# General Study of Hydrides

Strictly speaking the binary compounds of hydrogen with other elements whose electronegativity is lower than that of hydrogen are called hydrides. Thus according to this definition, the term hydride is not generally used for the compounds like H_2O, H_2S, NH_3, PH_3, H_2S, HF, HCl, HBr etc. Thus this term is not usually used for the binary compounds of hydrogen with non-metals. On the basis of the type of bonding in the hydrides, these are classified into the following classes by Gibb (1941). (A) *Ionic or salt-like hydrides.* (B) *Covalent or molecular hydrides.* (C) *Metallic or interstitial or alloy type hydrides.* (D) *Complex hydrides.* (E) *Borderline hydrides.*

A. Ionic or Salt-like Hydrides

These hydrides are given by the elements of groups IA (Fr is an exception), IIA (Be and Mg are exceptions) and some highly electropositive lanthanides and actinides. Examples are : LiH, CaH_2 etc.

### Preperation

(*i*) **By heating metal in a current of H_2.** The alkali and alkaline earth metals give hydrides when heated at different temperatures in a current of H_2.

$$2M + H_2 \xrightarrow{400°C} 2MH$$
$$(M = \text{Na or K})$$

$$M + H_2 \xrightarrow{150-300°C} MH_2$$
$$(M = \text{Ca, Sr, Ba})$$
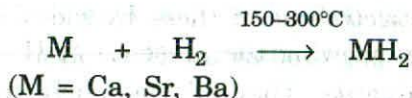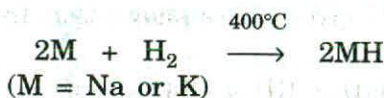
Li placed in an iron boat kept in a hard glass tube combines with H_2 at 600°C to give LiH.

(*ii*) **By heating carbonates in a current of H_2.** RbH and CsH are prepared by heating their carbonates in a current of H_2 at 620–650°C. In this reaction the presence of Mg is essential.

$$\text{In presence of Mg}$$
$$Rb_2CO_3 + 2H_2 \longrightarrow 2RbH + CO_2 + H_2O$$
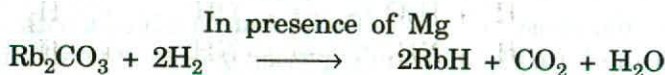
(*iii*) **By heating metal nitride in a current of H_2.** By this method LiH can be prepared.

$$2LiN_3 + 3H_2 \longrightarrow 6LiH + N_2$$

(*iv*) **Alexander's method.** CaH_2 is prepared by heating CaO with metallic Mg in a current of H_2 at 250°C and 50 cm. pressure of hydrogen.

$$CaO + Mg + H_2 \longrightarrow CaH_2 + MgO$$

A yield of 99.2% of CaH_2 is obtained in 2 hours.

Properties

(*i*) **Physical Properties.** The saline hydrides are crystalline compounds with ionic lattices. The crystals are somewhat denser than the metal from which they are made because of strong polar bonds existing in the ionic lattices. As ionic compounds, these possess high melting and boiling points and are electrically conducting in the fused state. Excepting LiH they decompose on fusion. They are stoichiometric compounds.

(*ii*) **Thermal stability and order of reactivity.** Hydrides of Li, Ca and Sr are most stable while others decompose above 400°C. Their thermal stability decreases with increasing size of the cation in a group. Thus the order of stability of the hydrides of Li to Cs and of Ca to Ba is as follows :

$$LiH > NaH > KH > RbH > CsH$$
$$CaH_2 > SrH_2 > BaH_2$$

The values of heats of formation (in Kcal/mole) of the above hydrides given below support this order.

Group $\longrightarrow$	I A	II A
Hydrides $\longrightarrow$	LiH, NaH, KH, RbH, CsH	CaH_2, SrH_2, BaH_2
Heat of formation (K.cal/mole) $\longrightarrow$	21.6, 13.9, 14.4, 13.5, 13.0 $\longrightarrow$ decreasing $\longrightarrow$	45.1, 42.3, 40.9 $\longrightarrow$ decreasing $\longrightarrow$

The relative order of stability given above shows that the order of reactivity is as :

$$LiH < NaH < KH < RbH < CsH$$
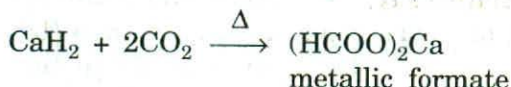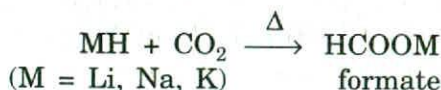
(*iii*) **Presence of H⁻ ion.** Electrolysis of these hydrides in the fused state liberates hydrogen at the anode, showing the presence of H^- ion in them.

(*iv*) **Action of protonic solvents.** They all vigorously react with protonic solvents (*i.e.* solvents giving H^+ ions) such as H_2O, C_2H_5OH and NH_3 forming H_2 and a base.

$$\underset{\substack{\text{Protonic} \\ \text{solvents}}}{MH} \rightleftharpoons M^+ + H^-$$

$$H^- + H_2O \longrightarrow OH^- + H_2$$
$$H^- + NH_3 \longrightarrow NH_2^- + H$$
$$H^- + C_2H_5OH \longrightarrow OC_2H_5^- + H_2$$
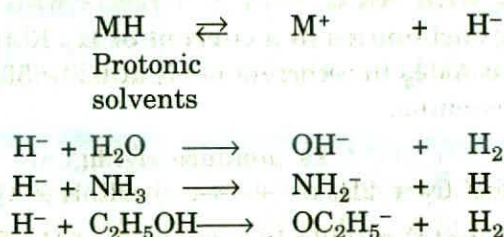
(*v*) **Reducing property.** All these hydrides show reducing properties at high temperatures which is probably due to the formation of atomic hydrogen. Thus

they reduce the refractory metal oxides (*e.g.* Fe_3O_4) to free metal, CO_2 to formate, sulphates to sulphides and chlorides to hydrides.

$$NaH + Fe_3O_4 \longrightarrow 3Fe + 4NaOH$$

$$\underset{(M = Li,\ Na,\ K)}{MH} + CO_2 \xrightarrow{\Delta} \underset{formate}{HCOOM}$$

$$CaH_2 + 2CO_2 \xrightarrow{\Delta} \underset{metallic\ formate}{(HCOO)_2Ca}$$

$$2CaH_2 + PbSO_4 \longrightarrow PbS + 2Ca(OH)_2$$

$$4NaH + SiCl_4 \longrightarrow SiH_4 + 4NaCl$$

(*vi*) Since these hydrides are ionic in nature, their bonds are not directed in space and hence the molecules of thee hydrides have no geometry. Typical type of gattering of these molecules in crystal gives specific type of lattice, *e.g.*, alkali metal hydrides possess face-centred cubic lattice while alkaline earth metal hydrides possess orthorhombic lattice. The radius of H^- ion in these hydrides decreases with the decrease in electropositive character of the metal.

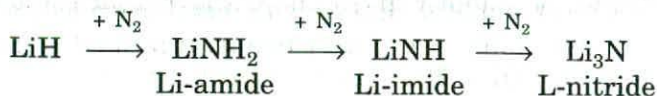(*vii*) **Decomposition by SO_2.** These are decomposed by SO_2 forming hyposulphites.

$$2KH + 2SO_2 \longrightarrow K_2S_2O_4 + H_2 \uparrow$$

$$CaH_2 + 2SO_2 \longrightarrow CaS_2O_4 + H_2 \uparrow$$

(*viii*) **Reaction with N_2.** (*a*) Alkaline earth metal hydrides react with N_2 to form nitrides.

$$3CaH_2 + N_2 \longrightarrow Ca_3N_2 + 3H_2$$

(*b*) LiH is oxidised by N_2, forming $LiNH_2$, Li_2NH and finally Li_3N.

$$LiH \xrightarrow{+ N_2} \underset{Li\text{-}amide}{LiNH_2} \xrightarrow{+ N_2} \underset{Li\text{-}imide}{LiNH} \xrightarrow{+ N_2} \underset{L\text{-}nitride}{Li_3N}$$

CsH, the most reactive hydride, gives $CsNH_2$ when heated with N_2.

$$CsH \xrightarrow[heat]{+ N_2} CsNH_2$$
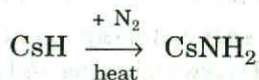
(*ix*) **Reaction with $AlCl_3$.** Only LiH reacts with $AlCl_3$ in ether forming $LiAlH_4$.

$$4LiH + AlCl_3 \text{ (in ether)} \longrightarrow LiAlH_4 + 3LiCl$$
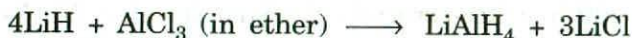
Uses

Ionic hydrides are used as condensing agents in Claisen and Aldol condensations. These hydrides, as shown above, are hydrolysed by water and give large quantities of H_2. Thus these hydrides are used as reducing agents. Other uses of LiH, NaH and CaH_2 which are ionic hydrides can be found in subsequent pages.

Some Ionic Hydrides

Let us discuss the methods of preparation, properties, uses and structure of some ionic hydrides like LiH, NaH, KH, (alkali metal hydrides), CaH_2, (alkaline earth metal hydride). These are discussed as follows :

1. Lithium hydride, LiH

Preparation. (*i*) It is prepared by passing H_2 gas over heated lithium at 700–800°C.

$$2Li + H_2 \xrightarrow{700-800°C} 2LiH$$
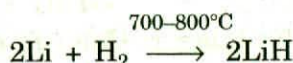
(*ii*) It can also be prepared by heating Li_3N in a current of H_2.

$$Li_3N + 3H_2 \longrightarrow 6LiH + N_2.$$
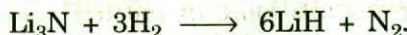
Properties. (*i*) It is a hard white solid with m.pt. = 680°C.

(*ii*) It reacts with H_2O evolving H_2
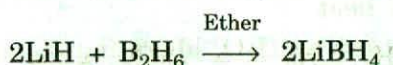
$$LiH + H_2O \longrightarrow LiOH + H_2 \uparrow$$

(*iii*) When an etheral solution of LiH is treated with anhydrous $AlCl_3$, lithium aluminium hydride ($LiAlH_4$) is obtained

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl.$$

(*iv*) Fused LiH, on electrolysis, gives Li at the cathode and H_2 at the anode like other ionic compounds.

(*v*) With B_2H_6 in ether medium it gives lithium borohydride, $LiBH_4$

$$2LiH + B_2H_6 \xrightarrow{Ether} 2LiBH_4$$

(*vi*) It turns blue on exposure to light without any change in composition.

(*vii*) LiH is the most stable of all the alkali metal hydrides and also chemically active. It is remarkably stable at ordinary temperature and is not affected by dry gases like Cl_2, HCl and O_2.

(*viii*) It is a powerful reducing agent and hence reduces oxides, chlorides, sulphides and also CO_2 to carbon.

Uses. It is used (*i*) as a strong reducing agent in synthetic organic chemistry. (*ii*) in the preparation of $LiAlH_4$ which is a valuable reducing agent. (*iii*) as a convenient source of H_2 for air-sea rescue balloons. (*iv*) for making borohydrides like $LiBH_4$ which are used in jet propulsion.

Structure. Its crystal has face-centred cubic structure (*i.e.* NaCl). The metal-hydrogen distance has been determined accurately by X-ray diffraction technique.

2. Sodium hydride, NaH

Preparation. It is prepared by passing pure and dry H_2 over metallic sodium kept in a nickel boat and heated in a glass tube at 365°C. After the reaction, colourless crystals of NaH are deposited on the upper portion of the tube a little away form the nickel boat.

Properties. (*i*) It is a colourles crystalline substance.

(*ii*) On beating above 330°C it is decomposed into its elements.

(*iii*) It is decomposed by H_2O evolving H_2

$$NaH + H_2O \longrightarrow NaOH + H_2$$

(*iv*) It absorbs CO_2 forming sodium formate, HCOONa
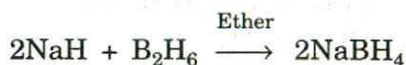
$$NaH + CO_2 \longrightarrow HCOONa$$

(*v*) On electrolysis, fused NaH gives H_2 at the anode and Na goes to cathode.

(*vi*) NaH reacts with $B(OCH_3)_3$ to form sodium borohydride, $NaBH_4$ which is used as a reducing agent.

$$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3NaOCH_3$$

(*vii*) NaH reacts with B_2H_6 in ether medium to give $NaBH_4$.

$$2NaH + B_2H_6 \xrightarrow{\text{Ether}} 2NaBH_4$$

Uses. (*i*) NaH is used to prepare $NaBH_4$ (as shown above) which is a valuable reducing agent.

(*ii*) NaH itself is also used as a reducing agent in organic chemistry.

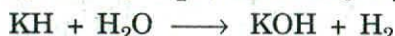**Structure.** NaH has a face-centred cubic lattice.

3. Potassium hydride, KH

Preparation. It is prepared by heating potassium in the atmosphere of H_2 at 360°C.

Properties. (*i*) It forms white needle-like crystalline solid.

(*ii*) It ignites spontaneously in Cl_2 or O_2

(*iii*) It is decomposed by heat

(*iv*) It also gets decomposed by H_2O, liberating H_2 gas

$$KH + H_2O \longrightarrow KOH + H_2$$

(*v*) In presence of moist CO_2 it is converted into HCOOK

$$KH + CO_2 \longrightarrow HCOOK.$$

Structure. It has NaCl like structure.

4. Calcium hydride or hydrolith, CaH_2

Preparation. It is prepared by passing H_2 over fused calcium metal at 400–500°C.

Properties. (*i*) It is a colourless crystalline compound of density 1.90.

(*ii*) On electrolysis of the fused salt, H_2 is evolved at the anode.

(*iii*) It is stable in air but is violently decomposed by cold water, giving slaked lime, $Ca(OH)_2$ and H_2

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

(*iv*) It combines with CO_2 to form calcium formate.

$$CaH_2 + CO_2 \longrightarrow (HCOO)_2Ca$$

Uses. (*i*) It is used for millitary purposes as a source of H_2 for balloons and hence the name of *hydrolith*.

(*ii*) It is used as a reducing agent in the metallurgical processes in organic chemistry and to determine the traces of water in organic solvents.

Structure. X-ray differaction has shown that Ca^{2+} ions in CaH_2 are in a slightly distorted hexagonally close-packed arrangement. The unit cell of this hydride is orthorhombic.

B. Covalent or Molecular Hydrides

These hydrides are given by most of p-block elements. Some elements (*e.g.* Sn, Pb, Sb, Bi, Te, Po and halogens) give only mononuclear hydrides while the elements like, B, Al, Ga, In, C, Si, N, O, S give mononuclear as well as polynuclear (or polymeric) hydrides as shown below :
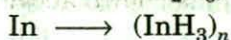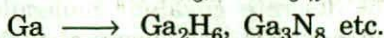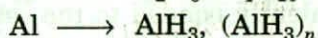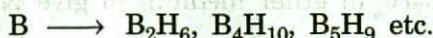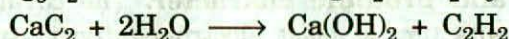
$$B \longrightarrow B_2H_6, \ B_4H_{10}, \ B_5H_9 \ \text{etc.}$$
$$Al \longrightarrow AlH_3, \ (AlH_3)_n$$
$$Ga \longrightarrow Ga_2H_6, \ Ga_3N_8 \ \text{etc.}$$
$$In \longrightarrow (InH_3)_n$$
$$C \longrightarrow CH_4 \ \text{and other higher hydrocarbons}$$
$$Si \longrightarrow SiH_4, \ Si_2H_6, \ Si_3H_8 \ \text{etc.}$$
$$N \longrightarrow NH_3, \ N_2H_4$$
$$S \longrightarrow H_2S, \ H_2S_3, \ H_2S_5$$
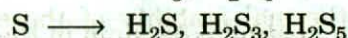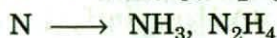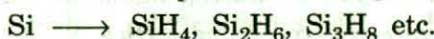
Excepting the hydrides of B, Al and Ga, the simplest hydrides of other elements can be formulated as AH_{8-n} where A is the element whose hydrides are being considered and n is the number of valence electrons in atom, A.

Preparation

(*i*) By the direct union of the free element with H_2 at elevated temperature.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$
$$2H_2 + O_2 \longrightarrow 2H_2O$$
$$H_2 + X_2 \longrightarrow 2HX$$
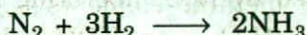
(*ii*) By the hydrolysis of compounds like borides, silicides, and similar compounds. The hydrolysis may be affected either by H_2O only or by dil. acid solutions.

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$$
$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$
$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + NH_3$$
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3$$
$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S$$
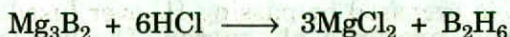
(*iii*) By the reduction of appropriate anhydrous chlorides in ether solution by $Li[AlH_4]$.
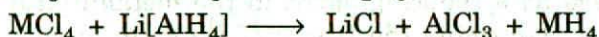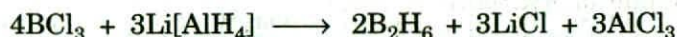
$$4BCl_3 + 3Li[AlH_4] \longrightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$$
$$MCl_4 + Li[AlH_4] \longrightarrow LiCl + AlCl_3 + MH_4$$
$$(M = Si, Ge \ or \ Sn)$$

(*iv*) By the decomposition of a carbide with alkalies.

$$Be_2C + 4KOH \longrightarrow 2Be(OK)_2 + CH_4$$

(*v*) Halogen hydrides, HX, may be obtained by heating double compounds such as HF. KF

$$HF.KF \xrightarrow{\text{heat}} HF + KF$$

(*vi*) **Paneth and Rabino-Witsch's method.** These persons prepared SnH_4 by electrolysing a sulphuric acid solution of $SnSO_4$ containing glucose. The cell used had Pb-electrodes and the temperature kept was below 50–60°C.

Properties

(*i*) The hydrogen atoms are covalently bonded to the central atom in these hydrides. The hydrides consist of discrete covalent molecules which are held together by weak van der Waals forces and in some cases by hydrogen bonds. As a result, hydrides are gases, liquids and (in few cases) solids of low melting and boiling points. The volatality is decreased in those hydrides in which hydrogen bonding occurs (*e.g.* NH_3, H_2O, HF) or where the hydrides are either dimeric [*e.g.* $(BH_3)_2$, $(GaH_3)_2$] or polymeric [*e.g.* $(AlH_3)_x$, $(InH_3)_x$].

(*ii*) **Thermal stability.** The thermal stability of these hydrides within a group decreases with the increasing atomic number (or atomic radius) of the element forming the hydride. Thus as the metallic character of the central atom increases, the thermal stability decreases. For example :

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$
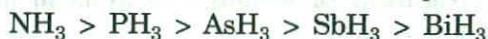
Note that N in NH_3 is a non-metal and Bi in BiH_3 is a metal. Thus the hydrides of the predominantly metallic elements (*e.g.* PbH_4, BiH_3, PoH_2) are particularly unstable.

The stability of the hydrides of the elements of second period increases with the increase in electronegativity of the central atom, *e.g.*,

$$CH_4 < NH_3 < H_2O < HF$$
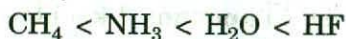
Note that the atomic radii of the elements decrease on proceeding from left to right in a period.

(*iii*) **Hydridic and protonic character.** The covalent hydrides of more electropositive elements (*i.e.* of least electronegativity) such as those of Be, B and Al behave as if they possess "*hydridic*" character. Thus these hydrides react with H_2O to form H_2.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

The hydrides of more electronegative elements such as those of oxygen family and halogens react as if the H-atoms have protonic character. Thus such hydrides react with bases to form salts.

$$\underset{\text{Hydride}}{HCl} + \underset{\text{Base}}{NH_3} \longrightarrow \underset{\text{Salt}}{NH_4Cl}$$
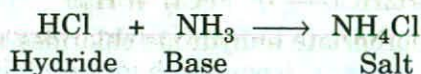
The formation of the salt, NH_4Cl probably occurs as follows :

$$\underset{\text{Hydride}}{HCl} \longrightarrow H^+ + Cl^-$$

$$NH_3 + H^+ \longrightarrow NH_4^+$$
$$\text{Base}$$
$$NH_4^+ + Cl^- \longrightarrow NH_4Cl$$
$$\text{Salt}$$

The hydrides of the elements of intermediate electronegativity such as those of group IV A show no marked hydridic or protonic character. These hydrides may, however, exhibit either hydridic or protonic character depending on the experimental conditions, *e.g.*, mono-germane, GeH_4, reacts with HBr to form H_2 and with sodium amide, $NaNH_2$ (which is a base) to give sodium germyl, $NaGeH_3$.
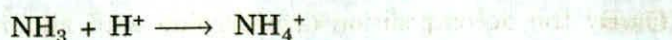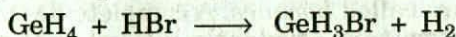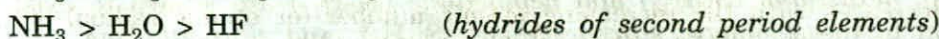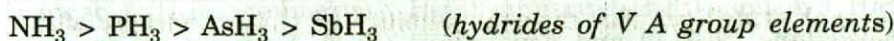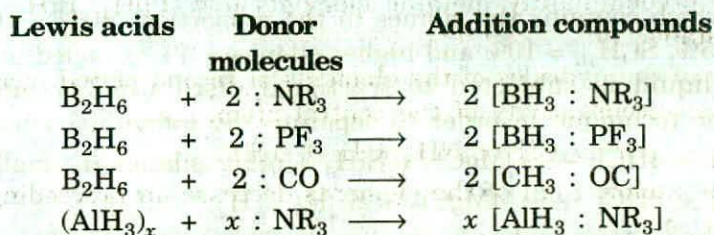
$$GeH_4 + HBr \longrightarrow GeH_3Br + H_2$$
$$GeH_4 + NaNH_3 \longrightarrow NaGeH_3 + NH_3$$

(*iv*) **Property of behaving as Lewis base.** Covalent hydrides that have one or more lone pairs of electrons behave as Lewis bases. This property of behaving as Lewis base decreases on proceeding down a group and from left to right across a period. Thus this property for the hydrides from NH_3 to SbH_3 and from NH_3 to HF is in the following order :

$NH_3 > PH_3 > AsH_3 > SbH_3$ (*hydrides of V A group elements*)
$NH_3 > H_2O > HF$ (*hydrides of second period elements*)

(*v*) **Formation of addition compounds.** The known hydrides of III A group elements [*e.g.* B_2H_6, $(AlH_3)_x$] are electron-deficient molecules and so behave as strong Lewis acids and hence form addition compound with a variety of donor molecules such as CO, PF_3, NR_3 etc.

Lewis acids	Donor molecules	Addition compounds
B_2H_6	$+ \quad 2 : NR_3 \longrightarrow$	$2\,[BH_3 : NR_3]$
B_2H_6	$+ \quad 2 : PF_3 \longrightarrow$	$2\,[BH_3 : PF_3]$
B_2H_6	$+ \quad 2 : CO \longrightarrow$	$2\,[CH_3 : OC]$
$(AlH_3)_x$	$+ \quad x : NR_3 \longrightarrow$	$x\,[AlH_3 : NR_3]$

(*vi*) *Formation of complex hydrides.* The covalent hydrides react with ionic hydrides to form complex hydrides, *e.g.*,

Covalent hydrides	Ionic hydrides	Complex hydrides
AlH_3	$+ \quad LiH \longrightarrow$	$Li\,[AlH_4]$
		Li-Al-hydride
		(complex hydride of Al)
B_2H_6	$+ \quad 2MH \longrightarrow$	$2M\,[BH_4]$
	(M = Li, Na)	Li- or Na-borohydride
		(complex hydride of B)
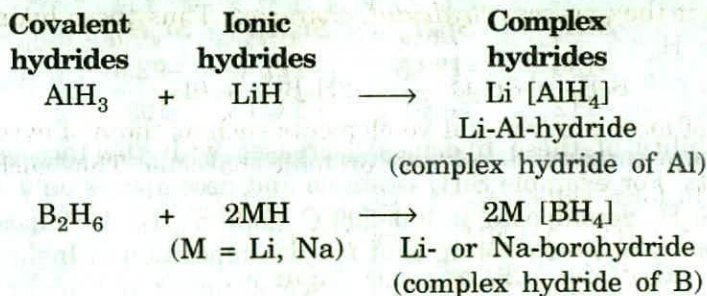
(*vii*) In polymeric covalent hydrides like $(AlH_3)_n$, $(InH_3)_n$ etc. the metal atoms are linked together by hydrogen bridges.

Uses

(*i*) Boron hydrides (called boranes) which are covalent hydrides are used as fuels and fuel additives, *e.g.* diborane (B_2H_6) is used as a high energy fuel and propallent. It is also used in welding.

(*ii*) Silane (SiH_4) which is a covalent hydride is used as a source for the preparation of silicon of high purity which is used in transistors. It is also used as a reducing agent.
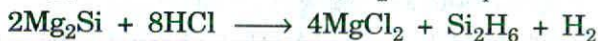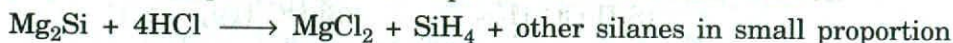
Hydrides of Boron : Boranes

Hydrides of boron are called *boranes*. A complete description of these hydrides is given in chapter 24. These hydrides are covalent hydrides.

Hydrides of Silicon : Silanes

General Discussion

Hydrides of silicon are called *silanes*. These are also covalent hydrides and are represented by the general formula Si_n (H_{2n+2}). The silanes namely *monosilane* or *silane* (SiH_4), *disilane* (Si_2H_6), *trisilane* (Si_3H_8), *tetrasilane* (Si_4H_{10}), *pentasilane* (Si_5H_{12}), *hexasilane* (Si_6H_{14}) and *heptasilane* (Si_7H_{14}) are known to exist. In addition to these silanes, *silicoacetylene*, $(Si_2H_2)_n$ and *silico-ethylene*, $(Si_2H_4)_n$ are also known. These compounds were studied by Stock and his students in 1926.

When 20% HCl acts on Mg_2Si (prepared by heating a mixture of Mg and SiO_2 in the absence of air) in an atmosphere of H_2, a mixture of silanes is obtained. This mixture which contains the silanes in the proportion, SiH_4 = 40%, Si_2H_6 = 30%, Si_3H_8 = 15%, Si_4H_{10} = 10% and higher silanes = 5% is cooled in liq. N_2 and the resulting liquid is subjected to fractional distillation or vapour phase chromatographic technique in order to separate the individual silanes.

$$Mg_2Si + 4HCl \longrightarrow MgCl_2 + SiH_4 + \text{other silanes in small proportion}$$
$$2Mg_2Si + 8HCl \longrightarrow 4MgCl_2 + Si_2H_6 + H_2$$

These compounds are analogous to alkanes. These are colourless and volatile covalent hydrides. The melting and boiling points of the first four members as given below show that these increase with the increase of their molecular weights.

	SiH_4	Si_2H_6	Si_3H_8	Si_4H_{10}
M.pts.(°C)	−185	−132.5	−117	−92.5
B.pts.(°C)	−112	−15	53	109

Thermal stability of these hydrides decreases with the increase of their molecular weights. For example SiH_4 is stable and decomposes only at red heat into H_2 and Si; Si_2H_6 decomposes at 400–500°C while Si_6H_{14} decomposes at room temperature. Here it is worth noting that the decomposition of higher silanes is not complete and gives a mixture of simple gaseous silanes and solid unsaturated hydrides. For example :

$$Si_5H_{12} \xrightarrow{\text{Heat}} 2\ SiH + Si_2H_6 + SiH_4$$

SiH_4 and Si_2H_6 are colourless gases at room temperature while higher silanes are colourless liquids. These compounds are very poisnous and produce headache and sickness when inhaled in small quantities. In low concentration they have stupefying and chocolate like odour, but in high concentration their odour resembles that of H_2S.

Chemically silanes are very reactive and burn spontaneously in air or oxygen. For example :
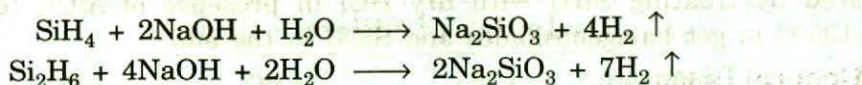
$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$
$$Si_4H_{10} + 13/2\ O_2 \longrightarrow 4\ SiO_2 + 5H_2O$$
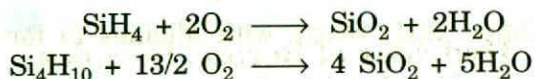
Silanes are stable towards neutral or acidic water, but in the presence of even a trace of a base in water, they form silicates with the liberation of H_2. For example :

$$SiH_4 + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 4H_2 \uparrow$$
$$Si_2H_6 + 4NaOH + 2H_2O \longrightarrow 2Na_2SiO_3 + 7H_2 \uparrow$$
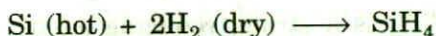
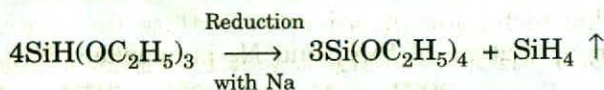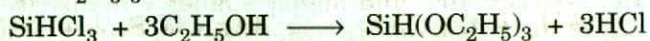Now let us discuss some silanes in detail.

1. Monosilane, SiH_4

This compound is also called *silico-methane* or *silicane*.

Preparation. (*i*) SiH_4 can be prepared by passing dry H_2 over hot silicon in an electric arc.

$$Si\ (hot) + 2H_2\ (dry) \longrightarrow SiH_4$$

(*ii*) *Johnson's method (1935).* According to this method pure SiH_4 is formed by decomposing Mg_2Si with NH_4Br in liq. NH_3.

(*iii*) Silico-chloroform, $SiHCl_3$, on treatment with C_2H_2OH gives ethyl silico orthoformate, $SiH(OC_2H_5)_3$ which on reduction with Na gives pure SiH_4.

$$SiHCl_3 + 3C_2H_5OH \longrightarrow SiH(OC_2H_5)_3 + 3HCl$$

$$4SiH(OC_2H_5)_3 \xrightarrow[\text{with Na}]{\text{Reduction}} 3Si(OC_2H_5)_4 + SiH_4 \uparrow$$

(*iv*) Pure SiH_4 can also be formed by reducing $SiCl_4$ with $LiAlH_4$ dissolved in ether at 0°C.

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$
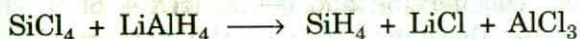
Properties. (*i*) It is a colourless gas which can be liquefied at –112°C and solidified at –185°C. It has faint odour.

(*ii*) *Action of air.* When pure, SiH_4 is not inflammable in air but in the presence of H_2 and other hydrides of silicon, it spontaneously burns in air with a bright flame to form SiO_2 and H_2O.

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$
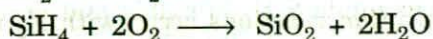
(*iii*) *Action of heat.* (*Decomposition*). When heated to 400°C it breaks down into its elements.

$$SiH_4 \xrightarrow{400°C} Si + 2H_2$$
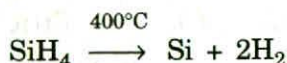
(*iv*) *Precipitation reactions.* SiH_4 gives a precipitate of copper silicide, Cu_2Si when passed in solution of copper salt like $CuSO_4$. Similarly silver metal is obtained from $AgNO_3$ solution.

$$2CuSO_4 + SiH_4 \longrightarrow \underset{\text{ppt.}}{Cu_2Si} + 2H_2SO_4$$

$$4AgNO_3 + SiH_4 \longrightarrow \underset{\text{ppt.}}{4Ag} + 4HNO_3 + Si$$

(*v*) *Action of alkalies.* SiH_4 reacts with alkalies to form silicate with the liberation of H_2

$$SiH_4 + 2\ NaOH + H_2O \longrightarrow Na_2SiO_3 + 4\ H_2 \uparrow$$

(*vi*) *Action of dry HCl (Replacement reaction).* Hydrogen of SiH_4 can be replaced by treating SiH_4 with dry HCl in presence of $AlCl_3$ (catalyst) at 100–125°C to get halogenosilanes and $SiCl_4$ in the end.

$$SiH_4 \underset{(-H_2)}{\overset{+\ HCl}{\longrightarrow}} SiH_3Cl \underset{(-H_2)}{\overset{+\ HCl}{\longrightarrow}} SiH_2Cl_2 \underset{(-H_2)}{\overset{+\ HCl}{\longrightarrow}} SiHCl \underset{(-H_2)}{\overset{+\ HCl}{\longrightarrow}} SiCl_4$$

(*vii*) *Action of alkali metals.* When SiH_4 is treated with potassium in glyme (1, 2-dimethoxy ethane) at –78°C, potassium derivative, $KSiH_3$ is obtained.
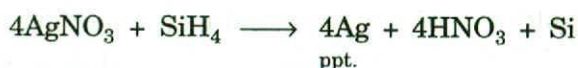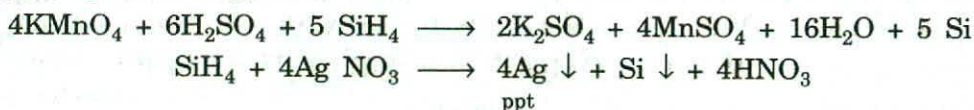
$$2\ SiH_4 + 2\ K \longrightarrow 2\ KSiH_3 + H_2$$

(*viii*) *Reducing properties.* SiH_4 is a strong reducing agent, since it reduces acidified $KMnO_4$ to $MnSO_4$, Hg (II) to Hg (I or 0), Fe (III) to Fe(II), Ag (I) to metallic Ag etc. Thus when SiH_4 is passed through silver salt solution like $AgNO_3$, precipitate of Ag is obtained.

$$4KMnO_4 + 6H_2SO_4 + 5\ SiH_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 16H_2O + 5\ Si$$

$$SiH_4 + 4Ag\ NO_3 \longrightarrow \underset{\text{ppt}}{4Ag \downarrow + Si \downarrow} + 4HNO_3$$

(*ix*) When a mixture of SiH_4 and N_2 is sparked, NH_3 is produced.

$$2SiH_4 + N_2 \longrightarrow 2Si + 2NH_3 + H_2$$
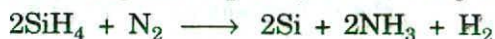
(*x*) *Reaction with X_2, $COCl_2$, $SnCl_4$ etc.* Si is precipitated.

$$SiH_4 + 2\ X_2 \longrightarrow \underset{\text{ppt.}}{4HX + Si}$$

$$SiH_4 + 2COCl_2 \longrightarrow 4HCl + Si + 2CO$$

$$SiH_4 + SnCl_4 \longrightarrow 4HCl + Si + Sn$$
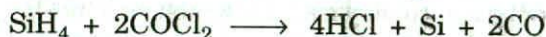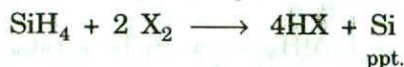
Excess of Cl_2 gives $SiCl_4$ directly

$$SiH_4 + 4Cl_2 \longrightarrow SiCl_4 + 4HCl$$

In some cases substitution reactions occur with X_2 molecules. For example :

$$SiH_4 + Cl_2 \longrightarrow SiH_3Cl + HCl$$

$$SiH_3Cl + Cl_2 \longrightarrow SiH_2Cl_2 + HCl$$

$$SiH_2Cl_2 + Cl_2 \longrightarrow SiHCl_3 + HCl$$

$$SiHCl_3 + Cl_2 \longrightarrow SiCl_4 + HCl$$
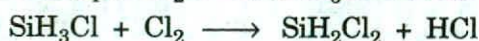
(xi) *Reaction with H_2O*. If the gas is bubbled through H_2O, then as it comes in contact with air, each bubble ignites giving vertex ring of finely divided SiO_2. SiO_2 may further form silicic acid, H_2SiO_3

$$SiH_4 + 2H_2O \longrightarrow SiO_2 + 4H_2$$
$$SiO_2 + H_2O \longrightarrow H_2SiO_3$$
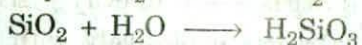
Uses. (i) SiH_4 is used as a source for the preparation of silicon of high purity which is produced by the pyrolysis and is used in transistors.

(ii) It is also used as a reducing agent.

2. Disilane, Si_2H_6

This compound is also called *silicoethane*.

Preparation. (i) When Mg_2Si is treated with dil HCl, a mixture of silicon hydrides is obtained. The fraction, obtained at $-100°C$ contains Si_2H_6 and SiH_4. Si_2H_6 is removed by refraction at $-100°C$. 400 mls. of Si_2H_6 are obtained from 100 gms of Mg_2Si.

(ii) It is best prepared by the reaction of Si_2Cl_6 with $Li[AlH_4]$ in ether solution

$$2Si_2Cl_6 + 3Li\,[AlH_4] \longrightarrow Si_2H_6 + 3LiCl + 3AlCl_3$$

(iii) It is also prepared by the action of conc. HCl acid on lithium silicide (Li_6Si_2)

$$Li_6Si_6 + 6HCl \longrightarrow 6LiCl + Si_2H_6$$

Properties. (i) It is a colourless liquid with more repulsive smell than SiH_4, b.pt = $-15°C$, m.pt = $-132°C$.

(ii) *Decomposition*. It is stable at ordinary temperature but decomposes into its elements at 200°C in absence of air.

$$Si_2H_6 \xrightarrow{\text{Heat (200°C)}} 2Si + 3H_2$$
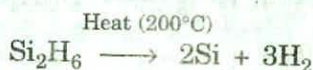
(iii) *Reactions with alkalies*. It reacts with alkalies to form silicates with the liberation of H_2.

$$Si_2H_6 + 4KOH + 2H_2O \longrightarrow 2K_2SiO_3 + 7H_2$$
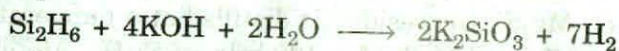
(iv) *Reaction with $CHCl_3$ and CCl_4*. $SiCl_4$ is formed in each case.

$$Si_2H_6 + 3CHCl_3 \longrightarrow 2\,SiCl_4 + 4H_2 + 3C + HCl$$
$$Si_2H_6 + 2CCl_4 \longrightarrow 2\,SiCl_4 + 3H_2 + 2C.$$
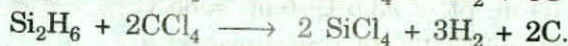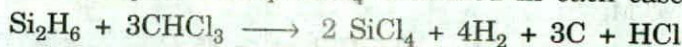
It explodes violently when mixed with CCl_4.

(v) *Solubility*. Si_2H_6 is soluble in CS_2, C_6H_6 and alcohol but sparingly soluble in H_2O with which it gives H_2SiO_3

$$Si_2H_6 + 6H_2O \longrightarrow 2H_2SiO_3 + 7H_2$$

(vi) *Action of air*. It inflames spontaneously in air and may even explode.

$$Si_2H_6 + 2O_2 \longrightarrow 2\,SiO_2 + 3H_2$$
$$2\,Si_2H_6 + 7O_2 \longrightarrow 4\,SiO_2 + 6H_2O$$

(vii) *Hydrolysis*. It is hydrolysed by H_2O containing even traces of alkali, giving H_2 and hydrated silica, $SiO_2.nH_2O$.

$$Si_2H_6 + (4 + 2n)H_2O \longrightarrow 2[SiO_2.nH_2O] + 7H_2 \uparrow$$

(viii) *Reducing properties.* It reduces $KMnO_4$, $K_2Cr_2O_7$, $FeCl_3$, $AgNO_3$, $HgCl_2$ etc.

$$6FeCl_3 + Si_2H_6 \longrightarrow 6FeCl_2 + 2Si + 6HCl$$
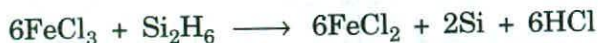
(ix) *Action of halogens.* It reacts explosively with halogens.

$$Si_2H_6 + 3X_2 \longrightarrow 2Si + 6HX$$

3. Trisilane, Si_3H_8

This compound is also called *silico-propane.*

Preparation. When Mg_2Si is treated with dil. HCl acid, a mixture of silanes is obtained. After removal of Si_2H_6 the residue is fractionated at $-60°C$ and refractionated at $-70°C$ to obtain Si_3H_8. 180 mls. of Si_3H_8 are obtained from 100 gms of Mg_2Si.

Properties. (i) It is a bright mobile colourless liquid with m.pt. $= -117°C$ and b.pt. $= 53°C$.

(ii) It inflames instantaneously in air with a loud detonation.

$$Si_3H_8 + 3O_2 \longrightarrow 3SiO_2 + 4H_2$$

(iii) *Decomposition.* Alkalies decompose it to Ni_2SiO_3 with the liberation of H_2.

$$Si_3H_8 + 6NaOH + 3H_2O \longrightarrow 3Na_2SiO_3 + 10H_2 \uparrow$$
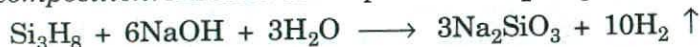
It is also decomposed by H_2O

$$Si_3H_8 + 6H_2O \longrightarrow 3SiO_2 + 10H_2 \uparrow$$

(iv) *Reaction with $CHCl_3$.* It also reacts with $CHCl_3$

$$Si_3H_8 + 4CHCl_3 \longrightarrow Si_3H_4Cl_4 + 4CH_2Cl_2$$

4. Tetrasilane, Si_4H_{10}

This compound is also called *silicobutane.*

Preparation. After removing the lower silanes from the mixture obtained by the action of dil. HCl on Mg_2Si, the residue is distilled at a temperature of $-25°C$ which is redistilled at $-35°C$ to get Si_4H_{10}. 100 mls. of Si_4H_{10} are obtained from 100 gms. of Mg_2Si.

Properties. (i) m .pt. $= 93.5°C$, b.pt. $= 85°C$

(ii) It is a colourless liquid.

(iii) It resembles Si_3H_8 in chemical properties.

5. Penta and hexa silanes (Si_5H_{12} and Si_6H_{14})

Si_5H_{12} and Si_6H_{14} can also be obtained from the reaction products obtained by treating Mg_2Si with dil. HCl. The liquid obtained after the removal of the series of silicon hydrides by fractional distillation, contains small quantities of Si_5H_{12} and Si_6H_{14}. 50 mls. and 35 mls. of Si_5H_{12} and Si_6H_{14} respectively are obtained from 100 gms. of Mg_2Si.

6. Silico ethylene, $(Si_2H_4)_n$

It is prepared by the action of HCl on calcium monosilicide, Ca_2Si_2

$$nCa_2Si_2 + 4nHCl \longrightarrow 2nCaCl_2 + (Si_2H_4)_n$$

7. Silico acetylene, $(Si_2H_2)_n$

It is prepared by the action of cal. silicide on HCl.

$$nCaSi_2 + 2nHCl \longrightarrow nCaCl_2 + (Si_2H_2)_n$$

Structure of Silanes

These compounds have the structures which are similar to those of the corresponding saturated hydrocarbons. The structure of these compounds are given below :

Monosilane (SiH_4)   Disilane (Si_2H_6)   Trisilane (Si_3H_8)   Tetrasilane (Si_4H_{10})

Pentasilane (Si_5H_{12})   Hexasilane (Si_6H_{14})
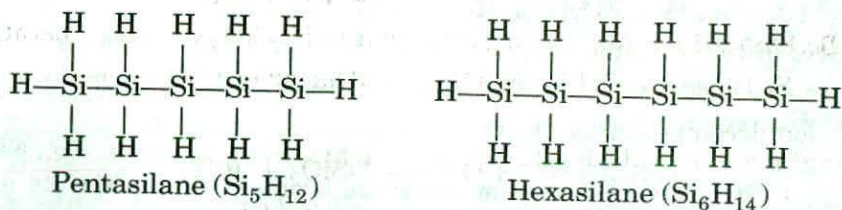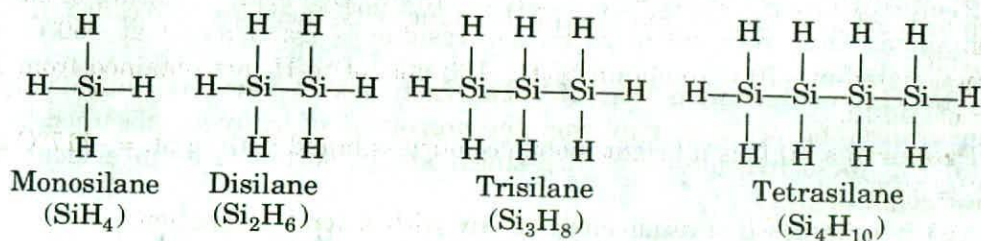
Differences between Alkanes and Silanes

1. In the hydrocarbon series, the number of C-atoms in a chain can apparently have any value but in case of silanes the maximum number of Si-atoms is seven which is found in hepta silane (Si_7H_{14}). This is because of the fact that relatively weak Si—Si bond makes unstable silanes linked with large number of Si-atoms.

2. SiH_4 gets hydrolysed while CH_4 does not. This is because maximum covalency of carbon is four which is attained in CH_4. Thus CH_4 is resistant to the attack of electron-donating molecules. The maximum covalency of silicon atom is six. In SiH_4 molecule only four covalent bonds are present. It is, therefore, possible for SiH_4 to accept lone pair of electrons from the donor group such as water.

C. Metallic (or Interstitial or Alloy-type) Hydrides

Many d-block elements (e.g. Ti, Pd, Zr, V, Nb etc.), lanthanides and actinides (e.g. La, Ce, Pr etc.) at elevated temperature absorb hydrogen into the holes or interstices existing between the atoms comprising the metallic lattice without changing the original crystal structure of the metal and thus give hydrides which are called metallic hydrides. Examples of such hydrides are : $TiH_{1.73}$, $VH_{0.6}$, $ZrH_{1.92}$, $PdH_{0.6}$, $TaB_{0.76}$, $CeH_{2.69}$, $PrH_{2.7}$ etc.

Thus these hydrides are interstitial combinations of hydrogen and the metals and it is for this reason that these are called interstitial hydrides.

The densities of these hydrides are usually lower than those of the parent metal. This fact suggests that these hydrides are interstitial in nature and the metal lattices expand. On the other hand, their electronegativity values are fairly close to those of IA (alkali metals) and IIA (alkaline earth metals) groups are they have fairly high heats of formation. These facts indicate that these hydrides may be regarded as a transition between the salt-like and interstitial, e.g. although CuH, NiH_2, CoH_2, FeH_2, CrH_3 have stoichiometric formulae, these do not resemble salt-like hydrides. Since these hydrides possess metallic properties such as hardness, lusture and electrical conductivity, these are also called metallic hydrides.

The chemical composition of these hydrides is variable, since varying temperature and pressure may vary the proportion of hydrogen absorbed by the metal, i.e. these hydrides have non-stoichiometric formulae as in evident from those given below :

$$TiH_{1.73}, \ PdH_{0.6}, \ ZrH_{1.92}, \ VH_{0.6}, \ NbH_{0.86}, \ TaH_{0.76},$$
$$LaH_{2.76}, \ CeH_{2.69}, \ PrH_{2.7}, \ ThH_{3.07}.$$
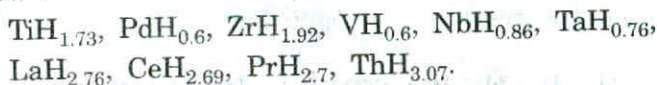
In view of the variable composition of these hydrides, it has been suggested that these are not chemical compounds but are regarded as metals containing absorbed hydrogen.

Certain metallic hydrides do possess stoichiometric formulae, e.g.. NiH_2, CoH_2, FeH_2 and CrH_3. When phenol magnesium bromide, $C_6H_5 \ Mg \ Br$ solution is mixed with metal (II) chloride and H_2 is passed through, black precipitates of NiH_2, CoH_2 and FeH_2 are formed.

$$MCl_2 + 2C_6H_5MgBr \longrightarrow M(C_6H_6)_2 + MgBr_2 + MgCl_2$$
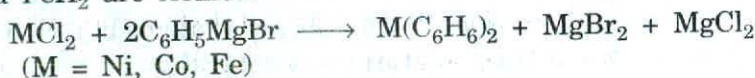$$(M = Ni, \ Co, \ Fe)$$

$$M(C_6H_5)_2 + 2H_2 \longrightarrow 2C_6H_6 + MH_2$$

A number of metals possess the remarkable property of combining relatively larger quantities of hydrogen either at room temperature or at high temperatures, e.g. Fe, Cu, Ni, Pt etc. absorb increasing quantities of hydrogen at increasing temperature. Certain metals such as Rh, Ta etc. absorb lesser quantities at high temperature.

The absorption of hydrogen by certain metals such as Cu, Ag, Cr, Mo, U, Fe, Co, Ni and Pt is endothermic, while that by other metals such as Ti, Th, Zr, V, Nb, Ta and Pd is exothermic. Pd, after absorbing hydrogen, becomes very reactive and has strong reducing properties. This suggests that hydrogen is held in metal at its surface in the atomic state. The difference in temperatures at which various metals absorb hydrogen is presumably due to the difference in the energy of activation of the reaction $H_2 \rightleftarrows 2H$, occurring at the metallic surface.

The absorbed hydrogen can be expelled from the interstices simply by heating the hydrides and by increasing the gas pressure. Thus these hydrides are good reducing agents.

D. Complex Hydrides

Some of the hydrides contain borohydride (BH_4^-) and aluminium hydride (AlH_4^-) ions. These hydrides are called complex hydrides. Lithium borohydride ($LiBH_4$), sodium borohydride ($NaBH_4$), beryllium borohydride [$Be(BH_4)_2$], aluminium borohydride [$Al(BH_4)_3$] and lithium aluminium hydride ($LiAlH_4$) are the most important examples of complex hydrides. In these hydrides hydrogen atoms are covalently bonded to the trivalent metal atom.

Such hydrides can be obtained by the action of an excess of alkali metal hydride on the appropriate trihalide. For example :

$$4NaH + BF_3 \xrightarrow{\text{Ether}} NaBH_4 + 3NaF$$

$$4LiH + AlCl_3 \xrightarrow{\text{Ether}} LiAlH_4 + 3LiCl$$
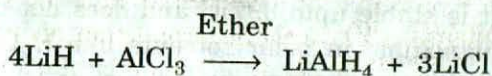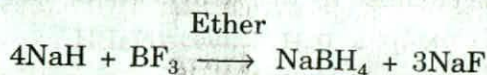
Although these hydrides have no free H^- ions, they show many reactions of ionic hydrides, but the reactions are smoother.

Some Complex Hydrides

1. **Lithium Borohydride, $LiBH_4$.** *Preparation.* It is prepared :

(*i*) By the action of $NaBH_4$ on LiCl.

$$LiCl + NaBH_4 \longrightarrow LiBH_4 + NaCl.$$

(*ii*) By the action of B_2H_4 on lithium ethyl (LiC_2H_5) or LiH suspended in ether.

$$2B_2H_6 + 2LiC_2B_5 \longrightarrow 3LiBH_4 + B(C_2H_5)_3$$

$$B_2H_6 + 2LiH \longrightarrow 2LiBH_4$$
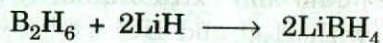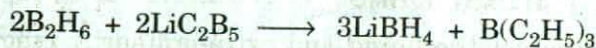
(*iii*) By the action of $Al(CH_4)_3$ on LiC_2H_5 in benzene.

$$Al(BH_4)_3 + 3LiC_2H_5 \longrightarrow 3LiBH_4 + Al(C_2H_5)_3.$$

Properties. (*i*) It is a white solid. In the absence of air it melts (decomposes) at 275°C, evolving H_2. It is soluble in polar solvents like H_2O.

(*ii*) It reacts with H_2O even in cold, with CH_2OH down to 100°C and with HCl down to –80°C. In all these reactions H_2 is evolved.

$$LiBH_4 + 2H_2O \longrightarrow LiBO_2 + 4H_2 \uparrow$$

$$LiBH_4 + 4CH_3OH \longrightarrow LiOCH_3 + B(OCH_3)_3 + 4H_2 \uparrow$$

$$2LiBH_4 + 2HCl \longrightarrow 2LiCl + B_2H_6 + 2H_2 \uparrow$$
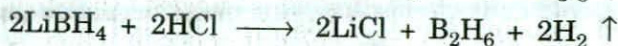
(*iii*) It reacts with I_2 at 125°C to form BI_3.

(*iv*) It can reduce $FeCl_3$ into free Fe metal and non-metallic halides (*e.g.* $SiCl_4$) to their hydrides (*e.g.* SiH_4)

$$2FeCl_3 + 6LiBH_4 \longrightarrow 6LiCl + 3H_2 + 2B_2H_6 + 2Fe.$$

Thus $LiBH_4$ is a powerful reducing agent.

Uses. Due to the liberation of H_2 gas in some reactions mentioned above, it is used as a reducing agent in organic as well as in inorganic chemistry.

2. Sodium Borohydride, NaBH₄

Preparation (*i*) It is obtained by treating NaH with methyl borate, $B(OCH_3)_3$ in tetrahydrofuran (THF) solvent.

$$4NaH + 4B(OCH_3)_3 \xrightarrow{\text{THF solvent}} NaBH_4 + 3NaB\ (OCH_3)_4$$
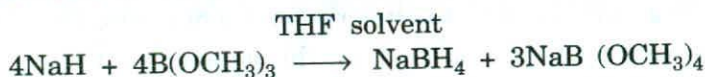
(*ii*) It can also be obtained by the action of B_2H_6 on NaH suspended in ether.

$$2NaH + B_2H_6 \longrightarrow 2NaBH_4$$
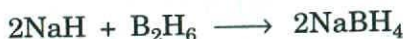
Properties. (*i*) It is stable upto 397°C and does not decompose water in the cold. Like $LiBH_4$ it is soluble in polar solvents like H_2O.

(*ii*) It reacts with HCl and BF_3 to produce B_2H_6

$$2NaBH_4 + 2HCl \longrightarrow 2NaCl + 2H_2 + B_2H_6$$

$$3NaBH_4 + BF_3 \xrightarrow{\text{Diglyme}} 2NaF + 2B_2H_6.$$
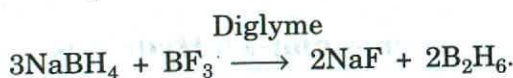
3. Aluminium borohydride, Al(BH₄)₃

It is prepared by the following reactions :

$$Al_2(CH_3)_6 + 4B_2H_6 \longrightarrow 2B(CH_3)_3 + 2Al(BH_4)_3$$

$$6LiBH_4 + Al_2Cl_6 \xrightarrow{\text{warm}} 6LiCl + 2Al(BH_4)_3$$
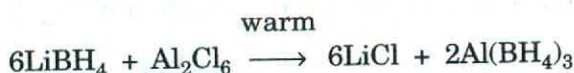
It is a colourless volatile liquid and extra-ordinarily reactive. It dissolves in non-polar solvents. It reacts with H_2O and HCl.

$$Al(BH_4)_3 + 12H_2O \longrightarrow 3H_3BO_3 + Al(OH)_3 + 12H_2$$

$$2Al(BH_4)_3 + 6HCl \xrightarrow{-80°C} Al_2Cl_6 + 2B_2H_6 + 3H_2$$
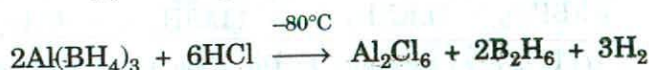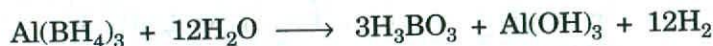
$Al(BH_4)_3$ also reacts with metallic halides and forms metallic borohydrides, if these are stable or otherwise H-atoms of $Al(BH_4)_3$ are substituted by halogens.

$$nAl(BH_4)_3 + 3M^{n+}X_n \longrightarrow 3M^{n+}(BH_4)_n + nAlX_3$$

$$Al(BH_4)_3 + M^{n+}X_n \longrightarrow Al(BX_4)_3 + M^{n+}H_n$$

If is a good reducing agent. If has covalent character which makes it soluble in non-polar solvents. If can also form addition compounds with amines.

Like B_2H_6 it also adjusts with three-centred bond in the Al—H—B group.

Structure of [BH₄]⁻ ion. The borohydride ion (BH^-_4) has tetrahedral shape which results from sp^3 sybridisation of $\bar{B}$ ($\bar{B} = 2s^2sp^2$). For details see chapter 8.

4. Lithium Aluminium Hydride, Li[AlH₄]

This compound was discovered by Finholt, Bond and Schlesinger 1947.

Preparation. It is best prepared by the action of LiH on an ether solution of $AlCl_3$

$$4LiH + AlCl_3 \xrightarrow{\text{Ether}} \underset{\text{(soluble)}}{LiAlH_4} + \underset{\text{(ppt)}}{3LiCl \downarrow}$$
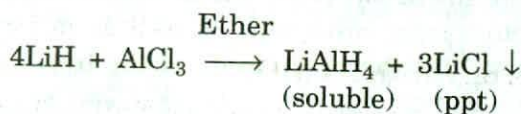
$LiAlH_4$ remains in solution in ether while LiCl is insoluble in it. The precipitated LiCl is filtered off, the ether is evaporated and $LiAlH_4$ remains in solution. If this solution is allowed to stand before filtration and then evaporated, $LiAlH_4$ of 99% purity is obtained.

Properties. (*i*) It is a non-volatile colourless crystalline solid which is stable to air in the cold. It is soluble in ether and other organic solvents.

(*ii*) If is decomposed by H_2O, liberating H_2 gas

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2 \uparrow$$
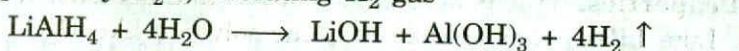
(*iii*) When heated, it gets decomposed according to the equation :

$$2LiAlH_4 \xrightarrow{\Delta} 2LiH + 2Al + 3H_2 \uparrow$$

(*iv*) Its etheral solution reduces (*a*) $SiCl_4$ to SiH_4

$$LiAlH_4 + SiCl_4 \longrightarrow LiCl + AlCl_3 + SiH_4$$

(*b*) $Zn(CH_3)_2$ to ZnH_2
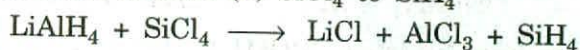
$$LiAlH_4 + Zn(CH_3)_2 \longrightarrow ZnH_2 + Li[AlH_2(CH_3)_2]$$

(*c*) aldehydes to alcohols

$$4RCHO + LiAlH_4 \longrightarrow (R—CH_2O)_4LiAl \xrightarrow{+ 4H_2O} 4R—CH_2OH + LiOH + Al(OH)_3$$
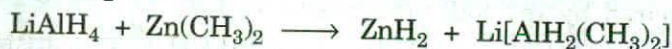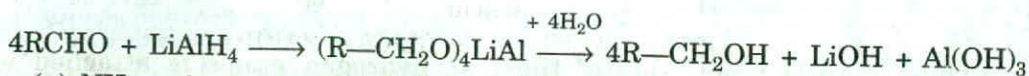
(*v*) NH_3, primary amines and secondary amines react with it to from H_2.

$$LiAlH_4 + 4NH_3 \longrightarrow LiAl(NH_2)_4 + 4H_3$$

$$LiAlH_4 + 4RNH_2 \longrightarrow LiAl(RNH)_4 + 4H_2$$

$$LiAlH_4 + 4R_2NH \longrightarrow LiAl(R_2N)_4 + 4H_2$$

(*vi*) It also reacts with diborane (B_2H_6) to form lithium borohydride, $Li[BH_4]$ and aluminum borobydride, $Al[BH_4]_3$.

$$LiAlH_4 + 2B_2H_6 \longrightarrow Li[BH_4] + Al[BH_4]_3$$
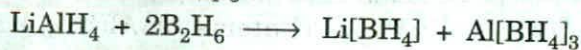
(*vii*) BCl_3 reacts to give B_2H_6.

$$3LiAlH_4 + 4BCl_3 \longrightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$$

(*viii*) It converts the chlorides of Si, Sn, B, Al etc. into their hydrides.

$$LiAlH_4 + SiCl_4 \xrightarrow{\text{Ether}} SiH_4 + LiCl + AlCl_3$$

$$LiAlH_4 + SnCl_4 \xrightarrow{\text{Ether}} SnH_4 + LiCl + AlCl_3$$

$$LiAlH_4 + 4BCl_3 \xrightarrow{\text{Ether}} 2B_2H_6 + 3LiCl + 3AlCl_3$$

$$LiAlH_4 + AlCl_3 \xrightarrow{\text{Ether}} 4AlH_3 + 3LiCl.$$
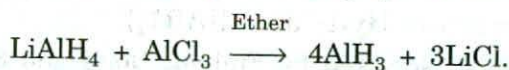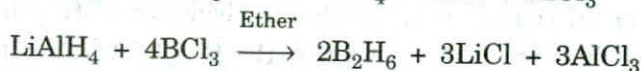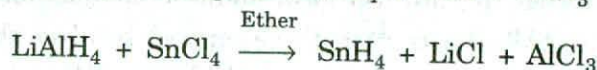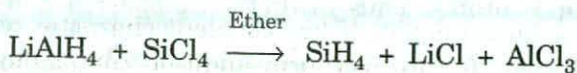
Uses. (*i*) It is used for reducing almost all the compounds containing a carbonyl group, $> C = O$ like ketones, carboxylic acids and their derivatives to alcohols (*See* above).

(*ii*) It is also used for the preparation of the hydrides of Si, B, Al etc from their chlorides (*See* above).

Structure. It is an ionic complex hydride containing the complex anion *viz* alumino hydride anion, $[AlH_4]^-$ ion which is ionically attached with Li^+ cation. $[AlH_4]^-$ ion is formed by the coordination of the hydride ion (H^-) (Lewis base) obtained from LiH molecule to AlH_3 molecule (Lewis acid).

$$LiH \longrightarrow Li^+ + H^-$$

$$
\begin{array}{c}
H \\
| \\
H-Al \\
| \\
H
\end{array}
+ : \quad H^- \longrightarrow
\left[
\begin{array}{c}
H \\
| \\
H? Al \longleftarrow H \\
| \\
H
\end{array}
\right]^-
$$

  Lewis acid   Lewis base   Complex anion
  (acceptor)   (donor)

$$
Li^+ +
\left[
\begin{array}{c}
H \\
| \\
H-Al \longleftarrow H \\
| \\
H
\end{array}
\right]^-
\longrightarrow
Li^+
\left[
\begin{array}{c}
H \\
| \\
H-Al \longleftarrow H \\
| \\
H
\end{array}
\right]^-
$$
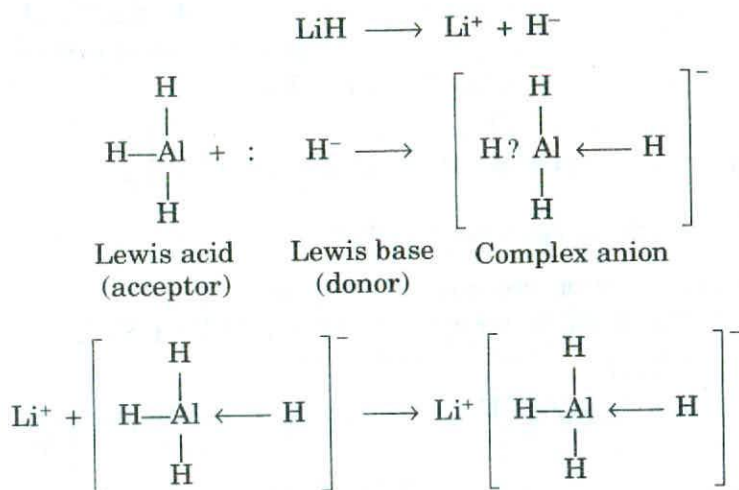
Thus in $[AlH_4]^-$ ion, one of the four hydrogen atoms is attached with Al-atom by a coordinate bond while the remaining three H-atoms are covalently attached.

Shape of $[AlH_4]^-$ ion. Due to the presence of one unit of negative charge on $[AlH_4]^-$ ion, Al atom (central atom) can be regarded as having 4 electrons instead of 3 in its valence-shell $[Al(3s^2p^1) + e^- \longrightarrow Al(3s^2p^2)]$. The Lewis structure of this ion,

$$
\left[
\begin{array}{c}
H \\
| \\
H-Al-H \\
| \\
H
\end{array}
\right]^-
$$

shows that Al atom uses all its 4 electrons in forming four

σ-bonds with four H atoms. Thus in this ion $\sigma\text{-}bps = 4$ and $lps = 0$ and hence $\sigma\text{-}bps + lps = 4$. Consequently Al atom is supposed to be sp^3 hybridised in the given complex ion as shown in Fig. 16.1.

Fig. 16.1. sp^3 hybridisation undergone by Al atom in its excited state.
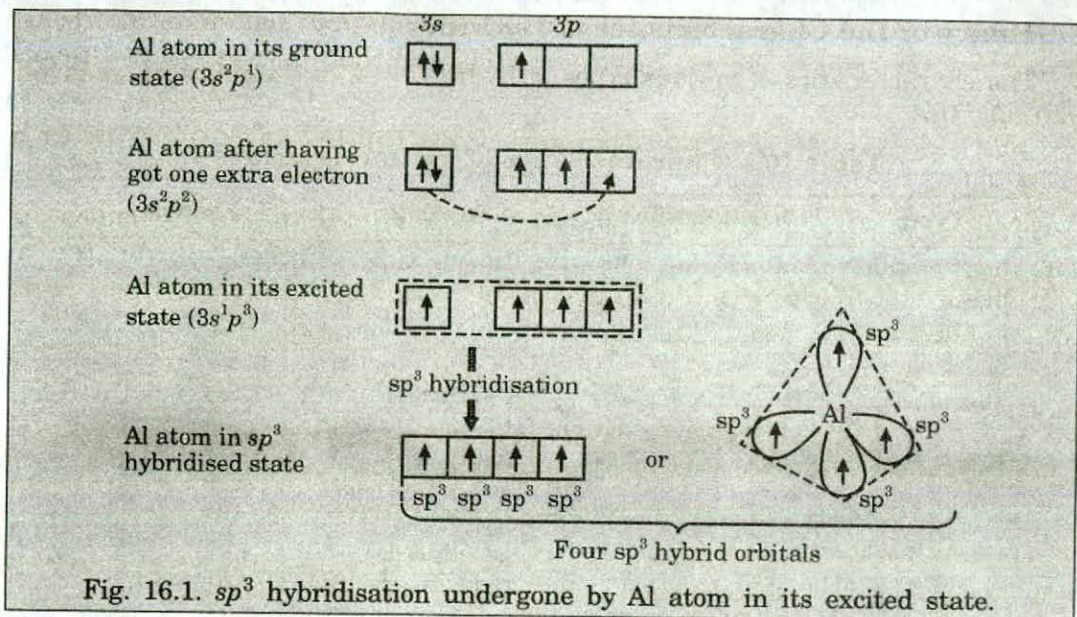
Each of the four sp^3 hybrid orbitals on Al atom is singly filled. Each of these hybrid orbitals overlaps along the axis with the half-filled $1s$ orbital on H-atom and forms four Al–H σ-bonds and consequently $[AlH_4]^-$ ion has a tetrahedral shape (See Fig. 16.2.)

Fig. 16.2. Pictorial representation of the formation of four σ-bonds in $[AlH_4]^-$ ion which has tetrahedral shape.
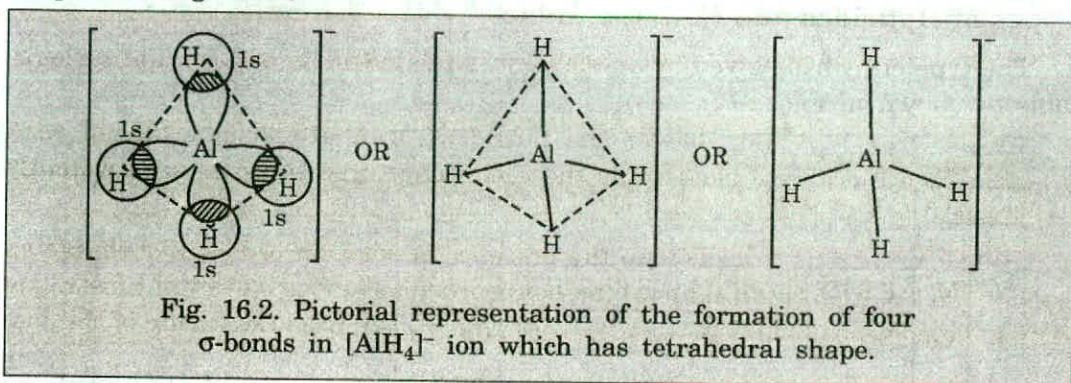
E. Borderline Hydrides

There are a number of hydrides which do not fall into any of the above four types. Examples of such hydrides are BeH_2, MgH_2, CuH, ZnH_2, CdH_2, HgH_2 etc. Such hydrides are not easily formed from the elements but are generally prepared by special methods. Not all of these hydrides have been obtained in a crystalline state suitable for X-ray examination. These hydrides are volatile but not ionic and relatively much less stable than the ionic hydrides. BeH_2 and MgH_2 have properties of both ionic and covalent hydrides while CuH, ZnH_2, CdH_2, HgH_2 etc. have the properties which are intermediate between those of covalent and metallic hydrides. In none of these hydrides the type of bonding has been established.

Summary of the Characteristics of Hydrides

The characteristics of various types of hydrides can be summarised as given in Table 16.1.

Table 16.1. Characteristics of various hydrides

Type	Characteristics	Bonding	Examples
1. Ionic or salt-like	Salt-like, resemble chlorides	Largely ionic	LiH, NaH, CaH_2
2. Covalent or molecular			
(i) Mononuclear	Gases or volatile liquids, non-conductors	Covalent	CH_4, H_2S, HF, H_2O
(ii) Polynuclear	Solids, non-conductors	Covalent, metal atoms ore linked together by hydrogen bridges.	$(AlH_3)_n$, $(InH_3)_n$
3. Metallic or interstitial	Possess parental properties such as brittleness, lustrue, electrical conductivity etc.	Partly ionic with residual metallic bonds.	$TiH_{1.73}$, $VH_{0.6}$, $LaH_{2.76}$

Types of Hydrides and Periodic Table

The type of hydride given by an element is related to its position the periodic table as shown in Fig. 16.3.

Fig.16.3. Relation between the type of hydrides given by an element and its position in the periodic table.

Question with Answers

Q.1 What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions ?

Ans : Electron-deficient hydrides do not have sufficient number of electrons to form normal covalent bonds. Therefore, to make up this deficiency, they generally exist in polymeric froms such as B_2H_6, B_4H_{10}, $(AlH_3)_n$, etc.

Further to make up this deficiency of electrons, they react with many metals, non-metals and their compounds. Hence, electron-deficient hydrides are very reactive as shown below :

$$B_2H_6 \ (g) + 3O_2 \ (g) \longrightarrow B_2O_3 \ (g) + 3H_2O \ (g)$$

$$2NaH \ (s) + B_2H_6 \ (g) \xrightarrow{\text{Diethyl ether}} 2Na^+ \ [BH_4]^- \ (s)$$
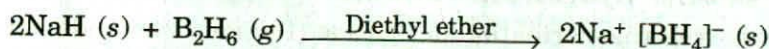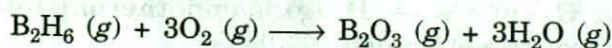
$$\text{Sod. borohydride}$$

Being electron-deficient compounds, they act as Lewis acids and thus form complexes with Lewis bases. For Example.

$$
\begin{array}{cccl}
B_2H_6 & + & 2NMe_3 & \longrightarrow \quad [2H_3B \overset{\cdot\cdot}{\leftarrow} NMe_3] \\
\text{Diborane} & & \text{Trimethylamine} & \qquad \text{Complex} \\
B_2H_6 & + & 2 : CO & \longrightarrow \quad [2H_3B \leftarrow CO] \\
& & \text{Carbon monoxide} & \qquad \text{Complex}
\end{array}
$$
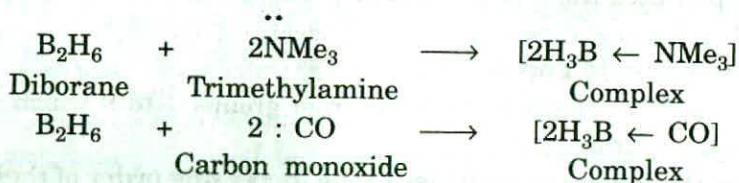
Q.2 Explain the following :

(i) Boiling points of hydrides of N, O and F are much higher than those of their subsequent groups elements.

Ans : The hydrides of N, O and F are NH_3, H_2O and HF respectively. On the basis of masses of NH_3, H_2O and HF, their boiling points are expected to be lower than the hydrides of the subsequent group members (*i.e.* PH_3, H_2S and HCl). However, due to high electronegativity of N, O and F, their hydrides undergo extensive intermolecular H-bonding. As a result, the boiling points of NH_3, H_2O and HF are much higher than the hydrides of their subseqent group members (*i.e.* PH_3, H_2S and HCl)

(ii) Phosphorus atom can form PH_3 but not PH_5.

Ans : Although P shows oxidation state of +3 and +5, it cannot form PH_5. Due to high Δ_{H-H} (435.88KJ mol^{-1}) and slightly negative $\Delta_{eg}H$ (−73KJ mol^{-1}) dihydrogen acts only as a weak oxidising agent. Therefore, it can oxidise P to + 3 oxidation state but not to its highlest oxidation state of +5. Thus, P forms PH_3 but not PH_5.

(iii) H_2 produced by the reaction between saline hydride and H_2O cannot be extingnished by CO_2.

Ans : Saline hydrides (such as NaH, CaH_2, etc.) react with water voilently to form the corresponding metal hydroxides with the evolution of dihydrogen.

$$NaH \ (s) + H_2O \ (l) \longrightarrow NaOH \ (aq) + H_2 \ (g)$$

$$CaH_2 \ (s) + 2 \ H_2O \ (l) \longrightarrow Ca \ (OH)_2 \ (aq) + 2 \ H_2 \ (g)$$
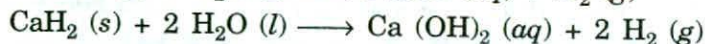
These reactions are so exothermic that the eveled H_2 catches fire. The fire so produced cannot be exitingished by CO_2 because it gets reduced by the hot metal hydride to form sodium formate.

$$NaH + CO_2 \longrightarrow HCOONa$$

However, sand is useful since it is a highly stable solid.

(iv) Beryllium forms a covalent hydride while calcium forms an ionic hybride.

Ans : Because of higher electronegativity (E.N. = 1.5), Be forms covalent hydride while due to lower electronegativity (E.N. = 1.0) Ca forms ionic hydride.

(v) The process $1/2$ H_2 (g) + $e^- \rightarrow$ H^- (g) is endothermic (ΔH = +151KJ mol^{-1}), yet salt-like hydrides are known.

Ans : It is true that formation of hydride (H^-) ion is an endothermic process, yet alkali and alkaline earth metals form salt-like hydrides. This is due to the reason that high lattice energy raleased (energy releasd during the formation of solid metal hydrides from their corresponding gaseous ions, *i.e.*, M^+ and H^-) more than compensates the energy needed for the formation of H^- ions from H_2 gas.

Q.3 What is hydride gap ?

Ans : The region of the periodic table from groups 7 to 9 which donot form hydrides is called hydride gap.

Q.4 Arrange the following hydrides in the increasing order of their property mentioned in braket.

(*i*) LiH, NaH, CsH (Inoic character).

(*ii*) NaH, MgH_2, H_2O (reducing property).

(*iii*) CaH_2, BeH_2, TiH_2 (Electrical conductance).

Ans : (*i*) Electronegative decreases down the group from Li to Cs, therefore, the ionic character of their hydrides increases in the same order, *i.e.*, *LiH < NaH < CsH*.

(*ii*) Ionic hydrides are powerful reducing agents. Both MgH_2 and H_2O are covalent hydrides but the bond dissociation energy of H_2O is much higher than that of MgH_2. Therefore, the reducing character increases in the order : $H_2O <$ MgH_2 < NaH.

(*iii*) BeH_2 is a covalent hydride, therefore it does not conduct electricity at all. CaH_2 conducts electricity in the fused state while TiH_2 conducts electricity at room temperature. Thus, the order of increasing electrical conductance is : $BeH_2 < CaH_2 < TiH_2$.

Q.5 (*i*) What is the nature of hydrides formed by the elements with atomic numbers : 15, 19, 23 and 44. (*ii*) Give the chemical equations to show their reaction with H_2O.

Ans : (i) Nature of hydrides. (*a*) Element with Z = 15 is a non-metal (*i.e.* P) and hence forms covalent hydride (*i.e.* PH_3).

(*b*) Element with Z = 19 is an alkali metal (*i.e.* K) nad hence forms saline or ionic hydride (*i.e.* K^+ H^-).

(c) Element with atomic number $Z = 23$ is a transition metal (i.e V) of group 3 and hence forms a metallic or interstitial hydride (i.e. $VH_{0.56}$).

(d) Element with $Z = 44$ is a transition metal (i.e. Ru) of group 8 and hence does not form any hydride (hydride gap).

(ii) **Reaction with water.** Only ionic hydrides react with water evoling H_2 gas. Thus :

$$2\ KH\ (s) + 2\ H_2O\ (s) \longrightarrow 2\ KOH\ (aq) + 2\ H_2\ (q)$$
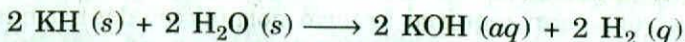
Q.6 Classify the following hybrides : BeH_2, AsH_3, B_2H_6, LaH_3 and $LiAlH_4$.

Ans : BeH_2 - polymeric, AsH_3 - covalent, B_2H_6 - electron deficient or Lewis acid, LaH_3 - metallic or interstitial, $LiAlH_4$ - complex.

Q.7 How will you explain that metallic hydrides can be used to store hydrogen.

Ans : In metallic hydrides, hydrogen is adsorbed as H-atoms. Due to the inclusion of H-atoms, the metal lattic expands and thus becomes less stable. Therefore, when the metallic hydride is heated, it decomposes to form hydrogen and very finely divided metal.

The hydrogen thus evolved can be used as a fuel. Thus, transition metals or their alloys can be used to store and transport hydrogen to be used as fuel. This is called hydrogen economy.

Q.8 How can saline hydrides remove traces of water from organic compounds ?

Ans : Saline hydrides (i.e, NaH, CaH_2, etc.) react with water forming their corresponding metal hydroxides with the liberation of H_2 gas. Thus, traces of water present in organic solvents can be easily removed by distiliing them over saline hydrides when H_2 escapes into the atmosphere, metal hydroxide is left in the flask while dry organic solvent distils over.

Alternatively, organic compounds containing traces of water can be dried by placing them in a desiccator containing saline hydrides at the bottom for a few hours or preferably overnight.

Q.9 Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as Lewis acid or base ? Justify your answer.

Ans : Carbon hydrides of the type (C_nH_{2n+2}) are electron-precise hydrides. In other words, they have exact number of electrons required to from covalent bonds. Therefore, they do not have any tendency to either gain or lose electrons and hence they neither act as Lewis acids nor Lewis bases.

Q.10 Give an example each of an ionic hydride and a covalent hydride.

Ans : Ionic : NaH or CaH_2.

Covalent : H_2O, B_2H_6, CH_4, etc.

Q.11 What do you understand by (i) electron-deficient hydrides (ii) electron-precise hydrides (iii) electron-rich hydrides. Give suitable examples.

Ans : (i) Hydrides of group 13 (i.e., BH_3, AlH_3, etc.) do not have sufficient number of electrons to form normal covalent bonds and hence are called electron-

deficient hydrides. To make up this deficiency, they generally exist in polymeric forms such as B_2H_6, B_4H_{10}, $(AlH_3)_n$, etc.

(*ii*) Hydrides of group 14 (*i.e.*, CH_4, SiH_4, GeH_4, SnH_4, PbH_4) have exact number of electrons to form covalent bonds and hence are called electron-precise hydrides. All these hydrides have tetrahedral shapes.

(*iii*)Hydrides of group 15, 16 and 17 (*i.e.*, NH_3, PH_3, H_2O, H_2S, HF, HCl, etc.) have more electrons than required to form normal covalent bonds and hence are called electron-rich hydrides. The excess electrons in these hydrides are present as lone pairs of electrons.

Q.12 What do you understand by the term "non-stoichiometric hydrides" ? Do you expect this type of the hydrides to be formed by alkali metals ? Justify your answer.

Ans : Hydrides which are deficient in hydogen and in which the ratio of the metal to hydrogen is fractional are called non-stoichimetric hydrides. Furthermore, even this fractional ratio is not fixed but varies with the temperature and the pressure. This type of hydrides are formed by *d*-and *f*-block elements. In these hydrides, the hydrogen atoms occupy holes in the metal lattice. Usually some holes always remain unoccupied and hence these metals form non-stoichiometric hydrides.

Since alkali metals are highly reducing, they transfer their lone electron to the H-atom, thereby forming H^- ions. In other words, alkali metal hydrides are ionic in which H^- ions occupy holes in the lattice. Since a hydride ion is formed by complete transfer of an electron, the ratio of metal to hydrogen is always fixed and hence alkali metals form only stoichimetric hydrides. In other words, alkali metals do not form non-stoichometric hydrides.

Q.13 (*a*) What is hydrolith ? How is it prepared ?

(*b*) Write the structures of two complex metal hydrides which are used as reducing agents.

(*c*) What type of elements form interstitial hydrides.

(*d*) Write two uses of interstitial hydrides ?

Ans : (*a*) Hydrolith is calcium hydride, CaH_2. It is prepared as :

$$Ca + H_2 \xrightarrow{\Delta} CaH_2 \text{ (hydrolith)}$$
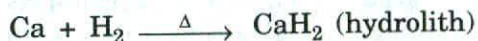
(*b*) $LiAlH_4$ and $NaBH_4$.

(*c*) *d*-and *f*-block elements.

(*d*) Interestitial hydrides are used : (*i*) in storing H_2 and (*ii*) as catalysts for hydrogenation reactions.

University Questions

1. What are hydrides? How are they classified? Compare the properties of hydrides of B, Si and Be. *(Delhi 86)*

2. What are hydrides ? Give their preparation, properties and uses. *(Delhi 84; Delhi Hons. 86; Raj. 83)*

3. What are covalent hydrides ? How do their stability, basicity and acid strength vary in a group? *(Raj. 85)*

4. What are silicon hydrides? How are they prepared? Describe their properties and applications. *(Meerut B.Sc. 84)*

5. Discuss the structure of borohydride ion. *(Delhi Hons. 80)*

6. (a) What are polymeric hydrides ? Discuss the preparation and structure of beryllium hydride.

   (b) What are interstial hydrides ? How do these differ from other hydrides? *(Himachal Pradesh 2000)*

7. What are hydrides ? How are they classified ? Give important methods to obtain boron and silicon hydrides. *(Lucknow 2000)*

8. Write a short note on $LiAlH_4$. *(Lucknow 2001)*

9. Hydrides of alkali metals are basic in nature but those of halogens are acidic. Explain why ? *(C.S.J.M. Kanpur 2007)*

10. Give preparation, properties and uses of $LiAlH_4$. *(Meerut 2008)*

11. Complete and balance the equation :

$$2Li + AlH_4 \xrightarrow{\Delta} \ldots + 2Al + \ldots$$

(Meerut 2009)

Heavy Water (D₂O)

Occurence of D_2O

(*i*) Washburn and Urey showed that the residual water obtained at the end of prolonged electrolysis of a large volume of ordinary water containing some alkali contains heavy water which is deuterium oxide.

(*ii*) It is also found in minute quantities on the leaves of banyan trees and in rain-water.

(*iii*) It is also found in the last remains obtained by the melting of snow by sun on the hills as in Himalayans.

Preparation of D_2O

Heavy water is prepared by the following methods :

1. By multi-stage electrolysis of ordinary water. (*Taylor, Eyring and Frost process*) This method was described by Taylor, Erying and Frost in 1933. Heavy water is largely prepared by the multi-stage (*i.e.* continuous and prolonged) electrolysis of ordinary water containing calculated quantity of NaOH.

Electrolytic cell and procedure. The cell used in this process is shown in Fig. 17.1 and has been designed by Brown, Degget and Urey. It consists of a steel cell (45 cm long and 10 cm in diameter). The cell itself acts as a cathode while
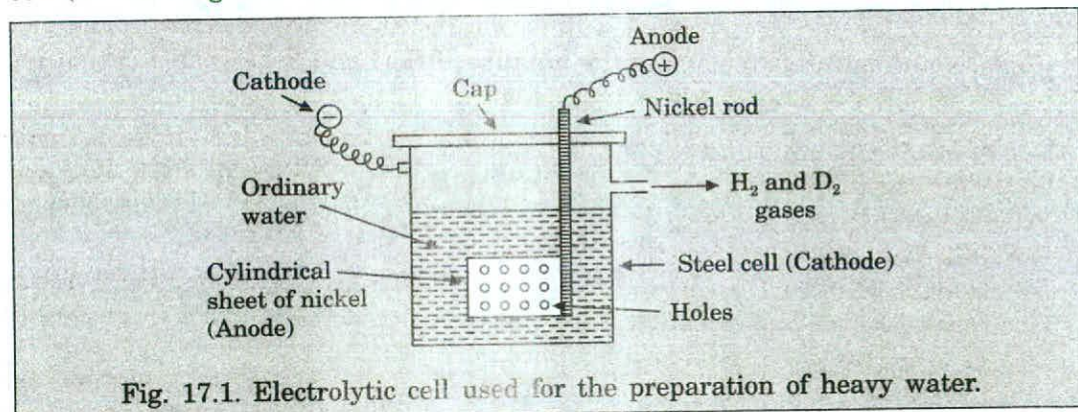
Fig. 17.1. Electrolytic cell used for the preparation of heavy water.

a cylindrical sheet of nickel having a number of holes punched into it (*i.e.* a perforated cylindrical sheet of nickel) serves as the anode.

In actual practice a large number of such cells is used so that the electrolysis of ordinary water may be done in several stages *i.e. the electrolysis of water is continuous and prolonged.* Thus by the continuous and prolonged electrolysis, the

concentration of heavy water goes on increasing gradually in the residual water left behind at the end of each stage of electrolysis. Usually the process of electrolysis is complete in seven stages as discussed below :

First stage : Thirty electrolytic cells, joined together in series, are used in this stage. Each cell is charged with 77 litres of a 8% solution of NaOH in ordinary water, *i.e.* 2310 litres of ordinary water are electrolysed in this stage. A current of 110 volts is used and the electrolysis is carried out for about 72 hours. The gases liberated during the electrolysis at the end of this stage contain protium (H_2) and O_2 which are discarded. At the end of 72 hours the total volume of the charge reduces to about $\frac{1}{6}$ th of its original volume. The alkali present is neutralised by passing CO_2 in it.

Second stage : The residual water obtained from the first stage is again electrolysed using six cells. The gases evolved during electrolysis in this stage are separately burnt in a burner and the mixture of H_2O and D_2O formed by the burning of gases is sent back to the cells being used in the first stage. The process of electrolysis in this stage is continued till the residual water contains about 0.5% of D_2O.

Third stage : The residual water obtained from the second stage is further electrolysed, till the residual water contains about 2.5% of heavy water. The gases evolved in this stage are separately burnt, as usual, in a burner and the mixture of H_2O and D_2O formed is sent back to the cell being used in the second stage. The residual water obtained at the end of this stage consists of 2.5% of D_2O.

Fourth stage : The residual water obtained from the third stage is further electrolysed so that the residual water contains 8.0% of D_2O. The gases evolved are burnt as usual and the mixture of H_2O and D_2O formed is sent back to the cells being used in the third stage.

Fifth stage : The residual water obtained from the fourth stage is further electrolysed so that the residual water contains about 30.0% of D_2O. The gases produced are burnt as usual and the mixture of H_2O and D_2O formed is sent back to the cells being used in the fourth stage.

Sixth stage : The residual water obtained from the fifth stage is further electrolysed till the residual water obtained contains 93.0% of D_2O. The gases produced are burnt as usual and the mixture of H_2O and D_2O obtained is sent back to the cells being used in fifth stage.

Seventh stage : The residual water obtained from the sixth stage is further electrolysed so that the residual water obtained at the end of this stage contains 99% of D_2O. The gases produced here are burnt as usual and the mixture of H_2O and D_2O obtained is sent back into the cells being used in the sixth stage. 99% pure D_2O obtained in this stage also contains some impurities like alkali metals, ordinary water etc. Therefore, this heavy water is distilled and the distillate obtained is then electrolysed to get pure deuterium. The deuterium is then separately burnt in O_2 to get 100% pure D_2O.

A flow sheet diagram showing the preparation of D_2O by the multistage electrolysis of ordinary water is given in Fig. 17.2.

Ordinary water
($D_2O = 0.0\%$)

→ H_2 and O_2 (Discarded)

I stage
(30 cells) ← H_2O and D_2O

Residual water
($D_2O = 0.0\%$)

II stage
(6 cells) → H_2 and O_2 Burner ← O_2
              H_2O and D_2O

Residual water
($D_2O = 0.5\%$)

III stage → H_2 and O_2 Burner ← O_2
             H_2O and D_2O

Residual water
($D_2O = 2.5\%$)

IV stage → H_2 and O_2 Burner ← O_2
            H_2O and D_2O

Residual water
($D_2O = 8.0\%$)

V stage → H_2 and O_2 Burner ← O_2
           H_2O and D_2O

Residual water
($D_2O = 30.0\%$)

VI stage → H_2 and O_2 Burner ← O_2
            H_2O and D_2O

Residual water
($D_2O = 93.0\%$)

VII stage → H_2 and O_2 Burner ← O_2

Residual water
($D_2O = 99.0\%$ + some impurities)

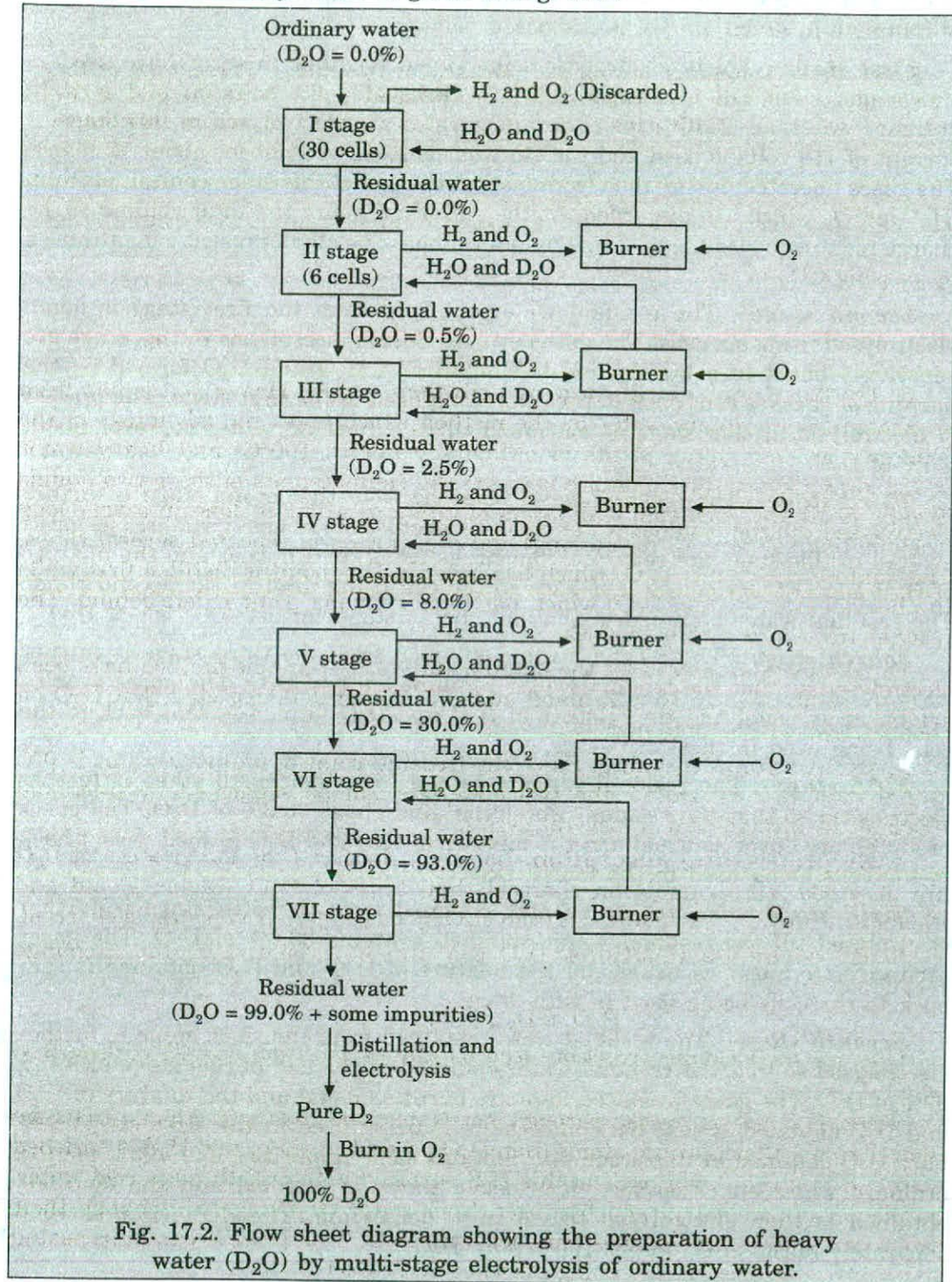Distillation and electrolysis

Pure D_2

Burn in O_2

100% D_2O

Fig. 17.2. Flow sheet diagram showing the preparation of heavy water (D_2O) by multi-stage electrolysis of ordinary water.

Taylor, Eyring and Frost started the electrolysis taking 2310 litres of ordinary water and obtained about 82% ml of D$_2$O. Data of their experiment are given in the following table :

Stage of electrolysis	Volume of ordinary water electrolysed (litres)	Density of the end product	Percentage of D$_2$O at the end of the stages mentioned
I	2310	0.998	—
II	340	0.999	0.5
III	52	1.001	2.5
IV	10.5	1.007	8.0
V	2	1.031	30.0
VI	0.42	1.098	93.0
VII	0.08	1.104	99.0

2. By fractional distillation of ordinary water. Heavy water has been separated from ordinary water by the method which takes the advantage of the difference in the boiling points of ordinary water (= 100°C) and heavy water (= 101.42° C). Since the difference between the boiling points of these two liquids is very small, the fractional distillation of ordinary water is done in a very long fractionating column (13 metre long) and the process is repeated several times. The lighter fraction (*i.e.* H$_2$O) which has lower boiling point is distilled first while the heavier fraction (*i.e.* D$_2$O) which has higher boiling point is left behind. The heavier fraction is richer in D$_2$O.

Distillation plants used for the manufacture of D$_2$O by this method have been recently established in New Zealand and U.S.A. and it is expected that D$_2$O on cheaper cost will be obtained.

3. By fractional freezing. Since the freezing point of ordinary water is 0°C and that of D$_2$O is 3.82°C, the two materials can be separated by fractional freezing. It is completed in several cycles.

4. By preferential adsorption. Based on the fact that the vapours of D$_2$O are adsorbed more rapidly on charcoal than those of H$_2$O, Taylor, Gould and Bleakney were able to separate D$_2$ from H$_2$O by passing their vapours on charcoal.

5. By exchange reactions. D$_2$O can also be prepared by the exchange reactions, *e.g.*

$$H_2O + D_2 \rightleftarrows D_2O + H_2$$
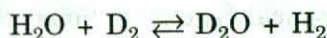
One specific exchange reaction used for the preparation of D$_2$O is discussed below :

When H$_2$S gas is passed through hot water, the hydrogen atoms exchange their places with deuterium atoms from D$_2$O present in water and H$_2$S is enriched with D$_2$S (Fig. 17.3). On passing this H$_2$S enriched with D$_2$S through cold water, the deuterium from D$_2$S and hydrogen from water (H$_2$O) again exchange their places and cold water becomes enriched with D$_2$O. This process can be repeated and cold water goes on becoming enriched with D$_2$O.
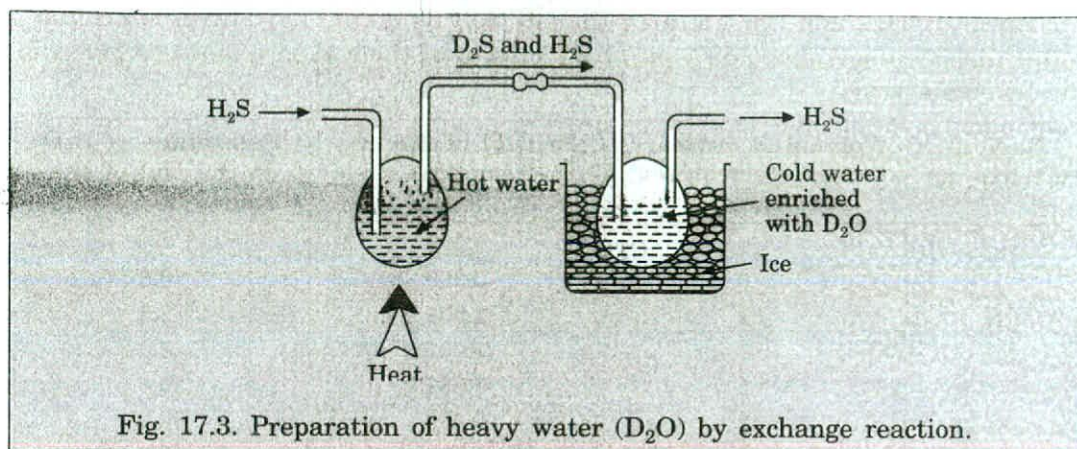
Fig. 17.3. Preparation of heavy water (D_2O) by exchange reaction.

6. Preparation of pure D_2O. Pure D_2O can be prepared by the action of D_2 gas on O_2 gas.

$$2D_2 + O_2 \longrightarrow 2D_2O$$

Manufacture of D_2O in India

In India *The Fertilizer Corporation of India* set up a heavy water plant at Nangal (Punjab) in 1962. Since here the electric supply is cheap, the method being used is of continuous and prolonged electrolysis of ordinary water. D_2O manufactured here is being supplied to the Atomic Energy Commission. Plants at Rourkel, Trombay, Namrup, Neyveli and Naharkatiya have also been set up.

Physical Properties of D_2O

(A) Similarities with H_2O. Like ordinary water, heavy water is a colourless, odourless and tasteless mobile liquid.

(B) Dissimilarities with H_2O. However, there are many physical properties of D_2O which are different from those of H_2O.

This fact is evident from the values of physical constants of H_2O and D_2O given in Table 17.1.

Chemical Properties of D_2O

D_2O behaves like H_2O in most of its chemical properties. However, D_2O reacts more slowly than H_2O in chemical reactions. Some of its chemical reactions are given below :

1. Electrolysis. A solution of D_2O containing P_2O_5 or Na_2CO_3. (The addition of P_2O_5 or Na_2CO_3 makes D_2O conductor), on electrolysis, decomposes into D_2 and O_2 which are evolved at cathode and anode respectively.

$$2D_2O \xrightarrow{\text{Electrolysis}} \underset{\text{(At cathode)}}{2D_2} + \underset{\text{(At anode)}}{O_2}$$
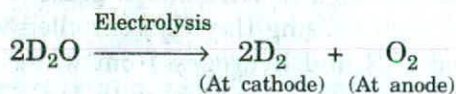
2. Action of metals. D_2O reacts with alkali and alkaline earth metals to liberate D_2 and heavy alkalies are formed.

$$2Na + 2D_2O \longrightarrow 2NaOD + D_2$$
$$Ca + 2D_2O \longrightarrow Ca(OD)_2 + D_2$$
<center>Heavy alkalies</center>

3. Action of metallic oxides. When D_2O reacts slowly with metallic oxides (*i.e.* basic oxides) like Na_2O, CaO etc., heavy alkalies are formed.

$$Na_2O + D_2O \longrightarrow 2NaOD$$
$$CaO + D_2O \longrightarrow Ca(OD)_2$$
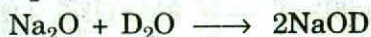
4. Action of non-metallic oxides. When D_2O reacts with non-metallic oxides (*i.e.* acidic oxides), deutero-acids are formed.

$$N_2O_5 + D_2O \longrightarrow 2DNO_3$$
<center>Deutero nitric acid</center>
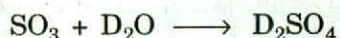
$$SO_3 + D_2O \longrightarrow D_2SO_4$$
<center>Deutero sulphuric acid</center>
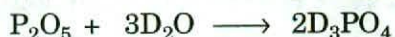
$$P_2O_5 + 3D_2O \longrightarrow 2D_3PO_4$$
<center>Deutero phosphoric acid</center>

Table 17.1. Physical constants of ordinary water (H_2O) and heavy water (D_2O)

Property	Ordinary water (H_2O)	Heavy water (D_2O)
Molecular weight	18.016	20.03
Density at 20°C	0.998	1.017
Boiling point (°C)	100.00	101.42
Melting point (*i.e.*, freezing point) (°C)	0.00	3.82
Temp. of maximum density	4.0	11.6
Max. density	1.0000 (at 4°C)	1.1073 (at 11.6 °C)
Specific heat at 20°C	1.0	1.018
Latent heat of fusion (cals/gm)	79.7	75.5
Latent heat of evaporation (*i.e.* vaporisation) (cals/gm)	539.0	557.0
Surface tension at 20°C (dynes/cm)	72.75	67.80
Refractive index at 20°C	1.3330	1.3284
Viscosity at 20°C (milli poises)	10.09	12.6
Dielectric constant	82.0	80.5
Dissociation constant (*i.e.*, ionic product) at 25°C	1.0×10^{-14}	0.3×10^{-14}
Ionic mobilities at 18°C		
K⁺	64.4	54.4
Cl⁻	65.5	55.3
Solubility of NaCl (gms/lit)	359	305
Critical temperature (°C)	374.2	374.1
Critical pressure (atm)	218.5	218.6
Molar freezing point depression (°C)	1.85	0.52

5. Action of metallic nitrides, phosphides etc. D_2O decomposes metallic nitrides, phosphides, arsenides and carbides to form the corresponding deutro compounds, *e.g.*

$$2AlN + 6D_2O \longrightarrow 2Al(OD)_3 + 2ND_3$$
<div align="center">Dutero ammonia</div>

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$
$$Ca_3P_2 + 6D_2O \longrightarrow 3Ca(OD)_3 + 2PD_3$$
<div align="center">Deutero phosphine</div>

$$Na_3As + 6D_2O \longrightarrow 3NaOD + AsD_3$$
<div align="center">Deutero arsine</div>

$$Al_4C_3 + 12D_2O \longrightarrow 4Al(OD)_3 + 2CD_4$$
<div align="center">Deutero methane</div>

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$
<div align="center">Deutero acetylene</div>
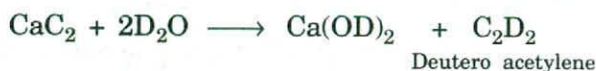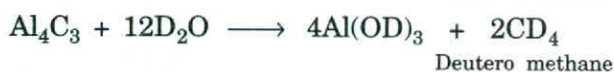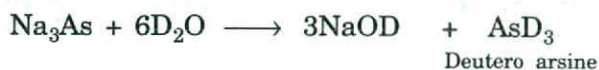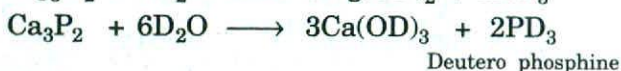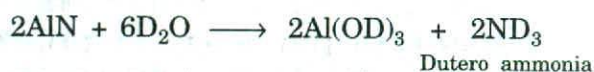
The melting points and boiling points of deutero compounds are generally higher than the analogous hydrogen compounds, *e.g.*, the melting and boiling points of ND_3 (m.pt. = 199.5°K, b.pt. = 242.0°K) are higher than those of NH_3 (m.pt. = 195.2°K, b.pt. 239.8°K.)

6. Formation of deuterates. Water (H_2O) gets associated with salts to form the crystalline salts called *hydrates*. Likewise heavy water (D_2O) also gets associated with salts to form crystalline salts called *deuterates or deutero-hydrates*. Examples of some deuterates are : $BeCl_2.4D_2O$; $CuSO_4.5D_2O$; $CoCl_3.6D_2O$; $NiCl_2.6D_2O$; $MgSO_4.7D_2O$.

In these deuterates D_2O acts as heavy water of crystallisation. These deuterates are obtained when solution of salts in D_2O are crystallised. For example :

$$CuSO_4.5H_2O + 5D_2O \xrightarrow[-5H_2O]{Crystalisation} CuSO_4.5D_2O$$
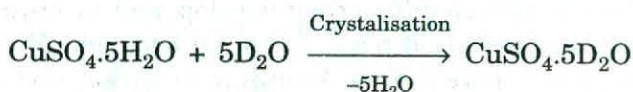
Deuterates are often analogous in composition with hydrates. The colour of deuterates of transition metals are lighter than those of hydrates, *e.g.* $CuSO_4.5D_2O$ has light blue colour while $CuSO_4.5H_2O$ has deep blue colour.

7. Action of compounds containing hydrogen : Exchange reactions. D_2O reacts with a number of compounds containing labile hydrogen atoms. In these reactions H atoms are partially or completely replaced by deuterium. Such reactions are called *exchange reactions*.

If the compounds contain ionic (*i.e.*, polar) hydrogen atoms, the exchange reactions occur more readily, *e.g.*

$$NaOH + D_2O \rightleftharpoons NaOD + HOD$$
$$HCl\ (aq) + D_2O \rightleftharpoons DCl + HOD$$
$$NH_4Cl + 4D_2O \rightleftharpoons ND_4Cl + 4HOD$$

The exchange reaction of NH_4Cl with D_2O takes place in steps as shown below :

$$NH_4Cl + D_2O \rightleftharpoons NH_3DCl + HOD$$
$$NH_3DCl + D_2O \rightleftharpoons NH_2D_2Cl + HOD$$
$$NH_2D_2Cl + D_2O \rightleftharpoons NHD_3Cl + HOD$$
$$NHD_3Cl + D_2O \rightleftharpoons ND_4Cl + HOD$$

On adding : $NH_4Cl + 4D_2O \rightleftharpoons ND_4Cl + 4HOD$
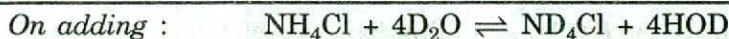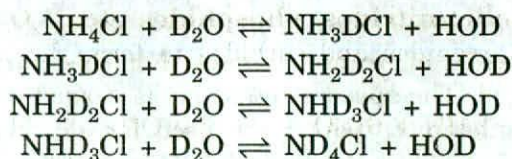
If the compounds contain non-ionic hydrogen atoms, the exchange reactions take place slowly and require the presence of a catalyst, *e.g.* C$_6$H$_6$ when treated with D$_2$O using nickel dispersed on kieselguhr at a temperature of 200°C leads to the formation of pure *hexa deutero-benzene.*

$$C_6H_6 + 3D_2O \rightleftharpoons \underset{\substack{\text{Hexa deutero-} \\ \text{benzene}}}{C_6D_6} + 3H_2O$$
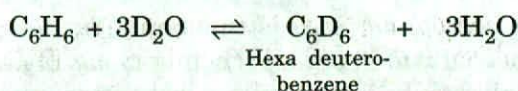
Hexammine cobaltic chloride, [Co(NH$_3$)$_6$]Cl$_3$ shows a slow e change reaction.

$$[Co(NH_3)_6]Cl_3 + D_2O \longrightarrow [Co(NH_3)_5(NH_2D)]Cl_3 + HOD$$
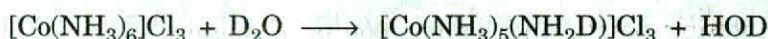
Exchange reactions have been used in determining the number of ionic and non-ionic hydrogen atoms present in a given compound, *e.g.*, treatment of hypophosphorous acid (H$_3$PO$_2$) with D$_2$O brings about the exchange of only one H atom of H$_3$PO$_2$ with deuterium.

$$H_3PO_2 + D_2O \longrightarrow H_2DPO_2 + HDO$$

This reaction shows the presence of only one ionic hydrogen atom in H$_3$PO$_2$, *i.e.* H$_3$PO$_2$ is a *mono basic acid.*

8. Physiological effects. Heavy water of high concentration retards the growth of plants and animals. Lewis has shown that tobacco seeds do not grow in D$_2$O, though under the same conditions they develop well in ordinary water. Pure D$_2$O kills small fish, tadpoles and mice, when fed on them. Mice and rats, on drinking D$_2$O, feel more and more thirsty. According to Taylor, it is a germicide and a bactericide. While water containing higher concentration of D$_2$O is poisonous, water containing small quantity of D$_2$O acts as a tonic and stimulates vegetable growth. Although D$_2$O is injurious to animal life, certain moulds have been found to flourish better in solutions richer in D$_2$O than in ordinary aqueous solutions.

9. Deuterolysis. Water brings about hydrolysis of certain inorganic chlorides and some other salts. D$_2$O also brings about a similar reaction which is called *deuterolysis.*

$$AlCl_3 + 3D_2O \longrightarrow Al(OD)_3 + 3DCl$$
$$BaS + 2D_2O \longrightarrow Ba(OD)_2 + D_2S$$
$$BiCl_3 + D_2O \longrightarrow BiOCl + 2DCl$$
$$SiCl_4 + 4D_2O \longrightarrow D_4SiO_4 + 4DCl$$
$$SOCl_2 + 2D_2O \longrightarrow D_4SO_3 + 2DCl$$
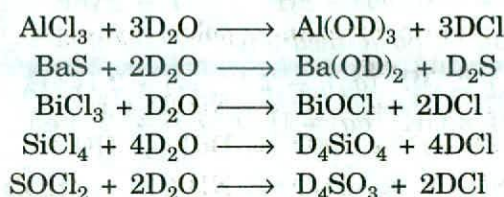
Uses of D$_2$O

Important uses of D$_2$O are :

(i) *As a moderator of neutrons in nuclear reactors.* Neuterons are used for bringing about the fission of uranium atoms. For this purpose the neutrons of *slow speed* are required. The speed of neutrons is slowed down by passing them through D_2O. Such substances which are used for slowing down the speed of neutrons are called *moderators.* Obviously D_2O here acts as a moderator.

(ii) *For the preperation of D_2.* D_2 can be prepared either by the electrolysis of DO or by the action of sodium metal on D_2O

$$2D_2O \xrightarrow{\text{Electrolysis}} 2D_2 + O_2$$
$$2D_2O + 2Na \longrightarrow 2NaOD + D_2$$

(iii) *As a tracer compound.* D_2O is commonly used as a tracer compound for studying reaction mechanism in organic chemistry *e.g.* D_2O has helped to elucidate the mechanism of electrophilic aromatic substitution reactions.

D_2O is also used as tracer in metabolic processes, *e.g.* when mice fed with labelled butyric acid, within hours all the deuterium was eliminated from the body indicating that it is a ready source of energy.

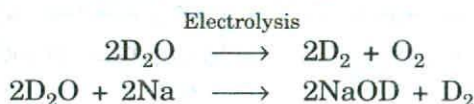(iv) Although D_2O injurious to animal life, yet certain moulds have been found to flourish better in solutions rich in D_2O than in ordinary aqueous solution.

(v) The ability of D_2O is to undergo exchange reactions has been used for studying the structure of some oxy-acids of phosphorus such as H_3PO_2 and H_3PO_3 by finding out the number of ionic hydrogen atoms in these compounds.

Question with Answers

Q.1 Give reactions to show that H_2O_2 can act as an OA as well as a RA.

Ans : H_2O_2 can act as an oxidising as well as a reducing agent both in acidic and basic media as illustrated below :

(i) *Oxidising agent (OA) in acidic medium*

$2 Fe^{2+} (aq) + 2 H^+ (aq) + H_2O_2 (aq) \rightarrow 2Fe^{3+} (aq) + 2 H_2O (l)$
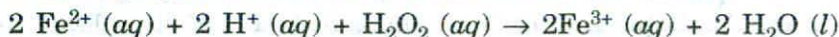
(ii) *Oxidising agent in basic medium*

$2 Mn^{2+} (aq) + H_2O_2 (aq) + 2 OH^- (aq) \rightarrow MnO_2 (s) + 2 H_2O (l)$

$2 Cr^{3+} (aq) + 3 H_2O_2 (aq) + 10OH^- (aq) \rightarrow 2 CrO_4^{2-} (aq) + 8 H_2O (l)$

(iii) *Reducing agent (RA) in acidic medium*

$2 MnO_4^- (aq) + 6H^+ (aq) + 5H_2O_2 (aq) \rightarrow 2Mn^{2+} (aq) + 8H_2O (l) + SO_2$
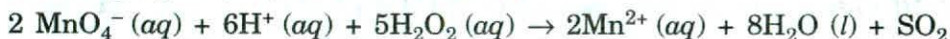
(iv) *Reducing agent in basic medium*

$I_2 (s) + H_2O_2 (aq) + 2 OH^- (aq) \rightarrow 2 I^- (aq) + 2 H_2O (l) + O_2 (g)$

$2[Fe (CN)_6]^{3-} (aq) + 2 OH^- (aq) + H_2O_2 (aq) \rightarrow 2 [Fe (CN)_6]^{4-} (aq) + 2H_2O(l)$
$+ O_2(g).$
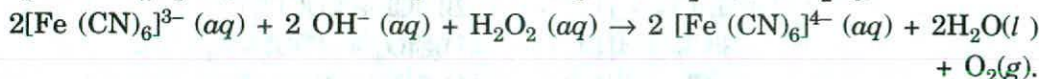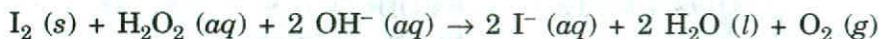
Q.2 10 ml of a given solution of H_2O_2 contains 0.91 g of H_2O_2. Express its strength in volume.

Ans : 68 g of H_2O_2 produce O_2 = 22400 ml at NTP.

$\therefore$ 0.91 g of H_2O_2 will produce $O_2 = \dfrac{22400 \times 0.91}{68} = 300$ ml at NTP

$\therefore$ Volume strength $= \dfrac{300}{10} = \mathbf{30}$

Q.3 Calculate the volume of 10 volume H_2O_2 solution that will react with 200 ml of 2 N $KMnO_4$ in acidic medium :

Ans : Normality of 10 volume $H_2O_2 = \dfrac{\text{Volume strength}}{5.6} = \dfrac{10}{5.6}$ N

Applying normality equation,

$$N_1V_1 = N_2V_2$$
$$(H_2O_2) \quad (KMnO_4)$$

$$\dfrac{10}{5.6} \times V_1 = 2 \times 200$$

or $\qquad V_1 = \dfrac{2 \times 200 \times 5.6}{10} = \mathbf{224\ cm^3}.$

Q.4 Calculate the molarity strength of H_2O_2 solution marked '30 volume'.

Ans : Morality = Volume strength/11.2 $= \dfrac{30}{11.2} = \mathbf{2.68\ M.}$

Q.5 Name two compounds which retard decomposition of H_2O_2 soultion.

Ans : Acetanilide, glycerol.

Q.6 How does H_2O_2 behave as a bleaching agent ?

Ans : The bleaching action of H_2O_2 is due to the *nascent oxygen* which it liberates on decomposition.

$$H_2O_2 \longrightarrow H_2O + O$$
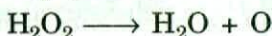
The nascent oxygen combines with colouring matter which, in turn, gets oxidised. Thus, the bleaching action of H_2O_2 is due to the *oxidation of colouring matter by nascent oxygen*. It is used for the bleaching of delicate materials like ivory, feather, silk, wool, etc.

Q.7 What do you mean by 15 volume H_2O_2 solution ?

Ans : 1 cm^3 of a 15 volume H_2O_2 solution gives 15 ml of O_2 at NTP.

Q.8 Calculate the percentage strength and strength in grams per liter of 10 volume hydrogen peroxide solution.

Ans : Hydrogen peroxide decomposes on heating according to the equation :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$2 \times 34\ g \qquad\qquad 22.4 \text{ liters at N.T.P.}$$
$$= 68\ g \qquad\qquad \text{or } 22400\ cm^3 \text{ at N.T.P.}$$
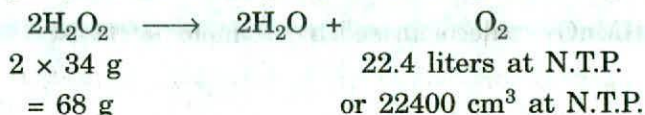
From the equation, 22.4 liters of O_2 at N.T.P. are obtained from 2×34 or 68 g of H_2O_2.

$\therefore$ 10 ml of O_2 at N.T.P. will be obtained from $\dfrac{68}{22400} \times 10$ g of H_2O_2

But 10 ml of O_2 at N.T.P. are produced from 1 ml of *10 volume* H_2O_2 solution

Thus, 1 ml of *10 volume* H_2O_2 solution contains $\dfrac{68}{22400} \times 10$ g of H_2O_2

$\therefore$ 100 ml of *10 volume* H_2O_2 solution will contain $\dfrac{68}{22400} \times \dfrac{10}{1} \times 100 = 3.036\text{g}$

Thus, a *10 volume* H_2O_2 solution is approx. 3%

Alternatively, 1000 ml of 10 volume H_2O_2 will contain $H_2O_2 = \dfrac{68}{22400} \times 10 \times$ 1000 = 30.36 g

Therefore, strength of H_2O_2 in 10 volume H_2O_2 = **30.36 g L^{-1}**

Q.9 Calculate the amount of H_2O_2 present in 10 ml of 25 volume H_2O_2 solution.

Ans : 10 ml of 25 volume H_2O_2 liberate O_2 = 10 × 25 = 250 ml at NTP

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$
$$68\text{ g} \qquad\qquad\qquad 22400\text{ml at NTP}$$
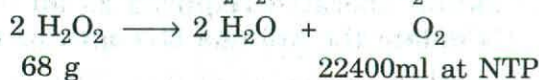
Amount of H_2O_2 that will liberate 250 ml of O_2 at NTP = $\dfrac{68 \times 250}{22400}$ = **0.759 g.**

Q.10 Complete the following equations :

(*i*) **PbS (*s*) + H_2O_2 (*aq*) → ....**

(*ii*) **MnO_4^- (*aq*) + H_2O_2 (*aq*) → ....**

Ans : (*i*) PbS (*s*) + 4 H_2O_2 (*aq*) → $PbSO_4$ (*s*) + 4 H_2O (*l*)

(*ii*) MnO_4^- (*aq*) + 5 H_2O_2 (*l*) + 6 H$^+$ (*aq*) → 2 Mn^{2+} (*aq*) + 8 H_2O (*l*) + 5O_2(*g*)
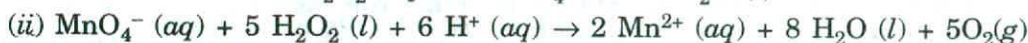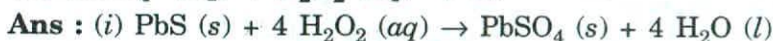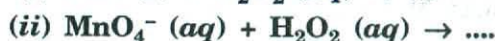
Q.11 What is perhydrol ?

Ans : Perhydrol is the trade name for H_2O_2 which is used as an antiseptive for washing wounds, teeth and ears.

Q.12 How many moles of H_2O_2 will be required for the neutralistaion of 1 mole of $KMnO_4$?

Ans : The reaction between H_2O_2 and acidified solution of $KMnO_4$ takes place as :

$$2\,KMnO_4 + 5\,H_2SO_4 + \quad 5\,H_2O_2 \quad \rightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2$$
2 moles   5 moles
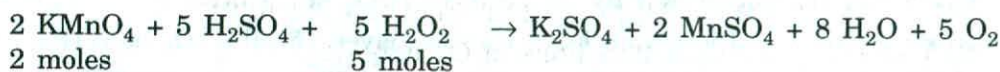
This equation shows that :

$\therefore$2 moles of $KMnO_4$ are decolourised by 5 moles of H_2O_2

$\therefore$1 mole of $KMnO_4$ is decolourised by $\dfrac{5}{2}$ moles of H_2O_2

$\therefore$ Answer is $\dfrac{5}{2}$ moles of H_2O_2

Q.13 How is heavy water produced from ordinary water ?

Ans : It is obtained by repeated electrolysis of ordinary water containing 3% NaOH.

Q.14 What is the importance of heavy water with regard to nuclear power generation ?

Ans : It is used as a moderator to slow down the neutrons produced as a result of fission and thus helps to control the nuclear reactions.

Q.15 How is D$_2$O$_2$ prepared ?

Ans : D$_2$O$_2$ is prepared by distillation of potassium persulphate (K$_2$S$_2$O$_8$) with D$_2$O.

Q.16 What happens when chloroform is treated with heavy water in presence of an alkali ?

Ans : Deuterochloform (CDCl$_3$) is formed.

$$CHCl_3 + D_2O \xrightarrow{\quad OH^- \quad} CDCl_3 + DOH.$$
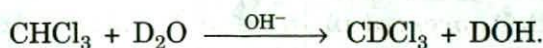
Q.17 To a 25 ml H$_2$O$_2$ solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 ml of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H$_2$O$_2$ solution.

Ans : Step 1. *To determine the normality of H$_2$O$_2$ solution.*

Let the normalitiy of the H$_2$O$_2$ solution be N$_1$. According to the question,

25 ml of N$_1$H$_2$O$_2$ ≡ 20 ml of 0.3 N Na$_2$S$_2$O$_3$ solution

or $25 \times N_1 = 20 \times 0.3$

or $N_1 = \dfrac{20 \times 0.3}{25} = \textbf{0.24 N}$

*Thus, the normality of the given H$_2$O$_2$ solution = **0.24 N***

Step 2. *To determine the amount of H$_2$O$_2$ in 25 ml solution*

1000 ml of N$_1$H$_2$O$_2$ solution contain H$_2$O$_2$ = 17 g   (Eq.wt. of H$_2$O$_2$ = 17)

∴ 25 ml of 0.24 N H$_2$O$_2$ solution will contain H$_2$O$_2$ = $\dfrac{17 \times 25 \times 24}{1000 \times 100}$ = **0.102 g**

Step 3. *To determine the volume strength of H$_2$O$_2$ solution.*

Consider the chemical equation,

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$
$$2 \times 34 = 68\ g \qquad 22.4\ \text{liters of } O_2 \text{ at N.T.P.}$$
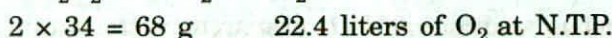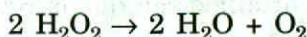
68 g of H$_2$O$_2$ give O$_2$ = 22.4 liters of O$_2$ at N.T.P.

∴ 0.102 g of H$_2$O$_2$ will give O$_2$ = $\dfrac{22.4 \times 1000 \times 0.102}{68}$ = 33.6 ml at N.T.P.

Now, 25 ml of H$_2$O$_2$ solution give O$_2$ = 33.6 ml at N.T.P.

∴ 1 ml of H$_2$O$_2$ solution will give O$_2$ = $\dfrac{33.6}{25}$ = **1.344 ml**

*Thus, the volume strength of the given H$_2$O$_2$ solution = **1.344***

Q.18 Explain the following :

(*i*) **Electrolysis of ordinary water occurs faster than that of heavy water ?**

Ans : Due to lower bond dissociation energy of protium bonds in H–O–H than deuterium bonds in D–O–D, electrolysis of H_2O occurs much faster than that of D_2O.

(ii) Although D_2O resembles H_2O chemically, yet it is a toxic subtance.

Ans : D_2O is toxic, since D^+ reacts at a much slower rate as compared to H^+ in ezyme-catalyzed reactions.

(iii) When H_2O_2 is added to blood, rapid evolution of a gas occurs.

Ans : The enzyme present in the blood catalyses the oxidation of H_2O_2 and hence rapid evolution of O_2 takes place.

$$2H_2O_2 \xrightarrow[\text{in blood}]{\text{Enzyme present}} 2\,H_2O + O_2 \uparrow$$
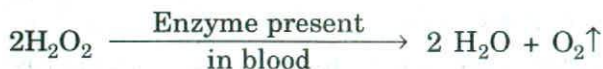
(iv) Ionic compounds (e.g. NaCl) are less soluble in D_2O than in H_2O.

Ans : Since D_2O has lower value of dielectric constant than H_2O, ionic compounds are less soluble in D_2O than in H_2O.

(v) Heavy water cannot be used for drinking purpose.

Ans : Heavy water is injurious to human beings, plants and animals since it slows down the rates of reactions occurring in them. Thus, heavy water does not support life so well as does ordinary water.

(vi) Hydrated barium peroxide is used in the preparation of hydrogen peroxide instead of anhydrous peroxide ?

Ans : If anhydrous barium peroxide is used in the preparation of H_2O_2, the $BaSO_4$ formed during the reaction forms an insoluble protective coating on the surface of solid barium peroxide.

$$BaO_2\,(s) + H_2SO_4\,(aq) \longrightarrow BaSO_4 + H_2O_2\,(aq)$$
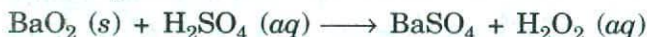
$BaSO_4$ thus formed prevents further action of the acid and ultimately the reaction stops. If, however, hydrated barium peroxide (in the form of thin paste) is used, the water of crystallization does not allow $BaSO_4$ to deposit on the surface of BaO_2 and the reaction goes to completion.

(vii) Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide.

Ans : The aqueous solution of H_2O_2 prepared by the action of dil. H_2SO_4 on hydrated BaO_2 has impurities of heavy metal ions like Ba^{2+}, Pb^{2+}, etc. These catalyse the decomposition of H_2O_2. Therefore, H_2O_2 perpared by the action of dil. H_2SO_4 on hydrated BaO_2 does not have good keeping qualities. If, however, phosphoric acid is used, the impurities of heavy metal ions are precipitated as insoluble phosphates. As a result, the resulting solution of H_2O_2 has good keeping qualities.

(viii) Red litmus paper turns white in the solution of Na_2O_2 but the same paper turns blue in the solution of Na_2O.

Ans : Na_2O_2 reacts with H_2O to produce H_2O_2.

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

It is due to the bleaching property of H_2O_2 that the red litmus paper turns white. Na_2O gives NaOH with H_2O.

$$Na_2O + H_2O \rightarrow 2\ NaOH$$
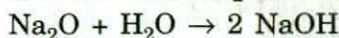
NaOH thus produced turns red litmus paper blue.

(*ix*) **A mixture of hydrazine (NH$_2$ – NH$_2$) and H$_2$O$_2$ with Cu (II) catalyst is used as a rocket propellant.**

Ans : The reaction between hydrazine and H_2O_2 is highly exthermic and is accompaned by a large increase in the volume of the products and hence this mixture is used as a rocket propellant.

$$NH_2\text{–}NH_2\ (l) + 2H_2O_2\ (l) \xrightarrow{\ \ Cu\ (II)\ \ } N_2\ (g) \uparrow + 4\ H_2O\ (g) \uparrow$$
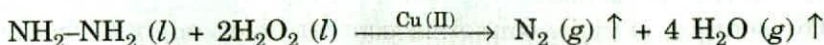
(*x*) **Statues coated with white lead on long exposure to atmosphere turn black and the original colour can be restored on treatment with H$_2$O$_2$.**

Ans : On long exposure to atmosphere, white lead (PbO_2) is converted into black PbS due to the action of H_2S present in the atmosphere. As a result, statues turn black.

$$PbO_2 + 2\ H_2S \rightarrow PbS + 2\ H_2O$$

On treatment of these blackned statues with H_2O_2, the black PbS gets oxidised to white $PbSO_4$ and the colour is restored.

$$PbS + 4\ H_2O_2 \rightarrow PbSO_4 + 4\ H_2O$$

Q.19 A 5.0 cm^3 solution of H$_2$O$_2$ liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H$_2$O$_2$ solution in terms of volume strength at STP.

Ans : (*a*) $2\ KI + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + 2\ H_2O + I_2$

From the above equation,

$$H_2O_2 \equiv I_2$$
$$34\ g\ of\ H_2O_2 \equiv 254\ g\ of\ I_2$$
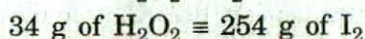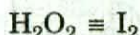
$\therefore$ 0.508 g of I_2 will be liberated from $H_2O_2 = \dfrac{34}{254} \times 0.508 = \mathbf{0.068\ g}$

(*b*) The decomposition of H_2O_2 occurs as :

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$
$$2 \times 34 = 68\ g \qquad 22400\ cm^3\ at\ NTP$$
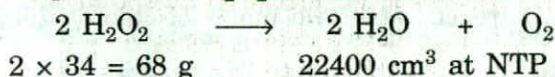
$\therefore$ 0.068 of H_2O_2 upon decomposition will give $O_2 = \dfrac{22400}{68} \times 0.068$

$$= \mathbf{22.4\ ml}$$

(*c*) Now 5.0 cm^3 of H_2O_2 solution gives $O_2 = 22.4$ cm^3 at STP

$\therefore$ 1.0 cm^3 of H_2O_2 solution will give $O_2 = \dfrac{22.4}{5} = 4.48$ cm^3 at STP

Thus, volume strength of given H_2O_2 solution = **4.48**.

University Questions

1. How is anhydrous H_2O_2 obtained from barium peroxide?   (*Madras 85*)

2. How does H_2O_2 manufactured?   (*Madurai 85*)

3. Discuss the constitution of H_2O_2.   (*Meerut 89;*

Allahabad 86, 87; Bundelkhand 88)

4. Explain the following :

(*i*) H_2O_2 acts both as an oxidising as well as a reducing agent.

(*ii*) The mixture of hydrazine (N_2H_4) and H_2O_2 with a Cu (II) catalyst is used as a rocket propellant ?   (*I.I.T. 87*)

(*iii*) The solution of H_2O_2 cannot be concentrated simply by heating.

(*iv*) H_2O_2 is used for restoring old paintings in the museum.   (*REE 87*)

5. What happens when :

(*i*) an alkaline solution of potassium ferricyanide is treated with H_2O.

(*I.I.T. 82*)

(*ii*) H_2O_2 reacts with H_2S.

(*iii*) H_2O_2 reacts with acidified solution of $KMnO_4$ solution.   (*I.I.T. 73*)

(*iv*) H_2O_2 reacts with Ag_2O.

(*v*) H_2O_2 reacts with PbS

(*vi*) H_2O_2 and ether is added to an acidic solution of $K_2Cr_2O_7$.

(*vii*) H_2O_2 is treated with O_3.

(*viii*) H_2O_2 is added to an acidic solution of $FeSO_4$.   (*REE 85*)

(*ix*) Complete and balance the following equations :

(*a*) $H_2O_2 + N_2H_4 \longrightarrow$ .....   (*Meerut 85*)

(*b*) $H_2O_2 + C_6H_6 \longrightarrow$ .....   (*Madurai 85*)

(*c*) $H_2O_2 + PbO_2 \longrightarrow$ .....   (*Madurai 85*)

(*d*) $H_2O_2 + H^+ + MnO_4^- \longrightarrow$ .....   (*Raj. 85*)

(*e*) $H_2O_2 + H_2SO_4 + KMnO_4 \longrightarrow MnSO_4 + K_2SO_4 + H_2O + \longrightarrow$ .....

(*I.I.T. 75; MLNR 85*)

(*f*) $H_2O_2 + HO.SO_2.Cl \longrightarrow$ .....   (*Delhi 85*)

(*x*) H_2O_2 reacts with Caro's acid.   (*Delhi 87; Calcutta 86*)

(*xi*) One mole of H_2O_2 reacts with two moles of chlorosulphonic acid.

(*Meerut 84 S*)

(*xii*) A solution of K_2CrO_4 containing H_2O_2 is acidified with H_2SO_4 in presence of ether or pyridine.   (*Delhi 87*)

6. Describe the preparation, properties and uses of heavy water.

Allahabad 89; Kanpur 80, 81, 82; Agra 80, 81; Lucknow 81, 84;

7. Starting from deuterium how would you prepare D_2O?   (*MD Rohtak 84*)

8. How does heavy water react with CaC_2, C_2H_2, H_2SO_4, P_2O_5, Mg_3N_2.

9. Discuss the following properties of H_2O_2 (*i*) Oxidising properties (*ii*) Reducing properties (*iii*) Acidic properties.   (*Madras 95, Maduria 85, Delhi 83*)

10. Give methods of preparation, properties and uses of heavy water.

(*Kanpur 2000, Avadh 2000*)

General Characteristics of Group 1 (I A) Elements : Alkali Metals

Group IA of the long form of periodic table contains six elements (excluding hydrogen) which are *Lithium* (Li), *Sodium* (Na), *Potassium* (K), *Rubedium* (Rb), *Caesium* (C) and *Francium* (Fr). These elements are collectly called alkali metals, since they form strongly alkaline oxides and hydroxides. Fr is a radioactive element.

Position of Alkali Metals in the Periodic Table

The inclusion of the alkali metals in the same sub-group of the periodic table is justified by the following general properties of these elements.

I. Electronic Configurations

The electronic configurations of the atoms of alkali metals are given in the following table :

Element	At. No.	Complete electronic configuration	Valence-shell electronic configuration
Li	3	2, 1	$2s^1$
Na	11	2, 8, 1	$3s^1$
K	19	2, 8, 8, 1	$4s^1$
Rb	37	2, 8, 18, 8, 1	$5s^1$
Cs	55	2, 8, 18, 18, 8, 1	$6s^1$
Fr	87	2, 8, 18, 32, 18, 8, 1	$7s^1$

These configurations show that the ultimate shells of these elements have *one s* electron (s^1 electron) while the penultimate shell contains *eight* (s^2p^6) electrons (Li is an exception). When this valence-shell electron is lost, the alkali metals are converted into M^+ ions which have inert gas configuration. Since the additional electron enters *ns*-orbital, these are *s*-block elements.

It is due the similarity in the electronic configirations of the atoms of alkali metals as shown above in the table that the alkali metals have similar physical and chemical properties as discussed below :

II. Similarities in Physical Properties and Gradation in Them

Some of the physical properties of alkali metals are given in Table 18.1, and are discussed below :

1. Physical state. With the exception of Li, the alkali metals are *extremely soft* and *readily fused*. They are highly malleable (*i.e.*, can be pressed out into

sheets) and ductile (*i.e.*, can be drawn into wires). When freshly cut, they have a bright lustre which is quickly tarnished as soon as metal comes in contact with atmosphere.

Table 18.1. Some physical properties of alkali metals

Property	Li	Na	K	Rb	Cs
Atomic weight	6.94	22.99	39.10	85.47	132.91
Abundance (% of earth's crust)	0.0065	2.74	2.47	0.028	3.2×10^{-4}
Atomic volume (c.c)	12.97	23.68	45.36	55.80	69.95
Atomic (*i.e.*, metallic) radius for coordination number 12 (A°)	1.55	1.90	2.35	2.48	2.67
Covalent radius (A°)	1.23	1.54	2.03	2.16	2.35
Ionic (crystal) radius of M^+ ions for coordination number 6 (A°)	0.60	0.95	1.33	1.48	1.69
Specific heat at °C	0.941	0.293	0.17	0.08	0.049
Ionic potential of M^+ ions (*i.e.*, charge/radius value)	1.67	1.05	0.75	0.68	0.59
Melting point (°C)	180.5	97.8	63.7	38.9	28.7
Boiling point (°C)	1330	892	760	688	670
Ionisation energies (KJ/mole)					
I_1	520.3	495.8	418.9	403.0	375.7
I_2	7298.1	4562.4	3051.4	2633.0	2230.0
Standard oxidation potential of $M (s) \rightarrow M^+ (aq) + e^-$ reaction (volt)	+ 3.04	2.71	+ 2.99	+ 2.99	+ 2.99
Sublimation energy (eV/atom)	1.7472	1.2432	1.0320	0.9840	0.9024
Hydration energy (eV/ion)	5.904	3.792	3.696	3.360	0.624
Electronegativity	1.0	0.9	0.8	0.8	0.7
Colour of the flame	Crimson red	Golden yellow	Violet	Violet	Violet
Oxidation states	+ 1	+ 1	+ 1	+ 1	+ 1
Heat of atomisation at 25°C (eV/atom)	1.7472	1.2432	1.0320	0.9840	0.9024
Ionic conduction of M^+ ion (Ω^{-1})	33.5	43.5	64.6	67.5	68.0

2. Atomic volume, atomic and ionic radii. As we move from lithium to caesium, an extra shell of electrons is added to each element. The addition of an extra shell increases the atomic volume. We find, therefore, that *there is an increase of atomic and ionic radii* (of M^+ ions) *as we move from lithium to caesium.*

Elements	Li	Na	K	Rb	Cs
Atomic volume (c.c.)	12.97	23.68	45.36	55.80	69.95
Atomic (*i.e.*, metallic) radii for coordination number 12 (A°)	1.55	1.90	2.35	2.48	2.67
Covalent radii (A°)	1.23	1.54	2.03	2.16	2.35
Ionic (crystal) radii of M^+ ion for coordination number 6 (A°)	0.60	0.95	1.33	1.48	1.69

3. Density. The densities of alkali metals are *quite low* due to the large atomic volumes. Li, Na and K are *lighter than water. The densities increase with the increase in atomic number from Li to Cs* indicating that greater atomic weight more than compensates for the bigger size of the atoms. K is, however, lighter than Na which is due to an unusual increase in atomic size of K.

Elements	Li	Na	K	Rb	Cs
Densities at 0°C (g/c.c)	0.534	0.972	0.859	1.525	1.903

4. Melting and boiling points. The melting and boiling points are *very low* because of the presence of weak interatomic bonds in the solid state of the alkali metals. These bonds are due to their atomic radii and mainly due to their electronic configuration having a *single valence electron* as compared to large *number of available vacant orbitals.* As the size of the metal atoms increases, the repulsion of the non-bonding electron also increases. This increase in the repulsion of the non-bonding electron *decreases the melting and boiling points of alkali metals, when we move from Li to Cs.*

Elements		Li	Na	K	Rb	Cs
Melting point (°C)	:	18.5	97.8	63.7	38.9	28.7
Boiling point (°C)	:	1330	892	760	688	670

5. Heats of atomisation. Alkali metals have low heats of atomisation which are indicative of the fact that here are weak interatomic bonds in alkali metals.

Elements	Li	Na	K	Rb	Cs
Heats of atomisation at 25°C (eV/atom)	1.7472	1.2432	1.0320	0.9840	0.9024

6. Ionisation energies. We know that alkali metals have only one electron in their outermost shell (ns^1 electron). This ns^1 electron is so *weakly held* with the nucleus that it can be removed very easily. Alkali metals, therefore, have *low ionisation energies.*

As the distance of ns^1 electron from the nucleus increases on moving from Li to Cs, its removal becomes more and more easy as we proceed from Li to Cs,. *i.e.,* the amount of energy (ionisation energy) used in the removal of ns^1 electron is maximum in case of Li while in case of Cs it is the minimum. *Consequently the ionisatson energies of alkali metals go on decreasing from Li to Cs* as shown below :

Elements :	Li	Na	K	Rb	Cs
Ionisation energies (KJ/mole) :	520.3	495.8	418.9	403.0	375.7

—————Values decreasing—————→

The second ionisation energies are fairly high, since the loss of the second electron from M^+ cation which has a noble gas configuration is quite difficult.

7. Electropositive (*i.e.,* metallic) character. The elements which have a strong tendency to lose their outermost electrons to form the cations are said to be electropositive or metallic elements. In case of alkali metals we have seen that ns^1 electron in these metals is weakly bound with the nucleus and hence can be easily removed from the atom to form M^+ cation.

$$M \longrightarrow M^+ + e^-$$

Thus these metals have a strong tendency to lose their ns^1 electron to form M^+ cation and hence show *strong electropositive or metallic character*. Because of the successive increase in the distance of ns^1 electron from the nucleus on proceeding from Li to Cs, the tendency of the atoms to lose ns^1 electron goes on increasing from Li to Cs, *i.e.*, Li atom loses its ns^1 electron with great difficulty and hence shows *minimum electropositive character*, while Cs atom loses the same quite readily and hence shows *maximum electropositive character*. Thus the electropositive character of alkali metals *increases* from Li to Cs. Note that ionisation energies of alkali metals *decrease* from Li to Cs.

8. Photo electric effect. (Effect of light). The ns^1 electron in the atoms of alkali metals is so loosely held with the nucleus that even the low energy photons (*i.e.* light) can eject this ns electron from the surface of these metals. This property of emitting the electron even on the exposure of light permits these (especially K and Cs) to be used in photo electric cells which are sensitive to blue light.

9. Reducing properties. It is well known that an oxidising agent is a substance which can accept electrons, while a reducing agent is a substance which can lose electrons. Since, as we have seen above, alkali metals have a strong tendency to lose their ns electron, they act as strong reducing agents.

The tendency of alkali metals to act as strong reducing agents is evident from the fact that these metals can liberate H_2 from H_2O and acids.

$$2M + 2H_2O \longrightarrow 2MOH + H_2 \uparrow$$
$$2M + 2HCl \longrightarrow 2MCl + H_2 \uparrow$$
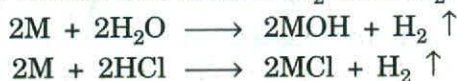
We have already seen that Li atom loses, its ns^1 electron with great difficulty (*i.e.* its ionisation energy is maximum) while Cs loses the same most readily (*i.e.* its ionisation energy is minimum). Consequently Li atom should have minimum reducing power while Cs atom should have maximum reducing power among the alkali metals. In other words, we can also say that Li atom, because of its maximum ionisation energy, should have minimum reducing power and Cs atom, because of its minimum ionisation energy, should have maximum reducing power.

Now let us examine the values of standard oxidation potentials (E° values) of alkali metals as given below and correlate these values with the reducing power of alkali metals.

$$Li(s) \longrightarrow Li^+ (aq) + e^- ; \qquad E° = + 3.04 \text{ volts}$$
$$Na(s) \longrightarrow Na^+ (aq) + e^- ; \qquad E° = + 2.71$$
$$K(s) \longrightarrow K^+ (aq) + e^- ; \qquad E = + 2.92$$
$$Rb(s) \longrightarrow Rb^+ (aq) + e^- ; \qquad E° = + 2.92$$
$$Cs(s) \longrightarrow Cs^+ (aq) + e^- ; \qquad E° = + 2.92$$
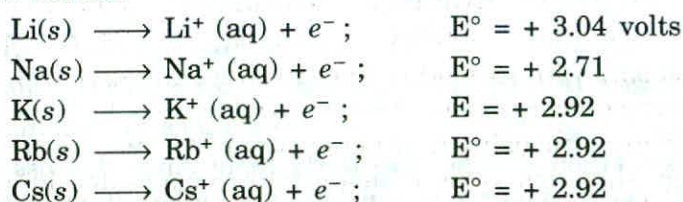
The high values of oxidation potentials show that alkali metals can lose their ns^1 electron quite readily and hence have a strong tendency to act as reducing agents. Since the value of oxidation potential for Li atom is the highest, it should lose its ns^1 electron most readily and hence should have the maximum reducing power.

Thus we see that on the basis of ionisation energy values, Li atom should have minimum reducing power while on the basis of oxidation potential values it should have maximum reducing power. As a matter of fact Li atom has the maximum reducing power in aqueous condition. Then how to explain this discrepancy regarding the reducing power of Li atom? This can be explained as follows :

As a matter of fact the conversion of an alkali metal in the solid state, $M(s)$ in contact with water into M^+ (aq) cation represented by :

$$M(s) \longrightarrow M^+(aq) + e^-,$$

which represents the reducing power of M in aqueous medium takes place through the following three steps :

1st step. In this step the metal in the solid state, $M(s)$ is evaporated to the gaseous state, $M(g)$. In this process *energy is required* which is called *sublimation energy.* For alkali metals sublimation energies are almost the same (Li = 1.7472 eV, Na = 1.2432, K = 1.0320, Rb = 0.9849, Cs = 0.9024)

$$M(s) + Sublimation\ energy \longrightarrow M(g)$$

2nd step. In this step the outer electron of $M(g)$ obtained in 1st step is pulled off to form $M^+(g)$ cation. In this process as well *energy is required* which is called *ionisation energy.*

$$M(g) + Ionisation\ energy \longrightarrow M(g) + e^-$$

As already said the value of ionisation energy of Li atom is the maximum

3rd step. In this step the gaseous cation, $M^+(g)$ formed in 2nd step gets hydrated to form $M^+(aq)$. In this process energy is *liberated*. This energy is called *hydration energy.*

$$M^+(g) + H_2O \longrightarrow M^+(aq) + Hydration\ energy$$
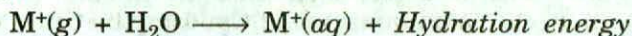
Li^+ ion, being the smallest in size, gets hydrated to the maximum extent (*i.e.* maximum water molecules can attach to Li^+ ion) and hence Li^+ ion has the maximum value of hydration energy (Li = 5.904 eV, Na^+ = 3.792, K^+ = 3.696, Rb^+ = 3.360, Cs^+ = 0.624).

The four energy terms *viz.*, standard oxidition potential ($E°$), sublimation energy (S), ionisation energy (I) and hydration energy (H) are related as :

$$E \quad = \quad H \quad - \quad I \quad - \quad S$$

Oxidation $\quad$ Hydration $\quad$ Ionisation $\quad$ Sublimation

potential $\qquad$ energy $\qquad$ energy $\qquad$ energy

When we compare with each other the values of sublimation energy, ionisation energy and hydration energy of Li atom, we find that its hydration energy value is maximum. Hence, although ionisation energy of Li atom required in 2nd step is also very high, this high value is more than compensated by the large value of hydration energy (of Li^+ ion) released in 3rd step. This maximum value of hydration energy is responsible for the maximum value of oxidation potential of Li atom which makes this atom have the maximum reducing power in contact with water (*i.e.*, in hydrous condition). In other words *the maximum reducing power of Li atom in contact with water is due to its maximum hydration energy.*

Here it should be noted that the reducing power of alkali metals in the dry state (*i.e.*, in anhydrous condition) depends on their ionisation energy values. Li atom which has the maximum ionisation energy has *maximum* reducing power.

10. Electronegativity. We have seen that alkali metals have a strong tendency to lose their ns^1 electron and hence have electropositive character. Because of this electropositive character, these metals have very little electronegative character. In other words alkali metals have *low values* of electronegativity, *i.e.*, they have little tendency to attract electrons towards themselves.

Now since their electropositive character increases from Li to Cs, their electronegative character (*i.e.* electronegativity values) decreases in the same order.

Elements :	Li	Na	K	Rb	Cs
Electronegativity :	1.0	0.9	0.8	0.8	0.7

11. Coloration to the flame. We have seen that the outer electron (*i.e.* ns^1 electron) of the atom of alkali metals is *loosely held with the nucleus* and hence it can be easily *excited* to the higher energy levels even by a small amount of heat energy (*e.g.* by heating the metals or their salts into bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic spectrum and hence the colour is imparted by the atom to the flame. Since the amount of energy absorbed during the excitation process is different in different atoms, different colours are imparted by the atoms to the flame, *e.g.* Li—*Crimson red*, Na—*Golden yellow*, K, Rb and Cs—*Violet*. The property of alkali metals to give colouration in the bunsen flame has been used to detect their presence in salts by a test, known as *flame test*.

12. Electrical conductivity. The individual atoms in the crystal structure of the metals (*i.e.* metal structure) are held together by the valence-electrons. In alkali metals, this binding is relatively weak, since the valence-electrons are loosely held. These loosely held electrons are, therefore, free to move throughout the metal structure with the result that the alkali metals have high conductivity, *i.e.* these are good conductors of electricity and heat.

13. Oxidation states. We have already seen that alkali metals can lose their ns^1 electron quite easily to form the unipositive ion, M^+. The loss of second electron from M^+ cation to form M^{2+} cation is very difficult, since M^+ cation has the configuration of its nearest noble gas which is very stable.

| Atom (M)		M^+ cation	
Li—2, 1		Li$^+$— 2	or $[He]_2$
Na—2, 8, 1		Na$^+$— 2, 8	or $[Ne]_{10}$
K—2, 8, 8, 1		K$^+$— 2, 8, 8	or $[Ar]_{18}$
Rb—2, 8, 18, 8, 1		Rb$^+$— 2, 8, 18, 8	or $[Kr]_{36}$
Cs—2, 8, 18, 18, 8, 1		Cs$^+$— 2, 8, 18, 18, 8	or $[Xe]_{54}$

Thus we see that the alkali metals can lose only one electron (*viz.* ns^1 electron) and hence show only + 1 oxidation state. It is evident from the configurations of

M^+ cations given above that these cations have *no unpaired electrons* and hence are *diamagnetic* and *colourless*. All the compounds of alkali metals are *colourless*, with the exception of those in which the anions are coloured, *e.g.* permanganates and dichromates.

14. Formation of ionic compounds. We have seen that ns^1 electron in alkali metals can be removed quite readily to form M^+ cations and hence these metals show highly electropositive character. Because of this character alkali metals react readily with highly electronegative elements by the transfer of their ns^1 electron to form the ionic compounds.

However alkali metals also show covalent bonding in certain compounds, *e.g.*, the vapours of alkali metals contain *diatomic molecules* like Na_2, Cs_2 in which the atoms are covalently bonded with each other. The strength of covalent bond in these diatomic molecules *decreases from Li to Cs*. Organometallic compounds like CH_3Li, C_2H_5Li, $C_6H_5CH_2Na$ are also covalent compounds.

15. Hydration of ions, hydrated radii and hydration energy. The alkali metals are extensively hydrated :

$$M^+(g) + aq \longrightarrow [M(aq)]^+$$
$$\text{Hydrated}$$
$$\text{cation}$$
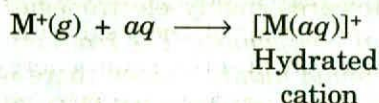
The smaller the cation, the greater is the degree of its hydration. Thus the *degree of hydration of M^+ ions decreases on moving from Li^+ to Cs^+.* As a result of this decrease in hydration degree, the ionic radii of M^+ ions in water (known as **hydrated radii**) decrease from Li^+ to Cs^+.

Hydrated ions	:	$Li^+(aq)$	$Na^+(aq)$	$K^+(aq)$	$Rb^+(aq)$	$Cs^+(aq)$
Hydrated radii (A°) :		3.40 >	2.76 >	2.32 >	2.28 >	2.27

With the decrease of hydrated radii from Li to Cs^+, the ionic conductance of these hydrated cations increases in the order :

$$Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$$
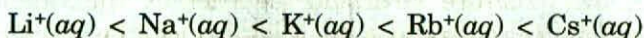
Hydration of ions is an *exothermic process*. The energy released when one gm mole of an ion in the gaseous state is dissolved in water to get it hydrated is called **hydration energy,** *i.e.* it is the energy released in the hydration of $M^+(g)$ ions :

$$M^+(g) + aq \longrightarrow [M(aq)]^+ \text{ +Energy released (Hydration}$$
$$\text{Aqua or} \qquad \text{energy)}$$
$$\text{hydrated}$$
$$\text{cation}$$
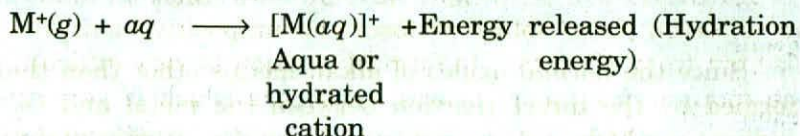
Since the degree of hydration of M ions decreases from Li^+ to Cs^+, the hydration energy of these ions also decreases in the same order :

M^+ ions :		L^+	Na^+	K^+	Rb^+	Cs^+
Hydration energy of M^+ ions (Kcal/mole)	:	121 >	−95 >	−76 >	−69 >	−62

Negative sign associated with these values indicates the release of energy. It is obvious that Li^+ ion has the highest hydration energy and is, therefore, most

extensively hydrated. Due to the extensive hydration of Li^+ ion, several lithium salts are hydrated to form *solvates* (*e.g.* $LiClO_4.3H_2O$) while the salts of other alkali metals are not hydrated.

16. Polarising power of alkali metal cations. When alkali metal cations approach near an anion, the cation attracts the outer-most electrons of the anion and repels the nucleus. Thus the distortion or polarisation of the anion takes place. This distortion results in the sharing of electrons between two oppositely charged ions, *i.e.* the bond between the cation and anion becomes partly covalent in character. In general the smaller cations polarise the anions more effectively than bigger ones. Therefore, the lithium salts are slightly covalent while other alkali metal Baits are ionic.

III. Similarities in Chemical Properties and Gradation in Them

1. Reactivity. We have seen that the first ionisation energies and electronegativities of alkali metals are the lowest of all the elements and their heats of atomisation are relatively low. These properties make the alkali metals highly reactive especially towards highly electronegative elements like Cl_2 and O_2 with which they give *ionic compounds. The reactivity of these metals increases with the increase of their atomic number,* since there is a steady decrease in the ionisation energies, *e.g.*, Li reacts *slowly* with H_2O; Na reacts *vigrously*; K, Rb and Cs reat with *increasing violence.*

2. Formation of oxides (Reaction with O_2 or air). Alkali metals react with O_2 or air rapidly and thus get tarnished due to the formation of their oxide on the surface of the metals. It is for this reason that alkali metals are stored in kerosene or paraffin oil.

Preparation. Li when burnt in O_2 gives mainly *lithium monoxide,* (*normal oxide*) Li_2O.

$$4\ Li + O_2 \longrightarrow 2\ Li_2O$$

Na when burnt in O_2 forms *sodium peroxide,* Na_2O_2

$$2Na + O_2 \longrightarrow Na_2O_2$$

Other alkali metals react with O_2 to form *super oxide* of MO_2 type.

$$M + O_2 \longrightarrow MO_2$$
$$(M = K, Rb, Cs)$$
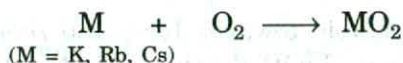
Since the normal oxides of alkali metals other than that of Li (Li_2O) are not formed by the direct reaction between the metal and O_2, they are formed by indirect methods, *e.g.*, *by reducing peroxides, nitrites and nitrates with the metal itself.*

$$2Na_2O_2 + 4Na \longrightarrow 4Na_2O$$
$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$
$$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$$

Properties. Normal oxides (O^{2-}) react with H_2O to form hydroxides by proton exchange.

Gains proton

$$O^{2-} + H_2O \rightleftarrows OH^- + OH^-$$

Loses proton
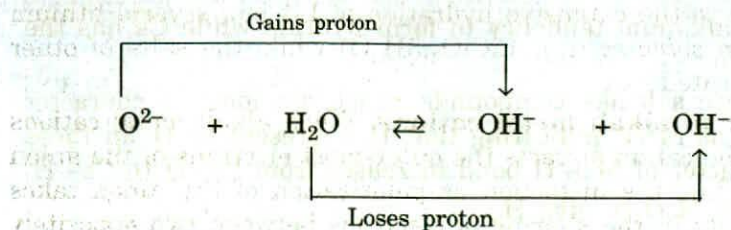
The peroxides (O_2^{2-}) and superoxides (O_2^-) are *strong oxidising agents* and react with H_2O to give H_2O_2 and O_2.

$$\underset{\text{Peroxide}}{O_2^{2-}} + 2H_2O \longrightarrow 2OH^- + H_2O_2$$

$$\underset{\text{Super oxide}}{2[O—O]^-} + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$$

Normal oxides have *anti-fluorite structure* and are ionic in nature since they contain *monoxide ion*, O^{2-}. Peroxides contain *peroxide ion*, O_2^{2-} or $[—O—O—]^{2-}$.

The super oxide ion has a *three-electron bond* as shown below :

$$\left(:\overset{..}{O} \overset{\cdots}{\text{———}} \overset{..}{O}: \right)^{-}$$

The presence of one unpaired electron in it makes this ion *paramagnetic* and *coloured.*

3. Formation of hydroxides. *Preparation.* Hydroxides of alkali metals can be prepared by treating the normal oxides or the metals with H_2O.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$2\,Li + 2H_2O \longrightarrow 2\,LiOH + H_2$$
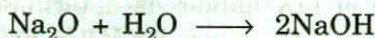
Properties. (i) Alkali metal hydroxides are crystalline solids. These are ionic compounds and are highly soluble in water and alcohol.

(ii) Since the alkali metals are highly electropositive, their hydroxides are the strongest bases known. Since the electropositive character of the metals increases from Li to Cs, *the basic character of their hydroxides increases from LiOH to CsOH.*

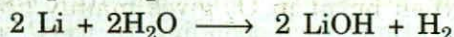(iii) All the hydroxides are stable towards heat and *their thermal stability increases from* LiOH *to* CsOH. e.g., LiOH decomposes at red heat, forming Li_2O while the other hydroxides do not decompose even at red heat. They melt, without decomposing and are good conductors of electricity in the fused state. At 400°C, the hydroxides consist of dimers, $(MOH)_2$.

(iv) With the increase in the size of the cation, the internuclear distance between the oxygen of OH^- ion and the metal cation also increases and hence the ionisation of the hydroxides increases from LiOH to CsOH.

4. Formation of hydrides : Actioia of H_2. *Preparation.* The alkali metals, on heating, react with hydrogen to give white crystalline *salt-like* hydrides. Since the electropositive character of alkali metals increases from Li to Cs, the ease with which these metals react with H_2 to form the hydrides decreases from

Li to Cs, *i.e.*, Li has the maximum tendency to form hydride while Cs has the minimum tendency to do so.

Properties. (*i*) These are salt-like compounds which are ionic in character and hence are represented as M^+H^- indicating that H is present as H^- in these compounds. The ionic character of M —H bond increases from Li—H to Cs—H.

(*ii*) Hydrides react with H_2O to give H_2.

$$MH + H_2O \longrightarrow MOH + H_2$$

Due to this property these are used as reducing agents.

(*iii*) On electrolysis of fused hydrides, H_2 is liberated at the anode

(*iv*) They all dissociate at a very high temperature. The stability of these hydrides decreases from LiH to CsH.

5. Formation of halides : Action of halogens. *Preparation*. Alkali metals combine directly with halogens to form halides of MX type. *As the electropositive character increases from Li to Cs, the ease with which the alkali metals form halides increases from Li to Cs.*

Properties. The halides have generally high melting and boiling points, are good conductors of electricity in the fused state and are readily soluble in water.

The halides essentially have ionic character and are, therefore, represented as M^+X^-. *The ionic character of MX halides increases with the increase of atomic radius on moving down the group.* Thus LiX has the least ionic character (*i.e.*, maximum covalent character) while CsX has the maximum ionic character (*i.e.* minimum covalent character).

Structure. The structure of MX halides is determined by *radius ratio and lattice energy effects*. The radius ratio values for M^+Cl^- chlorides and coordination numbers (C.N's) of M^+ cations corresponding to these values are given below (observed C.N's are also given in the last column).

M^+Cl^- chlorides	M^+/Cl^- radius ratio values	Expected C.N's	Observed C.N's
LiCl	0.328	4	6
NaCl	0.524	6	6
KCl	0.732	6	6
RbCl	0.822	8	6 or 8
CsCl	0.930	8	8

An examination of the table shows that the expected C.N's for Na, K, Rb and Cs are the same as their observed C.N's while for Li the observed C.N. is higher. This anomalous behaviour of Li is due to higher lattice energy of LiCl.

6. Action of liquid ammonia. The alkali metals dissolve in liquid ammonia without the evolution of H_2 gas.

Some of the properties of the solution obtained are given below :

(*i*) *Colour.* *The dilute solutions* of all the alkali metals are blue in colour. The absorption spectra of the solutions of all the alkali metals are the same. The

blue colour of the solutions results from the excitation of free electrons to high energy levels ($1s \rightarrow 2p$ *transition*). This type of transition gives absorption band near 1500 A° in red the region of the spectrum and, therefore, the solution looks blue in the transmitted light. The *concentrated solutions* of alkali metals have *deep bronze colour.*

(*ii*) ***Electrical conductivity.*** The concentrated solutions are remarkably good conductors of electricity. As solutions they conduct electric current better than any other known solutions. The high electrical conductivity of these solutions in due to the presence of *ammoniated electrons,* $[e(NH_3)_y]^-$

$$M + (x + y) NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The presence of *unpaired ammoniated electrons* in the solution makes the solution *paramagnetic.*

(*iii*) ***Stability.*** In the absence of any impurity, these solutions are quite stable, but if kept for a long time or in presence of a catalyst like platinum black, iron oxide etc., or ultraviolet light, these solutions decompose to form metal amide (MNH_2) and H_2.

$$2M + 2NH_3 \xrightarrow{\text{Catalyst}} 2MNH_2 + H_2 \uparrow$$
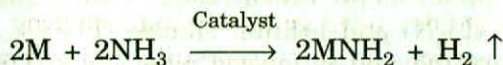
With the increase in the electropositive character of the metal, the stability of these solutions decreases down the group.

(*iv*) ***Reducing power.*** These solutions are good reducing agents. Their reducing property is due to the presence of free ammoniated electrons. Thus these solutions

(*a*) reduce metal halides to free metals.

(*b*) reduce $NaNO_2$ to Na_2NO_2 (sodium hydronitrite) which is an orange coloured extremely explosive solid.

(*c*) remove hydrogen atoms from acetylenic hydrocarbons.

$$CH_3 \equiv CH + e^- \longrightarrow CH_3 \equiv C^- + H$$
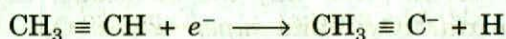
(*d*) remove halogen atoms from organic molecules.

$$C_2H_5Cl + 2e^- \longrightarrow C_2H_5^- + Cl^-$$

(*v*) ***Reversible nature.*** By careful evaporation of these solutions, the alkali metals can be recovered.

7. Formation of amalgams : Action of mercury. Alkali metals dissolve readily in mercurry and form the *amalgams.* This process is very *exothemic.* The formation of amalgams is an example of the formation of an alloy of alkali metals with Hg.

8. Nature of carbonates, bicarbonates and nitrates. The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) are highly stable to heat. *With increase of electropositive character from Li to Cs, the stability of these salts increases.*

Their nitrates decompose on strong heating to the corresponding nitrite and O_2 (Exception is $LiNO_3$).

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2 \uparrow$$
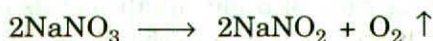
Anomalous Properties of Lithium : Dissimilarities with Other Alkali Metals

From the general properties of alkali metals discussed above it may be seen that Li differs in many properties from the other alkali metals.

The main reasons due to which it shows anomalous properties are :

(a) The size of Li atom and Li^+ ion is the smallest of all the alkali metal ions.

(b) The polarising power of Li ion is the greatest of all the alkali metal ions.

(c) Li has the highest ionisation energy and electronegativity as compared to other alkali metals.

Points of Differences. Following are the main points of differences between Li and other alkali metals.

1. The greatest polarising power of Li^+ ion results in its tendency towards *solvation* and *covalent bond formation*. Thus the salts of Li are covalent and are, therefore, more soluble in non-polar solvents (*e.g.* organic solvents). However, the salts of other alkali metals are insoluble in organic solvents.

2. Li is the only alkali metal which reacts with nitrogen and silicon to form ionic lithium nitride (Li_3N) and lithium silicide (Li_6Si_2). Li_6Si_2 is a dark violet and hygroscopic compound and is formed when Li and Si are heated together.

3. Li is much harder and lighter than the other alkali metals.

4. Its melting and boiling points are rather high and it can be melted in dry air without losing its brilliancy.

5. Due to its high ionisation energy, Li does not react with O_2 below 0°C; reacts *slowly* with H_2O to liberate H_2 or with liquid Br_2.

6. Li is the *least reactive* metal of all the alkali metals.

7. Li^+ ion shows a tendency to form complexes with NH_3, H_2O (to form hydrates) and forms a large number of organo lithium compounds.

8. When burnt in air, Li gives only the *monoxide*, Li_2O (O^{2-}) while other alkali metals form *peroxide* (O_2^{2-}) and *super oxides* (O_2^-).

9. When acetylene gas is passed over heated Li metal, it does not form lithium acetylide, while other alkali metals do form metal acetylides.

10. Li when heated in NH_3 forms imide, Li_2NH while other alkali metals form amides, MNH_2.

11. Li is the only alkali metal whose salts (*e.g.* LiCl) may undergo hydrolysis.

12. Due to the *low electropositive character* of Li, its various salts (*e.g.* Li_2CO_3, $LiNO_3$) are less stable and, therefore, decompose to give oxide, *e.g.*

$$2\ LiOH \xrightarrow{\text{Red heat}} Li_2O + H_2O$$
$$4\ LiNO_3 \longrightarrow 2\ Li_2O + 4\ NO_2 + O_2$$
$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
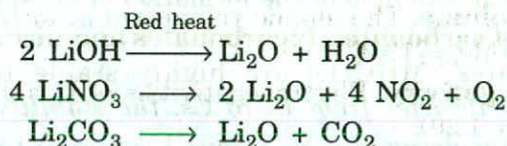
13. Some of the salts of Li like Li_2CO_3, Li_3PO_4 and LiF are *insoluble* in H_2O while the corresponding salts of other alkali metals are *soluble*. The solubility of the salts of other alkali metals is due to the weak electrostatic force of attraction.

14. Li_2O dissolves in H_2O quietly while other oxides do go more energetically.

15. LiOH is considerably *less soluble* in H_2O and is a *much weaker base* than NaOH or KOH.

LiOH decomposes at red heat forming Li_2O, whereas other alkali metal hydroxides sublime unchanged as $(MOH)_2$.

16. LiCl is deliquescent and is soluble in alcohol as well as in pyridine. It forms the hydrate, $LiCl.2H_2O$. Chlorides of other alkali metals do not show this behaviour.

17. $LiCO_3$ decomposes on heating to from Li_2O and CO_2 while other carbonates do not decompose. The small size of Li^+ io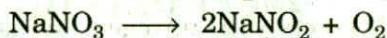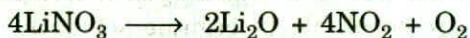n makes Li_2O lattice *more stable* than Li_2CO_3 lattice. However, the large size of other alkali metal ions make M_2O lattices *less stable* than M_2CO_3 lattice and hence they decompose.

18. $LiNO_3$, on heating, forms Li_2O, NO_2 and O_2 while other alkali metal nitrates form nitrites and O_2.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$
$$NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

19. Lithium hydro suiphide, LiSH is thermally unstable while the hydro sulphides of other alkali metals are so stable that they can be fused without extensive decomposition.

20. Lithium per chlorate, $LiClO_4$ is remarkably soluble in alcohol, acetone and ethyl acetone, while the per chlorates of other alkali metals are almost insoluble in these solvents. The solubility of $LiClO_4$ is due to strong solvation of Li^+ ion.

21. Li_2SO_4 is the only alkali metal sulplate which does not form double salts such as alums.

Diagonal Relationship of Li with Mg : Similarities between Li and Mg

It has been observed that Li resembles more in its many properties with the element, Mg, lying at its right in 3rd period (*i.e.* diagonally opposite element) than with other members of its own sub-group I A. This type of similarity between Li and Mg is called diagonal relationship.

Following are the points which show that Li resembles Mg in many respects, *i.e.* Li and Mg have diagonal relationship.

1. Atomic and ionic radii. The atomic radii of Li and Mg are comparable (Li = 1.225 Å, Mg = 1.365 Å). The ionic radious of Li^+ (= 0.60 Å) is closer to that of Mg^{2+} (= 0.65 Å) than to that of Na^+ (= 0.95 Å).

2. Atomic volume. The atomic volumes of solid Li and Mg are quite similar (Li = 12.97 c.c., Mg = 13.97 c.c.)

3. Electronegativity. Electronegativities of Li and Mg are quite comparable (Li = 1.00, Mg = 1.20).

4. High polarising power (*i.e.* ionic potential) and its effects. Li^+ and Mg^{2+} both the ions have high polarising power, *i.e.*, charge/radius ratio of both the ions is high.

It is due to this high polarising power that both the ions have great tendency to form hydrates with a definite number of water molecules, *i.e.* a number of salts of these ions crystallise from water with a definite number of water molecules of crystallisation to form the hydrates. Some of the hydrates are given below :

$$LiCl.2H_2O; \quad LiClO_4.3H_2O; \quad LiNO_3.3H_2O$$

$$MgCl_2.6H_2O; \quad Mg(ClO_4)_2.6H_2O; \quad Mg(NO_3)_2.6H_2O$$
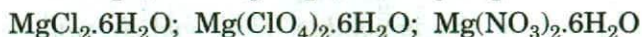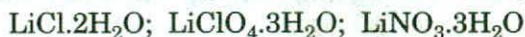
It is also because of the strong polarising power of Li^+ and Mg^{2+} ions on the charge cloud of halide ions that their halides have appreciable covalent character.

Because of the strong polarising power of Li^+ and Mg^{2+} ions on the charge cloud of the ions like NO_3^- and CO_3^{2-}, their nitrates and carbonates show *low thermal stability*, *i.e.* they decompose easily on heating to give out NO_2 and CO_2 respectively.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

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

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$
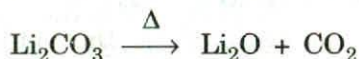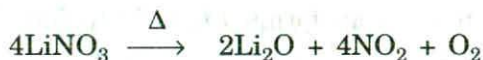
5. Enthalpies of vaporisation. Enthalpies of both the elements are comparable.

6. Melting points. Li and Mg have higher melting points than the other members of their respective groups. Their melting points are comparable with each other (Li = 1336°C, Mg = 1100°C).

7. Hardness. Li and Mg are harder than the other members of their respective groups. Hardness of Li is comparable with that of Mg.

8. Action of H_2O. Like Mg, Li decomposes water *slowly* to liberate H_2.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$
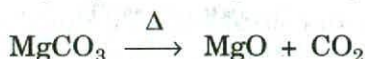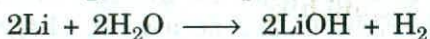
9. Action of N_2. Both the elements combine with N_2 on heating to form their *ionic nitrides*, Li_3N and Mg_3N_2.

Both the nitrides readily decompose H_2O to liberate NH_3.

$$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$
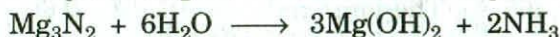
10. Action of Cl_2. Both the elements form their chlorides, LiCl and $MgCl_2$, on heating with dry Cl_2,

$$2Li + Cl_2 \longrightarrow 2LiCl$$

$$Mg + Cl_2 \longrightarrow MgCl_2$$

Both the chlorides have many similar properties, *e.g.* (*i*) Both are deliquescent solids (*ii*) Both are soluble in water and alcohol (*iii*) Both form hydrates *viz.* LiCl. $2H_2O$ and $MgCl_2.$ $6H_2O$ (*iv*) Both undergo hydrolysis in hot water.

11. Combination with carbon. On heating, both the elements combine with carbon to form the carbides, Li_2C_2 and MgC_2.

12. Action of air or O_2. Li, when burnt in air or O_2, forms *lithium oxide*, Li_2O (which is a *normal oxide*). Mg ribon, under similar conditions, forms *magnesium oxide*, MgO (which is also a *normal oxide*). Like Li_2O, MgO does not combine with further quantity of O_2 to form the *peroxide* (M_2O_2) or *superoxide* (MO_2).

13. Nature of hydroxides. Of all the alkali metal hydro-oxides, LiOH is *less soluble in water, less basic and decomposes on heating* to form Li_2O. Likewise $Mg(OH)_2$ is also *sparingly soluble, less basic* and *decomposes on heating* to form MgO.

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

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$
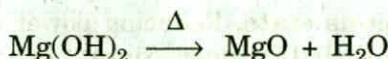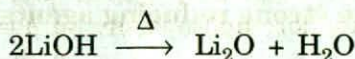
14. Solubility of salts. The solubility of lithium salts resembles that of the corresponding magnesium salts, *e.g. fluorides, carbonates* and *phosphates* of the both the metals are *insoluble in water* while the *chlorides, bromides, iodides and perchlorates are soluble in oxygenated organic solvents.*

15. Unstability of hydrosulphides. Lithium hydrosulphide, LiSH is unstable under ordinary conditions. Magnesium hydrosulphide, $Mg(SH)_2$, is also unstable in aqueous solution and decomposes to form $Mg(OH)_2$, liberating H_2S

$$Mg(SH)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2H_2S$$

16. Like $MgSO_4$, Li_2SO_4 does not form alums.

17. Due to their covalent nature, the alkyls of Li and Mg are soluble in organic solvents, *e.g.* $LiAlH_4$, RMgX are soluble in either. Alkyls of Li undergo reactions similar to Grignard reagents (RMgX).

18. Li^+ and Mg^{2+} ions are strongly hydrated.

Cause of Diagonal Relationship

Why Li resembles in its many properties with its diagonally opposite element *viz.*, Mg can be explained as follows on the basis of the *concept of electronegativity.*

We know that electronegativity increases from left to right in a period and decreases on descending a group. Thus, Be is more electronegative than Li (Be = 1.5; Li = 1.0; Be > Li) and Mg is slightly less electronegative than Be. (Be = 1.5, Mg = 1.2; Be > Mg). Li and Mg being slightly less electronegative than Be have almost the same value of electronegative and hence have many similar properties, *i.e.* they show diagonal relationship with each other.

Position of Lithium in the Periodic Table

Li is present in group IA with Na, K, Rb, Cs and Fr, Li resembles not only with the elements of its own sub-group but also resembles with its diagonally related element namely Mg. The position of Li in the periodic table is, therefore, justified because of the following facts.

(*i*) It resembles with the elements of its own sub-group.

(*ii*) It shows a regular gradation with the elements of its own sub-group.

(*iii*) It resembles with the diagonally related element namely Mg.

(*i*) and (*ii*) have been discussed under *"Position of Alkali Metals in the Period Table"* while (*iii*) has been discussed under *"Diagonal Relationship of Li with Mg"*.

Questions with Answers

Q.1 Explain the following :

(*i*) **Alkali metals are strong reducing agents in the gaseous state and in the aqueous solution ?**

Ans : (*i*) **In the gaseous state.** Reducing power of alkali metals (M) in the gaseous state depends on their IE values. Since these metals have low IE values, they can lose their ns^1 electrons quite readily to get oxidised to M^+ (*g*) ion and hence act as strong reducing agents.

(*ii*) **In aqueous solution.** Reducing power of alkali metals in aqueous solution depends on their E^o_{ox} values for the oxidation half reaction, M (*s*) → M^+ (*aq*) + e^-. Since E^o_{ox} values for alkali metals are fairly high, these metals can readily be oxidised to M^+ (*aq*) in aqueous solution and hence act as strong reducing agents.

(*iii*) **In the gaseous state, the reducing power (R.P.) of alkali metals is in the order : Li < Na < K < Pb < Cs.**

Ans : We know that R.P. of alkali metals in the gaseous state depends on the value of their IE values. Lower is the value of IE of an alkali metal [M (*s*)], more quickly it will be oxidised to M^+ (*g*) ion and hence higher will be its R.P. Thus with the decrease of IE values, the R.P. of alkali metals increases. Now since IE values decrease on moving down the group from Li to Cs (Li = 520.3, Na = 495.3, K = 418.9, Rb = 403.0, Cs = 375.7 KJ mol^{-1}), the R.P. of these metals increases in the same direction. Thus :

$$Li < Na < K < Rb < Cs$$

R.P. increase $\longrightarrow$

This order shows that Li metal is the weakest R.A. in the gaseous state.

(*iv*) **In the aqueous solution, the reducing power (R.P.) of alkali metals is in the order : Li > Na < K < Rb.**

Ans : We know that R.P. of alkali metals in aqueous solution depends on E^o_{ox} value for the oxidation half reaction, M (*s*) M^+ (*aq*) + e^-. Higher is the value of E^o_{ox}, more quickly the metal, M (*s*) is oxidised M^+ (*aq*) ion and hence higher is the R.P. of the metal. E^o_{ox} values for M/M^+ couples are as : Li/Li^+ = +3.04 V, Na/Na^+ = +2.71V, K/K^+ = +2.92V and Rb/Rb^+ = +2.99V. Now since E^o_{ox} for Li/Li^+ couple is the maximum, Li metal is oxidised to Li^+ (*aq*) ion most readily and hence is the strongest reducing agent (R.A.). Since E^o_{ox} values for other couples increase from Na/Na^+ to Rb/Rb^+, the R.P. of Na, K and Rb also increases from Na to Rb (Na < K < Rb). Thus the overoll order of R.P. of alkali metals in aqueous solution is as :

$$\text{Li} \quad | \quad > \text{Na} < \text{K} < \text{Rb}$$

Maximum R.P. | — R.P. increases →

(Strongest R.A.) |

Note : The oxidation half-reaction, $M\ (s) \to M^+\ (aq) + e^-$ is actually the sum of the following reactions :

$M\ (s) \longrightarrow M\ (g)$; ΔH = Energy absorbed

= Sublimition energy of $M\ (s)$ atom.

$M\ (g) \longrightarrow M^+\ (g) + e^-$; ΔH = Energy absorbed

= IE of $M\ (g)$ atom

$M^+\ (g) + aq \longrightarrow M^+\ (aq)$; ΔH = Energy released

= Hydration energy of $M^+\ (g)$ ion

On adding : $M\ (s) \longrightarrow M^+\ (aq) + e^-$
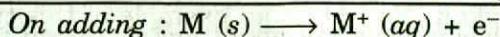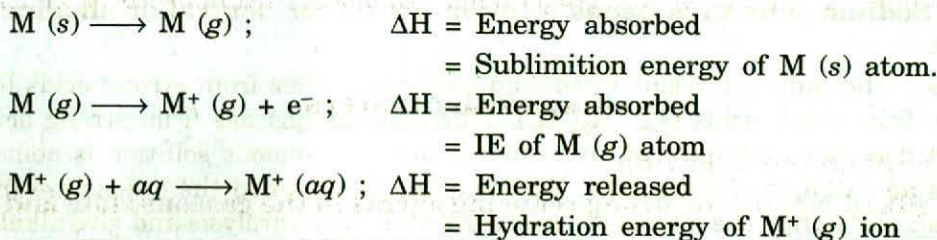
Since Li^+ ion is the smallest in size, the hydration energy of this ion is maximum and hence E°_{ox} value for the oxidation half-reaction, $Li\ (s) \to Li^+\ (aq) + e^-$ or for Li/Li^+ couple is also maximum.

(iv) Alkali metals are paramagnetic but their salt are diamagnetic.

Ans : Alkali metals contain one upaired electron (ns^1) and hence are paramagnetic. However, during salt formation, this unpaired electron is transferred to the non-metalic atom forming its anion. As a result, salt has paired electrons both in the cation as well as in the anion and hence alkali metals salts are diamagnetic in nature.

(v) Alkali metals impart colour to the flame.

Ans : Alkali metals have low ionization energies. Their valence electrons easily absorb energy from the flame and are excited to higher energy levels. When they return to the ground state, the energy is emitted back.

(vi) Sodium has higher melting point than potassium.

Ans : On going from Na to K, the size of the atom increases and hence the metallic bonding weakens. In other words sodium has higher melting point than potassium because of stronger metallic bonding.

(vii) Sodium fire in the laboratory should not be extinguished by pouring water.

Ans : Sodium reacts violently with water producing H_2 gas $(2\ Na + 2\ H_2O \to 2\ NaOH + H_2)$ which also cathes fire. As a result, the fire spreads rather than being extinguished. Therefore, H_2O should not be used for extinguishing sodium fire. Instead pyrene (CCl_4) should be used.

(viii) Table salt gets wet in rainy season.

Ans : Pure NaCl is not hygroscopic but table salt is impure NaCl containing impurities of Na_2SO_4, $CaSO_4$, $MgCl_2$ and $CaCl_2$. All of these, being hygroscopic, absorb moisture from air in rainy season. As a result, table salt gets wet.
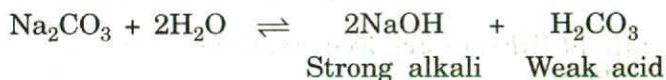
(ix) Alkali metals donot occur free in nature ?   (Roorkee 1980)
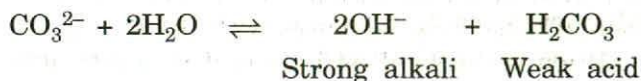
Ans : Since alkali metals are placed at the extrem left of the periodic table, they have the lowest IE values. Due to lowest IE values, these metals are extremely reactive. For example they readily combine with O_2, moisture and CO_2 of the atmosphere and many other substances. Due to their high reactivity, these matals donot occur free in nature.

(x) Sodium salts in aqueous solution are either neutral or alkaline in nature.

Ans : The anions present in sodium salts are either from strong acids (e.g. HCl) or from weak acids (e.g. H_2CO_3). When the anions are from strong acids, the salt does not undrego hydrolysis and hence the aqueous solution is neutral. NaCl is an example of such salts. On the other hand, when the anions are from the weak acids, then the anions of these salts undergo hydrolysis and give alkaline solution due to the formation of strong akali. Na_2CO_3 is an example of this type of salts.

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$$
$$\text{Strong alkali} \quad \text{Weak acid}$$

or

$$CO_3{}^{2-} + 2H_2O \rightleftharpoons 2OH^- + H_2CO_3$$
$$\text{Strong alkali} \quad \text{Weak acid}$$

(xi) Alkali metals are obtained by the electrolysis of their moten salt and not by the electrolysis of their aqueous solution.

Ans : The aqueous solution of alkali metal salt contains alkali metal cation, salt anions, H^+ and OH^- ions. When this solution is electrolysed, H^+ ions present in the solution are discharged at cathode as H_2 in preference to alkali metals cations, since discharge potential of H^+ ions is lower than that of alkali metal cations. Thus instead of getting alkali metal on cathode, we get H_2 gas. On the other hand, when a molten salt of alkali metal is electrolysed, only alkali metal cation gets discharged on cathode, since the salt does not contain H^+ ions.

(xii) When K, Rb and Cs are heated in the excess of air, they prefer to form superoxides ($O_2{}^-$) and not oxides (O^{2-}) and peroxides ($O_2{}^{2-}$).

Ans : K^+, Rb^+ and Cs^+ ions are large cations. Hence these cations stabilise large anions. Now since superoxide ion ($O_2{}^-$) is larger than oxide (O^{2-}) and peroxide ($O_2{}^{2-}$) ions, K^+, Rb^+ and Cs^+ ions stabilise the larger anoin viz superoxide ion ($O_2{}^-$).

(xiii) Superoxides of alkali metals are paramagnetic but normal oxides are diamagnetic.

or KO$_2$ is paramagnetic.

Ans : Superoxides of alakli metals contain superoxide ion ($O_2{}^-$) whose structure

is $\ddot{\text{:O}} - \ddot{\text{O}}\ddot{\text{:}}$ or $\left(\ddot{\text{:O}} \cdots \ddot{\text{O}}\ddot{\text{:}}\right)^-$. Since this structure has one unpaired electron,

alkali metal superoxides are paramagnetic. Normal oxides of alkali matals contain

oxide ion (O^{2-}) whose structure is $\overset{\cdot\cdot}{\underset{\cdot\cdot}{:O:}}{}^{2-}$. Since this structure has all the electrons

in the paired state, alkali metal oxides are diamagnetic.

Q.2 Give the reasons for the following :

(i) Alkali metals are used in photoelectric cells.   (*Kurukshetra 1995*)

or Cerium can be used in photoelectric cells but lithium cannot.

Ans : Since, in each period of the periodic table, the alkali metals have the lowest values of IE, these metals can release electrons readily when exposed to light even of low energy. Since Li has the highest value of IE amongst alkali metals, this metal cannot release the electron readily and hence cannot be used in photoelectric cells. On the other hand, since Cs has the lowest value of IE, this metal can readily release the electron and hence is used in photoelectric cells.

(ii) Lithium is most extensively hydrated among alkali metals.

(*M.D. Rohtak 1994*)

or Several salts of lithium are hydrated while the salts of other alkali metals are not hydrated.

Ans : We know that alkali metal ions are hydrated in aqueous solution. The degree of hydration of these ions decreases with the increase in the size of these ions. Thus since Li^+ ion is the smallest in size, it is hydrated in aqueous solution to the maximum extent. It is due to the maximum hydration of Li^+ ion that its several salts are hydrated (*e.g.* $LiClO_4$. $3 H_2O$). Since other alkali metals ions are hydrated to lesser extent, their salts are not hydrated.

(iii) In aqueous solution, Li^+ ion has the lowest mobility.

Ans : Among alkali metal cations (M^+), since Li^+ ion is the smallest ion, it is hydrated in aqueous solution to the maximum extent. Due to its maximum hydration, the hydrated Li^+ ion, Li^+ (*aq*) becomes heaviest and hence ionic mobility (conductance) of Li^+ ion in aqueous solution is the lowest.

(iv) In aqueous solution, Li^+ ion moves through the solution less rapidly than other alkali metal ions.

Ans : Since Li^+ ion is the smallest in size than other alkali metals ions, it gets hydrated by H_2O molecules to the maximum extent and hence its hydrated ion, [Li (*aq*)]$^+$ is the heaviest than other hydrated ions. Due to its heaviest nature, [Li (*aq*)]$^+$ ion moves through the solution less rapidly than each of the other hydrated ions.

(v) Conductivity of Li^+ ion in aqueous solution is smaller than that of Cs^+ ion, though the former ion is much lighter than the latter ion.

(*Kurukshetra 1994, Madras 1995*).

Ans : We know that alkali metal ions are hydrated in aqueous solution. The degree of hydration of these ions decreases with the increase in their size. Thus, since Li^+ ion is smaller in size than Cs^+ ion, Li^+ ion is hydrated to greater extent than Cs^+ ion. Due to greater hydration of Li^+ ion, Li^+ (*aq*) ion becomes heavier than Cs^+ (*aq*) ion [Li^+ (*aq*) > Cs^+ (*aq*)]. Being heavier, Li^+ (*aq*) ion has smaller

conductivity than Cs^+ (aq) ion. Thus the conductivity of Li^+ ion in aqueous solution is smaller than that of Cs^+ ion.

(vi) Na is less reactive than K.

Ans : We know that electropositive character and reactivity of alkali metals depend on the ease with which the metal loses its ns^1 electron. Since the ionisation energies of alkali metals decrease down the group, the ease with which these metals lose their ns^1 electron increases in the same direction and hence electropositive character and reactivity of these metals also increase in the same direction. Thus, since Na has higher IE value than K, this metal is less reactive than K.

(vii) The softness of alkali metals increases down the group with increasing atomic number. *(I.I.T. 1986)*

Ans : Softness of metals depends on the strength of metallic bond holding the atoms of the metal together. Since the size of alkali metal atoms increases down the group, the metallic bond holding the atoms together becomes weaker and weaker. With the weakening of metallic bond, the softness of akali metals increases.

(viii) Na metal can be used for drying directly ether but not ethanol ? *(I.I.T. 1982)*

Ans : Na-metal can be usd for drying diethyl ether, since the metal does not react with this compound. On the other hand, since Na-metal reacts with ethanol (C_2H_5OH) as shown below, this metal cannot be used for drying ethanol.

$$Na + 2\ C_2H_5OH \longrightarrow 2\ C_2H_5ONa + H_2$$

(ix) Alkali metals are normally kept in kerosene oil.

Ans : This is because in the air they are easily oxidized to oxides which may dissolve in the moisture of the air to from hydroxides. These hydroxides combine with CO_2 present in the atmosphere and form M_2CO_3.

$$4M + O_2 \xrightarrow{\quad Oxidation \quad} 2\ M_2O$$

$$M_2O + H_2O \longrightarrow 2\ MOH$$

$$2\ MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$$
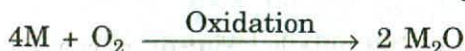
(x) Alkali metals do not form bivalent cation (M^{2+}). *(Banglore 1995, Punjab 1996, Magadh 1996).*

Ans : General electronic configuration of alkali metal atoms is..., $(n-1)s^2$ $(n-1)p^6, ns^1$. For the formation of bivalent cation (M^{2+}) two electrons have to be removed from the alkali metal atoms as shown below :

$$M\ (g) \xrightarrow[(-e^-)]{+IE_1} M^+\ (g) + e^-$$

$$M^+\ (g) \xrightarrow[(-e^-)]{+IE_2} M^{2+}\ (g) + e^-$$
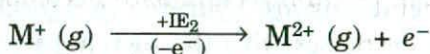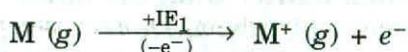
For the formation of M^+ (g) ion the electron is removed from ns orbital. Due to low IE values ns^1 electron is easily lost and hence M^+ (g) ion is quite easily formed.

On the other hand, for the formation of M^{2+} (g) ion the electron is removed from $(n - 1)s^2$ $(n - 1)p^6$ configuration (noble gas configuration). Since this configuration is extremely stable, IE_2 values are fairly high and hence M^{2+} (g) ion is not formed.

(xi) Solution of alkali metals in liq. NH_3 are blue coloured, conducting, paramagnetic and has reducing natrue.   **(G.N. Dev 1994)**

Ans : All alkali metals dissolve in anhydrous liq. NH_3 and give alkali metal – NH_3 solutions. In these solutions ammoniated cations, $[M (NH_3)_x]^+$ and ammoniated electrons, $[e (NH_3)_y]^-$ are fromd.

$$M \longrightarrow M^+ + e^-$$
$$M^+ + xNH_3 \longrightarrow [M (NH)_x]^+$$
$$e^- + yNH_3 \longrightarrow [e (NH_3)_y]^-$$

On adding : $M + (x + y) NH_3 \longrightarrow [M (NH_3)_x]^+ + [e (NH_3)_y]^-$

These solutions have the follwoing characteristics which can be explained on the basis of the presence of $[M (NH_3)_x]^+$ and $[e (NH_3)_y]^-$ in the solution.

(i) Blue Colour. (a) These solutions have blue colour. This colour is due to the excitation of free $[e (NH_3)_y]^-$. When ordinary light falls on these solutions, the free ammoniated electrons, $[e (NH_3)_y]^-$ get exited to higher energy levels by absorbing energy. Since the absorption of energy t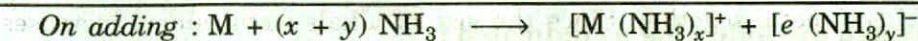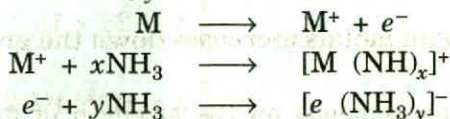akes place in red portion of the visible region, the colour of the transmitted light is blue due to which the solution appears blue. In short we can say that the blue colour of the solution is due to the presence of ammoniated electrons.

(b) With the increase in the concentration of alkali metal in liq. NH_3, the blue colour starts changing to that of metallic copper after which no more metal dissoves in liq. NH_3.

(ii) Conducting nature. The blue solution is conducting due to the presence of $[M (NH_3)_x]^+$ and $[e (NH_3)_y]^-$ in solution.

(iii) Paramagnetic nature. The blue solution is paramagnetic due to the presence of unpaired electrons in the cavities of ammonical solution.

(iv) Reducing property. The blue solution slows strong reducing properties due to the presence of free ammoniated electrons, $[e (NH_3)_y]^-$ in the solution.

(xii) LiF is most soluble among the fluorides of alkali metals.

Ans : Due to lesser degree of polarization, LiF will be most ionic hence most soluble in water.

(xiii) $NaHCO_3$ is known in solid state but $Ca(HCO_3)_2$ is not isolated in solid state.

Ans : Calcium bicarbonate is fromed only when CO_2 is passed through aqueous solution of $Ca(OH)_2$. On evaportion, calcium bicarbonate decomposes to calcium carbonate.

(xiv) Li is the only alkali metal that forms nutride directly.

Ans : Li and Mg have diagonal relationship with each other. Now since Mg forms nitride (Mg_3N_2), Li also forms nitide (Li_3N)

$$6Li\ (s) + N_2\ (g) \xrightarrow{\ \Delta\ } 2Li_3N\ (s)$$

Q.3 Atomic radius of Li atom is 1.23A° and ionic radius of Li⁺ ion is 0.76 A°. Calculate the volume occupied by valence electron.

Ans : The electronic configurations of Li atom and Li⁺ ion are as : Li = $1s^2$, $2s^1$ and Li⁺ = $1s^2$. Obviously valence electron is $2s^1$ electron. Hence :

Volume occupied by valence electron = Volume of Li atom − Volume of Li⁺ ion

$$= \frac{4}{3}\pi (r_{Li})^3 - \frac{4}{3}\pi (r_{Li^+})^3$$

$$= \frac{4}{3}\pi (1.23 \times 10^{-8})^3 - \frac{4}{3}\pi (0.76 \times 10^{-8})^3$$

$$= \frac{4}{3}\pi \times 10^{-24} [(1.23)^3 - (0.76)^3] \text{ (Ans)}.$$

Q.4 Arrange the following as indicated :

(a) LiOH, NaOH, KOH (Increasing order of solubility in water)

(b) $LiHCO_3$, $NaHCO_3$, $KHCO_3$ (Increasing order of solubility in water)

(c) Li_2CO_3, Na_2CO_3, K_2CO_3 (Increasing order of solubility in water)

(d) LiCl, NaCl, KCl, RbCl, CsCl (Increasing order of lattice energy)

(e) LiF, LiCl, LiBr, LiI (Increasing order of lattice energy)

(f) NaF, NaCl, NaBr, NaI (Increasing order of lattice energy)

(g) Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ (Increasing order of size of hydrated ion).

Ans :   (a) LiOH < NaOH < KOH

(b) $LiHCO_3$ < $NaHCO_3$, $KHCO_3$

(c) Li_2CO_3 < Na_2CO_3 < K_2CO_3

(d) CsCl < RbCl < KCl < NaCl < LiCl

(e) LiI < LiBr < LiCl < LiF

(f) NaI < NaBr < NaCl < NaF

(g) Cs⁺ < Rb⁺ < K⁺ < Na⁺ < Li⁺.

Q.5 Arrange the follwoing as specified :

(i) MgO, SrO, K_2O, NiO and Cs_2O (increasing order of basic character)
[I.I.T 1991]

(ii) LiCl, LiBr, LiI (decreasing order of order of covalent character)
[Roorkee 1987]

(iii) KCl, KBr, KI (decreasing order of solubility in water)

(iv) $NaHCO_3$, $KHCO_3$, $Mg (HCO_3)_2$, $Ca (HCO_3)_2$ (Increasing order of solubility)
[M.L.N.R. 1984]

(v) LiF, NaF, KF, RbF and CsF (increasing order of lattic energy)

(vi) Li, Na, K (decreasing order of reducing nature in solution)

Ans : (i) NiO < MgO < SrO < K_2O > Cs_2O

(ii) LiI > LiBr > LiCl

(iii) KI > KBr > KCl

(iv) $NaHCO_3 < KHCO_3 < Mg\ (HCO_3)_2 < Ca(HCO_3)_2$

(v) $CsF < RbF < KF < NaF < LiF$

(vi) $Li > K > Na$

Q.6 Amongst LiF and LiI which has more covalent character and why ?
[Roorkee 1980; I.I.T. 1986]

Ans : LiI is more covalent . According to Fajan's rule, Li^+ will be able to polarise the bigger ion, I^-, more than the smaller ion, F^-. More polarisation brings more covalent character.

Q.7 Calculate heat of formation of NaCl from the following data. Hydration energy of Na^+ = –389.4 KJ mol⁻¹, hydration energy of Cl^- = –382.3 KJ mol⁻¹ and lattice energy of NaCl = –776 KJ mol⁻¹.

Ans : We know that heat of solution of NaCl, $[\Delta H_{solu}]_{NaCl}$ is given by :

$$[\Delta H_{solu}]_{NaCl} = \text{Hydration energy of NaCl} - \text{Lattic energy of NaCl}$$

$$= [\Delta H_{hyd}]_{NaCl} - [\Delta H_{lat}]_{NaCl}$$

$$= [(\Delta H_{hyd})_{Na}{}^+ + (\Delta H_{hyd})_{Cl}{}^-] - [\Delta H_{lat}]_{NaCl}$$

$$= [-389.4 + (-382.3)] - (-776.0)$$

$$= -7771.7 - 776.0 = + 4.3 \text{ KJ mol}^{-1} \text{ (Ans)}.$$

University Questions

1. Explain the following :

(i) Alkali metals are obtained by the electrolysis of their molten salts and not by the electrolysis of their aqueous solution.   (*REE 84*)

(ii) Alkali metals show on oxidation station + 1 only.

OR

Alkali metals are univalent.   (*Agra 89*)

(iii) Lattice energy of the fluorides of alkali metals decreases from LiF (= 1032 kJ mole⁻¹) to CsF (726 kJ mol⁻¹).

(iv) Degree of hydration of alkali metal ions decreases from Li^+ to Cs^+.

(v) Alkali metals are good reducing agents.   (*Agra 89, REE 81, 83*)

(vi) Alkali metals have low m.pts.

(vii) Alkali metals give characteristic colour to the bunsen flame.

(viii) Alkali metals have body-centered cubic structures.

(ix) Na is stored under kerosene.   (*IIT 70*)

(x) Alkali metals do not occur free in nature.   (*REE 80*)

(xi) Alkali metals form M^+ cations instead of M^{2+} cations.

(xii) Alkali metals do not form dipositive ions. (*Raj. 82S, 86; Jodhpur 84*)

(xiii) Solutions of alkali metals in liquid NH_3 are blue in colour.

(xiv) Group IA elements are poor complexing agents.   (*Jodhpur 86*)

(xv) Alkali metals produce different colours in Bunsen flame. (*Delhi 83*)

(xvi) Alkali metals are active in metallic character.   (*MD Rohtak, 83*)

(xvii) Alkali metals lose electrons even when exposed to light.

(*MD Rohtak 84*)

(*xviii*)Li^+ ions is most extensively hydrated amongst alkali metals.
$$\text{(Delhi 85)}$$
(*xix*) Of all the alkali metals, Li has the highest oxidation potential.
$$\text{(Meerut 83)}$$
(*xx*) Li^+ ion in aqueous solution are the poorest conductor of electricity as compared to other alkali aqua ions.   (*Delhi 88*)
(*xxi*) Alkali metals have low ionisation potentials.   (*Agra 89*)

2. Explain the following :
   (*i*) Salts of lithium are covalent while those of other alkali metals are ionic.
   (*ii*) Li-salts are insoluble in H_2O while those of other alkali metals are soluble.
   (*iii*) In general alkali metals form ionic compounds.   (*Agra 89*)

3. Explain the following :
   (*i*) Li, on burning in O_2, gives normal oxide (mono oxide, Li_2O), Na forms peroxide (Na_2O_2) and Rb and Cs form Super oxides (MO_2).
$$\text{(Punjab 85)}$$
   (*ii*) Super oxides of alkali metals are paramagnetic in character.
$$\text{(Delhi Hons. 85)}$$

4. How does Li_2CO_3 differ from K_2CO_3?   (*Madras 86*)

5. Explain the following:
   (*i*) Li_2CO_2, on heating, gives CO_2 but the carbonates of other alkali metals do not.
   (*ii*) L_2CO_2 decomposes on heating to give CO_2 while Na_2CO_3 does not decompose.   (*GND 82*)
   (*iii*) $NaHCO_3$ is quite stable and exists as solid while $LiHCO_3$ exists only in aqueous solution.   (*Delhi Hons. 82*)

6. Explain the following :
   (*i*) In spite of the fact that Li is an alkali metal, lithium halide is covalent in nature.   (*Punjab 85, Jodhpur 86*)
   (*ii*) LiCl is soluble in organic solvents while the chlorides of other alkali metals are not.   (*Meerut 83*)
   (*iii*) Li is soluble in water while LiF is not.   (*Jodhpur 87*)

7. Explain the following giving appropriate reason for your answer : Super oxides of alkali metals are coloured.   (*Delhi 99*)

8. Which is a stronger base: KOH or $Ba(OH)_2$?   (*Delhi 99*)

9. Hydroxides of 1st group are strong bases. Explain why.
$$\text{(Himachal Pradesh 99)}$$

10. Explain the following :
    (*a*) Lithium forms normal oxide, sodium forms peroxide and potassium, rubedium and caesium for superoxides.
    (*b*) Li_2CO_3 is unstable while other alkali metal carbonates are relatively more stable.
    (*c*) Alkali metals give coloured solutions in liq. NH_3.
$$\text{(Himachal Pradesh 2000)}$$

11. Explain why Li resembles Mg in certain properties.   (*Lucknow 2001*)

12. Alkali metals are univalent strong reducing agents and have low ionisation potential. Explain.   (*C.S.J.M. Kanpur 2007*)

13. Write a short note on "Diagonal relationship between Li and Mg".
$$\text{(C.S.J.M. Kanpur 2005, 2006, 2009)}$$

14. Discuss the position of Li in the period table.   (*Meerut 2009*)

Chemistry of Lithium and Its Compounds

<div align="center">| Lithium |</div>

History

While analysing the minerals *petalite* and *spodumene* in the laboratory of *Berzelius, Arfvedson* in 1817 resported the discovery of a new metal which was called *lithium*. Later on *Bunsen* and *Mathiessen* isolated lithium by the electrolysis of fused lithium chloride in 1855. The word lithium which means *stony* was given to this metal because it was then believed that this metal was confined to the mineral kingdom only.

Occurrence

Lithium is rare but widely distributed in the earth crust. In traces it occurs in soils, milk, blood, muscular tissues, lungs, seawater, meteorites and ashes of plants like sugar, beat, tobacco, coffee and in many mineral springs etc. Important minerals of lithium are :

1. Aluminosilicates. These include the following minerals.

(a) *Lepidolite or lithia mica*, $(Li, Na, K)_2 Al_2 (SiO_3)_3 (F, OH)_2$. It contains 2˘6% of Li.

(b) *Spodumene*, $LiAl(SiO_3)_2$. It contains 3.8˘5.6% of Li.

(c) *Petalite*, $Li Al(Si_2O_5)_2$. It contains 2˘3% of Li.

2. Phosphates. These are mainly of the following minerals.

(a) *Triphylite*, $(Li, Na)_3PO_4 . (Fe, Mn)_3(PO_4)_2$. It is a double phosphate of Li Na, Fe and Mn and contains 1.6˘3.7% of Li.

(b) *Amblygonite*, $Li(AlF) PO_4$. It contains 7˘10% of Li.

Occurence in India

Lithium mainly occurs in India as *lepidolite* in Bihar, Kashmir Karnataka and Rajasthan.

Extraction of Lithium

The extraction of lithium involves the following two steps :

1. Preparation of LiCl. LiCl can be prepared either from *spodumene ore*, $LiAl (SiO_3)_2$ or from triphylite ore as shown below :

(i) *Preparation of LiCl from spodumene ore, LiAl(SiO₃)₂.* LiCl can be prepared from spodumene ore by using any of the following two methods :

(a) *Acid treatment method.* The finely powdered spodumene is digested (boiled) with conc. H_2SO_4.

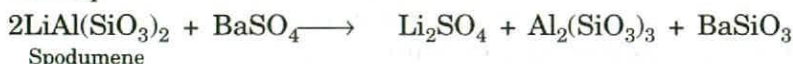$$2LiAl(SiO_3)_2 + 4H_2SO_4 \longrightarrow Li_2SO_4 + Al_2(SO_4)_3 + 4H_2SiO_3$$
Spodumene   Silicic acid
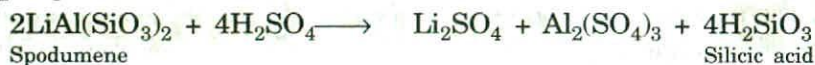
The digested mass is evaporated to dryness to convert H_2SiO_3 formed during the process into insoluble *hydrated silica*, $SiO_2.H_2O$.

$$HSiO_3 \longrightarrow SiO_2.H_2O$$

The filtrate is heated with Na_2CO_3 to precipitate the impurities of Mg, Al and Fe. At this stage, the solution is, however, too dilute for the precipitation of Li_2CO_3. The filtrate after concentration is treated with excess of Na_2CO_3 to precipitate Li_2CO_3. The precipitate of Li_2CO_3 is filtered and converted into LiCl by the treatment of HCl.

$$Li_2SO_4 + Na_2CO_3 \longrightarrow Li_2CO_3 + Na_2SO_4$$
$$Li_2CO_3 + 2HCl \longrightarrow 2LiCl + H_2O + CO_2$$

(b) *Fusion method.* The finely powdered spodumene is fused with a mixture of $BaCO_3$ and $BaSO_4$.

$$2LiAl(SiO_3)_2 + BaSO_4 \longrightarrow Li_2SO_4 + Al_2(SiO_3)_3 + BaSiO_3$$
Spodumene

$$2LiAl(SiO_3)_2 + BaCO_3 \longrightarrow Li_2CO_3 + Al_2(SiO_3)_3 + BaSiO_3$$

From the fused mass two layers are separated : *upper layer* which consists of Li_2SO_4 and *lower layer* which contains the silicates of Al and Ba. The lower layer is rejected whereas the upper layer is separated, dissolved in water and treated with $BaCl_2$ when insoluble $BaSO_4$ and soluble LiCl are obtained.

$$Li_2SO_4 + BaCl_2 \longrightarrow 2LiCl + BaSO_4$$
(Soluble)   (Insoluble)
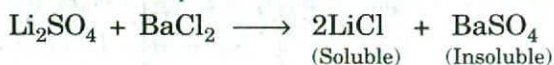
The filtrate of LiCl is evaporated to dryness and then is purified by the extracting it with alcohol.

(ii) *Preparation of LiCl from triphylite ore.* The finely powdered triphylite mineral is digested with conc. HCl. H_3PO_4 so liberated is removed by precipitation with $FeCl_3$ in presence of CH_3COONH_4 and CH_3COOH as in qualitative analysis. The filtrate which consists mostly of LiCl, NaCl and $MnCl_2$ is evaporated to dryness, extracted with hot water and Mn is removed as MnS by the treatment of *excess* of BaS solution.

$$MnCl_2 + BaS \longrightarrow MnS + BaCl_2$$
ppt.
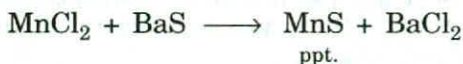
The filtrate is then treated with dil. H_2SO_4 to remove the excess of barium as insoluble $BaSO_4$ which is again removed by filtration. Now the filtrate containing Li_2SO_4 and Na_2SO_4 is evaporated along with oxalic acid. Lithium and sodium oxalates are formed which on ignition yield Li_2CO_3, Na_2CO_3 and CO. When these carbonates are treated with HCl, a mixture of LiCl and NaCl is obtained. From the mixture, LiCl is dissolved out in pyridine while NaCl remains insoluble. From this solution LiCl is obtained by distilling away pyridine.

2. To get Li metal by the electrolysis of LiCl. LiCl obtained as above is electrolysed to get Li metal. If an aqueous solution of LiCl is electrolysed, no lithium metal is obtained but there is only liberation of hydrogen at the cathode. In electrolytic process, therefore, aqueous solution of LiCl is not used. A fused mixture of LiCl and KCl is electrolysed at 400°C. The addition of KCl lowers the melting point (fusion temperature) of LiCl from 610°C to about 400°C so that the formation of lithium metal fog is prevented and increases the electrical conductivity of LiCl.

The electrolysis is carried out in an electrolytic cell shown in Fig. 19.1. The cell is made of steel with a refractory lining and consists of a steel cathode and graphite anode. The anode and cathode are separated from each other by a cast iron enclosure having iron gauze in its lower portion. The cell is operated at 400⁀ 420°C and the voltage is maintained between 8 to 9 volts. On passing the electric current, Li^+ ions are discharged in preference to K^+ ions at the cathode and Cl^- ions at the anode. The molten lithium containing about 1.3% of potassium, being lighter, rises to the surface of the fused mixture of electrolyte in the cast iron enclosure surrounding the cathode and is collected under a bell to protect it from contact with air. The metal is removed intermittently and stored either in well-stoppered bottles or in liquids like water-free ether, naphtha or petroleum. Metal obtained by this method is 99% pure.
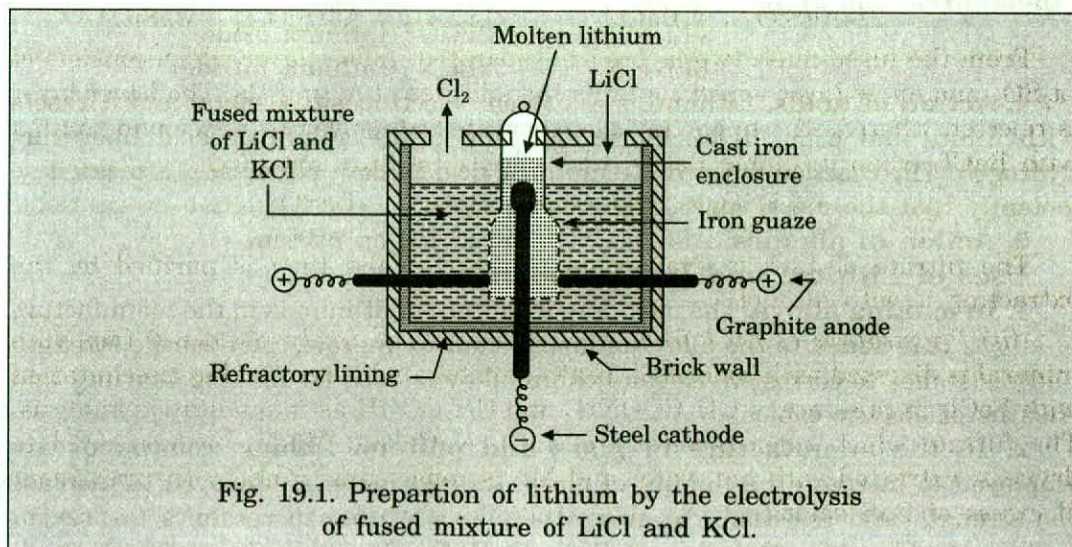
Fig. 19.1. Prepartion of lithium by the electrolysis
of fused mixture of LiCl and KCl.

The following reactions take place :

Ionisation : $LiCl \rightleftarrows Li^+ + Cl^-$

Cathode process : $Li^+ + e^- \longrightarrow Li$

Anode process : $Cl^- \longrightarrow Cl + e^-$

                                $Cl + Cl \longrightarrow Cl_2$
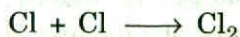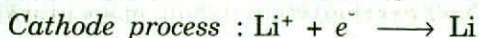
Cl_2 gas which is a valuable by-product is removed from the **outlet of the** anodic compartment.

Lithium may also be obtained by the electrolysis of conc. solution of LiCl in pyridine, ethanol or acetone.

Physical Properties

Lithium is a silvery white metal which melts at 186°C. It is harder than sodium or potassium but is extremely light. Its density which is 0.534 at 20°C *is the lowest of all the metals*. When volatilized, it imparts a red colour to the flame. It is a good conductor of heat and electricity. It forms an amalgam and alloys with a number of other metals. It has the highest specific heat of any element (0.9408).

Chemical Properties

1. Formation of compounds. When heated above its fusion point, it combines with hydrogen, nitrogen, sulphur, halogen and carbon dioxide.

$$2Li + H_2 \longrightarrow 2LiH \quad \text{(Lithium hydride)}$$
$$6Li + N_2 \longrightarrow 2Li_3N \quad \text{(Lithium nitride)}$$
$$2Li + Cl_2 \longrightarrow 2LiCl \quad \text{(Lithium chloride)}$$

2. Action of water. It reacts with water forming the hydroxide and liberating hydrogen but unlike sodium or potassium it does not fuse on water as its m.pt. is higher

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

3. Action of Air. It is not affected in dry air but is oxidised when moisture is present. Heated in air above 180°C, it burns with a brilliant light forming lithium oxide and lithium nitride.

$$4Li + O_2 \longrightarrow 2Li_2O \quad \text{(Lithium oxide)}$$
$$6Li + N_2 \longrightarrow 2Li_3N \quad \text{(Lithium nitride)}$$

4. Action of acids. Lithium is a strongly electropositive metal and it reacts with dilute and conc. hydrochloric acid and dilute sulphuric acid liberating hydrogen. The reaction with conc. sulphuric acid is slow. Nitric acid attacks it so violently that the metal melts and catches fire.

5. Action of alkalies. Alkalies have no action on lithium.

Uses of Lithium and Its Compounds

1. In making alloys. The most important use of lithium is in the manufacture of alloys. It is added to the alloys of magnesium to improve their tensile strength and resistance to corrosion. A lead-lithium alloy is used for making bearings and sheaths of electric cables.

2. In the manufacture of glass and pottery. Lithium compounds are employed to increase the fluidity of glass. Its carbonate is employed to increase the strength and resistance of glass. Its salts are used in ceramics to prevent surface cracking of pottery.

3. As deoxidiser. It is employed as a deoxidiser in the purification of nickel and copper.

4. In medicine. Its citrate and salicylate are employed in medicine for relieving gout since lithium urate is fairly soluble in water. Its compounds have also been used in the synthesis of vitamin A and some pharmaceuticals.

5. In lubricants. Its hydroxide is used in the manufacture of high quality lubricating greases which can withstand extreme variations of temperature.

6. In thermonuclear energy. It is finding increasing use as an ingredient of high energy fuels for propulsion of intercontinental rockets.

Compounds of Lithium

1. Lithium Chloride, LiCl

Preparation. It is prepared by burning the metal in Cl_2 or by adding HCl to its hydroxide or carbonate

$$2Li + Cl \longrightarrow 2LiCl$$
$$LiOH + HCl \longrightarrow LiCl + H_2O$$
$$Li_2CO_3 + 2HCl \longrightarrow 2LiCl + H_2O + CO_2 \uparrow$$
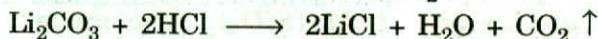
The resulting solution is completely evaporated at white heat in a current of hydrogen chloride when anhydrous salt is obtained.

Manufacture. It can be manufactured from spodumene and triphylite minerals as described under *"Extraction of Lithium"*.

Properties. It is a white crystalline solid with m.pt. = 606°C and b.pt. = 1350°C. Unlike the other alkali metal chlorides, it is the most *deliquescent* substance and is extremely solube in water. The fact that LiCl is also soluble in organic solvents shows that it has partial covalent character. It is due to its covalent character that it is hydrolysed by water. It crystallises as anhydrous salt from its aqueous solution above 98°C and as $LiCl.H_2O$, $LiCl.2H_2O$ and $LiCl.3H_2O$ at lower temperatures. It absorbs NH_3 both in solution and in the dry state to give the *ammoniates* like $LiCl.NH_3$, $LiCl.2NH_3$, $LiCl.3NH_3$ and $LiCl.4NH_3$. It also forms a number of double salts with chlorides of Fe, Co, Ni, Cu, Mn etc. It is the most volatile of all the alkali metal chlorides and, on being heated above the fusion point, it loses its chlorine.

Uses. It is used (*i*) in the preparation of metal by electrolysis (*ii*) in air-conditioning plants in the form of aqueous solution (35-40%) for humidity control (*iii*) in pyrotechny (*iv*) as a constituent for cleaning and soldering fluxes for Al and Mg (*v*) In Ni-Fe accumulators.

Structure. It is primarily an ionic compound. The formation of ionic bond by the transfer of one electron from Li atom to Cl atom can be explained as we do in NaCl.

$$Li^* + \cdot \ddot{C}l \colon \to [\,Li\,]^+ \left[\begin{array}{c} \ddot{} \\ {}^* \ddot{C}l \colon \\ \cdots \end{array} \right] \text{ or } Li^+Cl^-$$
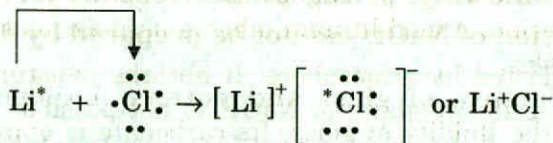
2. Lithium Carbonate, Li_2CO_3

Preparation. When $(NH_4)_2CO_3$ solution is added to a solution of lithium salt like LiCl in presence of NH_3, white preciptate of Li_2CO_3 is produced.

$$2\ LiCl + (NH_4)_2CO_3 \longrightarrow \underset{\text{ppt.}}{Li_2CO_3} + 2NH_4Cl$$
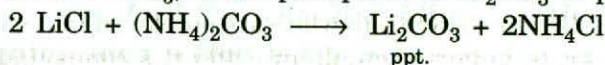
The preciptate is filtered and dried.

Manufacture. (a) *From amblygonite, Li(AlF) PO_4.* The mineral is ground to fine powder which is heated with $CaSO_4$ solution so that Li_3PO_4 and $AlPO_4$ present in the mineral are converted into soluble Li_2SO_4 and $Al_2 (SO_4)_3$ respectively

$$2Li_3PO_4 + 3CaSO_4 \longrightarrow \underset{\text{soluble}}{2Li_2SO_4} + \underset{\text{ppt.}}{Ca_3(PO_4)_2}$$

$$2AlPO_4 + 3CaSO_4 \longrightarrow \underset{\text{soluble}}{Al_2(SO_4)_3} + \underset{\text{ppt.}}{Ca_3(PO_4)_2}$$
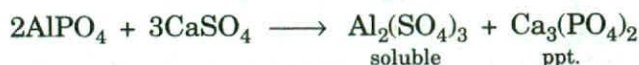
The filtrate containing Li_2SO_4 and $Al_2(SO_4)_3$ is treated with Na_2CO_3 whereby Li_2CO_3 is precipitated.

$$Li_2SO_4 + Na_2CO_3 \longrightarrow \underset{\text{ppt.}}{Li_2CO_3} + Na_2SO_4$$

(b) From spodumene, LiAl (SiO₃)₂. The preparation of Li_2CO_3 from spodumene can be obtained by the acid treatment method as described under the extraction of lithium.

Properties. (*i*) It is a white crystalline substance, very sparingly soluble in water and insoluble in alcohol. It is more soluble in cold water than in hot. Its m.pt. is 618°C and density is 2.11.

(*ii*) *Action of heat.* When heated above 600°C, it gets decomposed into its oxide (Li_2O) and CO_2.

(*iii*) *Action of CO₂.* When CO_2 is passed through a suspension of Li_2CO_3 in water, the latter dissolves forming $LiHCO_3$.

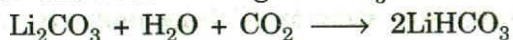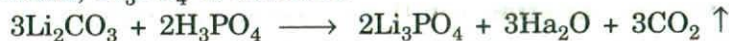$$Li_2CO_3 + H_2O + CO_2 \longrightarrow 2LiHCO_3$$

The solution of $LiHCO_3$ is used in medicine as a remedy for gout and rheumatism under the name of *lithia water.*

(*iv*) *Action H₃PO₄.* When Li_2CO_3 is dissolved in H_3PO_4 and the solution so obtained is evaporated, Li_3PO_4 is obtained.

$$3Li_2CO_3 + 2H_3PO_4 \longrightarrow 2Li_3PO_4 + 3Ha_2O + 3CO_2 \uparrow$$

Uses. Li_2CO_3 is used (*i*) as a starting material for the production of other lithium compounds (*ii*) in glass industry for preparing glass transparent to ultra-violet light.

Questions with Answers

Q.1 Explain the following, giving proper reasons for your answer :

(*i*) Standard solution of NaOH cannot be prepared by direct weighing.

Ans : NaOH is affected by atmosphere. It absorbs moisture and CO_2 from atmosphere. Thus, accurate weighing of NaOH is not possible.

(*ii*) The hydoxides of aluminium and iron are insoluble in water but NaOH is used to separate one from the other.   **[I.I.T 1991]**

Ans : $Al(OH)_3$ dissolves in excess of NaOH forming a soluble compound, sodium meta aluminate, $NaAlO_2$

$$Al(OH)_3 + NaOH \to NaAlO_2 + 2 H_2O$$
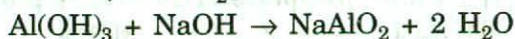
(*iii*) The inside surface of a glass bottle containing caustic soda becomes dull.

Ans : Silica is present in glass. It dissolves in NaOH slowly and forms soluble sodium silicate (Na_2SiO_3) and thus inside surface becomes dull.

$$2 NaOH + SiO_2 \text{ (silica)} \to Na_2SiO_3 + H_2O$$

Q.2 A certain compound (X) is used in the laboratory for analysis. Its aqueous solution gives th following reactions :

(i) **On addition to copper sulphate, a brown precipitate is obtained which turns white on addition of excess of $Na_2S_2O_3$ solution.**

(ii) **On addition of Ag^+ ion solution, a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.**

Identify (X) and give equations for the reactions at steps (i) and (ii).

(Roorkee 1991)

Ans : X is KI.

(i) $2 CuSO_4 + 4KI \longrightarrow 2 CuI_2 + 2 K_2SO_4$

$CuI_2 \longrightarrow Cu_2I_2 + I_2$

(White)

$I_2 + 2 Na_2S_2O_3 \longrightarrow 2 NaI + Na_2S_4O_6$

(ii) $Ag^+ + KI \longrightarrow AgI + K^+$
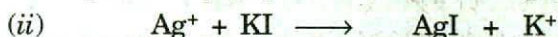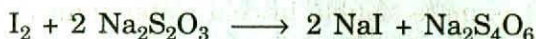
Yellow ppt.

(Insoluble in NH_4OH)

Q.3 When 16.78 g of a white solid X were heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y, dissolved in water to give an alkaline solution, which with excess of barium chloride solution gave a white precipitate, Z. The precipitate effervesced with acid giving off carbon dioxide. Identity A, B and Y and write down the equation for the thermal decomposition of X.

[I.I.T. 1984]

Ans : X is $NaHCO_3$

$2 NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$
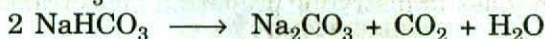
$(X) \qquad\qquad (Y) \qquad (A) \quad (B)$

Q.4 Solvay process used for the manufacture of Na_2CO_3 can be represented by the follwoing scheme.
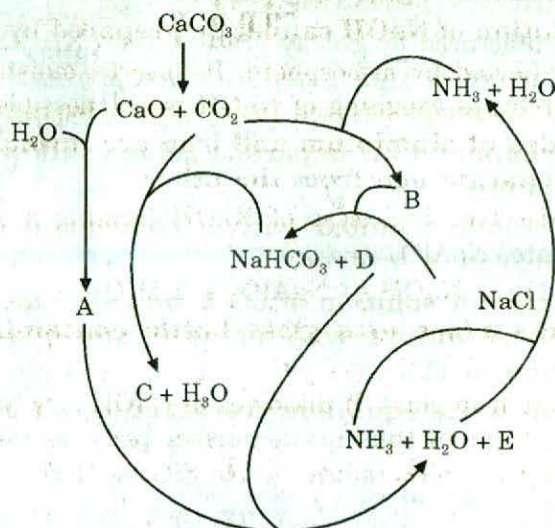
Identity A, B, C, D and E.   (*I.I.T 1999*)

Ans : The reactions taking place in the scheme are :

(*i*) $NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$
$$(B)$$

(*ii*) $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$
$$(B) \qquad\qquad\qquad\qquad (D)$$

(*iii*) $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$
$$(C)$$

(*iv*) $CaO + H_2O \longrightarrow Ca(OH)_2$
$$(A)$$

(*v*) $Ca(OH)_2 + 2NaCl \longrightarrow 2\,NH_3 + 2\,H_2O + CaCl_2$
$$(A) \qquad (D) \qquad\qquad\qquad\qquad (E)$$
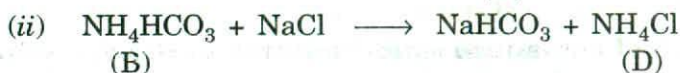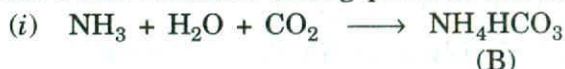
Thus : A = Ca$(OH)_2$, B = NH_4HCO_3, C = Na_2CO_3, D = NH_4Cl and E = $CaCl_2$.

Q.5 Na_2CO_3 is made by Solvay process but the same process cannot be extended to the manufacture of K_2CO_3. Explain.   (*I.I.T. 1981*)

Ans : We know than Solvay process used for the manufacture of Na_2CO_3 consists of the following steps :

(*i*) CO_2 gas is passed through commercial brine solution (NaCl) when $NaHCO_3$ (an insoluble compound) is produced as an intermediate compound.

$$NaCl + NH_3 + H_2O + CO_2 \longrightarrow NaHCO_3 + NH_4Cl.$$

The formation of $NaHCO_3$ actually takes place through the following two steps :

(*a*) $NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$

(*b*) $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$
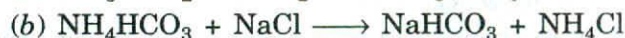
$$\text{Intremediate}$$
$$\text{(Insoluble)}$$

(*ii*) $NaHCO_3$ obtained as above gets decomposed, on heating, to give Na_2CO_3

$$2\,NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$
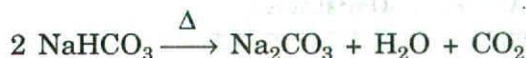
If K_2CO_3 is manufactured by Solvay process, then $KHCO_3$ will be formed as an intermediate in accordance with step (*b*) given above. Now since $KHCO_3$ is very soluble in H_2O, it cannot be used to get K_2CO_3 by heating it.

Q.6 A certain compound (*X*) imparts a golden yellow flame and shows the following reactions :

(*i*) **Zinc powder when boiled with a concentrated solution of (*X*) dissolves and hydrogen is evolved.**

(*ii*) **When an aqueous solution of (*X*) is added to an aqueous solution of stannous chloride, a white precipitate is obtained first which dissolves in excess of solution of (*X*).**

Identify (*X*) and write equations for reactions at steps (*i*) and (*ii*).
                                                                       (*Roorkee 1991*)
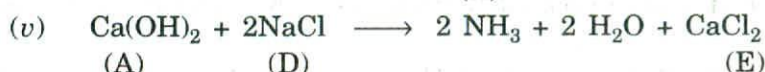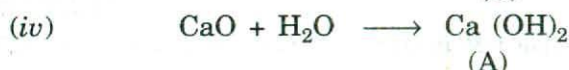
Ans : *X* is NaOH

(i) $Zn + 2\,NaOH \longrightarrow Na_2ZnO_2 + H_2$

(ii) $SnCl_2 + 2\,NaOH \longrightarrow Sn\,(OH)_2 + 2\,NaCl$

         $Sn\,(OH)_2 + 2\,NaOH \longrightarrow Na_2SnO_2 + 2\,H_2O$

                     Soluble
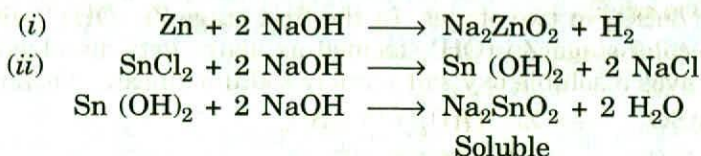
Q.7 Gradual addition of potassium iodide solution to Bi (N$_3$)$_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write the chemical equation for the above reactions. **[I.I.T. 1996]**

Ans : At first, Bi (NO$_3$)$_3$ undergoes hydrolysis. Nitric acid is formed. Which oxidises KI to iodine. The liberated iodine dissolves in KI to form yellow solution of KI$_3$.

$$Bi\,(NO_3)_3 + H_2O \longrightarrow [Bi\,(OH)\,(NO_3)_2] + HNO_3$$

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO_2 + O$$

$$2\,KI + H_2O + O \longrightarrow 2\,KOH + I_2$$

                              Dark brown

$$I_2 + KI \longrightarrow KI_3$$

                 Yellow solution

Q.8 Write balanced equations for the reaction between caustic soda and (a) Zn (b) AgNO$_3$ (c) Phosphorus (d) Arsenion oxide (As$_2$O$_3$) (e) I$_2$ (f) ZnSO$_4$ solution (g) AlCl$_3$ solution. **(MLNR 1979)**

Ans : (a) NaOH reacts with Zn to form sodium zincate (Na$_2$ZnO$_2$) and H$_2$ gas is evolved.

$$Zn + 2\,NaOH \longrightarrow Na_2ZnO_2 + H_2$$

(b) AgNO$_3$ reacts with NaOH in two stages. In the first stage unstable hydroxide of Ag (AgOH) is formed. In the second stage this hydroxide gets decomposed into insoluble oxide of Ag (Ag$_2$O).

$$2\,AgNO_3 + 2\,NaOH \longrightarrow 2\,AgOH + NaNO_3$$

                         (Unstable)

$$2\,AgOH \longrightarrow Ag_2O + H_2O$$
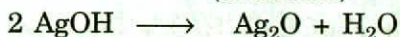
                 Stable (Brown)

(c) White (yellow) phosphorus, when heated with NaOH solution, evolves phosphine (PH$_3$) and sodium hypophosphite (NaH$_2$PO$_2$) is also formed.

$$P_4 + 3\,NaOH + 3\,H_2O \longrightarrow 3\,NaH_2PO_2 + PH_3$$

(d) Since As$_2$O$_3$ is an acidic oxide, salt *viz.* sodium arsenite (NaAsO$_2$) is formed.

$$2\,NaOH + As_2O_3 \longrightarrow 2\,NaAsO_2 + H_2O$$

(e) With cold and dil. NaOH solution, sodium iodide (NaI) and sodium hypoiodite (NaIO) are formed. But with hot concentrated NaOH solution, sodium iodide (NaI) and sodium iodate (NaIO)$_3$ are obtained.

$$2\,NaOH + I_2 \longrightarrow NaI + NaIO + H_2O$$

Dilute and cold.

$$6\,NaOH + 3\,I_2 \longrightarrow 5NaI + NaIO_3 + 3\,H_2O$$
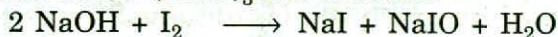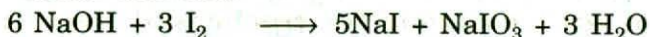
Hot and concentrated

(f) NaOH reacts with $ZnSO_4$ in two stages. In the first stage $Zn(OH)_2$ (white ppt.) is formed. In the second stage $Zn(OH)_2$ formed as above gets dissolved in the excess of NaOH and gives a soluble oxy salt namely sodium zincate, Na_2ZnO_2.

$$2\ NaOH + ZnSO_4 \longrightarrow Zn(OH)_2 + Na_2SO_4$$
$$\text{White ppt.}$$

$$Zn(OH)_2 + 2\ NaOH \longrightarrow Na_2ZnO_2 + 2\ H_2O$$
$$\text{(Soluble)}$$

$$4\ NaOH + ZnSO_4 \longrightarrow Na_2ZnO_2 + 2\ H_2O + Na_2SO_4$$
$$\text{(Soluble)}$$

(g) NaOH reacts with $AlCl_3$ in two stages. In the first stage $Al(OH)_3$ (white ppt.) is formed and in the second stage white ppt. of $Al(OH)_3$ formed gets dissolved in the excess of NaOH and gives a soluble oxy salt namely sodium aluminate $(NaAlO_2)$.

$$3\ NaOH + AlCl_3 \longrightarrow Al(OH)_3 + 3\ NaCl$$
$$\text{White ppt.}$$

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2\ H_2O$$
$$\text{(Soluble)}$$

$$4\ NaOH + AlCl_3 \longrightarrow NaAlO_2 + 2\ H_2O + 3\ NaCl$$
$$\text{(Soluble)}$$
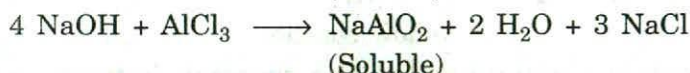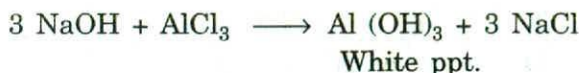
Q.9 What are the compounds *U, V, W, X, Y, Z, A, B, C* in the following road map problems ?

$$NaCl + H_2SO_4\ (conc.) \longrightarrow U + \text{Gas } V$$

$$V + MnO_2 \xrightarrow{\Delta} \text{Gas } W + MnCl_2 + H_2O$$

$$U + NaCl \xrightarrow{\Delta} X + V$$

$$X + Coke + CaCO_3 \longrightarrow Y + Z$$

$$CaCO_3 \xrightarrow{\Delta} A + B \text{ (colourless and odourless gas)}$$

$$A + H_2O \longrightarrow C$$

$$C + Y \rightarrow NaOH + CaCO_3$$

Ans : $NaCl + H_2SO_4\ (conc.) \longrightarrow \underset{(U)}{NaHSO_4} + \underset{(V)}{HCl\ (g)}$

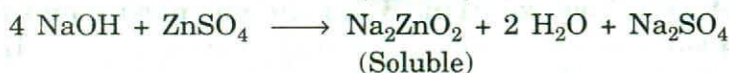$\underset{(V)}{MnO_2 + 4\ HCl\ (g)} \longrightarrow \underset{(W)}{MnCl_2 + Cl_2} + 2\ H_2O$

$\underset{(U)}{NaHSO_4 + NaCl} \xrightarrow{\Delta} \underset{(X)}{Na_2SO_4} + \underset{(V)}{HCl}$

$\underset{(X)}{Na_2SO_4 + CaCO_3} \longrightarrow \underset{(Y)}{Na_2CO_3} + \underset{(Z)}{CaSO_4}$

$CaCO_3 \xrightarrow{\Delta} \underset{(A)}{CaO} + \underset{(B)}{CO_2\ (g)}$

$\underset{(A)}{CaO + H_2O} \longrightarrow \underset{(C)}{Ca(OH)_2}$

$\underset{(C)}{Ca(OH)_2} + \underset{(Y)}{Na_2CO_3} \longrightarrow 2\ NaOH + CaCO_3$
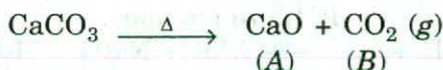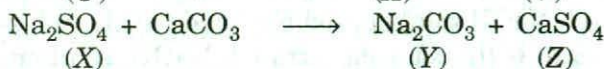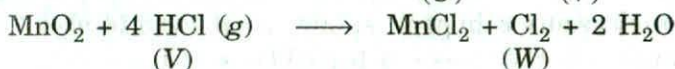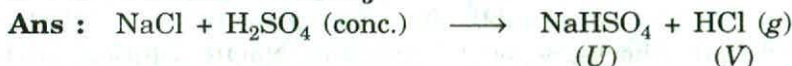
Q.10 From the following reactions identity A, B, C and D and write their formulae.

$A\ (aq) + Zn \longrightarrow B\ (g)$

$A\ (aq) + C \xrightarrow{\Delta} PH_3$
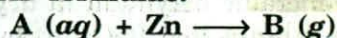
$A\ (aq) + NH_4Cl \longrightarrow D\ (g)$ **(Roorkee 1987)**

Ans : A = NaOH, sodium hydroxide; B = H_2, hydrogen; C = P_4, phosphorus; D = NH_3, ammonia.

Q.11 State the reasons :

(i) **The addition of NH_4OH to $ZnSO_4$ solution produces white precipitate but no precipitate is formed if it contain NH_4Cl.**

(Roorkee 1980)

(ii) **The addition of NaOH to a solution of $ZnCl_2$ produces a white precipitate which dissolves on further addition of NaOH.**   **(Roorkee 1980)**

Ans : (i) NH_4OH is a weak hydroxide. It ionises slightly furnishing OH^- ions. However, OH^- ions produced are sufficient to cause precipitation of $Zn(OH)_2$ as its solubility product is exceeded.

$$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$$
$$\text{White ppt.}$$

In presence of NH_4Cl, the ionisation of NH_4OH is further suppressed and sufficient OH^- ions are not available to cause precipitation as the solubility product is not exceeded.

(ii) $2NaOH + ZnCl_2 \longrightarrow Zn(OH)_2 + 2NaCl$

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2Zn(OH)_4 \longrightarrow Na_2ZnO_2 + 2H_2O$$

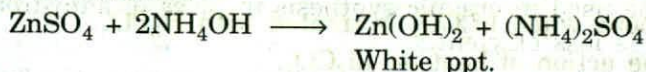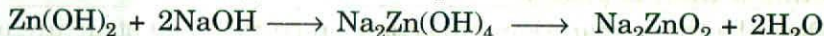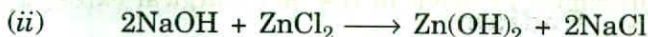NaOH pricipitates insoluble hydroxides of metals from their soluble salts since zinc metal is amphoteric in nature. Since $Zn(OH)_2$ precipitate so formed is amphoteric in nature, on adding excess of NaOH a soluble complex $Na_2Zn(OH)_4$ is formed.

Q.12 What happens when :

(i) **Excess of NaOH solution is added slowly to $ZnCl_2$ solution.**

(ii) **Excess of NH_4OH solution is added to $ZnCl_2$ solution.**

(iii) **ZnO is treated with excess of NaOH solution.**

Ans : (i) First a white precipitate of $Zn(OH)_2$ is formed which dissolves in excess of NaOH forming $Na_2Zn(OH)_4$.

(ii) A white $Zn(OH)_2$ precipitated is first formed of which dissolves in excess of NH_4OH forming $[Zn(NH_3)_4](OH)_2$, which is a soluble complex.

(iii) ZnO dissolves in NaOH forming a soluble complex, $Na_2Zn(OH)_4$,

$$ZnO + 2\ NaOH + H_2O \longrightarrow Na_2Zn(OH)_4$$
$$\text{insoluble} \qquad\qquad\qquad \text{soluble}$$
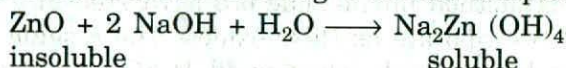
Q.13 Identity A, B, C and D and give their chemical formulae :

$A + NaOH \xrightarrow{\Delta} NaCl + NH_3 + H_2O$

$NH_3 + CO_2 + H_2O \longrightarrow B$

$B + NaCl \longrightarrow C + NH_4Cl$

$C \longrightarrow Na_2CO_3 + H_2O + D.$

Ans : A = NH_4Cl, ammonium chloride ; B = NH_4HCO_3, ammonium bicarbonate; C = $NaHCO_3$, sodium bicarbonate ; D = CO_2, carbon dioxide.

University Questions

1. Give the ores, extraction and isolation of pure lithium.
   (Meerut 89; Garhwal 88)

2. Clarify the following points of the extraction of lithium from its ores :
   (*i*) How is LiCl obtained from NaCl and KCl.
   (*ii*) How is metallic Li obtained from LiCl ?   *(Gorakhpur 84)*

3. Describe the properties of lithium.   *(Meerut 88)*

4. What are the uses of lithium metal and its compounds.   *(Delhi 86;*
   Madras 85; Agra 84, 85; Rohilkhand 84; Gorakhpur 80, 84;
   Lucknow 81; Bhopal 80; Kanpur 82; Meerut 84, 86, 88)

5. Give an account of the preparation, properties, uses and structure of LiCl.
   (Meerut 82, 82 S, 89)

6. What happens when Li metal is heated with H_2, N_2 and Cl.

7. How is Li_2CO_3 manufactured from amblygonite ore.

8. What happens when Li_2CO_3 is treated with H_3PO_4.

9. What is the action of heat on Li_2CO_3.

10. Give the method of preparation, properties and uses of KI.   *(MLNR 78)*

11. (*a*) Discuss the role of alkali metals as a source of energy.
    (*b*) Give the chemical principles involved in the metallurgical extraction of lithium from Lepidolite.
    (*c*) Describe the preparation, important properties, and structure of lithium tetrahydroaluminate.   *(Allahabad 99)*

12. Explain why alkali metals are good reducing agents.   *(Kanpur 2000)*

13. How will you get LiCl from lepidolyte?   *(Kumaon 2000)*

14. How is lithium obtained from its ores ? Discuss its anomolous behaviour.
    (Lucknow 2001)

General Characteristics of Group 2 (IIA) Elements : Alkaline Earth Metals

Group IIA of the long form of the periodic table consists of *six* elements which are : *Breyllium* (Be), *Magnesium* (Mg), *Calcium* (Ca), *Strontium* (Sr), *Barium* (Ba), and *Radium* (Ra).

The oxides of the three metals *viz.*, Ca, Sr and Ba were known much earlier than the metals themselves and were called *alkaline earths*, since they were alkaline in character and occured in nature as earths [*lime* (CaO), *strontia* (SrO) and *baryta* (BaO)]. Later, when Ca, Sr and Ba were discovered, they were named *alkaline earth metals*. Now this term is used to include all the elements of Group II A. Although Ra has similar properties as alkaline earth metals, but being radioactive, it is studied separately along with other radioactive elements.

Position of Alkaline Earth Metals in the Periodic Table

The inclusion of the alkaline earth metals in the same subgroup is justified by the following points :

I. Electronic Configurations.

The electronic configurations of the alkaline earth metals (Group II A) are given below :

Element	At No.	Complete electronic configuration	Valence-shell electronic configuration
Be	4	2, 2	$2s^2$
Mg	12	2, 8, 2	$3s^2$
Ca	20	2, 8, 8, 2	$4s^2$
Sr	38	2, 8, 18, 8, 2	$5s^2$
Ba	56	2, 8, 18, 18, 8, 2	$6s^2$
Ra	88	2, 8, 18, 32, 18, 8, 2	$7s^2$

These configurations show that the ultimate shell of these elements has *two* s-electrons (s^2 electrons) while the penultimate shell contains *eight* (s^2p^6 electrons.) When the two s-electrons of the valence-shell are lost, alkaline earth metals are converted into M^{2+} ions which have inert gas configuration. Since the additional electron enters the *ns*-orbital, these elements are called s-block elements.

II. Similarities in Physical Properties and Gradation in Them

Some of the physical properties of alkaline earth metals are given in Table 20.1 and are discussed as follows :

Table 20.1. Some physical properties of alkaline earth metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (% of earth's crust)	6.0×10^{-4}	2.0	3.45	0.915	0.040	1.3×10^{-10}
Density (gm/c.c.)	1.84	1.74	1.55	2.54	3.75	6.00
Melting point (°C)	1277	650	838	763	714	700
Boiling point (°C)	2770	1107	1440	1380	1640	—
Atomic volume (c.c.)	4.90	13.97	25.9	34.54	36.7	38.0
Atomic (i.e., metallic) radius for coordination number 12(Å)	1.12	1.60	1.97	2.15	2.22	—
Covalent radius (Å)	0.90	1.36	1.74	1.91	1.98	—
Ionic (crystal) radius of M^{2+} ion for coordination number 6(Å)	0.31	0.65	0.99	1.13	1.35	140
Ionisation energies (KJ/mole)						
I_1	899.5	737.7	829.8	547.5	502.9	509.4
I_2	1757.1	1450.7	1145.4	1064.3	965.2	979.06
$I_1 + I_2$	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46
Oxidation state	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for $M(s) \longrightarrow M^{2+}(aq) + 2e^-$	1.70	2.37	2.87	2.89	2.90	2.92
Heat of automisation at 25°C and 1 atm. pressure (KJ/mole)	327.26	146.89	181.21	163.21	175.77	—
Heat of hydration (KJ/mole)	2385.45	1925.1	1653.07	1485.67	1276.42	—
Ionic potential of M^{2+} ion (i.e., charge/radius ratio)	6.66	3.08	2.12	1.82	1.55	1.33

1. **Physical state.** The elements of this group have a greyish white lustre when freshly cut and are malleable and ductile.

2. **Density.** Density decreases slightly upto Ca after which it increases. Irregular variation of the density is due to the difference in the crystal structure of these elements. By comparing the densities of these elements with those of alkali metals, it may be seen that these elements are *denser* (*i.e.*, have higher density) than the alkali metals in the same period. This is due to the fact that the elements of Group IIA can be packed more tightly due to their *greater nuclear charge* and *smaller size.*

3. **Melting and boiling points.** Melting and boiling points of these elements do not show any regular trend. *These are, however, higher than those of alkali*

metals. This is because the alkaline earth metals have *two valence electrons* and are *much strongly bonded* in the solid state than the alkali metals.

4. Atomic volume, atomic and ionic radii. Because of the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume *increases* from Be to Ra. With the increases of atomic volume *the atomic and ionic radii* (of M^{2+} ions) *also increase from Be to Ra.* The atomic radii of these elements are, however, smaller than those of alkali metals in the same period. This is due to the fact that the alkaline earth metals have higher nuclear charge which tends to draw the orbit electrons towards the nucleus. The smaller values of atomic radii result in that the alkaline earth metals are *harder, have higher densities* and *higher melting points* than the alkali metals.

Elements	:	Be	Mg	Ca	Sr	Ba	Ra
Atomic volume (c.c.)	:	4.90	13.97	25.9	34.54	36.7	38.09
Atomic radii (Å)	:	1.12	1.60	1.97	2.15	2.22	—
Ionic radii of M^{2+} ions (Å)	:	0.31	0.65	0.99	1.13	1.35	1.40

5. Colour and magnetic properties of M^{2+} ions. Since the outer-shell electronic configuration of M^{2+} ions are similar to those of inert gases (s^2 or s^2p^6 configuration), these ions have *no unpaired electrons* and consequently are *diamagnetic and colourless.*

6. Ionisation energies. *The first and second ionisation energies of these elements decrease with the increase of atomic radii from* Be to Ba. However, both these values for Ra are slightly higher than those of Ba.

Elements		Be	Mg	Ca	Sr	Ba	Ra
Ionisation energies							
(KJ/mole)	I_1 :	899.5	737.7	589.8	549.5	502.9	509.4
	I_2 :	1757.1	1450.7	1145.4	1064.3	965.2	979.06

7. Electropositive character. Although the ionisation energies of these elements are higher than those of alkali metals, yet these are sufficiently low to make these metals to *lose readily their ns^2 electrons to form M^{2+} ions* :

$$M_1 \longrightarrow M^{2+} + 2e^-$$

These metals, therefore, show strong electropositive character which increases from Be to Ba. Since these metals have higher ionisation energies than the alkali metals, *these are not strongly electropositive as the alkali metals.*

8. Formation of divalent ions and oxidation states. In view of the fact that first ionisation potenials of these metals are lower than the second ionisation potentials, it appears that these metals should form univalent ions rather than divalent ions. But actually these elements give divalent ions. This anomaly is because of the fact that M^{2+} ions are extensively hydrated to form the hydrated ions, $[M(H_2O)_x]^{2+}$ and in this process a large amount of energy, known as *energy of hydration* is released.

$$M^{2+} + xH_2O \longrightarrow [M(H_2O)_x]^{2+} + \textit{Energy of hydration}$$
Hydrated cation
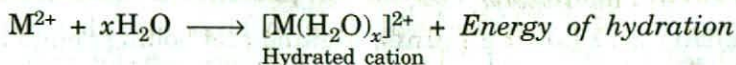
This energy of hydration more than counterbalances the higher value of second ionisation energy.

Because of the fact that Be has the highest ionisation energy, it has the least tendency to form Be^{2+} ion. Consequently, its compounds with nitrogen, oxygen, sulphur, halogens etc., are *covalent* while the corresponding compounds of Mg, Ca, Sr, and Be are *ionic*.

9. Hydration of alkaline earth metals. The values of the heats of hydration of M^{2+} ions (*i.e.* hydration energy) show that *these decrease with the increase in ionic radii of M^{2+} ions.*

Alkaline earth metal ions :	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Radii for M^{2+} ions (Å) :	0.31	0.65	0.92	1.13	1.35
Heats of hydration of M^{2+} ions (KJ/mole) :	2385.45	1925.1	1653.07	1485.67	1276.42

Since the hydration energies for alkaline earth metal ions are larger than those of alkali metals ions, the alkaline earth metal compounds are more extensively hydrated than those of alkali metals, *e.g.* magnesium chloride and calcium chloride exist as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$ respectively while sodium chloride and potassium chloride do not from hydrates.

With the decrease of hydration energies from Be^{2+} to Ba^{2+}, the ionic mobilities (*i.e.* ionic conductance) of these ions increase in the same order.

10. Electronegativities. These are *small* and *decrease from Be to Ba.*

11. Flame colouration. In the flame tests their electrons absorb energy and are excited to higher energy levels. When reverting to lower levels, they give out extra energy which appears as visible light of characteristic colours as shown below :

Ca—*Brick red*; Sr—*Crimson*;

Ba—*Apple green*; Ra—*Red*.

Be and Mg do not give any colour to the flame. This is because the atoms are smaller and hence their electrons are more strongly attracted by the nucleus. Hence these electrons are not excited to the higher energy levels by the energy of the flame.

12. Polarising power of M^{2+} cations. In this group the ionic radius increases from Be to Ra, whereas the ionic charge remains the same. Therefore, polarising power of M^{2+} cations decreases from Be^{2+} to Ra^{2+}. In general, smaller ions polarise the anions more effectively than the bigger ones. Therefore, Be^{2+} has a tendency to form covalent compounds.

13. Conductivity. Since two valence electrons are free to move throughout the metal structure, the alkaline earth metals are good conductors of heat and electricity.

14. Reducing properties : Oxidation potentials. Alkaline earth metals have two electrons in their valence shell. Due to large size they are comparatively easily oxidised to M^{2+} ions. They are, therefore, *strong reducing agents*. On moving down, the oxidation potentials increase due to increase in electropositive

character, since the strength as a reducing agent *increases* downwards from Be to Ba.

The oxidation potentials of alkaline earth metals are *lower* than those of alkali metals because of their *higher sublimation* and *ionisation energies*. Hence alkaline earth metals are *weaker* reducing agents than the alkali metals.

III. Similarities in Chemical Properties and Gradation in Them

1. Formation of oxides (*a*) Normal oxides of MO type. *Preparation*. The alkaline earth metals form the normal oxides of MO type which are obtained by heating the metal in O_2 or by heating their carbonates at high temperature, *e.g.*

$$Ca + O_2 \xrightarrow{\Delta} CaO$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$
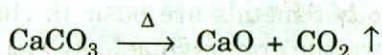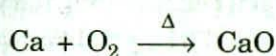
Properties. (*i*) These oxides are extremely stable white crystalline solids due to their *high crystal lattice energy* obtained by packing *doubly-charged ions* in a sodium chloride type of lattice.

(*ii*) Excepting BeO which has a *wurtzite* (4 : 4) structure, all other oxides have the sodium chloride (6 : 6) structure.

(*iii*) BeO and MgO are quite insoluble in H_2O while CaO, SrO and BaO react with H_2O to give soluble hydroxides, $M(OH)_2$ which are *strong bases.*

(*iv*) BeO is *not* at all *basic in nature*; in fact it is *amphoteric* since it reacts with acids to form salts and with alkalies to give beryllates.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$
$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$
$$\text{Sod. beryllate}$$
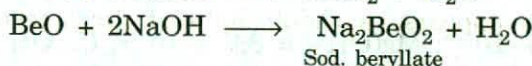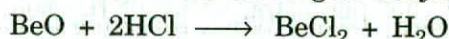
The oxides of other metals are basic in character. Their basic character increases on moving down the group.

(*v*) Due to *small size* of Be^{2+} ion, BeO is *covalent* while other oxides are ionic. Although BeO is covalent, yet is has a higher melting point and is harder than the oxides of other metals, as it is *polymeric*. Each Be atom is *tetrahedrally* coordinated by four oxygen atoms.

(*b*) **Peroxides. *Preparation*.** The peroxides of heavier metals (Ca, Sr, Ba etc.) can be obtained on heating the normal oxides with O_2 at high temperature.

$$2BaO + O_2 \longrightarrow 2BaO_2$$

Properties. The peroxides are white, ionic solids having peroxide anion, $[O-O]^{2-}$. They react with acids to produce H_2O_2.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

2. Formation of hydroxides. *Preparation*. The hydroxides, $M(OH)_2$ are obtained :

(*a*) by the reaction of the metals with H_2O, *e.g.*
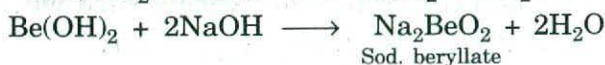
$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + O_2$$

Be does not react with H_2O even at elevated temperature, Mg reacts only with steam while other metals react with cold water as well.

(b) by the reaction of the oxides (excepting MgO) with H_2O, e.g.

$$MO + H_2O \longrightarrow M(OH)_2$$

Properties. (i) The heats of formation of hydroxides increase from $Be(OH)_2$ to $Ba(OH)_2$.

(ii) $Be(OH)_2$ is *not at all basic*; in fact it is *amphoteric*, since it reacts with acids to form salts and with alkalies to give beryllates.

$$Be(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$\text{Sod. beryllate}$$

The hydroxides of other metals are basic in character. Their basic character increases on moving down the group. Thus $Mg(OH)_2$ is *weakly basic* while $Ba(OH)_2$ is the *strongest base*. The increase in basic character of the hydroxides on moving down the group is due to the fact that with the increase in size of M^{2+} cation both the *polarity* of M—OH bond and the *internuclear distance* between oxygen of OH^- ion and the metal atom *increase*. As a result of this, there is greater ionisation of $M(OH)_2$ and hence basic character increases.

(iii) Due to *high polarising power of small Be^{2+} ion*, $Be(OH)_2$ is *covalent* while other hydroxides are *ionic*.

(iv) $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in H_2O while the hydroxides of other metals are slightly soluble. Their solubility increases on moving down the group as shown by the increasing value of the solubility products of these hydroxides.

$Be(OH)_2 = 1.6 \times 10^{-26}$; $Mg(OH)_2 = 8.9 \times 10^{-12}$; $Ca(OH)_2 = 1.3 \times 10^{-4}$;
$Sr(OH)_2 = 3.2 \times 10^{-4}$; $Ba(OH)_2 = 5.4 \times 10^{-2}$

3. Formation of halides. *Preparation*. The halides, MX_2 of these metals can be obtained :

(a) by heating the metals with halogens at appropriate temperatures,

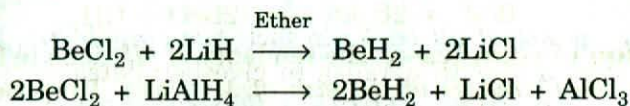(b) by reacting the metal carbonates with dil. halogen acids.

Properties. Halides of Be (e.g. $BeCl_2$, BeF_2) are covalent and, therefore, do not conduct electricity in fused state. They are hygroscopic and fume in air due to hydrolysis. They have low melting points. The covalent character of the halides of Be is due to *high polarising power of small Be^{2+} cation.*

The chlorides and fluorides of other alkaline earth metals are *ionic solids* and hence good conductors of electricity in the fused as well as in the dissolved state. The melting points and conductivity increases on moving down the group due to the increase in the ionic character of the halides. They are hygroscopic and readily form hydrates, e.g. $MgCl_2.6H_2O$, $CaCl_2.6H_2O$. The solubility of halides in water decreases on moving down the group due to the decrease in their hydration energy with the increasing size of the metal ion. The fluorides, MF_2 are almost insoluble in water.
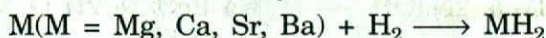
Most of the anhydrous halides of alkaline earth metals crystallise in the fluorite type structure.

4. Formation of hydrides. All the elements of this group form the hydrides of MH_2 type.

Preparation. BeH_2 cannot be prepared by the direct combination of Be and H_2. It is, however, prepared by reducing $BeCl_2$ by LiH or $LiAlH_4$.

$$BeCl_2 + 2LiH \xrightarrow{\text{Ether}} BeH_2 + 2LiCl$$

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

Mg, Ca, Sr and Ba form their hydrides when heated with H_2.

$$M(M = Mg, Ca, Sr, Ba) + H_2 \longrightarrow MH_2$$

Properties. (i) BeH_2 is a *covalent compound*, MgH_2 is *partly ionic* (*i.e. almost covalent*) in nature while the hydrides of other metals are ionic solids due to their greater electropositive character.

(ii) They react with H_2O, liberating H_2. Thus they are used as *reducing agents*.

$$MH_2 + 2H_2O \longrightarrow M(OH)_2 + H_2$$

5. Formation of carbonates. (i) All the carbonates decompose on heating at appropriate temperature, evolving CO_2.

$$MCO_3 \xrightarrow{\Delta} CO_2 + MO$$
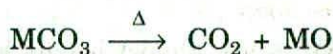
The stability of the carbonates of these metals *increases on moving down the group*. This is illustrated by the values of the decomposition temperatures of these carbonates as given below :

$$BeCO_3 = 25°C, \ MgCO_3 = 540°C, \ CaCO_3 = 900°C,$$
$$SrCO_3 = 1290°C, \ BaCO_3 = 1360°C.$$
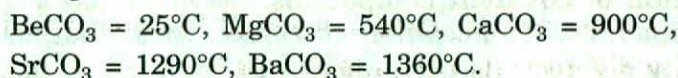
The marked instability of $BeCO_3$ is due to *strong polarising effect of small Be^{2+} cation* on the large polarisable CO_3^{2-} ion.

(ii) Carbonates are insoluble in water and, therefore, occur as solid rock minerals in nature. However, they dissolve in H_2O containing CO_2 due to the formation of bicarbonates.

$$\underset{\text{(Insoluble)}}{CaCO_3} + CO_2 + H_2 \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2}$$
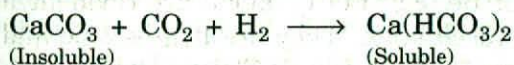
6. Formation of nitrides. All the elements burn in nitrogen to form nitrides, M_3N_2, *e.g.*

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

These react with H_2O to liberate NH_3 *e.g.*

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

Be_3N_2 is *volatile* while other nitrides are *not so*.

7. Formation of carbides. When the elements from Mg to Ba or their oxides are heated with carbon, carbides (MC_2) are obtained, *e.g.*

$$CaO + 3C \longrightarrow CaC_2 + CO$$

All these carbides are *ionic in nature* and have NaCl type structure with M^{2+} replacing Na^+ and $[C \equiv C]^{2-}$ replacing Cl^-. On treatment with H_2O, they liberate *acetylene*.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$$

When Be is heated with carbon, it gives the carbide, Be_2C and not BeC_2. This carbide with H_2O gives *methane*.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$

8. Formation of complexes. The tendency of M^{2+} ions to form the complexes *decreases with the increases of the size of M^{2+} ions*. Thus Be^{2+} ion, on account of its small size, forms many stable complexes such as $[BeF_3]^-$, $[BeF_4]^{2-}$, while Ba^{2+} forms *very few complexes*.

9. Solubility of sulphates and chromates. Calcium sulphate is sufficiently soluble in water, whilst strontium and barium sulphates are almost insoluble but calcium and strontium chromates are soluble in acetic acid medium while barium chromate is insoluble.

Anomalous Behaviour of Beryllium : Dissimilarities with Other Alkaline Earth Metals

Beryllium, the first element of the group differs from rest of alkaline earth metals due to its small atomic size (0.90 Å) and comparitively high electronegativity (1.5). The main points of difference are :

1. Hardness. Beryllium is the hardest of all the elements of its group.

2. Melting and boiling points. The melting and boiling points of beryllium are the highest.

3. Formation of covalent compounds. Beryllium has a tendency to form covalent compounds. Thus, when it reacts with another element, the electronegativity difference is not so large and the bond is, therefore, covalent.

4. Reaction with water. Beryllium does not react with water even at high temperatures. Other alkaline earth metals decompose water liberating H_2 gas.

$$Mg + H_2O \longrightarrow MgO + H_2$$

5. Reaction with hydrogen. Beryllium does not react with hydrogen directly to form its hydride. Its hydride, however, has been prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.

6. Reaction with alkalies. Beryllium reacts with alkalies to form hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2 \uparrow$$
$$\text{Sodium} \atop \text{beryllate}$$
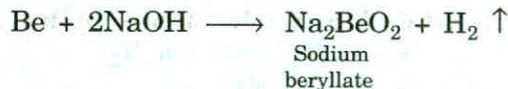
Other alkaline earth metals do not react with alkalies.

7. Behaviour of oxides and hydroxides. The oxides and hydroxides of beryllium are amphoteric, *i.e.*, dissolve in both acids and alkalies to form salts.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

The oxides and hydroxides of other alkaline earth metals are basic.

8. Behaviour of carbides. Beryllium carbide is decomposed by water to form methane (CH_4).

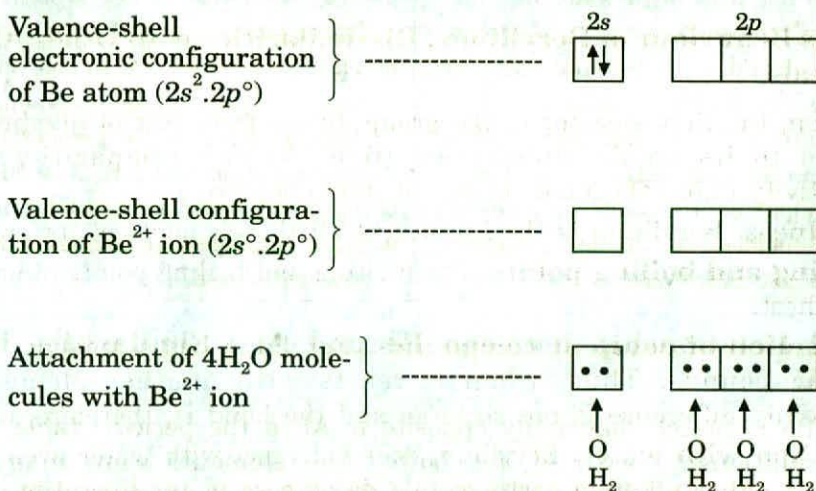$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

The carbides of other alkaline earth metals are decomposed by water to form accetylene (C_2H_2). For example :

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

9. Behaviour of nitrides. Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non-volatile.

10. Number of molecules of water of crystallisation. The salts of Be^{2+} ion cannot have more than four molecules of water of crystallisation while other alkaline earth metals have more than four molecules of water of crystallisation. This is explained as follows. In case of Be^{2+} ion there are only four orbitals (namely one $2s$ and three $2p$ orbitals) available in its outermost shell. These four orbitals can accept lone pairs of electrons denoted by O-atom on each of the water molecules as shown below :

Valence-shell electronic configuration of Be atom $(2s^2.2p^\circ)$

Valence-shell configuration of Be^{2+} ion $(2s^\circ.2p^\circ)$

Attachment of $4H_2O$ molecules with Be^{2+} ion

On the other hand, other alkaline earth metals like Mg can extend their co-ordination number to six by using one $3s$, three $3p$ and two $3d$ orbitals belonging to their outermost shell.

11. Formation of complex compounds. Be^{2+} ion, on account of its small size, forms many stable complex compounds like $[BeF_3]^-$, $[BeF_4]^{2-}$ while M^{2+} ions derived from other alkaline earth metals form very few complex compounds.

Comparison of Be and Mg with Other Alkaline Earth Metals (Ca, Sr, and Ba)

Beryllium and magnesium, although placed in the same group, differ from rest of the alkaline earth metals in a number of properties. Their similarities and dissimilarities with each other are given below.

Similarities

(i) Both Be, Mg and Ca, Sr, Ba have two electrons in their outermost shells.

(*ii*) Both have valency equal to two.

(*iii*) Both react with halogens to form halides of the general formula, MX_2.

(*iv*) Both combine directly with nitrogen to form nitrides.

(*v*) Both react with dilute acids to form hydrogen.

Dissimilarities

| Be, Mg	Ca, Sr, Ba
1. They are hard metals, Be is the hardest.	1. They are soft metals, Ba is the softest.
2. They do not give any colour to the flame.	2. They give characteristic colours to the flame.
3. They do not react with hydrogen.	3. They react with hydrogen to form hydrides.
4. They are not affected by dry air.	4. They are affected by dry air to form oxides.
5. They do not react with water at ordinary temperature.	5. They react with water to form hydrogen.
6. Their hydroxides are insoluble in water and are amphoteric or weakly basic.	6. Their hydroxides are soluble in water and are strongly alkaline.
7. Their carbonates are not precipitated in the presence of $NH_4Cl + NH_4OH$.	7. Their carbonates are precipitated in the presence of $NH_4Cl + NH_4OH$.
8. Their sulphates are soluble in water.	8. Their sulphates are insoluble in water.
9. Their sulphides are soluble in water and are not hydrolysed.	9. Their sulphides are soluble in water and are hydrolysed.

Diagonal Relationship between Be and Al : Similarities between Be and Al

Since Be is placed diagonally opposite to Al in the periodic table, it shows diagonal relationship with Al, *i.e.* both these elements show many similar properties. In fact the similarity between Be and Al is so striking that Be—Al pair is considered to be an ideal diagonal pair in the periodic table and hence the similarity between Be and Al is the best example of diagonal relationship. Their diagonal relationship is attributed because of the following reasons :

(*i*) Polarising powers (*i.e.* ionic potentials), which are equal to charge/radius ratio, of Be^{2+} (= 6.45) and Al^{3+} (= 6.00) are of similar magnitude as shown below :

Ion :	Be^{2+}	Al^{3+}
Charge on ion :	+ 2	+ 3
Ionic radius ($A°$) :	0.31	0.50
Polarising power (*i.e.* charge/radius ratio) :	2/0.31 = 6.45	3/0.50 = 6.0

(*ii*) The standard oxidation potential of Be(= + 1.70 volts) for the electrode reaction :

$$Be \longrightarrow Be^{2+} + 2e^-, \; E°_{ox} = + 1.70 \text{ volts}$$
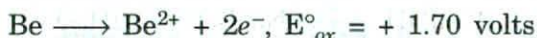
is very close to that of Al (= + 1.67 volts) for the electrode reaction :

$$Al \longrightarrow Al^{3+} + 3e^-, E°_{ox} = + 1.67 \text{ volts.}$$
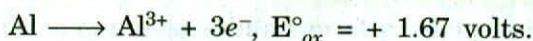
(iii) The electronegativity values of both the elements are the same (Be = 1.5, Al = 1.5)

(iv) Both the metals are weakly electropositive.

The following points show that Be and Al have many similar properties, i.e. they show diagonal relationship.

1. Ionic radii. The ionic radius of Be^{2+} (= 0.31 A°) is comparable with that of Al^{3+} (= 0.50 A°).

2. Extraction. Both the metals are obtained by the electrolysis of their fused salts in the presence of fluoride.

3. Heat of vaporisation. Heats of vaporisation of both the elements at their boiling points are comparable (Be = 73.9 k.cal/g.atom, Al = 67.9 k.cal/g.atom).
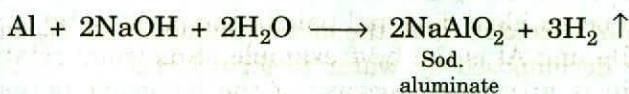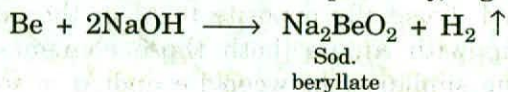
4. Occurrence. In nature both the elements occur together in beryl, $3BeO.Al_2O_3.6SiO_2$.

5. Formation of polymerised covalent hydrides. Both the elements form the polymerised hydrides which are covalent in nature.
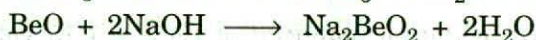
6. Formation of covalent compounds. Both Be and Al have small size and higher charge density and as such they have a strong tendency to form *covalent compounds*. Thus the compounds of both the elements have lower melting points, are soluble in organic solvents and get hydrolysed by water.

7. Action of HNO₃ (Passivity). Both Be and Al are rendered passive by HNO_3 due to the formation of an inert and impervious film of their oxide on the surface of the metals.

8. Action of alkalies. Both the metals dissolve in boiling alkalies liberating H_2 and forming *beryllates* and *aluminates* respectively, e.g.

$$Be + 2NaOH \longrightarrow \underset{\substack{\text{Sod.}\\\text{beryllate}}}{Na_2BeO_2} + H_2 \uparrow$$

$$Al + 2NaOH + 2H_2O \longrightarrow \underset{\substack{\text{Sod.}\\\text{aluminate}}}{2NaAlO_2} + 3H_2 \uparrow$$

9. Properties of oxides and hydroxides. Both the metals burn in O_2 and form oxides. The oxides and hydroxides of both the metals are *amphoteric in nature*, i.e. they are soluble in acids and alkalies as shown below :

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$
$$Al_2O_3 + 6HCl \longrightarrow AlCl_3 + 3H_2O$$
$$Be(OH)_2 + 2HCl \longrightarrow BeCl_3 + 2H_2O$$
$$Al(OH)_3 + 2HCl \longrightarrow AlCl_3 + 3H_2O$$
$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$
$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

Oxides of both the metals are extremely hard, non-volatile and have *very high melting point.*

10. Halildes. Both the metals react with halogens and form halides.

$$Be + Cl_2 \longrightarrow BeCl_2 \; ; \; 2Al + 3Cl_2 \longrightarrow AlCl_3$$
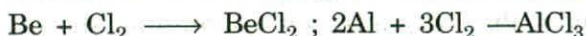
These halides have low melting points and are hydrolysed by water. The anhydrous halides (excepting fluorides) are covalent in nature and as such they dissolve in organic solvents and fume in moist air. Their halides also behave as Lewis acids.

11. Formation of carbides. Both the metals form carbides (Be_2C and Al_4C_3) which evolve methane on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$
$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$
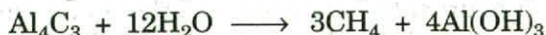
12. Formation of complexes. Be^{2+} and Al^{3+} ions have strong tendency to form chelate type complexes. For example Be^{2+} gives tetrahedral complexes like BeF_4^{2-} and $[Be(C_2O_4)_2]^{2-}$ while Al^{3+} forms octahedral complexes like AlF_6^{3-} and $[Al(C_2O_4)_3]^{3-}$

13. Properties of salts. Salts of both the metals like nitrates, sulphates and chlorides crystallise from aqueous solutions as hydrates. They get easily hydrolysed in solution. The extent of hydrolysis of the salts of both the metals is almost comparable.
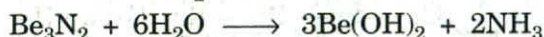
The carbonates of both the metals are unstable, except in an atmosphere of CO_2.

14. Formation of hydrated ions. Both the ions give hydrated ions in aqueous solution like $[Be(H_2O)_4]^{2+}$ and $[Al(H_2O)_6]^{3+}$.

15. Formation of bridged chlorides. Both the metals form bridged chlorides in vapour form. For example :
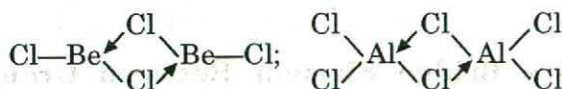
16. Formation of nitrides. Both the metals combine with N_2 and form nitrides. These nitrides are decomposed by water to form NH_3.

$$3Be + N_2 \longrightarrow Be_3N_2$$
$$2Al + N_2 \longrightarrow 2AlN$$
$$Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + 2NH_3$$
$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Comparison of Alkaline Earth Metals with Alkali Metals

(1) The metals calcium, barium and strontium have been isolated from their stable salts by similar electrolytic methods which are applied to the isolation of alkali metals. Beryllium and magnesium are also prepared by the electrolysis of their chlorides.

(2) These metals are, likewise, soft with silvery lustre and very light.

(3) They also *react with water* or *oxygen* with readiness and show much activity towards other substances.

(4) Magnesium and beryllium are comparatively *harder* and *more stable* metals, but in absorbing nitrogen, magnesium shows an analogy to lithium. They possess higher density and higher melting and boiling points.

(5) The *electropositive nature* continuously increases from beryllium to radium in the second group, as in the first group from lithium to caesium.

(6) The *oxides* of alkaline earth metals have less affinity towards water when compared to the oxides of alkali metals but they also dissolve in water to a fair extent (though much less when compared to Na_2O) with the evolution of a considerable amount of heat, and the solution obtained is alkaline. Their *hydroxides*, like alkali hydroxides, are good absorbents for carbon dioxide forming carbonates. But there is a difference between alkali *carbonates* and alkaline earth carbonates. With the exception of lithium carbonate, other alkali carbonates dissolve fairly in water and produce mild alkali solutions. But the carbonates of magnesium, calcium, strontium and barium are only sparingly soluble and come down as precipitates whenever they are formed in solution.

(7) Another contrast is in the behaviour of *bicarbonates*. Sodium and potassium bicarbonates are comparatively less soluble than their carbonates, but, on the contrary, magnesium and calcium bicarbonates are more soluble than the carbonates, and therefore, a fresh precipitate of magnesium or calcium carbonate can be redissolved by passing an excess of carbon dioxide.

(8) Alkali *sulphates* and *phosphates* are also soluble in water but calcium, strontium and barium sulphates and phosphates are much less soluble, and so is the case with their oxalates.

(9) In other salts as chlorides, acetates, nitrates, cyanides etc., the two series of salts are similar. But all these salts are not so important and not so extensively used as the alkali salts.

Magnesium Acts as a Bridge Element Between Groups II A and II B Elements

The sub-group A of the second group of periodic classification consists of the elements Be, Mg, Ca, Sr, Ba and Ra, whereas sub-group B consists of Zn, Cd and Hg. The branching of the two sub-groups occurs at magnesium as shown below :

$$Be-Mg\Big\langle \begin{matrix} Ca-Sr-Ba-Ra...Group\ IIA \\ -Zn-Cd-Hg\ \ ...Group\ IIB \end{matrix}$$
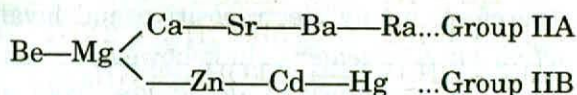
As we have said in the case of the first group, the metals of the sub-group B are the transitional ones of a long series, and the first metal in the second group of this transition is zinc and not magnesium, and necessary therefore, magnesium does not belong to sub-group B. It is a member of the main group, but being at the position where the branches of two sub-groups just begin, it shows similarity with calcium as well as with zinc. In fact it *resembles zinc more than it resembles calcium (See below)*. It is also seen that the electropositive character of the

elements increases from magnesium to radium whereas decreases gradually from magnesium to mercury. In other words, it gradually decreases from radium to mercury via magnesium. Magnesium thus links the two sub-groups and is therefore, regarded as a bridge element between them.

A. Magnesium resembles calcium. Both the metals resemble in the following respects :

(1) Both of them have similar electronic configuration, *i.e.* they have two electrons in their ultimate shell and eight electrons in their penultimate shell.

$$Mg_{12} \longrightarrow 1s^2, 2s^2p^4, 3s^2$$
$$Ca_{20} \longrightarrow 1s^2, 2s^2p^4, 3s^2p^6, 4s^2$$
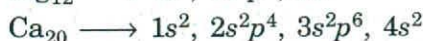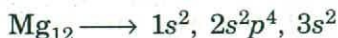
The metals are, therefore, highly electropositive and bivalent.

(2) Both are light silvery and white light metals which are mallable and ductile.

(3) Both of them occur as carbonates and sulphates in nature.

(4) Both form a number of deliquescent salts.

(5) When these metals are heated in a current of nitrogen, both form nitrides (Mg_3N_2 and Ca_3N_2).

(6) Both liberate H_2 when treated with very dil. HNO_3.

(7) Sulphides of both the metals are soluble in water and are not precipitated by passing H_2S in their salt solutions.

(8) Nitrates of both give oxide when heated.

(9) The oxides of both the metals (MgO and CaO) are basic in nature and stable towards heat.

B. Magnesium resembles zinc. Both of these metals resemble in the following respects :

(1) Both are malleable and ductile metals.

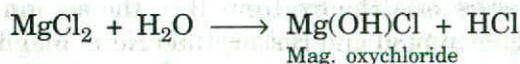(2) Both Mg and Zn *slowly* tranish in air while Ca *quickly* tranishes in air.

(3) Both have the same electronic configuration, *i.e.* they have two electrons in their outermost shell.

$$Mg_{12} \longrightarrow 1s^2, 2s^2p^6, 3s^2$$
$$Zn_{20} \longrightarrow 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2$$
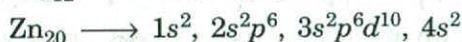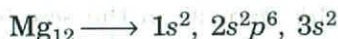
These metals are, therefore, highly electropositive and bivalent.

(4) Both have *no action on cold water*. They, however, react with steam to give metal oxides and H_2. Calcium, however, *decomposes cold water*.

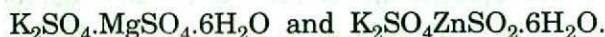(5) Salts of both the metals are *readily hydrolysed*.

$$MgCl_2 + H_2O \longrightarrow Mg(OH)Cl + HCl$$
$$\text{Mag. oxychloride}$$

$$ZnCl_2 + H_2O \longrightarrow Zn(OH)Cl + HCl$$
$$\text{Zinc oxychloride}$$

Calcium salts are *quite stable towards water*.

(6) Their sulphates are isomorphous (*e.g.* $MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$). These sulphates are *readily soluble in water and decompose on strong heating.*

$$2MgSO_4 \longrightarrow 2MgO + 2SO_2 + O_2$$
$$2ZnSO_4 \longrightarrow 2ZnO + 2SO_2 + O_2$$
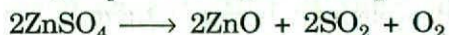
The sulphates also form double salts of the type

$$K_2SO_4.MgSO_4.6H_2O \text{ and } K_2SO_4ZnSO_2.6H_2O.$$

The sulphate of calcium. $C_2SO_4.2H_2O$ is *insoluble in water* and gives the anhydrous sulphate, C_2SO_4 on heating at 400°. Moreover, it does not form double salts as $MgSO_4$ and $ZnSO_4$ do.

(7) Both form double phosphates, *e.g.* $Mg(NH_4)PO_4$ and $Zn(NH_4)PO_4$. These are crystalline compounds, insoluble in water and give pyrophosphates on heating.

$$2Mg(NH_4)PO_4 \longrightarrow Mg_2P_2O_7 + H_2O + 2NH_3$$
$$2Zn(NH_4)PO_4 \longrightarrow Zn_2P_2O_7 + H_2O + 2NH_3$$
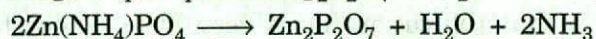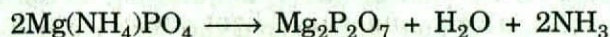
Calcium does not form such double phosphates.

(8) Their salts do not impart any characteristic colour to the flame while calcium salts give brick red colour to the flame.

(9) They do net form hydrides with hydrogen while calcium unites directly with hydrogen to form a salt-like hydride, CaH_2.

Questions with Answers

Q.1 Explain the following giving appropriate reasons for your answer.

(i) The solubility of $M_2^+ CO_3$ carbonates (M = alkali metals) increases while that of $M^{2+}CO_3$ carbonates (M = alkaline earth metals) decreases on moving down the group.

Ans : The variation in solubility of M_2CO_3 and MCO_3 carbonates on moving down the group can be explained on the basis of lattice energies of carbonates and hydration energies of M^+/M^{2+} ions.

In case of $M^+(CO_3)_2$ carbonates since the lattice energies of carbonates decrease down the group, the solubility of carbonates increases down the group. The decrease in lattic energies is due to the increase in the size of M^+ ions from Li^+ to Cs^+ down the group.

In case of $M^{2+}CO_3$ carbonates, since the size of CO_3^{2-} ion is much larger than that of M^{2+} ion, the lattice energies of $M^{2+}CO_3$ carbonates remain almost the same on moving down the group. Hence the decrease in solubility of $M^{2+}CO_3$ carbonates cannot be explained on the basis of lattice energies of $M^{2+}CO_3$ carbonates. The decrease in solubility of these carbonates down the group is due to the decrease of hydration energies of M^{2+} ions from Be^{2+} to Ba^{2+} ions (Be^{2+} = 2455, Mg^{2+} = 1920, Ca^{2+} = 1620, Sr^{2+} = 1480 and Ba^{2+} = 1360 KJ mol^{-1}). Hydration energies of M^{2+} ions decrease down the group because of the gradual increase in the size of M^{2+} ions on moving down the group.

(ii) $Be(OH)_2$ is insoluble but $Ba(OH)_2$ is fairly soluble in water.

(*Kurukshetra 1995*)

Ans : We know that, due to the increase in the size of M^{2+} ions on moving down the group from Be^{2+} to Ba^{2+}, lattice energies of hydroxides decrease from $Be(OH)_2$ to $Ba(OH)_2$. Thus $Be(OH)_2$ has maximum value of lattic energy and $Ba(OH)_2$ has the minimum value. Since $Be(OH)_2$ has maximum value of lattice energy, this hydroxide is insoluble. On the other hand, since $Ba(OH)_2$ has minimum value of lattice energy, this hydroxide is fairly soluble.

The answer of this question can also be given on the basis of covalent/ionic character of the hydroxides. Since Be^{2+} is smallest in size, $Be(OH)_2$ is primarily covalent and hence is insoluble. On the other hand, since Ba^{2+} is the largest in size, $Ba(OH)_2$ has least covalent character and hence is fairly soluble in water.

(*iii*) Ba (OH)$_2$ is highly soluble in water BaSO$_4$ is almost insoluble.

Ans : The size of the SO_4^{2-} ion in $BaSO_4$ is quite big as compared to that of OH^- ion in $Ba(OH)_2$. The SO_4^{2-} ion has masked the Ba^{2+} ion in $BaSO_4$ to a large extent with the result that the cation has a very little tendcy to get hydrated. On the other hand, the OH^- ions due to smaller size masks the Ba^{2+} ions to lesser extent which means that hydration energy released when $Ba(OH)_2$ dissolves in water is quite large. Therefore $Ba(OH)_2$ readily dissolves in water while $BaSO_4$ is almost insoluble.

(*iv*) BeO is insolube in water but BeSO$_4$ is soluble in water.

Ans : The lattice energy BeO is higher as compared to $BeSO_4$ because the size of O^{2-} ion is very small while SO_4^{2-} ion has bigger size. Since high lattice energy opposes the solubility of a substance in water, BeO is almost insoluble while $BeSO_4$ is isoluble in water.

(*v*) Na$_2$SO$_4$ is water soluble while BaSO$_4$ is not.

Ans : Lattice energy of Na_2SO_4 is less compared with that of $BaSO_4$ because of smaller charge density on Na^+ ion as compared to Ba^{2+} ions. Therefore, hydration energy released easily overcomes the lattice energy when Na_2SO_4 dissolves in water. But this is not possible in case of $BaSO_4$ when tried to be dissolved in water. Therefore, Na_2SO_4 is readily soluble in water while $BaSO_4$ in almost insoluble.

(*vi*) The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble.

Ans : The solubility of a particular salt in water is inversely proportional to the lattice energy. Now, the sizes of both Mg^{2+} and Ca^{2+} ions are smaller as compared to Na^+ and K^+ ions. This means that there is a stronger metallic bonding. As a result, the lattice energies of the compounds containing these ions are more and they are expected to be less soluble in water compared with the corresponding compounds of sodium and potassium.

(*vii*) BaSO$_4$ is insoluble where as BeSO$_4$ is soluble in water

Ans : The lattice energy of $BaSO_4$ is much more than its hydration energy and hence it is insoluble in water. But hydration energy of $BeSO_4$ is much higher than its lattice energy because of small size of Be^{2+} ions. Therefore, it is highly soluble in water

(*viii*) **BaO is soluble but BaSO$_4$ in insoluble in water.**

Ans : Both BaO and BaSO$_4$ are ionic compounds. However, the size of O^{2-} ion is much smaller than that of the SO$_4{}^{2-}$ ion. *Since a bigger anion stabilizes a bigger cation more than a smaller anion stabilizes a bigger cation*, the lattice energy of BaO is much smaller than that of BaSO$_4$ and hence BaO is soluble while BaSO$_4$ is insoluble in water.

(*ix*) **LiI is more soluble than KI in ethanol.**

Ans : Li$^+$ is much smaller than K$^+$ ion. Therefore, according to Fajans rule, Li$^+$ ion can polarize bigger I$^-$ ion to a greater extent than K$^+$ ion. As a result, LiI is more covalent than KI and hence is more soluble in organic solvents like enthanol.

Q.2 Be and Mg donot give characteristic colour to the flame while other alkaline earth metals do give. Explain why.

(**Punjab 1996 ; M.D. Rohtak 1997 ; Delhi 1997**)

Ans : When alkali earth metals or their salts are heated in a flame, they give a characteristic colour to the flame as shown below :

Ca	Sr	Ba	Ra
Brick red	*Crison*	*Apple green*	*Crimson*

Reason. When alkaline earth metals or their salts are heated in a flame, the electrons present in the outer most shell absorb energy of the flame. Since ionisation energies of Ca, Sr, Ba and Ra are comparatively low, the energy absorbd by the electrons is suficient to excite the electrons to higher energy levels. When these excited electros come back to the ground state levels, they emit the absorbed energy in the form of radiations having particular frequency or wavelength. It is due to the emission of energy that Ca, Sr, Ba and Ra give colour in the flame.

Since Be and Mg atoms are smaller in size, they have high values of ionisation energies and hence their electrons are bound to the nucleus very strongly. They, therefore, need greater amount of energy to get excited to higher enrgy levels. Now since the energy absorbed by the electrons from the flame is not sufficient to excite the electrons to go to higher energy levels, Be and Mg donot impart any colour to the flame.
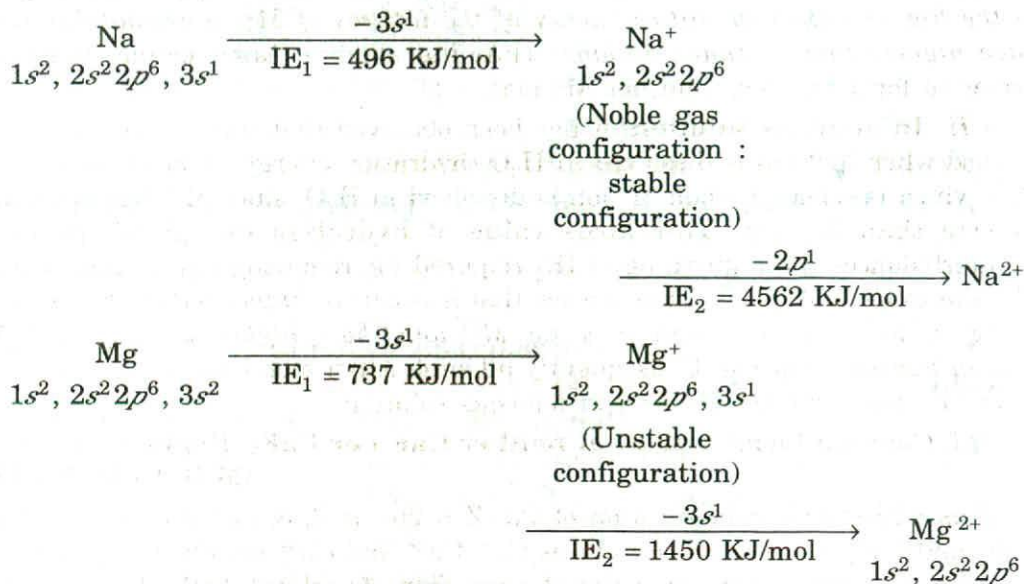
Q.3 IE$_1$ values of alkali metals are lower than those of the corresponding alkaline earth metals but IE$_2$ values of alkali metals are higher than those of the corresponding alkaline earth metals. Explain why ?

Ans : This can be explained by considering IE$_1$ and IE$_2$ values of Na (alkali metal) and Mg (alkaline earth metal) as given below :

Since Na atom is larger in size than Mg atom (Na = 186 pm, Mg = 160 pm), Na atom has lower value of IE$_1$ than Mg atom.

In case of alkali metals (*i.e.* Na) the second electron is to be removed from the monovalent cation (Na$^+$) which has already acquired a noble gas configuration *viz.* 1s^2, 2s^2 2p^6 which is a stable configuration. On the other hand, in alkaline earth metals (*i.e.* Mg), the second electron is to be removed from a monovalent cation (Mg$^+$) which still has one electron in the outer most shell (Mg$^+$ = 1s^2, 2s^2,

$2p^6$, $3s^1$). Thus the second electron in Mg can be removed easily and hence IE_2 of Mg is lower than that of Na.

$$\underset{1s^2,\ 2s^2 2p^6,\ 3s^1}{Na} \xrightarrow[\quad IE_1 = 496\ KJ/mol \quad]{-3s^1} \underset{\substack{1s^2,\ 2s^2 2p^6 \\ \text{(Noble gas} \\ \text{configuration :} \\ \text{stable} \\ \text{configuration)}}}{Na^+}$$

$$\xrightarrow[\quad IE_2 = 4562\ KJ/mol \quad]{-2p^1} Na^{2+}$$

$$\underset{1s^2,\ 2s^2 2p^6,\ 3s^2}{Mg} \xrightarrow[\quad IE_1 = 737\ KJ/mol \quad]{-3s^1} \underset{\substack{1s^2,\ 2s^2 2p^6,\ 3s^1 \\ \text{(Unstable} \\ \text{configuration)}}}{Mg^+}$$

$$\xrightarrow[\quad IE_2 = 1450\ KJ/mol \quad]{-3s^1} \underset{1s^2,\ 2s^2 2p^6}{Mg^{2+}}$$

IE_3 of Mg will be very high because the electron is to be removed from the stable noble gas configurtion of Mg^{2+}.

Q.4 Why do alkaline earth metals form bivalent ions (M^{2+}) through their second ionisation energy (IE_2) is much higher than their first ionisation energy (IE_1). (M.D. Rohtak 1997)

Ans : Since the values of IE_1 for alkaline earth metal atoms are much lower than those of IE_2, these metals should prefer to form monovalent ions (M^+) and not bivalent ions (M^{2+}). However, in practice, these metals form bivalent ions like Mg^{2+}, Ca^{2+} etc. Greater stability of M^{2+} ions as compared to that of M^+ ions can be explained as follows :

(*i*) Greater stability of M^{2+} ions as compared to M^+ ions can be explained on the basis of electronic configuration of these ions. We know that the E.C. of the atoms of alkaline earth metals (excepting Be) is 2, 8,... 8, 2. Thus E.C. of M^+ and M^{2+} ions is 2, 8, ...8, 1 and 2, 8, ...8 respectively. These configurations show that M^+ ions have one electron in their outer most shell while M^{2+} ions have 8 electrons (noble gas configuration) in their outer most shell. Since 8-electron configuration (noble gas configuration) of M^{2+} ions is more stable than 1-electron configuration of M^+ ions, M^{2+} ions are more stable than M^+ ions. Consequently alkaline earth metals prefer to form M^{2+} ions rather than M^+ ions.

(*ii*) **In the solid state,** the lattices (ionic solids) formed by M^{2+} ions are stronger (more stable) than those formed by M^+ ions. This is due to the fact that lattice energy released in the formation of lattices of M^{2+} ions is higher than that which is released in the formation of lattices of M^+ ions. Higher value of lattice energy released in the formation of lattices of M^{2+} ions is because of the fact that M^{2+} ions are smaller in size than M^+ ions (Smaller is the size of the cation,

higher is the value of lattice energy of its lattice). This higher value of lattice energy of lattices of M^{2+} ions conterbalances the high value of IE_2. Thus it is *due to the higher values of lattice energy of the lattices of M^{2+} ions that M^{2+} ions have higher stability than M^+ ions.* Thus the alkaline earth metal atoms (M) prefer to form M^{2+} ions and not M^+ ions.

(*iii*) **In aqueous solution,** it has been observed that the amount of energy releasd when M^{2+} ion is dissolved in H_2O (hydration energy) is much more than that which is released when M^+ ion is dissolved in H_2O, since M^{2+} ion is smaller in size than M^+ ion. This large value of hydration energy of M^{2+} ions counterbalances the high value of IE_2 required for removing two electrons from M atom to form M^{2+} ions. Thus we see that *it is due to higher value of hydration energy of M^{2+} ions that these ions (i.e. M^{2+} ions) have higher satbility than M^+ ions in aqueous solution.* Consequently alkaline earth metal atoms (M) prefer to form M^{2+} ions and not M^+ ions in aqueous solution.

Q.5 Calcium forms CaF_2, but neither CaF nor CaF_3. Explain why ?
                                                                   (M.D. Rohtak 1994)

Ans : Electronic configuration of Ca (Z = 20), is 2, 8, $3s^2$, $3p^6$, $4s^2$. In CaF, CaF_2 and CaF_3, Ca atom is present as Ca^+, Ca^{2+} and Ca^{3+} ion respectively. These ions are obtained by removing one electron from $4s$ orbital, both electrons from $4s$ orbital and two electrons from $4s$ orbital and one electron from $3p$ orbitals. The energies required for the removal of these electrons are equal to IE_1 IE_2 and IE_3 of Ca atom respectively. Value of IE_1 is much smaller than that of IE_2 and the value of IE_3 is very large ($IE_3 > IE_2 \gg IE_1$).

Now since the value of IE_1 is much smaller than that of IE_2, Ca should prefer to form CaF (Ca is present as Ca^+ in CaF) and not CaF_2 (Ca is present as Ca^{2+} in CaF_2). But Ca prefers to form CaF_2 instead of CaF. The preference for the formation of CaF_2 is due to the fact that CaF_2 has much more lattice energy than CaF has. Thus CaF_2 is more stable than CaF.

Formation of CaF_3 (Ca is present as Ca^{3+} in CaF_3) is not possible because the removal of three electrons from Ca atom to form Ca^{3+} ion requires a large amount of energy which is not available in chemical reaction.

Q.6 Explain why in aqueous solution $MgCl_2$ is more readily formed than MgCl.

or **Explain why in aqueous solution $MgCl_2$ is more stable than MgCl.**

or **Explain why in aqueous solution $MgCl_2$ exists but MgCl does not.**

Ans : The formation of one mole of MgCl and $MgCl_2$ in aqueous solution can be represented by the following equations :

$$Mg\ (s) + \frac{1}{2}\ Cl_2\ (g) + aq \rightarrow MgCl\ (aq)$$

$$Mg\ (s) + Cl_2\ (g) + aq \rightarrow MgCl_2\ (aq)$$
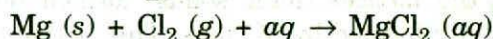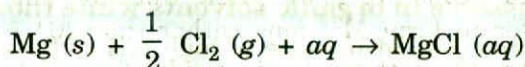
It has been observed that the values of $\Delta H°_f$ for MgCl (aq) and $MgCl_2$ (aq) both are negative but this value for $MgCl_2$ (aq) is more negative than that for MgCl (aq). Hence $MgCl_2$ (aq) is more readily fromed in aqueous solution than

MgCl (aq). In other words we can say that in aqueous solution $MgCl_2$ is more stable than MgCl or in aqueous solution $MgCl_2$ exists but MgCl dose not exist.

Q.7 Explain the following, giving reasons for your answer.

(i) Compounds of alkaline earth metals are more hydrated than those of alkali metals.

***or* The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts.   (I.I.T. 1997)**

Ans : Since alkaline earth metal ions (M^{2+}) are smaller in size than alkali metal ions (M^+), M^{2+} ions are more extentively hydrated than M^+ ions and hence compounds of M^{2+} ions are more hydrated than those of M^+ ions. For example magenisum chloride and calcium chloride exist as $MgCl_2. 6H_2O$ and $CaCl_2. 6H_2O$ while sodium chloride and potassium chloride exist as NaCl and KCl. Among alkali metals, only Li, because of its small size, forms hydrated salts like LiCl. $2H_2O$.

(ii) Mg^{2+} ion is more highly hydrated than Na^+ ion.

Ans : The positive charge density around Mg^{2+} ion is more than that around Na^+ ion due to its smaller size and more number of positive charges. Therefore, Mg^{2+} ion has a greater tendency to attract surrounding H_2O molecules than Na^+ ion. In other words, Mg^{2+} is more highly hydrated than Na^+ ion.

Q.8 How would you explain the following ?

(i) Group 2 metals (Mg and Ca) are harder and denser than group 1 metals (Na and K).

Ans : In metals belonging to the group 2, the atomic sizes are less as compared to the metals of the group 1 present in the same period. For example, size of Mg is smaller as compared to Na. This means that the atoms in group 2 metals are more closely packed as compared to those belonging to group 1 and the metallic bonds in them are also stronger. Therefore, the metals of group 2 are denser as compared to metals of group 1.

(ii) Halides of beryllium fume in moist air but other alkaline earth metal halides do not.

Ans : $BeCl_2$ being a salt of a weak base, $Be(OH)_2$ and a strong acid, HCl undergoes hydrolysis by water to form HCl which fumes in air. $BaCl_2$, on the other hand, being a salt of a strong base, Ba $(OH)_2$ and strong acid, HCl does not undergo hydrolysis by water to form HCl and hence does not fume in air.

$$BeCl_2 + 2\ H_2O \longrightarrow Be(OH)_2 + 2HCl\ ;$$
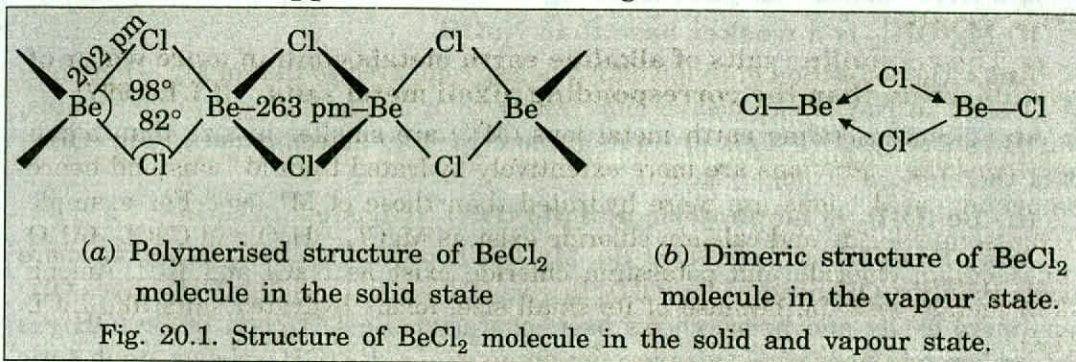$$BaCl_2 + H_2O \overset{}{\times\!\!\longrightarrow} Ba(OH)_2 + 2HCl$$
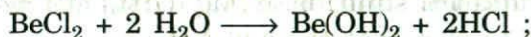
(iii) Halides of Be dissolve in organic solvents while those of Ba do not.

Ans : Halides of Be are covalent because of high $\Delta_i H$ of Be while those of Ba are ionic due to low $\Delta_i H$ of Ba.

(iv) Beryllium halides are polymeric.

Ans : The halides of Be are electron deficient covalent compounds since they have only four electrons in the valence shell. Therefore, to complete their octets,

they undergo polymerization to form polymerisd molecule. For example in the solid state, $BeCl_2$ molecule exists as a polymerised molecule whose structure is given at (a) of Fig. 20.1. In the vapour state $BeCl_2$ molecule exits as a chloro-bridged dimer, $(BeCl_2)_2$ as shown at (b) of Fig. 20.1.

(a) Polymerised structure of $BeCl_2$ molecule in the solid state

(b) Dimeric structure of $BeCl_2$ molecule in the vapour state.

Fig. 20.1. Structure of $BeCl_2$ molecule in the solid and vapour state.

(v) MgO is used as a refractory material.

Ans : MgO has high lattice energy due to greater charge and smaller ionic size of Mg^{2+} and O^{2-} ions. As a result, it has a very high melting point and hence is used as a refractory material.

(vi) $MgCl_2$ is more covalent than NaCl.

Ans : Since Mg^{2+} ion has higher charge than Na^+ ion, this ion palarises Cl^- ion more strongly in $MgCl_2$ than Na^+ ion polarises Cl^- ion in NaCl. Hence $MgCl_2$ is more covalent than NaCl.

(vii) The chemistry of beryllium is not essentially ionic. Justify the statement by making a reference to the nature of oxide, chloride and fluoride of beryllium.

Ans : The compounds of alkaline earth metals of group 2 are generally of ionic nature but those of beryllium are mostly covalent. Actually Be^{2+} ion due to very small size has a high positive charge density around it. It can easily polarise the O^{2-} ion or F^- or Cl^- ion in BeO, BeF_2 and $BeCl_2$ respectively. The oppositely charged ions mutually netralise their charges to large extent. Therefore, these compounds are almost covalent in nature.
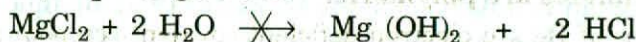
(viii) Mg_3N_2 when reacted with H_2O gives NH_3 but $MgCl_2$ does not give HCl with H_2O.

Ans : Since Mg_3N_2 is a salt of strong base [Mg $(OH)_2$] and weak acid (NH_3), it gets hydrolysed by H_2O to give $Mg(OH)_2$ and NH_3

$$Mg_3N_2 + 6\ H_2O \xrightarrow{\text{Hydrolysis}} Mg\ (OH)_2 + 2\ NH_3$$
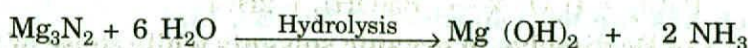
$$\text{Strong base} \qquad \text{Weak acid}$$

Since $MgCl_2$ is a salt of strong base [Mg(OH)$_2$] and strong acid (HCl), it is not hydrolysed by H_2O to give HCl

$$MgCl_2 + 2\ H_2O \xrightarrow{\;\;\;} Mg\ (OH)_2 + 2\ HCl$$

$$\text{Strong base} \quad \text{Strong acid}$$

(ix) Alkaline earth metals have greater tendency to form complexes than alkali metals.

Ans : Since alkaline earth metal cations (M^{2+}) have smaller size and higher charge than the alkali metal cations (M^+), M^{2+} ions have greater tendency to form complexes.

Q.9 Give reasons for the following :

(i) Mg(OH)$_2$ is a weaker base than NaOH.

Ans : The ionisation enthaply of Na is less compared to that of Mg. Therefore, M–O bond in NaOH can cleave more easily than in Mg (OH)$_2$. In other words, NaOH can releas OH$^-$ ions in solution more readilly as compared to Mg (OH)$_2$. It is therefore, a stronger base.

(ii) Be (OH)$_2$ is amphoteric and Mg (OH)$_2$ is basic.

Ans : Since IE of Mg < IE of Be, Mg–OH bond in Mg (OH)$_2$ is broken more easily than Be–OH bond in Be (OH)$_2$ to give OH$^-$ ions. Thus Mg (OH)$_2$ gives OH$^-$ ions more easily and hence shows basic character. Be–OH bond in Be (OH)$_2$ is not broken and hence OH$^-$ ions are not obtained, *i.e.* Be (OH)$_2$ shows amphoteric character.

(iii) Be (OH)$_2$ dissolves in NaOH but Mg(OH)$_2$ does not.

Ans : Be (OH)$_2$ is amphoteric and hence it dissolves in NaOH forming sodium beryllate (Na$_2$BeO$_2$).

$$Be (OH)_2 + 2\ NaOH \rightarrow Na_2BeO_2 + 2\ H_2O$$

Mg(OH)$_2$, on the other hand, being basic does not dissolves in NaOH.

Q.10 The enthalpy of formation of hypothetical CaCl (s) is found to be –180 KJmol^{-1} and that of CaCl$_2$ (s) is – 800 KJmol^{-1}. Calculate $\Delta H°_f$ for the disproportation reaction :

$$2\ CaCl\ (s) \rightarrow CaCl_2\ (s) + Ca\ (s)$$
$$(Ca = H) \qquad\qquad (Ca = +2) \qquad (Ca = 0)$$
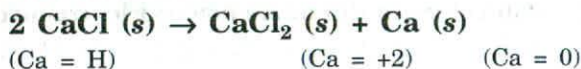
Ans : $\Delta H°_f$ of the given reaction

$$= \Delta H°_f\ (Products) - \Delta H°_f\ (Reactants)$$
$$= [\Delta H°_f\ (CaCl_2) + \Delta H°f\ (Ca)] - 2 \times \Delta H°_f\ (CaCl)$$
$$= [-800 + 0] -2 \times (-180)$$
$$= -800 + 360 = -440\ KJmol^{-1}\ (Ans)$$

Q.11 Answer the following with appropriate reason.

(i) Which are more electropositive ? Alkali metals or alkaline earth metals.

(ii) Which one is a covalent hydride ? BeH$_2$, NaH, CaH$_2$?

(iii) Whose aqueous solution is acidic ? NaCl, BaCl$_2$, BeCl$_2$?

(iv) Which has the least hardness ? Na, Be, Li, Ca.

(v) Which are stronger reducing agents ? Alkali metals or alkaline earth metals.

**Ans :** (i) *Alkali metals are more electropositive than alkaline earth metals.*

Reason. Since alkali metals have lower IE values than alkaline earth metals, these metals can lose their ns^1 electron more easily and hence show more electropositive character than alkaline earth metals.

(ii) *BeH$_2$ is a covalent hydride.*

Reason. Since Be is the first element in group II A, it has the smallest size and hence Be^{2+} ion has high polarising power. Consequently BeH_2 has high covalent character.

(*iii*) *Aqueous solution of BeCl$_2$ is acidic.*

Reason. Since $BeCl_2$ is a salt of weak base [Be(OH)$_2$ – amphoteric hydroxide] and strong acid (HCl), the hydrolysis of aqueous solution of this salt gives weak base and strong acid. Due to the formation of strong acid, the aqueous solution of $BeCl_2$ shows acidic property.

$$BeCl_2 + 2 \ H_2O \longrightarrow Be \ (OH)_2 \quad + \quad 2 \ HCl$$

Weak base   Strong acid

(Amphotoeric

hydroxide)
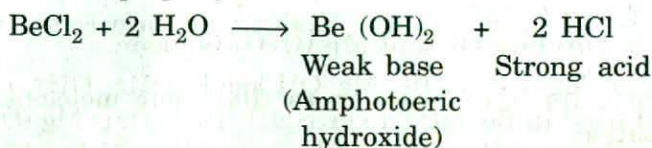
NaCl is a salt of strong acid (HCl) and strong base (NaOH). Simmilary $BaCl_2$ is also a salt of strong acid (HCl) and strong base *viz* Ba (OH)$_2$.

(*iv*) *Na metal has the least hardness.*

Reason. We know that, since with the increase in the size of atoms of a metal, the strength of the metallic bond holding the atoms of the metal together decreases, the hardness of the metal also decreases. On this basis, the relation between hardness of the given metals can be written as (*i*) Li > Na (*ii*) Be > Ca and (*iii*) Li < Be or Be > Li. These relations show that Na metal has the least hardness.

(*v*) *Alkali metals are stronger reducing agents than alkaline earth metals.*

Reason. Since $E°_{ox}$ values for alkali metals are higher than those for alkaline earth metals, alkali metals are stronger reducing agents than alkaline earth metals.

Q.12 Two metals (A) and (B) belong to the same group of the periodic table. Metal (A) froms an insoluble oxide (AO) but soluble sulphate (ASO$_4$) while metal (B) forms soluble oxide (BO) and insoluble sulphate (BSO$_4$). The hydroxide of (A) is soluble in NaOH while that of (B) is insoluble in NaOH. Identity the metals (A) and (B).

Ans : The formulae of oxides (AO, BO) and sulphates (ASO$_4$ and BSO$_4$) given in the question indicate that (A) and (B) metals belong to group II A. Now we know that among the oxides of alkaline earth metals (group II A), BeO is insoluble and BaO is soluble. Similarly, among the sulphates of alkaline earth metals, $BeSO_4$ is soluble and $BaSO_4$ is insoluble. Being amphoteric in nature, BeO reacts with NaOH to form Na_2BeO_2 while since BaO is strongly basic, it does not react with NaOH.

$BeO + 2 \ NaOH \rightarrow Na_2BeO_2 + 2 \ H_2O$

$BaO + NaOH \rightarrow$ No reaction
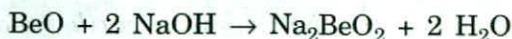
Thus the metals are A = Be and B = Ba.

University Questions

1. Explain the following :

   (*i*) Alkaline earth metals form M^{2+} ions but not M^+ ions.

   (Raj. 87; Agra 83)

   (*ii*) Although the value of 2nd ionisation potential of alkaline earth metal is higher than that of 1st ionisation potential, yet these metals form M^{2+} ions instead of M^+ ion. *(Gorakhpur 82; Allahabad 89)*

   (*iii*) Be^{2+} ion has a much stronger tendency to form complexes than Mg^{2+} ion. *(Meerut 80S)*

   (*iv*) Beryllium salts have never more than four molecules of water of crystallisation. *(Meerut 80)*

   (*v*) Be and Mg do not import any colour to the flame. *(Mysore 80)*

   (*vi*) The solubility of the sulphates of alkaline earth metals decreases whereas the solubility of their hydroxides increases on moving down the group.

   (Gorakhpur 82)

   (*vii*) The thermal stability of carbonates of alkaline earth metals increases in atomic numbers. *(Allahabad 87)*

   (*viii*) Alkaline earth metal salts import colour to the bunsen flame.

   (Delhi 89)

   (*ix*) $MgSO_4$ is more soluble in water than $BaSO_4$. *(Raj. 87)*

   (*x*) $BaSO_4$ is insoluble in water whereas $MgSO_4$ is soluble. *(Raj. 79)*

   (*xi*) Be^{2+} ion has a much stronger tendency to form complexes than Mg^{2+} ion. *(Meerut 80S)*

   (*xii*) CaO is a basic oxide whereas BeO is amphoteric. *(Allahabad 89)*

   (*xiii*) The first ionisation energy of Ca is much smaller than the second ionisation energy; but calcium forms only Ca^{2+} ions in solution.

   (Allahabad 86)

   (*xiv*) Alkaline earth metals form M^{2+} ions but not M^{3+} ions. *(Meerut 88)*

   (*xv*) Basic character of the hydroxides of alkaline earth metals increases on descending the group. *(Delhi 89)*

2. Compare a typical alkali metal with a typical alkaline earth metal with respect to ionisation potential, ionic size, melting points and hardness. Account for the similarities and differences. *(Jodhpur 85)*

3. Compare alkali metals with alkaline earth metals with respect to their electronic configuration, atomic and ionic radii, ionisation potential, oxidation state, polarising power and hydration energies. *(Meerut 84; GND 87)*

4. Explain the following :

   (*i*) The ionisation potential values of alkaline earth metals are higher than those of neighbouring alkali metals.

   (*ii*) Alkaline earth metals have greater tendency to form complexes than those of alkali metals. *(Delhi B.Sc. Hons. 81)*

(*iii*) The metals of group IIA are harder and have higher m. pts than those of group IA elements.   (*Raj. 84; Delhi 88, 89*)

(*iv*) The alkaline earth metals are harder than alkali metals.

(*v*) The hydroxide of group IIA metals are weaker than those of group IA metals.   (*Raj. 84*)

(*vi*) The carbonates of group IIA metals are less stable to heat than those of group IA metals.   (*Raj. 84*)

(*vii*) KOH is stronger base than $Ba(OH)_2$.   (*Punjab 85*)

(*viii*) Group IIA elements are smaller in size than group IA elements.
    (*Delhi 88*)

5. (*a*) Explain why the solubility of sulphates decreases while that of hydroxides increases as the size of cations increases from beryllium to barium in group 2 of the periodic table.

   (*b*) Compare and contrast the alkali metals with alkaline earth metals with respect to : (*i*) Electronic configuration and hardness (*ii*) Reducing properties and oxidation potentials (*iii*) Their carbonates and bicarbonates.   (*Allahabad 99*)

6. Discuss the anomalous behaviour of Be.   [*Gauhauti (General) 2000*]

7. How will you obtain ? (*i*) Beryllium from beryl (*ii*) Radium bromide from pitchblende.   (*Lucknow 2001*)

8. Explain why solubilities of alkaline earth metal sulphates decrease down the group.   (*Delhi 2002*)

9. Explain the hybridisation and structure of $BeCl_2$ molecule.
    (*C.S.J.M. Kanpur 2006*)

10. (*a*) Explain why $BeCl_2$ is more covalentthan $MgCl_2$.

    (*b*) Explain physical and chemical properties of II A group elements.
    (*Meerut 2006*)

11. Justify the position of alkaline earth metals in the periodic table.
    (*Meerut 2008*)

12. Which of the following is the most covalent? $BeCl_2$, $MgCl_2$, $CeCl_2$ and $SrCl_2$.   (*Agra 2008*)