iron materials by various techniques.
11. Write a short note on the Alkaline Earth metals and their compounds.
12. Show with examples that aluminium and zinc are amphoteric in nature.
13. Give brief description of the preparation and uses of :—
(a) Calomel, (b) Lithopone, (c) Nessler's Reagent.

CHAPTER 18

BORON AND ALUMINIUM

(Elements of Group III)

The elements of group III are divided into two sub-groups. These are :

Group IIIA

B — Boron
Al — Aluminium
Ga — Gallium
In — Indium
Tl — Thallium

Group IIIB

Sc — Scandium
Y — Yttrium
La — Lanthanum*

Boron and aluminium are the representative elements of group III of the Periodic Table. Scandium, yttrium, lanthanum and all the rare earth elements may be placed in the sub-group IIIB. Gallium, indium, thallium together with the representative elements boron and aluminium are being placed in the sub-group IIIA. The placements of the elements into A and B sub-groups in this group III and onward is a matter of convenience and sometimes the order is reversed. But boron and aluminium have more common characteristics with Ga, In and Tl and hence all these five may be considered to be the elements of group IIIA. The elements of the sub-group IIIA have 3 electrons s^2p^1 in the outermost energy levels beyond the core of inert gas configurations, whereas those of the sub-group IIIB have three electrons involving *d* and *f* electrons and in most cases the three electrons are beyond a set of 18 electron types. Again, the rare earth

* La and all the other rare earth elements from Ce(58) to Lu (71) may be considered to have similar chemistry and are classified under Rare Earth elements or Lanthanides.

elements together with Sc and Y constitute a group which is rather unique and the chemistry of these elements are discussed separately.

In the elements of group IIIA we encounter the situation where the non-metallic character tends to show itself as in the case of the starting element boron, although the metallic character increases as we go down the group with increasing atomic number.

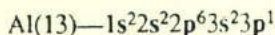
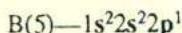
The Electronic Structure

The electronic configurations of the group IIIA elements are given in Table 18.1.

Table 18.1. Electronic configurations of group IIIA elements.

At. No.	Elements	Electronic configuration	Valence electrons
5	B	He core, $2s^2 2p^1$	$2s^2 2p^1$
13	Al	Ne core, $3s^2 3p^1$	$3s^2 3p^1$
31	Ga	Ar core, $3d^{10} 4s^2 4p^1$	$4s^2 4p^1$
49	In	Kr core, $4d^{10} 5s^2 5p^1$	$5s^2 5p^1$
81	Tl	Xe core, $4f^{14} 5d^{10} 6s^2 6p^1$	$6s^2 6p^1$

Thus, from the Table 18.1 we see that the elements of this group have three electrons in the outer orbitals : two are s electrons and one is p electron. The electronic configurations of B and Al may be separately shown as,



The third electron in p is loosely bond not only because it is unpaired but also because it is at higher energy level than s electrons.

Physical properties : Some of the physical properties of group IIIA elements are given in Table 18.2.

It is the unpaired p electron in the outermost orbital which is easily lost and hence the ionization potentials for the elements in this group are slightly less than those for the corresponding elements of group II containing paired electrons in their outer orbitals.

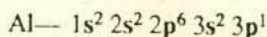
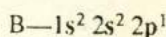
The first element, boron, in this group is distinctly a non-metal and its properties show diagonal relationship with silicon in the next group IV. Boron does not conduct electricity. But aluminium is a true metal with good electrical conductivity and other metallic properties. Some of the points of the comparative chemistry of boron and aluminium are enumerated hereafter.

Table 18.2. Physical properties of group IIIA elements.

Properties	B	Al	Ga	In	Tl
At. No.	5	13	31	49	81
At. wt.	10.82	26.97	70.10	114.80	204.60
Atomic radius (Å)	0.88	1.43	1.22	1.62	1.71
Ionic radius M^{+3} (Å)	0.20	0.50	0.62	0.81	0.95
Ionization potential $M^+(ev)$	8.03	6.00	6.00	5.80	6.10
Outer electron configuration	$2s^2 2p^1$	$3s^2 3p^1$	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$
Density (g/cm^3)	2.30	2.70	5.90	7.40	11.80
Melting point ($^{\circ}C$)	2300	658	29	155	303
Boiling Point ($^{\circ}C$)	2550	1800	1600	1450	1650
Oxidation potential (v)	—	Al/Al^{+3} +1.67	Ga/Ga^{+2} +0.53	In/In^{+2} +0.34	Tl/Tl^{+} +0.34
Electronegativity	2.00	1.50	1.80	1.50	1.44
Oxidation states	+3	+3	+1,+2,+3	+1,+2,+3	+1,+3

Comparative Chemistry of Boron And Aluminium

1. The electronic configurations of boron and aluminium,



indicate that in spite of the three electrons in the outermost energy level of the two elements ($s^2 p^1$), there are marked differences in some of the properties. The differences are due to the sizes of atoms and ions of the two elements. There is no real B^{+3} ion because the 3 electrons are held firmly. But Al^{+3} ion having ionic radius 0.5 Å forms many ionic compounds.

2. Some of the physical properties mentioned in Table 18.2 show that boron has a very high melting point (2300°C) and it is a non-metal or semi-metal having properties related to that of silicon. The non-metallic property is due to the small size and high charge of boron. Aluminium has comparatively low melting point (658°C) and is distinctly metallic because Al has a larger size than B, although the charge is the same. High ionization potential of B also gives it non-metallic character.

3. Aluminium is the third most abundant element in the earth's crust whereas boron is almost scarce probably due to the fact that boron nuclei had been transformed into other nuclei by cosmic rays. Boron shows allotropy which is not exhibited by aluminium.

4. Oxidation state of +3 is common both for boron and aluminium but boron has greater tendency to form covalent compounds particularly with hydrogen showing anomalous bonding. KBF_4 has a tetrahedral structure. Al shows coordination number of 4 as in Al_2Cl_6 and in $\text{Al}(\text{NH}_3)_4\text{Cl}_3$ having tetrahedral structure. $\text{Na}_3[\text{AlF}_6]$ has octahedral arrangement. The octahedral configuration of Al is due to the availability of the vacant 3d orbitals.

5. Boron forms more stable acidic oxide and stable borates are the principal salts of boron. Boric acid and borates occur in nature. Aluminium oxide is amphoteric and aluminates are unstable. The small size of B^{+3} ion pulls electrons to itself from H_2O and ruptures the OH bond giving H^+ ion. Hence $\text{B}(\text{OH})_3$ and B_2O_3 are acidic. The large Al^{+3} does not behave in this manner.

6. Halides, sulphates and nitrates of aluminium are common stable compounds of aluminium. Such compounds of boron are also formed but are less stable. Al forms both hydroxide and halide complexes. Aluminium sulphate gives a series of double sulphates known as alums. No such compounds are formed with B.

7. Both aluminium and boron form nitrides, AlN and BN . Boron forms oxide B_2O_3 , Al gives Al_2O_3 . Hydroxides are $\text{B}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$.

8. Boron forms B_2H_6 , B_4H_{10} and other hydrides. Al does not form similar hydrides.

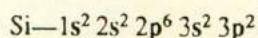
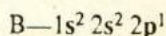
9. Al is less electronegative than B which has greater tendency to form covalent compounds than Al.

10. Aluminium is an extremely useful structural material whereas boron has only scientific applications.

In accordance with the diagonal relationships in the Periodic Table, boron has similarities in properties with Si and to some extent with carbon. The similarity arises mainly due to the atomic and ionic sizes which are close to each other in B, Si and C.

Comparison of Boron and Silicon

Boron and silicon are members of Group III and Group IV respectively but resemble in chemical properties closely. Boron is regarded as a "bridge element" because it forms a bridge between Group III and Group IV as in the case of Li and Be which are also bridge elements and show diagonal relationship. The similarity of chemical properties arises due to the fact that the ratio of nuclear charge to atomic radius, Z/r , is nearly the same indicating that the outermost electrons are attracted to the nucleus with about equal force. Electronic structures of B and Si are :



Similarities :

(1) B and Si belong to the class of semiconductor. They show increased electrical conductivity at high temperature. This property is unlike metallic characteristic.

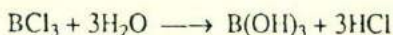
(2) B and Si have a number of allotropic forms and are non-metals with little metallic characteristic. Neither occurs free in nature. They are hard and have high melting points indicating strong bonding between the individual atoms. B and Si do not form cations.

(3) Boron and silicon resist the actions of acids and alkalis. On fusion with alkalis both form silicates and borates evolving H_2 .

(4) Boron and silicon form large number of hydrides similar to hydrocarbons.

Thus, we have, B_2H_6 , Si_2H_6 , and C_2H_6 although B_2H_6 has different structure.

(5) BCl_3 and $SiCl_4$ are covalent liquids at ordinary temperature. They are easily hydrolysed by water :



(6). B and Si form BF_3 and SiF_4 respectively which are colourless gases, covalent and are also easily hydrolysed forming acids.

(7). B_2O_3 and SiO_2 are acidic oxides and form giant molecules by linking of B—O—B, and Si—O—Si bonds in three dimensions respectively.

Dissimilarities :

- (1) B and Si have different electronic structures.
- (2) B and Si have different atomic radii.
- (3) Normal valence of B is 3 whereas that of Si is 4.
- (4) Hydrides of B have different structures than those of silicon hydrides which resemble hydrocarbons.
- (5) H_3BO_3 is more stable than H_4SiO_4 and occurs in nature.
- (6) Borates consists of BO_2^- and BO_3^{-3} ions whereas silicates are made of SiO_4 tetrahedra.

Gradation of Properties in the Group IIIA

Comparison of Al Group : Apart from the variation of properties mentioned in the Table 18.2, the following points regarding the gradation of properties of Group IIIA elements may be indicated :—

(1) Boron is a non-metal with melting point about $2300^\circ C$. Crystal structure of B and Al are different. Ga is a metal and almost liquid at ordinary temperature having m. p. $29^\circ C$.

Indium is a metal, soft and malleable, m. p. $150^\circ C$.

Tl is a metal, soft and malleable and marks paper like lead. The marking vanishes in moist air due to formation of $TlOH$ and Tl_2CO_3 . The mobile nature

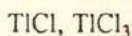
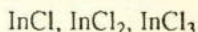
of the electrons in the outer orbitals increases with the increase in the atomic number.

(2) B has acidic properties and the hydroxide is acidic. Al is amphoteric, $\text{Al}(\text{OH})_3$ is insoluble but soluble in acids and alkalis. Ga is more acidic than Al. $\text{Ga}(\text{OH})_3$ is soluble in ammonia. In and Tl hydroxides are more basic.

(3) B is extracted from B_2O_3 by reaction with reactive metals. Al is extracted from Al_2O_3 by electrolytic process. Ga_2O_3 , In_2O_3 and Tl_2O_3 are easily reduced by hydrogen.

(4) B forms covalent compounds. Al is covalent but also ionic.

In and Tl form compounds having different oxidation states, such as,



5. Flame spectra—

<i>Element</i>	<i>Colour of flame</i>
B	In conc H_2SO_4 and alcohol, it gives green-edged flame due to the burning of ethyl borate
Al	No colour
Ga	Violet
In	Dark blue
Tl	Green

Extraction of Boron and Aluminium

Extraction of Boron

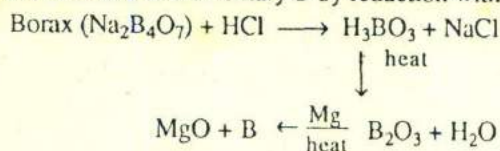
<i>Sources :</i>	Borax	—	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
	Boracite	—	$\text{Mg}_3\text{B}_8\text{O}_{11} \cdot \text{MgCl}_2$
	Colemanite	—	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
	Borocalcite	—	$\text{CaB}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$

It is also found as boric acid, H_3BO_3 , in the hot spring in volcanic regions.

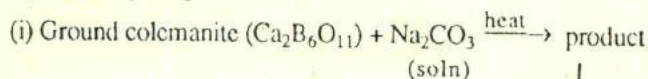
Elementary boron can be extracted by a number of methods starting from minerals and boron compounds.

Extraction of boron from minerals: The minerals are processed in order to convert them to B_2O_3 first. Borax or uincal is treated with hot conc

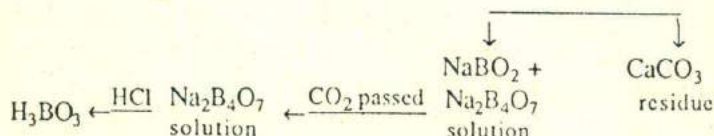
HCl, whereby sparingly soluble H_3BO_3 is deposited. This on heating gives B_2O_3 which is reduced to elementary B by reduction with Mg.



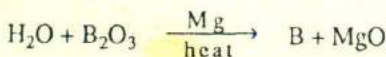
Colemanite and other minerals are treated differently as shown below either by Na_2CO_3 or by SO_2 :



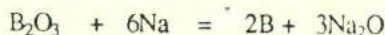
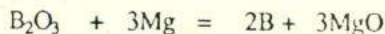
↓ filtered



↓ heat

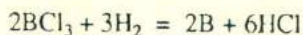


(ii) Ground colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11}$, is suspended in water and on passing SO_2 through the suspension CaSO_3 is precipitated out and H_3BO_3 is isolated from the hot solution on cooling. Elementary boron is obtained by the reduction of B_2O_3 with Mg or with Na :



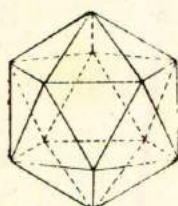
MgO remains in the solid product and is removed by dissolving in HCl. Na_2O is washed out by water. Boron prepared by reduction with Mg is impure in the form of a brown amorphous powder.

Pure boron is obtained by passing a mixture of BCl_3 and H_2 through an electric arc or a hot tube.



The mixture of BCl_3 and H_2 when passed through a tube containing an electrically heated tungsten (W) filament, pure crystalline boron is formed and deposited in layers on the filament. Boron is metalloid and a semiconductor. It occurs in three allotropic forms. The crystal lattice may consist of icosahedron units (20-sided structure).

An Icosahedron



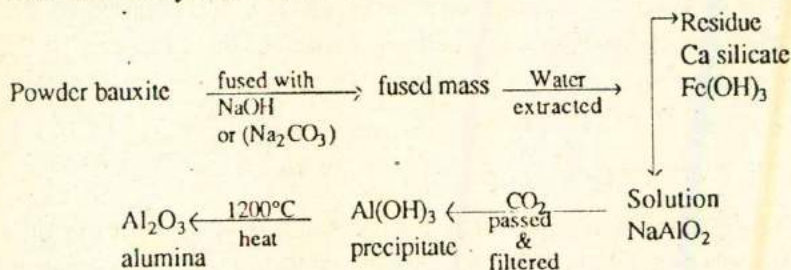
Extraction of Aluminium

Aluminium is the most abundant metal and the third most abundant element in the earth's crust. It does not occur free in nature and, although most abundant, it was not extracted from its minerals until the end of the 19th century because of the difficulties involved in its extraction.

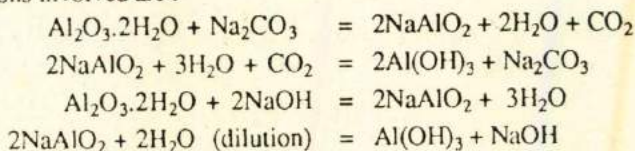
Sources :	Bauxite	—	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
	Diaspore	—	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	Corundum	—	Al_2O_3
	Cryolite	—	Na_3AlF_6

[N.B. Very large and widely distributed quantities of Al occur in aluminosilicates such as clays (kaolin), feldspar, mica etc]

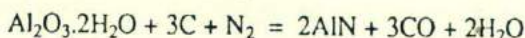
Hall and Baeyer's method :



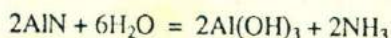
The reactions involved are :



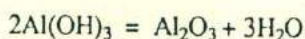
Serppek's process : This process is suitable for bauxite containing larger amount of silica. The ore is heated with carbon while a stream of nitrogen is passed over the heated mixture forming AlN :



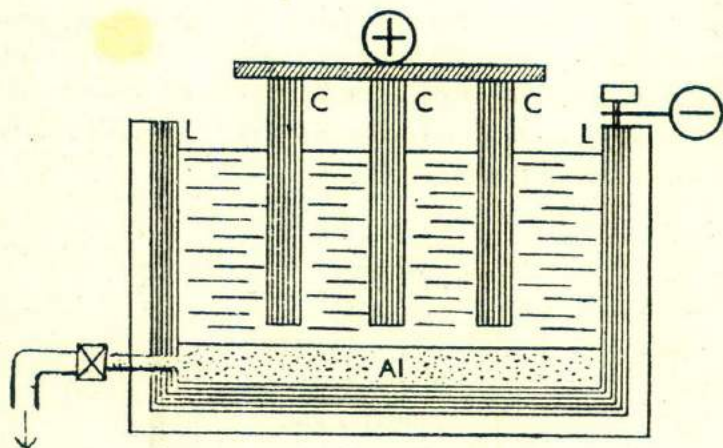
AlN on hydrolysis gives $\text{Al}(\text{OH})_3$:



$\text{Al}(\text{OH})_3$ on calcination produces alumina :



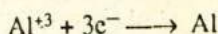
Electrometallurgy of aluminium (Hall-Herault Process) : The purified bauxite in the form of alumina obtained by the above mentioned processes is used as the starting material for electrometallurgy of Al. Alumina is dissolved in fused cryolite, Na_3AlF_6 , and the molten solution is electrolysed in a steel tank lined with carbon in the inside. The lining is made the cathode and the anode is also made of carbon rods which dip in the molten mass as shown in Fig. 18—1.



C—Carbon rods as anodes, L—Carbon lining as cathode, Al—Aluminium in the molten state

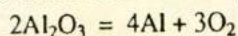
Fig. 18—1. Electrolytic cell for the manufacture of Al from Al_2O_3 .

The voltage of the cell is adjusted to ensure deposition of aluminium at the bottom but not of sodium which remains in the solution. Although Al_2O_3 is the raw material but in the molten condition in the cryolite, Na_3AlF_6 , the formation of some AlF_3 may take place. This on electrolysis gives Al at the cathode :



and at the anode : $6\text{F}^- + 6\text{e}^- \longrightarrow 3\text{F}_2$

The liberated F_2 immediately reacts with Al_2O_3 forming AlF_3 and oxygen which is evolved at the anode. The overall reaction, therefore, is,



Na_2AlF_6 acts as catalyst and lowers the melting point of Al_2O_3 mixture to 900°C . The molten Al is drawn off from the tap-hole and more Al_2O_3 is added to the fused electrolyte. The liberated O_2 attacks the carbon anode forming some CO and CO_2 . In a modified method, artificial mixture of fluorides are used instead of cryolite. The mixture has an approximate composition of $2\text{AlF}_3 \cdot 6\text{NaF} \cdot 3\text{CaF}_2$.

Al produced by the above methods is 99% pure and contains Cu, Fe, Si, Al_2O_3 etc. as impurities.

Electro-refining of aluminium : 99.9% pure Al is produced by the Hoopes Electrolytic Process. The fused bath consists of three layers. The bottom layer is a fused alloy of Cu-Al, the top layer is pure molten Al and the middle layer consists of the electrolyte of a fused mixture of BaF_2 , AlF_3 and NaF saturated with Al_2O_3 . The layers are maintained by the difference in their densities during electrolysis. The bottom layer is the anode and the top layer is the cathode as shown in Fig. 18—2.

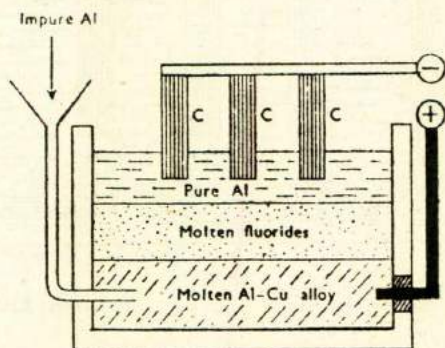


Fig. 18—2. Electro-refining of aluminium.

On electrolysis Al from Cu-Al alloy goes into solution in the middle layer as Al^{+3} , leaving the impurities behind at the anode. The Al^{+3} is now reduced at the cathode and the upper layer of Al grows which is drawn off and impure metal is added to the bottom layer. Al obtained is pure.

Uses of Boron and Aluminium

Uses of Boron : Boron as such has not many uses except in making special compounds of boron as boron carbides and borides. These are hard materials and used as abrasives. Boron rods are also used in nuclear reactors for controlling the neutron flux because boron acts as a good neutron absorber. Boron is used in the purification of pure copper for casting.

Other important useful compounds of boron are made from B_2O_3 , borax, boric acid and even directly from the minerals.

Uses of Aluminium

(1) Al is used in making cooking utensils because of its light weight, resistance to corrosion and chiefly because it is a good conductor of heat.

(2) Aeroplane bodies and other structural materials are made of Al.

(3) Aluminium is used in paints and pigments.

(4) For reflecting heat and light in reflecting mirrors.

(5) Making special types of alloys such as.

(a) **Duralumin** : Al—92.5%, Mg—1.5%, Cu—4%, Ni—2% (or Cu—2% and Ni—4%). This alloy is light but is strong as steel and specially used in aircraft. In order to further protect it from corrosive action of air, the alloy is given a coating of thin layer of pure Al, the product is known as Alcad.

(b) **Al—Bronze** : Cu—90%, Al—10%. This is golden in colour, has great tensile strength and is used in jewellery.

(c) **Alnico** : Fe—50%, Al—20%, Ni—2%, Co—10%. This is a magnetic alloy and can lift huge pieces of iron. This is produced by pressing the metals in powder form just below the melting point and is an example of a new metallurgical technique known as **Powder Metallurgy**.

(d) *Magnalium* : Al—95 to 70%, Mg—5 to 30%. It is used for producing cheap goods.

Aluminothermic process : This is also known as *Thermite process* or *Goldschmidt Thermic process*. Aluminium powder is used for this reaction for the purpose of reducing metallic oxides to metals particularly those of Cr, Mn, Mo, W etc. Fe_2O_3 can also be reduced to Fe by this process. The thermite consists of a mixture of metallic oxide with Al powder together with a little BaO_2 in a crucible lined with magnesia having a hole at the bottom. The thermite mixture is ignited with the help of a fuse of magnesium ribbon as shown in Fig. 18—3.

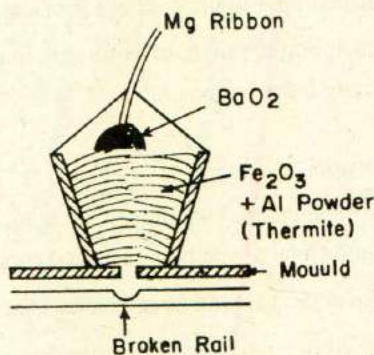
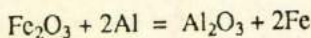


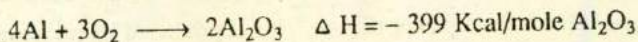
Fig. 18—3. Sketch of aluminothermic process.

Considerable temperature is generated upto 3000°C due to exothermic reaction so that Fe and Al_2O_3 become liquid :



The molten metal by suitable method may be used for welding broken pieces of steel, such as, rail and other materials.

Because of the high temperature in the thermite reaction which is not readily quenched by water, the thermite bombs have been used for incendiary purposes. The high temperature results from the high heat of formation of Al_2O_3 (solid) :



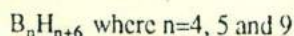
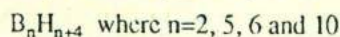
During the reaction with Fe_2O_3 , the heat evolved is sufficient to produce Fe and Al_2O_3 in the molten state.

Compounds of Boron and Aluminium

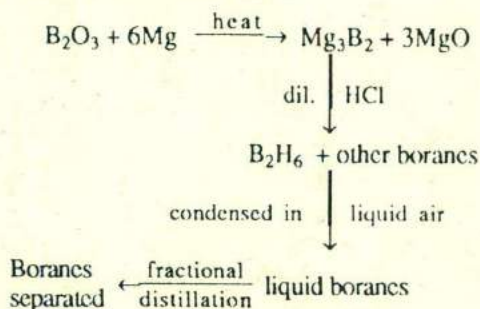
Some important compounds of boron and aluminium are described here briefly.

Compounds of Boron

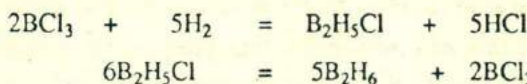
Boron hydrides : Boron forms a series of volatile hydrides similar to the hydrides of C and Si having compositions from B_2H_6 to $B_{10}H_{14}$. The simplest boron hydride, BH_3 , does not exist and is dimerized to B_2H_6 (diborane). The boron hydrides are generally known as boranes. There are two series of boranes :



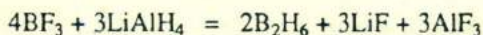
These are prepared by hydrolysis of Mg_3B_2 :



Diborane, B_2H_6 , has also been prepared by passing BCl_3 vapour and H_2 through a tube and subjecting the mixture to an electric discharge :



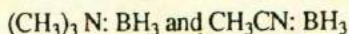
Diborane is more easily formed by the action of $LiAlH_4$ or LiH on BCl_3 in ether solution :



B_2H_6 decomposes slowly forming higher boranes. When heated to $300^\circ C$, B_2H_6 is decomposed to $B + H_2$. It is readily hydrolysed by water forming $H_3BO_3 + H_2$:

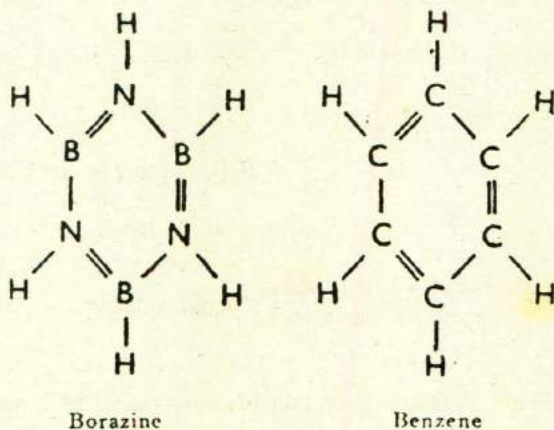


Many of the reactions of B_2H_6 give indication of the reaction of the "half molecule" BH_3 . Thus,



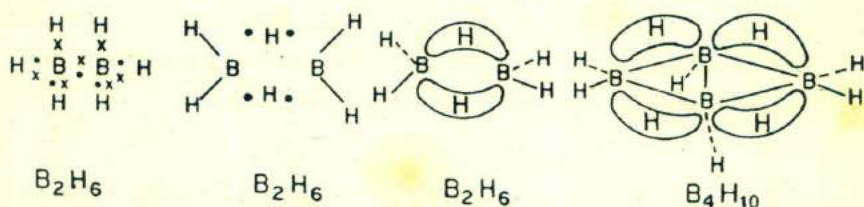
B_2H_6 and boranes are easily flammable in air. The boranes have been used as rocket fuel and jet fuel since they have high heats of combustion and low mol. wt. The energy obtained per g. of B_2H_6 is very high.

B_2H_6 has an interesting reaction with NH_3 giving first $B_2H_6 \cdot 2NH_3$ which on heating forms $B_3N_3H_6$ which is an electronic isomer of benzene known as *borazol* or *borazine* as shown below.



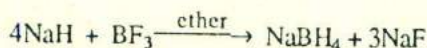
Structure of B_2H_6 : Much work has been done on the structure of boranes and this has been a puzzling problem in inorganic chemistry. An electronic structure for B_2H_6 cannot be written since there are only 12 electrons to form 7 covalent bonds between B and H in B_2H_6 . B_2H_6 is, therefore, regarded as an "electron deficient" compound. Various structures have been suggested and only two representative structures are given indicated by (I) and (II).

The modern view about the structures of B_2H_6 and other boron hydrides is that the bridge H atom between two B atoms participates in a three-centre bond formed by two electrons (single pair). Boron hydrides have prospective use as rocket fuels.

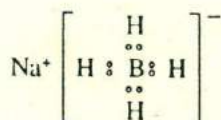


Each bridge H joins two B atoms by three-centre BHB bonds.

Sodium borohydrides, $NaBH_4$: This is obtained by the action of NaH on BF_3 in ether solution :

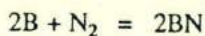


Similarly, $LiBH_4$ is also obtained. In this compounds 4H are covalently bonded to B forming BH_4^- ion (tetravalent B) having tetrahedral sp^3 structure.



$LiBH_4$ and other borohydrides are used as versatile reducing agents in organic chemistry and also in inorganic synthesis for the preparation of unstable hydrides.

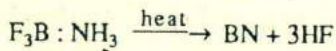
Boron nitride, BN: Boron forms quite a large number of compounds with B—N bonds. BN is formed by heating B in N_2 at $1000^\circ C$:



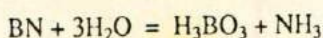
It is also made by reaction of BCl_3 and NH_3 :



Also by thermal decomposition of $F_3B : NH_3$:

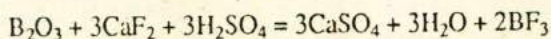


BN and graphite (C) have similar giant layer structure. This is because the atomic radius of C is almost equal to half the sum of the atomic radii of B and N. Carbon lies in between B and N in the Periodic Table. In BN the layers consist of alternate B and N atoms. It is very stable and has high melting point (3000°C). It reacts with water slowly to give H_3BO_3 and NH_3 :

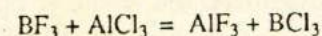


The presence of H_3BO_3 in hot spring of volcanic origin is attributed due to the hydrolysis of BN of volcanic origin. Boron nitride is very hard and the crystalline variety has the diamond-like hardness and is used as abrasive.

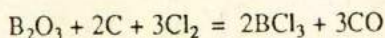
Boron halides, BX_3 : Boron fluoride is made by the action of B_2O_3 , H_2SO_4 and a fluoride, such as CaF_2 :



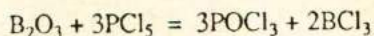
BCl_3 is made by the action of BF_3 on $AlCl_3$ by heat :



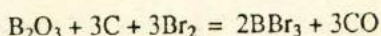
This is also made by heating B_2O_3 mixed with C and passing a stream of Cl_2 :



With PCl_5 :



BBr_3 is made in a similar manner from B_2O_3 , C and Br_2 :



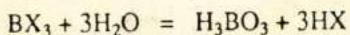
BI_3 is made by heating B in HI :



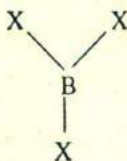
The boron halides can also be made by the direct union of B and the halogens but the method is inconvenient.

BF_3 is a gas, BCl_3 and BBr_3 are liquids and BI_3 is solid at ordinary temperature. They are covalent compounds and Lewis acids.

These are hydrolysed by H_2O to H_3BO_3 :



The three halogens in BX_3 are at the corners of an equilateral triangle giving structures :



This is due to the use of sp^2 hybrid bond orbitals by boron atom forming three equivalent bonds with 3 halogen atoms as illustrated in Fig. 2—10. page

BF_3 being a Lewis acid combines with HF to give BF_4^- and also salts like KBF_4 :

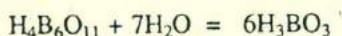
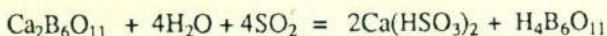


BF_3 is used as a versatile catalyst in organic chemistry.

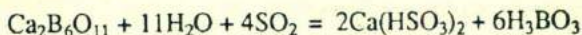
Boric acid, H_3BO_3 : Ortho-boric acid, H_3BO_3 , occurs in nature in the jets of steam known as soffioni in volcanic region since H_3BO_3 is volatile with steam.

(1) It is isolated by evaporating the water and crystallising solid H_3BO_3 .

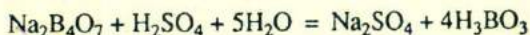
(2) H_3BO_3 can be obtained from colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, by passing SO_2 through a suspension of the mineral in water :



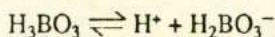
The overall reaction :



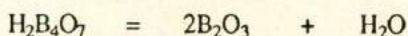
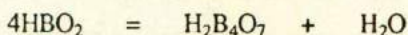
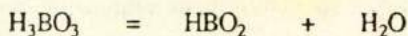
(3) Borax, $Na_2B_4O_7$, when treated with conc H_2SO_4 gives boric acid crystals :



Boric acid, also known as *boracic acid*, is a colourless crystalline substance and soapy to touch because of layer structure. It is sparingly soluble in cold water but dissolves in hot water forming a weak acid solution. It ionizes as,

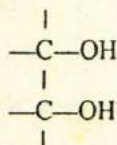


H_3BO_3 loses H_2O at 100°C forming meta-boric acid, HBO_2 , and at 140°C to tetraboric acid. On strong heating, it gives B_2O_3 :

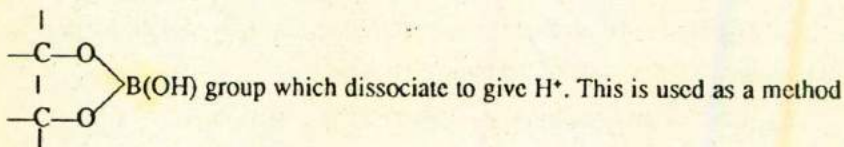


B_2O_3 forms a glassy mass and is mainly used to make borosilicate glasses which resist chemical action and heat.

H_3BO_3 is converted to a strong acid by adding to its solution some organic substances having the group :

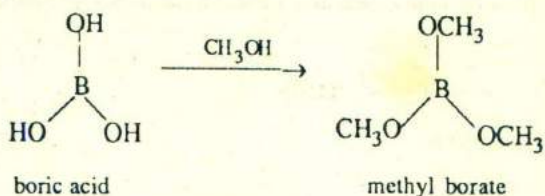


These are glycerine, glucose, mannitol etc. probably forming



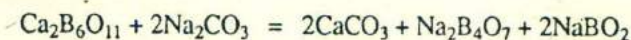
for the titrimetric determination of boric acid and boron with standard alkali solution in presence of phenolphthalein.

H_3BO_3 also forms methyl and ethyl borates which are volatile compounds and burn with green-edged flame on ignition and this is used to detect borate in qualitative test :

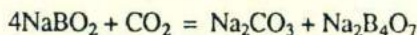


Boric acid is used as a mild antiseptic. H_3BO_3 is associated in the solid state to form a giant molecule through H-bonding.

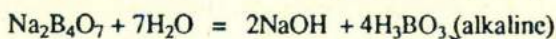
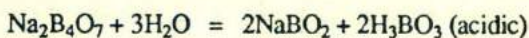
Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$: This is also known as sodium tetraborate or pyroborate. This occurs in nature known as "tincal". It is obtained : (i) from tincal by leaching the mineral with water and crystallising to $\text{Na}_2\text{B}_4\text{O}_7$; (ii) from colemanite by digesting the mineral with conc Na_2CO_3 solution to give $\text{Na}_2\text{B}_4\text{O}_7$ by double decomposition :



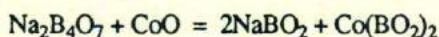
NaBO_2 is converted to $\text{Na}_2\text{B}_4\text{O}_7$ by CO_2 :



On crystallisation from aqueous solutions above 58°C , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is obtained, whereas below 58°C , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is obtained. A strong solution of $\text{Na}_2\text{B}_4\text{O}_7$ appears to be acidic whereas a dilute solution is strongly alkaline because NaOH formed is a strong base and H_3BO_3 is a weak acid :



Uses of Borax : (1) As a laboratory reagent for borax bead tests for some metals. When borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is heated on a platinum loop, it first swells due to the escape of H_2O and then melts to form a transparent glassy bead. If a pinch of salts of other metals is fused with it, the metals form metaborates of various colours. Thus, with CoO gives the following reaction :



$\text{Co}(\text{BO}_2)_2$ is coloured blue. Similarly, $\text{Cu}(\text{BO}_2)_2$ is blue-green, $\text{Cr}(\text{BO}_2)_3$ is green, and $\text{Mn}(\text{BO}_2)_2$ is amethyst or violet coloured. The colour also changes in

oxidizing and reducing flames and also gives different colours in the cold and hot conditions.

- (2) Borax is used as flux for solders.
- (3) Food preservation.
- (4) Buffer solutions.
- (5) Enamels, borosilicate glass, or "pyrex" glass.
- (6) Leather industry for soaking and cleaning hides.

Sodium peroxyborate (Sodium perborate), $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$:

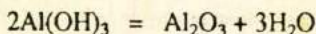
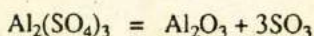
This is formed from borax solution when treated with NaOH and H_2O_2 giving transparent crystals of $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$. This is used as bleaching agent and as an antiseptic. Na-perborate can be formed by the action of sodium hydroperoxide, NaHO_2 , on H_3BO_3 . It liberates H_2O_2 on hydrolysis and is used as an oxidizing and a bleaching agent.

Compounds of Aluminium

Aluminium oxide (Alumina), Al_2O_3 : In the pure form Al_2O_3 occurs in nature as corundum. It is very hard and is used as abrasive for grinding and polishing. Bauxite is a mineral of Al_2O_3 containing large number of impurities. Emery contains Al_2O_3 together with Fe_2O_3 . Ruby contains Al_2O_3 and some Cr_2O_3 . Sapphire, amethyst etc. are also Al_2O_3 containing impurities. These are precious stones and are used as jewellery. Now-a-days all these are made by artificial processes and are largely used as bearings (jewels) in watches and other instruments. Artificial corundum is known as alundum. Large number of minerals containing Al_2O_3 , SiO_2 etc. also occur as precious stones, such as jade, topaz, garnet, aquamarine, tourmaline etc.

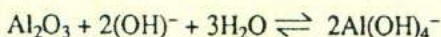
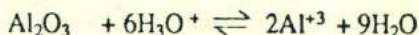
Finely divided Al_2O_3 is called *activated alumina* and is used as catalyst, dehydrating agents and in chromatography.

Pure Al_2O_3 is obtained by igniting $\text{Al}_2(\text{SO}_4)_3$, or $\text{Al}(\text{OH})_3$ or alum :

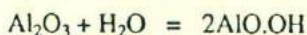


Naturally occurring Al_2O_3 is unreactive, but Al_2O_3 prepared in the laboratory is distinctly amphoteric. Al_2O_3 is used in Al metallurgy.

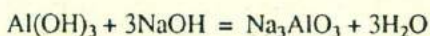
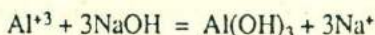
Al_2O_3 is amphoteric :



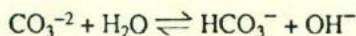
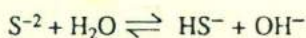
Freshly prepared alumina reacts slowly with water to give AlO.OH (disapore) :



Aluminium hydroxide., $\text{Al}(\text{OH})_3$: When alkali is added to a solution of Al-salts, the white gelatinous precipitate formed is $\text{Al}(\text{OH})_3$. In excess caustic alkalis the precipitate is soluble forming aluminate :



Solutions of sulphides and carbonates also precipitate $\text{Al}(\text{OH})_3$ due to hydrolysis of S^{-2} and CO_3^{-2} ions :



The gelatinous precipitate has great tendency to take up colouring matters, such as diazo compounds, alizarine etc. and forms beautiful colours known as "lakes". This is used in dyeing and mordanting of fabrics. Fast colour on cloth is imparted by dipping in a solution of Al-salt, such as Al-acetate. The fibre becomes impregnated with $\text{Al}(\text{OH})_3$ due to the hydrolysis of Al-salt. If the solution of Al-salt is mixed with a dye, the precipitate of $\text{Al}(\text{OH})_3$ is coloured which is absorbed in the fabrics which hold the colour fast. $\text{Al}(\text{OH})_3$ is known as a *Mordant* and the coloured product is called a *Lake*.

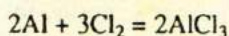
Aluminium hydroxide is also used for purification of water.

Aluminium halides, AlX_3 : Aluminium reacts readily with halogens rather vigorously forming AlX_3 . The fluoride, AlF_3 , is a definite ionic compound and is also obtained when Al is dissolved in HF or when $\text{Al}_2(\text{SO}_4)_3$ is

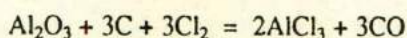
heated with NaF. AlF_3 is insoluble in water and not hydrolysed ordinarily but only when heated with steam.

Aluminium chloride, AlCl_3 , is obtained by various methods :—

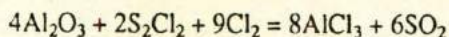
(i) Direct reaction between Al-metal and dry chlorine or hydrogen chloride gas in a heated tube gives anhydrous AlCl_3 which sublimes and collects in a receiver bottle out of contact with air :



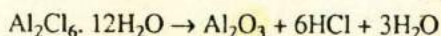
(ii) Alumina mixed with carbon heated in dry chlorine gives anhydrous AlCl_3 :



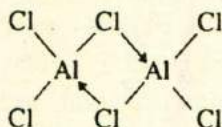
(iii) Alumina heated with sulphur chloride, S_2Cl_2 , vapour and chlorine :



AlCl_3 is a white crystalline substance which sublimes at 193°C and is soluble in organic solvents. This is very hygroscopic and a solution in water gives crystal of $\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ which cannot be made anhydrous because of hydrolysis :

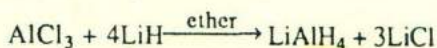


Measurement of vapour density indicates that AlCl_3 is a dimer having Al tetrahedrally bonded to four Cl. One Cl of each AlCl_3 donates a pair of electrons to be shared by the atom of the other molecule :



Anhydrous AlCl_3 is used as a catalyst in many organic reactions and in cracking process for making gasoline. Like BCl_3 it is a strong Lewis acid. In addition to their uses in organic chemistry, AlCl_3 and AlBr_3 are used to make complex Al-hydrides and alkyls, such as $\text{Al}_2(\text{CH}_3)_6$.

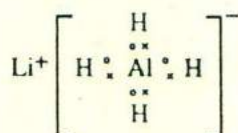
LiAlH_4 : Al does not react with H_2 , but AlCl_3 reacts with, say, LiH , in ether to form LiAlH_4 :



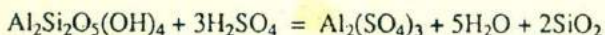
LiAlH_4 is decomposed by H_2O :



LiAlH_4 is an important reducing and hydrogenating reagent. The structure of LiAlH_4 contains Li^+ and AlH_4^- ions :



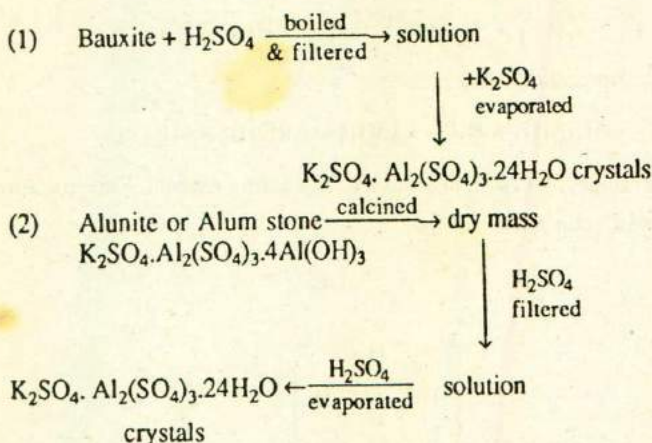
Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3$: This is prepared from freshly precipitated Al(OH)_3 and H_2SO_4 . Large quantities of $\text{Al}_2(\text{SO}_4)_3$ is produced by treating bauxite or clay with H_2SO_4 . The aqueous solution on crystallisation gives $\text{Al}_2(\text{SO}_4)_3$ with 18 or 9 H_2O depending on temperature:



$\text{Al}_2(\text{SO}_4)_3$ is the cheapest Al-salt soluble in water, and is used for (i) purification of water, (ii) dyeing of fabrics, (iii) in styptic or blood-clotting formulations, (iv) in tanning agents for hides, (v) water proofing and (vi) sizing of papers.

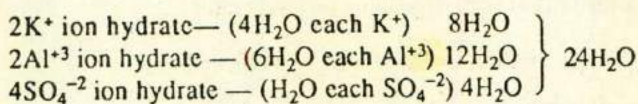
Alums : Alums are made from $\text{Al}_2(\text{SO}_4)_3$ which are quite numerous. Alums are double or mixed sulphates of Al and some other metal with usually $24\text{H}_2\text{O}$ in the double salt. The common alum is $\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$. K_2SO_4 may be replaced by sulphates of other alkali metals, silver, ammonium and also $\text{Al}_2(\text{SO}_4)_3$ may be replaced by sulphates of trivalent metal, such as Fe, Cr, Mn etc. Thus chrome alum is $\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$. Ferric alum, $\text{K}_2\text{SO}_4, \text{Fe}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$ etc.

Al-alum or potash alum, $\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$ is produced by the following processes :



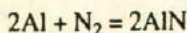
Alums are soluble in water and when strongly heated produce porous mass. Alums form very beautiful octahedral crystals.

Alums are mixed crystals and no complex ions are present. The solution gives the test of all the ions present in the crystals indicating complete dissociation. The distribution of 24 molecules of water is as follows :

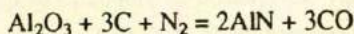


Alum is the most important commercial compound of Al and is used in (i) water purification, (ii) dyeing of fabrics, (iii) coagulation of colloidal solutions, (iv) tanning agents for hides, (v) sizing of paper etc.

Aluminium nitride, AlN : On heating, Al combines with N_2 forming AlN :

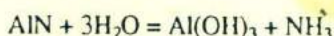


It is also obtained by strong heating of a mixture of bauxite and carbon in a current of N_2 :

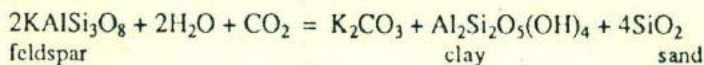


AlN is a covalent compound of high melting point. It forms a giant molecule having diamond-like structure. The structure is due to the presence of one pair of electrons in nitrogen atoms which are used to form coordinate bonds resulting in a three-dimensional lattice. AlN is isoelectronic with SiC and both

are physically similar. But AlN is rapidly attacked by water or dilute alkali to give ammonia and Al(OH)₃ :



Aluminium silicates : Many of the most important silicate rocks contain aluminium. Clay and sand are formed by the weathering of rocks. Weathering involves the thawing and freezing of water in the rocks, and the chemical action of water and carbon dioxide upon them. The chemical disintegration of feldspar may be represented by the equation :



The soluble potassium carbonate formed is largely removed by water, and sand-clay remains as soil. Pure clay shown above is white in colour and is called *kaolin*. Ordinary clay is coloured by compounds of iron and other metals. Kaolin is used for making porcelain china wares, white impure clays are used in the manufacture of earthen wares. The red colour in these earthen-wares is due to the presence of iron silicate. Porous products are obtained by firing, but by means of glazing agents they are made smooth, shining and water-tight. During firing sodium chloride is added in the kiln which makes Na-Al silicate which fills the pores. Better quality china and porcelain wares are glazed by means of feldspar, silica and red oxide during the second firing. The coloured glazes are imparted with the help of suitable metal oxides.

The Elements of Group IIIB

Scandium, Yttrium and the Rare Earths

Scandium(21) and Yttrium(39) are transition metals and have no relationship with the group of elements commonly known as *Rare Earths* so far as the electronic configurations are concerned. But their chemical properties have great similarity with those of the Rare Earths and the atomic numbers relationship places these in the same group IIIB. The Rare Earth elements generally known as *Lanthanides* have themselves been placed together in the

same position of the Periodic Table although starting from *Lanthanum* (57) to *Lutecium* (71), they consist of 15 elements. But generally Lanthanides start from Ce(58)

The Rare Earths (Lanthanides)

These elements from Ce(58) to Lu(71) have physical and chemical properties which are very similar. Their occurrence in nature together and the remarkable similarity in their properties have been attributed due to their similar electron arrangements. The increase in the nuclear charge (atomic number) from Ce (58) to Lu (71) is compensated by placement of the electrons in the 4f and 5d sub-levels rather than the outer orbitals. Their electron arrangements are shown in Table 18.3.

Table 18.3. Electron arrangements of the lanthanides.

Elements	At. No.	Electron configuration			
La	57	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$	$4f^0$	$5s^2 5p^6 5d^1$	$6s^2$
Ce	58		$4f^1$	$5s^2 5p^6 5d^1$	$6s^2$
Pr	59		$4f^3$	$5s^2 5p^6 5d^0$	$6s^2$
Nd	60		$4f^4$	$5s^2 5p^6 5d^0$	$6s^2$
Pm	61		$4f^5$	$5s^2 5p^6 5d^0$	$6s^2$
Sm	62		$4f^6$	$5s^2 5p^6 5d^0$	$6s^2$
Eu	63		$4f^7$	$5s^2 5p^6 5d^0$	$6s^2$
Gd	64		$4f^7$	$5s^2 5p^6 5d^1$	$6s^2$
Tb	65		$4f^9$	$5s^2 5p^6 5d^0$	$6s^2$
Dy	66		$4f^{10}$	$5s^2 5p^6 5d^0$	$6s^2$
Ho	67		$4f^{11}$	$5s^2 5p^6 5d^0$	$6s^2$
Er	68		$4f^{12}$	$5s^2 5p^6 5d^0$	$6s^2$
Tm	69		$4f^{13}$	$5s^2 5p^6 5d^0$	$6s^2$
Yb	70		$4f^{14}$	$5s^2 5p^6 5d^0$	$6s^2$
Lu	71		$4f^{14}$	$5s^2 5p^6 5d^1$	$6s^2$

Due to the filling up of 4f orbitals in the lanthanides a unique feature arises among these group of elements. The electrons in the 4f are nearer the nucleus and hence these are attracted more than the electrons in the outermost energy levels. Thus the atomic size of the elements and so also the ionic size

decrease from lanthanum to lutecium in a systematic manner. This decrease in the atomic or ionic sizes of the rare earth elements is known as *Lanthanide Contraction*.

The rare earth elements are often found together in the minerals. *Monazite sand* is the most important mineral in which the rare earths are present as phosphate together with thorium. There is one exception : element number 61, promethium, which does not occur in nature at all.

Separation of Rare Earths

Due to the Lanthanide contraction the rare earth elements resemble so closely that their separation from one another had been a great problem in chemistry. (1) Fractional crystallisation of their nitrates or double sulphates involving many hundreds of steps led only to partial separation. (2) Recently ion-exchange technique has been used to provide more effective and rapid separation of rare earths by selective absorption of the ions of rare earth on a column of an ion-exchange resin. The absorbed ions are then eluted out by a suitable solvent, such as ammonium acetate or citric acid. It has been observed that the rare earths are eluted out in the reverse order of their atomic number. That is, Lu first and La last. (3) Solvent extraction process has also been developed for the separation of lanthanides.

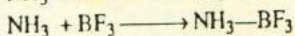
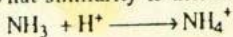
Properties : The rare earth elements are all silvery white metals of inner transition series with high densities. They form oxides of the general formula M_2O_3 and chlorides MX_3 . But Ce shows oxidation states of +4. The normal oxidation state of all the rare earths is +3. Some rare earths show oxidation state +2, e. g., Lu. The basicity of their hydroxides $M(OH)_3$ decreases due to decrease in the ionic size of M^{+3} ions in the group.

CeO_2 mixed with ThO_2 is used in gas mantles. "Misch metal", a mixture of iron and some rare earth metals, is used to make artificial flints for cigarette lighters. Rare earth fluorides are used as the core of the carbon used in the projectors in motion pictures.

QUESTIONS AND PROBLEMS

- How is borax prepared? Describe the chemistry of the borax bead test. Discuss the diagonal relationship between boron and silicon. Write electronic structure for NH_3 and BF_3 . These molecules combine to form

the addition compounds NH_3BF_3 . What is the electronic structure of this compound? What similarity is there in the following chemical reactions?



4. Justify the inclusion of iron and aluminium, widely separated groups of the periodic classifications into the same analytical group. Emphasize the difference between the compounds of these two elements.
5. Discuss the use of borax in analytical chemistry. Give balanced equations for the reaction involved.
6. Write a clear note on aluminothermit process with reactions involved.
7. What are the sources of aluminium metal? Describe its extraction and important properties.
8. Describe the preparation and properties of anhydrous aluminium chloride.
9. Write a short note on rare earths.
10. Write a short note on Thermit Process.
11. Compare the chemistry of boron and aluminium and their important compounds.
12. Describe the preparation, structure and properties of boron hydrides.
13. Starting with bauxite, how would you prepare—(a) different types of alumina, (b) anhydrous aluminium chloride, and (c) potash alum? Discuss properties and uses of metallic aluminium and its alloys.
14. How bauxite is purified for obtaining pure alumina? Describe the electrolytic process employed for the extraction and refining of aluminium. Discuss the important uses of the metal.
15. Write short note on extraction and refining of aluminium.
16. Compare the chemistry of Boron and Aluminium.
17. Compare the chemistry of Group III elements with particular reference to Boron and Aluminium.
18. Write a note on diborane.
19. Show with examples that aluminium is amphoteric in nature.
20. Give the structure of aluminium chloride.
21. Discuss similarity of properties of boron and silicon.
22. Al is a major metal in our society. Describe the chemistry of its recovery from ores.
23. Al is not recovered from the silicate ores which occur abundantly. Explain why.
24. pH is an important factor in the refining of Al. Why?

25. Why Anhydrous AlCl_3 behaves as a Lewis Acid?
26. Differentiate between the Baeyer Process, the Hall-Heralt process and the Hoopes Process of manufacture of Al.
27. Why alum is acidic in aqueous solution?
28. Explain lanthanide contractions.
29. How the rare earth metals are separated from one another?