s-BLOCK ELEMENTS

1. ALKALI METALS (GROUP 1)

The group 1 elements have ns^1 electronic configuration and are highly reactive metals

Elements	Atomic Number	Electronic Configuration
Lithium (Li)	3	[He] $2s^1$
Sodium (Na)	11	[Ne] $3s^1$
Potassium (K)	19	[Ar] $4s^1$
Rubidium (Rb)	37	[Kr] $5s^1$
Cesium (Cs)	55	[Xe] $6s^1$
Francium (Fr)	87	[Rn] $7s^1$

1.1 Physical Properties

1.1.1 Atomic Size

The atoms are largest in their corresponding periods. Atomic size increases in going down the group.

1.1.2 Oxidation State

The group 1 elements exhibit +1 oxidation state

1.1.3 Density

Alkali metals have large size which accounts for their low density

$$\text{Density} = \frac{\text{Atomic mass}}{\text{Atomic volume}}$$

Atomic weight increases from Li to Cs in the group and volume also increases but increase in atomic weight is more than increase in volume. Therefore density increases from Li to Cs.

Exception : Density of Na is more than that of K

order : $Li < K < Na < Rb < Cs$

1.1.4 Nature of Bonds

The electronegativity values being low, they combine with other elements to form Ionic bond.

1.1.5 Ionization Energy

The first ionisation energies for the atoms in this group are lower than those for any other group in the periodic table. The atoms are very large so the outer electron are held weakly by the nucleus hence the ionisation energy is not large. Ionization energy decreases on moving down the group.

1.1.6 Flame Test

Alkali metals have large size, when heated on the flame the electrons present in the valence shell move from lower energy level to higher energy level by absorption of heat from the flame. When they come back to the ground state, they emit the extra energy in the form of visible light to provide colour to the flame

Element	Colour
Li	Red
Na	Golden yellow
K	Violet
Rb	Red Violet
Cs	Blue

1.1.7 Standard Oxidation Potential

The measure of the tendency of donating electrons of a metal in water is called its electrode potential. If the concentration of metal ions is unity, then it is called as standard electrode potential. Lithium has the highest ionization potential but has an highest electrode potential due to highest hydration energy.

1.1.8 Hydration of Ions

The ions are heavily hydrated. The smaller the size of the ion, the greater is the degree of hydration. Thus the degree of hydration decreases down the group from Li^+ to Cs^+. Thus with the increase in hydration electrical conductivity decreases.

1.1.9 Lattice Energy

Salts of alkali metals are ionic solids. Lattice energy of salts of alkali metals having common anion decreases on descending down the group.

1.1.10 Solubility in Liquid Ammonia

$M + n\,NH_3 \rightarrow [M(NH_3)_x]^+ + e^-(NH_3)_y$

$(n = x + y)$

Dilute solutions of alkali metals in liquid ammonia are dark blue in colour and the main species present are solvated metal ions and solvated electrons. If the blue solution is allowed to stand, the colour fades until it dissappears owing to the formation of metal amide. The solutions of metal in liquid conduct electricity because of the presence of solvated electrons. The dilute solutions are paramagnetic because they contain free electrons.

1.1.11 Electronegativity Values

The electronegativity values are small which decrease from Li to Cs.

1.1.12 Reactivity

The reactivity of alkali metals goes on increasing in the following order.

$Li < Na < K < Rb < Cs$

1.1.13 Colourless and Diamagnetic ions

The property of an ion being colourless or coloured depends on the number of unpaired electrons present in the ion. If unpaired electrons are present in anion then these electrons can be excited by energy from light and show colour on coming back to the ground state. The ion which have unpaired electrons show magnetic properties whereas the ions having paired electrons nullify the magnetic fields of each other. Such ions are called diamagnetic ions.

Super oxides are para magnetic and coloured due to the presence of unpaired electrons.

1.1.14 Melting and Boiling Point

The cohesive energy is the force holding the atoms or ions together in the solid. The cohesive energy depends on the number of electrons that can participate in bonding. The cohesive force decreases down the group in alkali metals group as they have only one valence electron which participates in bonding and of the large size and diffusing nature of the outer bonding electron. The atoms become larger on descending down the group, so the bonds are weaker, the cohesive energy decreases and the softness of metal increases. Hence the melting point decreases down the group. Boiling point also decreases down the group.

1.2 Chemical Properties

Some common reactions of Group 1 metals

Reaction	Comment
$M + H_2O \rightarrow MOH + H_2$	Hydroxides are strongest base known
$Li + O_2 \rightarrow Li_2O$	Monoxide formed by Li and to a small extent by Na
$Na + O_2 \rightarrow Na_2O_2$	Peroxide formed by Na and to a small extent by Li
$K + O_2 \rightarrow KO_2$	Superoxide formed by K, Rb, Cs.
$M + H_2 \rightarrow MH$	Ionic salt like hydrides
$Li + N_2 \rightarrow Li_3N$	Nitride formed only by Li
$M + S \rightarrow M_2S$	All metals form sulphides
$M + X_2 \rightarrow MX$	All the meatls form halide
$M + NH_3 \rightarrow MNH_2$	All the metals form amides.

1.2.1 Reaction with Air

Group 1 elements are very reactive and tarnish rapidly in air. Cs burns spontaneously in air.

These metals form alkaline carbonates in moist air.

$2Na + O_2 \rightarrow 2\,Na_2O$

$Na_2O + H_2O\ (\text{mositure}) \rightarrow 2\,NaOH$

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

1.2.2 Reaction with O_2

Li forms Li_2O, Na forms two type of oxide

(M_2O, M_2O_2) and K, Rb, Cs forms superoxides (MO_2).

1.2.2.1 Basic Nature, Ionic Nature of the Oxides

Basic nature of oxides increases from Li to Cs due to increase in the size of cation

- Size of cation increases from Li to Cs. According to Fajan's Rule, ionic character of these oxides increases from Li to Cs.
- Solubility in water increases from Li to Cs oxides, due to increase in ionic character of these metal oxides.

1.2.3 Reaction with water

Group 1 metals react with water liberating H_2 and forming hydroxides.

$2\,Li + 2\,H_2O \rightarrow 2LiOH + H_2$

$2Na + 2\,H_2O \rightarrow 2NaOH + H_2$

$2K + 2\,H_2O \rightarrow 2\,KOH + H_2$

1.2.4 Reaction with Hydrogen

Group 1 metals reacts with H_2 to form ionic hydrides. Thermal stability of LiH is high.

Stability of hydrides :

$LiH > NaH > KH > RbH > CsH$

1.2.5 Reaction with dilute acids

Due to alkaline nature, these metals react rapidly with dilute acids and the rate of reaction increases from Li to Cs because of increase in basic character.

1.3 Compounds of Alkali Metal

1.3.1 Hydroxides

NaOH is often called as caustic soda. KOH is called caustic potash because of their corrosive properties. The caustic alkali are the strongest base in aqueous solution. The solubility of hydroxides increases down the group.

The bases react with acids to form salt and H_2O.

$KOH + HCl \rightarrow KCl + H_2O$

$NaOH + HCl \rightarrow NaCl + H_2O$

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

The bases liberate ammonia from ammonium salts

$NaOH + NH_4Cl \rightarrow NH_3 + NaCl + H_2O$

$KOH + NH_4Cl \rightarrow NH_3 + KCl + H_2O$

KOH resembles NaOH in all its reaction. but as KOH is much more expensive it is seldom used. However KOH is more soluble in alcohol, thus producing $C_2H_5O^-$ ions by the equilibrium

$C_2H_5OH + OH^- \rightleftharpoons C_2H_5O^- + H_2O$

This accounts for the use of alcoholic KOH in organic chemistry Group 1 hydroxides are thermally stable.

1.3.2 Oxides, Peroxides, Superoxides

Normal oxides - monoxide : The monoxides are ionic. They are strongly basic oxides and they react with water form strong bases.

$Na_2O + H_2O \rightarrow NaOH$

$K_2O + H_2O \rightarrow KOH$

Peroxides

Preparation :

$2Na + O_2\ (excess) \xrightarrow{300^\circ C} Na_2O_2$

$2Na_2O \xrightarrow{7400^\circ C} Na_2O_2 + Na\ (vapour)$

Properties

$Na_2O_2 + H_2SO_4\ (dil) \rightarrow Na_2SO_4 + H_2O_2$

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

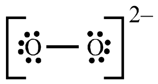
Na_2O_2 is a powerful oxidant Because it reacts with CO_2 in the air it has been used to purify the air in submarines

$Na_2O_2 + CO \rightarrow Na_2CO_3$

$Na_2O_2 + 2CO_2 \rightarrow Na_2CO_3 + O_2$

$Na_2O_2 + Cr^{3+} \rightarrow CrO_4^{2-}$

Structure



peroxide ion

O is sp^3 hydridised. The peroxide ion has 18 electrons which occupy the molecular orbitals as shown.

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_y^2 = \pi 2p_z^2, \pi^* 2p_y^2 = \pi^* 2P_z^1$

Bond order is 1 and it is diamagnetic

Superoxides (O_2^-)

Superoxides are ionic oxides $M^+O_2^-$

Preparation :

$M + O_2 \text{ (excess)} \rightarrow MO_2$

$(M = K, Rb, Cs)$

Superoxides are stronger oxidizing agents than peroxides. The stability of these superoxides is in the order

$KO_2 < RbO_2 < CsO_2$

Reactions

$KO_2 + H_2O \rightarrow KOH + H_2O_2 + 1/2\ O_2$

KO_2 is used in space capsules, submarines and breathing masks because it produces O_2 and removes CO_2

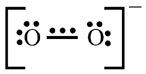
$4KO_2 + 2CO_2 \rightarrow 2\ K_2CO_3 + 3O_2$

$4KO_2 + 4CO_2 + 2\ H_2O \rightarrow 4KHCO_3 + O_2$

sodium superoxide cannot be prepared by burning metal in oxygen but it can be prepared by reacting sodium peroxide with O_2 at high temperature and pressure

$$Na_2O + O_2 \rightarrow 2NaO_2$$

Structure



The presence of one unpaired electron in 3 electron bond explains paramagnetic character. The superoxide has 17 electrons which give a bond order of 1.5 which occupy the molecular orbitals as shown

$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2, \pi^*2p_y^2 = \pi^*2P_z^1$

Stability of oxides : Normal oxide > peroxide > superoxide.

1.3.3 Carbonates and Bicarbonates

Group 1 metals form solid bicarbonates ($MHCO_3$). All alkali metals form carbonates of type M_2CO_3. Due to highly electro positive nature of the alkali metals their carbonates and bicarbonates are highly stable to heat (Li_2CO_3 decomposes easily by heat).

The exceptional behaviour of Li_2CO_3 can be explained by

(a) small size and strong polarisation of Li distorts the e^- cloud of the near by oxygen atom of the large CO_3^{2-} to such an extent that the C—O bond gets weakened.

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

(b) Replacement of the larger carbonate ion by a smaller ion leads to increased lattice energy and thus favours the decomposition.

$$M_2CO_3 \xrightarrow{\Delta} M_2O + CO_2\uparrow$$

$\mathbf{Na_2CO_3}$ is used as **washing soda.** $\mathbf{NaHCO_3}$ is used as **baking soda.** The crystal structure of $NaHCO_3$ and $KHCO_3$ both show hydrogen bonding. In $NaHCO_3$, the HCO_3^- linked into an infinite chain whilst in $KHCO_3$ a dimeric anion is formed.

Reactions

$2HNO_3 + K_2CO_3 \rightarrow 2KNO_3 + CO_2 + H_2O$

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

$M_2CO_3 + H_2O \rightleftharpoons 2M^+ + HCO_3^- + OH^-$

They hydrolyze to give basic solution.

1.3.4 Halides

All the metals in this group form halides of type MX.

Li^+ is the smallest ion in the group, it would be expected to form hydrated salts more readily than other metals.

Properties :

As evident from their following properties, alkali metal halides are ideal ionic compounds.

(i) All alkali halides except lithium fluoride are freely soluble in water (LiF is soluble in non-polar solvents).

(ii) They have high melting and boiling points.

(a) For the same alkali metal, the melting and boiling points decrease regularly in the order

Fluoride > chloride > bromide > iodide

This is explained on the basis of **lattice energy*** of these metal halides. For the same metal, lattice energy decreases with the decrease in electronegativity of the halogen. For example,

Metal Halide :	**NaF**	**NaCl**	**NaBr**	**NaI**
Lattice energy (kJ/mole) :	910	769	732	682
Melting point (K) :	1298	1081	1028	934

(b) For the same halide ion, the melting point of lithium halides are lower than those of the sodium halides. However, after sodium the melting points of halides decrease as we move down the group from Na to Cs. This abnormal behaviour shown by lithium halides is probably due to its covalent nature whereas sodium and other halides are ionic in nature. Amongst ionic halides, melting point decreases as lattice energy decreases as we move down the group i.e.,

NaCl >	KCl >	RbCl >	CsCl
1081 K	1045 K	990 K	918 K

(iii) **Solubility of halides of alkali metals :-** The solubilities of alkali metal halides show a gradation. For example, solubility of alkali metal fluorides in water increases regularly from lithium to caesium.

Metal fluoride :	**LiF**	**NaF**	**KF**	**RbF**	**CsF**
Solubility in water at 298 K (gm/litre) :	2-7	42	1020	1310	3700

In case of chlorides, LiCl has much higher solubility in water than NaCl. This is due to small size of Li^+ ion and much higher hydration energy. However, from NaCl to CsCl, solubility in water increases regularly due to decrease in their lattice energy.

(iv) They are good conductors of electricity in the fused state.

(v) They have ionic crystal structure. However, lithium halides have partly covalent character due to polarising power of Li ions.

The structure and stability (solubility) of alkali metal halides are explained by the lattice energy, and polarising power.

(a) **Lattice energy :-** Lattice energy is the energy released during the formation of a crystal lattice from the respective gaseous cations and anions; or it is the energy required to separate one mole of the solid ionic compound into its gaseous ions. Thus lattice energy (the force of attraction among the ions) is a direct measure of the stability of ionic crystals; higher the lattice energy of a compound lower will be its solubility in water.

When a crystal of an ionic compound comes in contact with a polar solvent such as water, the hydrogen end (positive pole) of the water molecule is attracted to a negative ion while the oxygen end (negative pole) is attracted to a positive ion. This attachment of polar solvent molecules to the ions is known as **solvation (or hydration,** if the solvent is water) of the ions. With the stabilization of the ions by solvation, a large amount of **solvation energy** (or **hydration energy)** is released which if exceeds the lattice energy of the crystal causes the dissolution of the ionic compound in the solvent. On the other hand, if the solvation energy is not enough to counteract the lattice energy, the substance remains insoluble as in case of lithium fluoride. The high lattice energy of lithium fluoride is due to the combination of small lithium ion with small fluoride ion. In general, for a given ion, the lattice energy increases as the size of the oppositely charged ion decreases.

(b) **Polarising power and polarisability (Fajan's rule) :-** Although an ionic bond in a compound like M^+X^- is considered to be 100% ionic, in some cases (e.g., lithium halides) it is found to have significant covalent character . According to Fajan, when the two oppositely charged ions approach each other, the nature of the bond between them depends upon the effect of one ion on the other.

When two oppositely charged ions approach each other, the positive ion attracts electrons present on the outermost shell of the anion and repels its positively charged nucleus. This results in the distortion, deformation or polarisation of the anion. Thus the power of a cation to distort the anion is known as its polarisation power and the tendency of the anion to get polarised by the cation is known as its **polarisability**. If the polarisation is quite small, an ionic bond is formed, while if the degree of polarisation is large, electrons are drawn from the anion to the cation by electrostatic attraction with the result the electron density between the two ions is increased and the resulting bond becomes covalent in character. In general, greater the polarisation power or polarisability of an ion greater will be its tendency to form covalent bond. Since polarisation power increases with the decrease in the size of the cation while polarisability increases with the increase in the size of the anion, in a compound consisting of large negative ions and small positive ions the polarization may be so marked that the bond becomes covalent. Thus lithium iodide, consisting of Li^+ ions (the smallest alkali metal ion) and I^- ions (the greatest halide ion), is found to be markedly covalent in nature.

Other examples of such ionic-covalent compounds are $AlCl_3$, $FeCl_3$, $SnCl_4$, etc.

Reactions

The alkali metal halides react with the halogen and interhalogen compounds forming ionic polyhalides.

$KI + I_2 \rightarrow K[I_3]$

$KBr + ICl \rightarrow K[Br\,ICl]$

$KF + BrF_3 \rightarrow K[BrF_4]$

1.3.5 Sulphates

They form sulphates of type M_2SO_4

1.4 Anomalous Behaviour of Lithium

Although lithium exhibits most of the characteristic properties of the group I elements, it differs, at the same time, in many respects from them. This anomalous behaviour of lithium is due to extremely small size of lithium atom and its ion. The small size of the Li^+ ion leads to its high charge density. Lithium ion, therefore, possesses the greatest polarising power out of all the alkali metal ions. Hence it exerts a great distorting effect on a negative ion. Consequently, the Li^+ ion has a remarkable tendency towards solvation and covalent bond formation. Further it is important to note that the polarising power of the Li^+ ion is similar to that of Mg^{2+} ion, hence the two elements (placed diagonally in the periodic table) resemble very much in their properties.

(i) Lithium is much harder than the other elements of group I (similarity with Mg which is also a hard metal).

(ii) The m.p. and b.p. of lithium are comparatively high.

(iii) Unlike other elements of this group, lithium is the least reactive as represented by the following points.

- **(a)** Unlike others, it is not affected by air.
- **(b)** Unlike others, it decomposes water very slowly (resemblance with Mg).
- **(c)** Unlike others, it hardly reacts with bromine.
- **(d)** On burning in oxygen, it forms only the monoxide Li_2O, while the others form peroxides (M_2O_2) too. Further, K, Rb and Cs form even the superoxide, MO_2.

(iv) Unlike other elements, it directly combines with nitrogen to form nitride, Li_3N (similarity with Mg):

(v) Lithium is much less electropositive and, therefore, several of its compounds (Li_2CO_3 and LiOH) are less stable (similarity with Mg). For example,

$$2LiOH \rightarrow Li_2O + H_2O$$

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

Hydroxides of other alkali metals sublime unchanged.

(vi) Lithium nitrate, on heating, gives nitrogen dioxide and oxygen leaving behind lithium oxide (similarity with $MgNO_3$), while sodium and potassium nitrates evolve only oxygen, thus leaving nitrites.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

$$[2Mg(NO_3)_2 \rightarrow 2\,MgO + 4NO_2 + O_2]$$

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

(vii) Most of the lithium salts (e.g., hydroxide, carbonate, oxalate, phosphate and fluoride) are sparingly soluble in water (similarity with Mg.) The corresponding salts of sodium and potassium are freely soluble in water.

(viii) Lithium halides and lithium alkyls are soluble in organic solvents, while those of Na and K are insoluble ; $MgCl_2$ is also soluble in alcohol.

(ix) Lithium chloride (like $MgCl_2$) undergoes hydrolysis in hot water though to a small extent; while $NaCl$ and KCl do not hydrolyse at all.

(x) Unlike sulphates of other alkali metals, lithium sulphate does not form alums.

(xi) Lithium compounds, particularly, lithium halides are partially covalent in nature. This is due to the tendency of Li^+ to draw electrons towards itself (polarising power). This explains the lower Value (e.g;, 6.25 D in LiI) of the dipole moment of lithium compounds than the expected (e.g., 11.5 D in LiI).

(xii) The ions and its compounds are more heavily hydrated than those of the other alkali metals (similarity with Mg.)

1.5 Extraction of Sodium

Sodium is obtained on large scale by two processes :

1.5.1 Castner's process

In this process, electrolysis of fused sodium hydroxide is carried out at 330°C using iron as cathode and nickel as anode.

$$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

At cathode : $2Na^+ + 2e^- \rightarrow 2Na$

At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

During electrolysis, oxygen and water are produced. Water formed at the anode gets partly evaporated and is partly broken down and hydrogen is discharged at cathode.

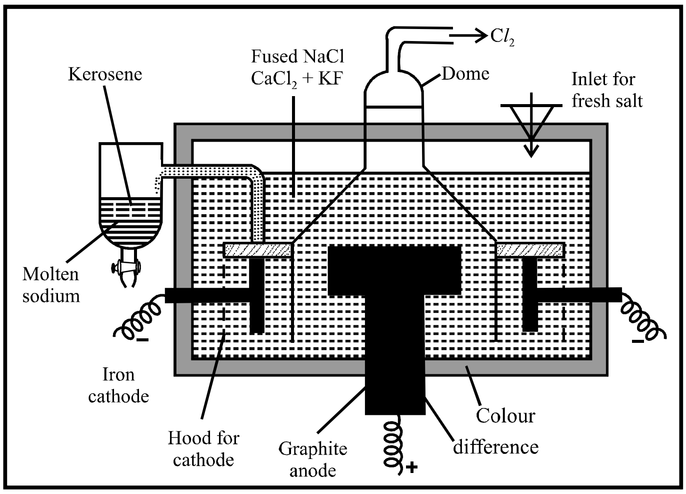
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : $2H^+ + 2e \rightarrow 2H \rightarrow H_2\uparrow$

1.5.2 Down's process

Now-a-days the metal is manufactured by Down's process. It involves the electrolysis of fused sodium chloride containing calcium chloride and potassium fluoride, using iron as cathode and graphite as anode, at about 600° C.

The cell consists of a steel tank lined with heat-resistant bricks. A circular graphite anode is placed in the centre of the cell which is surrounded by a cylindrical iron cathode. The anode and cathode are separated by a steel gauze cylinder through which fused charge can pass. The anode is covered by a dome-shaped steel hood which provides the outlet for the escape of chlorine gas. The molten metal liberated at the cathode moves up and flows into the receiver containing kerosene.



Reactions : $NaCl \rightleftharpoons Na^+ + Cl^-$

At Cathode : $2Na^+ + 2e^- \rightarrow 2Na$

At Anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

Sodium obtained by this method is 99.5% pure.

The electrolysis of pure sodium chloride presents the following difficulties :

(i) The fusion temperature of NaCl is high, i.e., 803°C (1076 K) which is difficult to maintain.

(ii) Sodium is volatile at this temperature and therefore, a part of it vapourises and forms a metallic fog.

(iii) At this temperature, the products of electrolysis, sodium and chlorine are corrosive and may attack the material of the cell.

To remove the above difficulties, pure sodium chloride is mixed with calcium chloride and potassium fluoride. Calcium chloride and potassium fluoride do not decompose at the voltage employed however, they lower the fusion temperature. The fusion temperature of a mixture containing 40% NaCl and 60% calcium chloride and a very small amount of potassium fluoride becomes about 600°C. The electrolysis of this mixture at 600°C is done in the electrolytic cell.

EXAMPLE – 1 Alkali metals are paramagnetic but their salts are diamagentic. Explain.

Sol. In metals, the outermost energy shell is singly occupied, but in cations, all the orbitals are doubly occupied (inert gas configuration).

e.g., Na, $1s^2, 2s^2\,2p^6, 3s^2\,3p^6, \boxed{4s^1}$ paramagnetic

Na^+ $1s^2, 2s^2\,2p^6, \boxed{3s^2 3p^6}$ Diamagnetic

EXAMPLE – 2 Alkali metals are good reducing agents. Explain.

Sol. Alkali metals act as strong reducing agents because they can lose valence electrons readily on account of low ionisation enthalpy values and high values of oxidation potential.

EXAMPLE – 3 Which alkali metal ion has the maximum polarising power and why ?

Sol. Li^+ ion has the maximum polarising power among the alkali metal ions. This is due to small size of Li^+ ion.

EXAMPLE – 4 Li^+ ion is far smaller than other alkali metal ions but it moves through a solution less rapidly than the others. Explain.

Or

The conductance of lithium salts is less in comparison to the salts of other alkali metals. Explain.

Sol. The dense charge of Li^+ attracts several water molecules around it, i.e., Li^+ ion has maximum degree of hydration. Thus, the size of the hydrated lithium ion is largest in comparison to the size of the other alkali metal ions which affects its movement in solution and the conductance is less.

Size : $[Li\,(aq)]^+ > [Na\,(aq)]^+ > [K\,(aq)]^+$

EXAMPLE – 5 Sodium salts in aqueous solutions are either neutral or alkaline in nature. Explain.

Sol. The anions in sodium salts are either from strong acids or weak acids. When anions are from strong acids, there is no hydrolysis and aqueous solutions are neutral ($NaCl$, $NaNO_3$, Na_2SO_4 solutions are neutral).

On the other hand, when anions are from weak acids, there is hydrolysis and the solutions are alkaline in nature. For example, in the case of sodium carbonate or bicarbonate, solns. are alkaline.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

EXAMPLE – 6 Why do K, Rb and Cs form superoxides in preference to oxides and peroxides on being heated in excess supply of air ?

Sol. K^+, Rb^+ and Cs^+ are large cations in size and superoxide ion (O_2^-) is larger in size in comparison to oxide (O^{2-}) and peroxide (O_2^{2-}) ion. A larger cation can stabilise a large anion and therefore, these metals form superoxides rather than oxides and peroxides.

EXAMPLE – 7 Why is KO_2 paramagnetic ?

Sol. The superoxide O_2^- is paramagnetic because of one unpaired electron in π^*2p molecular orbital.

$$KK\,\sigma\,(2s)^2\sigma^*\,(2s)^2\,\sigma\,(2p_x)^2\,\pi\,(2p_x)^2\,(\pi 2p_y)^2\pi^*\,(2p_x)^2\,\pi^*\,(2p_y)^1$$

EXAMPLE – 8 Among the alkali metals which element has :

(i) highest melting point

(ii) highest size of hydrated ion in solution

(iii) strongest reducing agent in solution

(iv) least electronegative

Sol. (i) Li, (ii) $[Li(aq)]^+$ (iii) Li, (iv) Cs

EXAMPLE – 9 What happens when following compounds are heated ?

(a) Li_2CO_3 (b) $Na_2CO_3.10H_2O$

(c) $LiNO_3$ (d) $NaNO_3$

Sol. $Li_2CO_3 \longrightarrow Li_2O + CO_2$

$Na_2CO_3\,.\,10H_2O \longrightarrow Na_2CO_3 + 10H_2O$

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

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

EXAMPLE – 10 (a) Arrange LiF, NaF, KF, RbF and CsF in order of increasing lattice energy.

(b) Arrange the following in order of the increasing covalent character.

MCl, MBr, MF, MI (where M = alkali metal)

Sol. (a) $CsF < RbF < KF < NaF < LiF$

(b) $MF < MCl < MBr < MI$

with increasing size of the anion, covalent character increases.

EXAMPLE – 11 Why a standard solution of sodium hydroxide cannot be prepared by weighing ?

Sol. NaOH is a deliquescent substance. It absorbs moisture and reacts with CO_2 of the atmosphere and both increase its mass. Thus, accurate weighing is difficult.

EXAMPLE – 12 What happens when :

(a) fused sodium reacts with dry ammonia.

(b) sodium hydrogen carbonate is heated.

(c) sodium hydroxide is heated with sulphur ?

Sol. (a) Sodamide is farmed with evolution of hydrogen

$$2Na + 2NH_3 + \rightarrow 2NaNH_2 + H_2$$

Sodamide

(b) Sodium carbonate is formed.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

(c) Sodium thiosulphate is formed.

$$4s + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$$

Sodium thiosulphate

EXAMPLE – 13 Give reasons for the following :

(i) LiCl is more covalent than NaCl

(ii) LiI has lower melting point then LiCl

(iii) $MgCl_2$ is more covalent than NaCl

(iv) CuCl is more covalent than NaCl

Sol. (i) Due to smaller size, Li^+ ion is more polarising than Na^+ and hence LiCl is more covalent than NaCl

(ii) Due to bigger size, I^- is more polarisable than Cl^- and hence LiI is more covalent than LiCl. Therefore, LiI has lower melting point than LiCl.

(iii) Due to higher charge, Mg^{2+} is more polarising than Na^+ and hence $MgCl_2$ is more covalent than NaCl.

(iv) Dut to pseudo inert gas configuration, Cu^+ is more polarising than Na^+, and hence CuCl is more covalent than NaCl.

EXAMPLE – 14 Identify (A), (B), (C) and (D) and give their chemical formulae.

(a) $(A) + NaOH \xrightarrow{Heat} NaCl + NH_3 + H_2O$

(b) $NH_3 + CO_2 + H_2O \longrightarrow (B)$

(c) $(B) + NaCl \longrightarrow (C) + NH_4Cl$

(d) $(C) \xrightarrow{Heat} Na_2CO_3 + H_2O + (D)$

Sol. (a) $NH_4Cl + NaOH \xrightarrow{Heat} NH_3 + NaCl + H_2O$

(A) is ammonium chloride (NH_4Cl).

(b) $NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$

(B) is ammonium bicarbonate (NH_4HCO_3).

(c) $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$

(C) is sodium bicarbonate ($NaHCO_3$).

(d) $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$

(D) is carbon dioxide (CO_2).

EXAMPLE – 15 Arrange the following as specified :

(i) MgO, SrO, K_2O and Cs_2O (increasing order of basic character)

(ii) LiCl, LiBr, LiI (decreasing order of covalent character)

(iii) $NaHCO_3, KHCO_3, Mg(HCO_3)_2, Ca(HCO_3)_2$ (decreasing solubility in water)

(iv) LiF, NaF, RbF, KF and CsF (in order of increasing lattice energy)

(v) Li, Na K (in order to decreasing reducing nature in solution)

Sol. (i) $MgO < SrO < K_2O < Cs_2O$

(ii) $LiI > LiBr > LiCl$

(iii) $NaHCO_3 < KHCO_3 < Mg\,(HCO_3)_2 < Ca(HCO_3)_2$

(iv) $CsF < RbF < KF < NaF < LiF$

(v) $Li > K > Na$

EXAMPLE – 16 (a) What happens when KO_2 reacts with water ? Give the balanced chemical equation.

(b) Predict giving reason the outcome of the reaction :

$$LiI + KF \longrightarrow$$

Sol. (a) When KO_2 reacts with water, oxygen is evolved and an alkaline solution containing potassium hydroxide and H_2O_2 is formed ?

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

(b) LiI reacts with KF i.e., anions are exchanged

$$LiI + KF \longrightarrow LiF + KI$$

The exchange occurs as stable compounds are formed i.e., larger cation stabilizes larger anion and smaller cation stabilizes smaller anion.

2. ALKALINE EARTH METALS

2.1 Introduction

The elements, **beryllium, magnesium, calcium, strontium, barium** and **radium,** constitute Group-II of the periodic table.

All these elements are metals. The oxides of calcium, strontium and barium were known much earlier than the metals themselves and they were called alkaline earths since they were alkaline and existed in the earth. Later, when the elements were discovered, they were named as alkaline earth metals. Radium corresponds to the alkaline earth metals in its chemical properties but, being a radioactive element, it is studied separately along with the other radioactive elements.

2.2 Physical Properties

2.2.1 Atomic size

Atomic size increases down the group.

2.2.2 Oxidation State

The group 2 elements exhibit +2 oxidation state.

2.2.3 Density

The size of group 2 elements are smaller than those of group1 thus these elements have higher density than group 1 elements. Density increases from Be to Ra

Exception : Density of Ca is less than Mg and density of Mg is less than Be.

2.2.4 Nature of bonds

Be mainly forms covalent compound. The rest of the elements in group 2 forms ionic bond.

2.2.5 Hydration energy

The hydration energies of the group 2 ions are four or five time greater than for group 1 ions due to their smaller size and increased charge. $\Delta H_{\text{hydration}}$ decreases down the group as the size of the ions increases.

2.2.6 Lattice Energy

Lattice energy of salts of alkali metals having common anion decreases on descending down the group.

2.2.7 Ionization Energy

Since the atoms are smaller than those in group1, the electrons are more tightly held so that the energy required to remove the first electron (first ionization energy) is greater than for group 1. Energy required to remove the second electron is nearly double than the first. Therefore energy required to produce divalent ions for group 2 elements is four times greater than the energy required to produce M^+ from group 1 metals.

2.2.8 Flame Test

When energy is supplied to these elements in a flame, their electrons are excited to higher energy states, as is the case with alkali metals under similar conditions. As the electrons drop back to the original energy level, the extra energy is emitted in the form of visible light with characteristic colours as given below :

Element	Colour
Ca	brick red
Sr	crimson red
Ba	grassy green
Ra	crimson

Beryllium and magnesium atoms are smaller. The electrons in these atoms are, therefore, more strongly bound. Hence these are not excited by the energy of the flame to higher energy states. These elements, therefore, do not give any colour in bunsen flame.

2.2.9 Standard oxidation potential

Standard Oxidation Potential of Alkaline Earth Metals

Element	Oxidation Reaction	Standard Oxidation Potential (volt)
Be	$Be \rightarrow Be^{2+} + 2e^-$	1·85
Mg	$Mg \rightarrow Mg^{2+} + 2e^-$	2·37
Ca	$Ca \rightarrow Ca^{2+} + 2e^-$	2·87
Sr	$Sr \rightarrow Sr^{2+} + 2e^-$	2·89
Ba	$Ba \rightarrow Ba^{2+} + 2e^-$	2·90

2.2.10 Solubility in liquid NH_3

The metals dissolve in liquid ammonia as do group 1 metals. Dilute solutions are blue in colour due to the formation of solvated e^-. The solution decomposes forming amides and evolving H_2

$$2NH_3 + 2e^- \rightarrow 2NH_2^- + H_2$$

2.2.11 Electronegative values

The electronegativity values of group 2 are low but are higher than the values of group 1. The value of decreases down the group.

2.2.12 Colourless and diamagnetism

The elements of alkaline earth metal group form M^{2+} ions, since it does not have any unpaired electron, it is diamagnetic and colourless

2.2.13 Melting and Boiling point

Since the cohesive force decreases down the group the melting point of elements of group 2 decreases down the group.

Exception : Mg has the lowest melting point.

Boiling points do not show regular trends. They are harder than alkali metals .

2.2.14 Metallic properties

Elements of Group-II have typical metallic properties. They show good metallic luster and high electrical as well as thermal conductivity.

GROUP – I & II

OXIDES

Sodium Oxide (Na_2O) :

Preparation :

(i) It is obtained by burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium.

$$2Na + ½O_2 \xrightarrow{180°} Na_2O$$

(ii) By heating sodium peroxide, nitrate or nitrate with sodium.

$$Na_2O_2 + 2Na \longrightarrow 2Na_2O$$

$$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$$

$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$

Properties :

(i) It is white amorphous mass.

(ii) It decomposes at 400°C into sodium peroxide and sodium

$$2Na_2O \xrightarrow{400°C} Na_2O_2 + 2Na$$

(iii) It dissolve violently in water, yielding caustic soda.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Sodium Peroxides (Na_2O_2) :

Preparation : It is formed by heating the metal in excess of air or oxygen at 300°C, which is free from moisture and CO_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

Properties :

(i) It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and Na_2CO_3.

(ii) In cold water (~0°C) produces H_2O_2 but at room temperature produces O_2. In ice-cold mineral acids also produces H_2O_2.

$$Na_2O_2 + 2H_2O \xrightarrow{\sim 0^\circ C} 2NaOH + H_2O_2$$

$$2Na_2O_2 + 2H_2O \xrightarrow{25^\circ C} 4NaOH + O_2$$

$$Na_2O_2 + H_2SO_4 \xrightarrow{\sim 0^\circ C} Na_2SO_4 + H_2O_2$$

(iii) It reacts with CO_2, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

(iv) It is an oxidising agent and oxidises charcoal, CO, NH_3, SO_2.

$3Na_2O_2 + 2C \longrightarrow 2Na_2CO_3 + 2Na$ [deposition of metallic Na]

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

$$Na_2O_2 + SO_2 \longrightarrow Na_2SO_4$$

$$3Na_2O_2 + 2NH_3 + \longrightarrow 6NaOH + N_2$$

(v) It contains peroxide ion $[—O—O—]^{-2}$

Uses :

(i) For preparing H_2O_2, O_2

(ii) Oxygenating the air in submarines

(iii) Oxidising agent in the laboratory.

Oxides of Potassium :

	Colours
K_2O	White
K_2O_2	White
K_2O_3	Red
KO_2	Bright Yellow
KO_3	Reddish brown needles

Preparations :

(i) $2KNO_3 + 10K \xrightarrow{\text{heating}} 6K_2O + N_2$

✹ $K_2O \xrightarrow{\text{heating}} K_2O$

(White) (Yellow)

✹ $K_2O + H_2O \longrightarrow 2KOH$

(ii) $2K + O_2 \xrightarrow[\text{air at 300°C}]{\text{Controlled}} K_2O_2$ [Props : Similar with Na_2O_2]

(iii) Passage of O_2 through a blue solution of K in liquid NH_3 yields oxides K_2O_2 (white), K_2O_3(red) and KO_2 (deep yellow) i.e.

$$\text{K in liq. } NH_3 \longrightarrow \underset{\text{white}}{K_2O_2} \longrightarrow \underset{\text{red}}{K_2O_3} \longrightarrow \underset{\text{yellow}}{KO_2}$$

✹ KO_2 reacts with H_2O and produces H_2O_2 and O_2 both

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

KO_3 : $\underset{\text{(Dry powdered)}}{KOH} + O_3 \text{ (ozonised oxygen)} \xrightarrow{-10^\circ \text{ to } 15^\circ C} \underset{\text{(orange solid)}}{KO_3}$

Magnesium Oxide (MgO) :-

It is also called magnesia and obtained by heating natural magnesite.

$$MgCO_3 \longrightarrow MgO + CO_2$$

Properties :

(i) It is white powder.

(ii) It's m.p. is 2850°C. Hence used in manufacture of refractory bricks for furnances.

(iii) It is very slightly soluble in water imparting alkaline reaction.

Calcium Oxide (CaO) :

It is commonly called as quick lime or lime and made by decomposing lime stone at a high temperature about 1000°C.

$$CaCO_3 \longrightarrow CaO + CO_2 + 42000 \text{ cal}$$

Properties :

(i) It is white amorphous powder of m.p. 2570°C.

(ii) It emits intense light (lime light), when heated in oxygen-hydrogen flame.

(iii) It is a basic oxide and combines with some acidic oxide e.g.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$CaO + CO_2 \longrightarrow CaCO_3$$

(iv) It combines with water to produce slaked lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Magnesium Peroxide (MgO_2) and Calcium Peroxide (CaO_2) :-

These are obtained by passing H_2O_2 in a suspension of $Mg(OH)_2$ and $Ca(OH)_2$.

Uses :

MgO_2 is used as an antiseptic in tooth paste and a bleaching agent.

HYDROXIDES

Sodium Hydroxides :

Preparation :

(i) Electrolysis of Brine :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At anode : $2Cl^- \longrightarrow Cl_2 + 2e$

At cathode : $Na + e^- \longrightarrow Na$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

(ii) Caustication of Na_2CO_3 (Gossage's method) :

$$\underset{\text{(suspension)}}{Na_2CO_3 + Ca(OH)_2} \rightleftharpoons 2NaOH + CaCO_3$$

Since the K_{sp} $(CaCO_3) < K_{sp}(Ca(OH)_2)$, the reaction shifts towards right.

Properties :

(i) It is white crystalline, deliquescent, highly corrosive solid.

(ii) It is stable towards heat.

(iii) It's aqueous solution is alkaline in nature and soapy in touch.

(iv) $FeCl_3 + 3NaOH \longrightarrow Fe(OH)_3 \downarrow + 3NaCl$

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 \uparrow + H_2O$$

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 \downarrow + 2NaCl$$

$$Zn(OH)_2 \downarrow + 2NaOH \xrightarrow{\text{Excess}} \underset{\text{Soluble}}{Na_2ZnO_2} + 2H_2O$$

[Same with $AlCl_3$, $SnCl_2$, $PbCl_2$]

(v) Acidic and amphoteric oxides gets dissolved easily e.g.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

(vi) Aluminium and Zn metal gives H_2 from NaOH

$$2Al + 2NaOH + 2H_2O \longrightarrow 3H_2 + 2NaAlO_2$$

(vii) Several non metals such as P, S, Cl etc. yield a hydride instead of hydrogen e.g.

$$4P + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

Potassium Hydroxide :

Preparation : Electrolysis of aqueous solution of KCl.

Properties : Same as NaOH

** (a) It is stronger base compared to NaOH.

(b) Solubility in water is more compared to NaOH.

(c) In alcohol, NaOH is sparingly soluble but KOH is highly soluble.

(d) As a reagent KOH is less frequently used but in absorption of CO_2, KOH is preferably used compared to NaOH. Because $KHCO_3$ formed is soluble whereas $NaHCO_3$ is insoluble.

Magnesium Hydroxide : It occurs in nature as the mineral brucite.

Preparation : It can be prepared by adding caustic soda solution to a solution of Mg-sulphate or chloride solution.

$$MgSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Mg(OH)_2$$

Properties :

(i) It can be dried at temperature upto 100°C only otherwise it breaks into its oxide at higher temperature.

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

(ii) It is slightly soluble in water imparting alkalinity.

(iii) It dissolves in NH_4Cl solution

$$Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$$

✸ Thus, $Mg(OH)_2$ is not therefore precipitated from a solution of Mg^{+2} ions by NH_4OH in presence of excess of NH_4Cl.

Calcium Hydroxide :

Preparation : By spraying water on quicklime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Properties :

(i) It is sparingly soluble in water.

(ii) It's solubility in hot water is less than that of cold water. Hence solubility decreases with increase in temperature.

(iii) It readily absorbs CO_2 as used as a test for the gas.

(iv) It is used as a mortar.

[Mortar is a mixture of slaked lime (1 Part) and saved (3 Parts) made into paste with water.]

CARBONATES

Sodium Carbonate :

Preparation :

(i) Leblanc Process :

$$NaCl + H_2SO_4(conc.) \xrightarrow{\text{mild heating}} NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \xrightarrow[\text{heated}]{\text{Strongly}} \underset{\text{(Salt Cake)}}{Na_2SO_4} + HCl$$

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO\uparrow$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS$$

(ii) Solvay Process :

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{150°C} Na_2CO_3 + H_2O + CO_2$$

Properties :

(i) Anhydrous Na_2CO_3 is called as soda ash, which does not decompose on heating but melts at 852ºC.

(ii) It forms number of hydrates.

(iii) Hydrated Na_2CO_3 is called washing soda ($Na_2CO_3.10\ H_2O$) and is prepared by Le Blanc process solvay process and electrolytic process.

(iii) Na_2CO_3 absorbs CO_2 yielding sparingly soluble sodium bicarbonate which can be calcined at 250º to get pure sodium carbonate.

$$Na_2CO_3 + H_2O + CO_2 \underset{250°C}{\rightleftharpoons} 2NaHCO_3$$

(iv) It dissolved in acid with effervescence of CO_2 and causticised by lime to give caustic soda.

$$Na_2CO_3 + HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

Uses : It is widely used in glass making as smelter.

Potassium Carbonate :

By leblanc process, it can be prepared but by solvay process it cannot be prepared because $KHCO_3$ is soluble in water.

Properties : It resembles with Na_2CO_3, m.p. is 900ºC but a mixture of Na_2CO_3 and K_2CO_3 melts at 712ºC.

Uses : It is used in glass manufacturing.

Calcium Carbonate :

It occurs in nature as marble, limestone, chalk, calcite etc. It is prepared by dissolving marble or limestone in HCl and removing iron and aluminium present, by precipitating with NH_3 and then adding $(NH_4)_2\ CO_3$ to the solution.

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2NH_4Cl$$

Properties :

(i) It is dissociates above 1000ºC as follows :

$$CaCO_3 \longrightarrow CaO + CO_2$$

(ii) It dissolves in water containing CO_2 forming $Ca(HCO_3)_2$ but is precipitated from the solution by boiling.

$$CaCO_3 \longrightarrow H_2O + CO_2 \underset{\text{boiling}}{\rightleftharpoons} Ca(HCO_3)_2$$

Magnesium Carbonate :

It occurs in nature as magnesite, isomorphous with calcite. It is obtained as a white precipitated by adding sodium bicarbonate to a solution of a magnesium salt but only basic carbonate, called magnesia alba, having the approximate composition $MgCO_3.\ Mg(OH)_2.\ 3H_2O$ is precipitated.

Properties : Same as $CaCO_3$.

BICARBONATES

Sodium bicarbonates :

Preparation : By absorption of CO_2 in Na_2CO_3 solution.

$$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3$$

Uses : It is used in medicine and as baking powder.

Potassium bicarbonates :

Preparation : Same as $NaHCO_3$

Properties : Same as $NaHCO_3$

But it is more alkaline and more soluble in water compared to $NaHCO_3$.

Magnesium bicarbonate :

$$MgCO_3 + CO_2 + H_2O \overset{\text{boiling}}{\rightleftharpoons} Mg(HCO_3)_2$$

Calcium bicarbonate :

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$$

CHLORIDES

Sodium Chloride : Prepared from brine containing 25% NaCl.

Properties :

(i) It is nonhygroscopic but the presence of $MgCl_2$ in common salt renders it hygroscopic.

(ii) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to –23°C.]

(iii) For melting ice and snow on road.

Potassium Chloride : It also occurs in nature as sylvite (KCl) or carnallite $KCl \,.\, MgCl_2 \,.\, 6H_2O$.

Uses : It is used as fertiliser.

Magnesium Chloride :

Preparation : By dissolving $MgCO_3$ in dil. HCl.

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

Properties :

(i) It crystallises as hexahydrate. $MgCl_2.\ 6H_2O$.

(ii) It is deliquescent solid.

(iii) This hydrate undergoes hydrolysis as follows :

$$MgCl_2 + H_2O \longrightarrow Mg(OH)Cl + HCl$$

$$Mg(OH)Cl \longrightarrow MgO + HCl$$

- Hence, anhy. $MgCl_2$ cannot be prepared by heating this hydrate.
- Because of the formation of HCl sea water cannot be used in marine boilers which corrodes the iron body.

(iv) Anhydrous $MgCl_2$ can be prepared by heating a double salt like. $MgClO_2.\ NH_4Cl.\ 6H_2O$ as follows :

$$MgCl_2 \,.\, NH_4Cl_2 \,.\, 6H_2O \xrightarrow[\Delta]{-H_2O} MgCl_2NH_4Cl$$

$$\xrightarrow[\Delta]{\text{strong}} MgCl_2 + NH_3 + HCl$$

Sorel Cement : It is a mixture of MgO and $MgCl_2$ (paste like) which sets to hard mass on standing. This is used in dental filling, flooring etc.

Calcium Chloride :

(i) It is the by-product in solvay process.

(ii) It may also be prepared by dissolving the carbonate in HCl

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Properties :

(i) It is deliquescent crystals.

(ii) It gets hydrolysed like $MgCl_2$ hence anhydrous $CaCl_2$ cannot be prepared.

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl$$

Hence, anhy. $CaCl_2$ is prepared by heating $CaCl_2.\ 6H_2O$ in a current of HCl (dry).

(iii) Anhy. $CaCl_2$ is used in drying gases and organic compounds but not NH_3 or alcohol due to the formation of $CaCl_2 \,.\, 8NH_3$ and $CaCl_2 \,.\, 4C_2H_5OH$.

SULPHATES

Sodium Sulphate :

Preparation :

It is formed in the Ist step of leblanc process by heating common salt with sulphuric acid.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

Thus the salt cake formed is crystallised out from its aqueous solution as $Na_2SO_4 \,.\, 10H_2O$. This is called as Glauber's salt.

- One interesting feature of the solubility of glauber's salt is ; when crystallised at below 32.4ºC, then $Na_2SO_4 . 10H_2O$ is obtained but above 32.4ºC, Na_2SO_4 (anhy.) comes out.

Properties : it is reduced to Na_2S when fused with carbon.

$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

Uses : It is used in medicine.

Potassium Sulphate :

It occurs in stassfurt potash beds as schonite K_2SO_4, $MgSO_4 . 6H_2O$ and Kainite, $KCl . MgSO_4 . 3H_2O$ from which it is obtained by solution in water and crystallisation. It separates from the solution as crystals whereas Na_2SO_4 comes as decahydrate.

Uses : It is used to prepare alum.

Magnesium Sulphate :

Preparation :

(i) It is obtained by dissolving kieserite $MgSO_4 . H_2O$ in boiling water and then crystallising the solution as a hepta hydrate. i.e. $MgSO_4 . 7H_2O$. It is called as **Epsom salt.**

(ii) It is also obtained by dissolving magnesite in hot dil. H_2SO_4.

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

or by dissolving dolomite ($CaCO_3 . MgCO_3$) in hot dil. H_2SO_4 and removing the insoluble $CaSO_4$ by filtration.

(iii) It is isomorphous with $FeSO_4 . 7H_2O$, $ZnSO_4 . 7H_2O$

Calcium Sulphate : It occurs as anhydrite $CaSO_4$ and as the dihydrate $CaSO_4 . 2H_2O$, gypsum, alabaster or satin-spar.

Properties :

(i)
$$\begin{tikzcd}
\text{Gypsum } (CaSO_4 . 2H_2O) \arrow[r, shift left, "120^\circ C"] & 2CaSO_4 . H_2O \text{ (Plaster of paris)} \arrow[l, shift left, "+H_2O"] \arrow[d, "200^\circ C"] \\
 & CaSO_4 \text{ (anhydrous)} \\[-2em]
 & \text{Dead burnt plaster}
\end{tikzcd}$$

(ii) Solubility of $CaSO_4$ at first increases upto a certain point and then decreases with rise of temperature.

(iii) Plaster of paris is used in wood making due to its porous body.

EXAMPLE – 17 (a) Mg_3N_2 when reacted with water, gives off NH_3 but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature. Why ?

(b) The crystalline salts of alkaline earth metals contain more water of crystallization than corresponding alkali metal salts. Why ?

Sol. (a) Mg_3N_2 is a salt of a strong base and weak acid (NH_3), hence its hydrolysis is possible.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$MgCl_2$ is a salt of a strong base, [$Mg(OH)_2$], and a strong acid, (HCl), and hence, its hydrolysis is not possible.

(b) Due to small size and high nuclear charge, alkaline earth metal ions have higher tendency of hydration in comparison to alkali metal ions. Thus, the salts of alkaline earth metals contain more water of crystallisation than the salts of alkali metals.

EXAMPLE – 18 What happens when :

(i) Beryllium carbide reacts with water.

(ii) Magnesium nitrate is heated.

(iii) Quick lime is heated in electric furnace with powdered coke.

(iv) NaOH solution is added to $ZnCl_2$ solution.

Sol. (i) Methane gas is evolved.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(ii) Brown coloured gas, NO_2, is evolved.

$$2Mg\,NO_3 \longrightarrow 2MgO + 4NO_2 + O_2$$

(iii) Calcium carbide is formed with evolution of CCl.

$$CaO + 3C \xrightarrow[\text{Arc}]{\text{Electric}} CaC_2 + CO$$

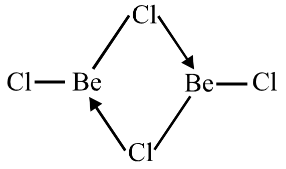
(iv) While precipitate of Zn $(OH)_2$ is formed which dissolves in excess of NaOH forming sodium zincate.

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{ppt.}}{Zn(OH)_2} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + 2H_2O$$

EXAMPLE – 19 Draw the structure of (i) $BeCl_2$ (vapour state) (ii) $BeCl_2$ (solid).

Sol. In vapour state, it has chlorobridged dimer structure which dissociates into linear monomer at 1000° C.

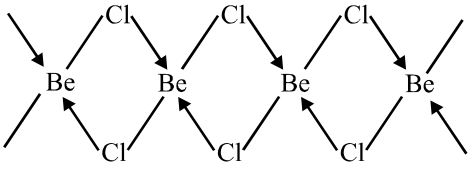


Dimer

Cl — Be — Cl

Monomer

In the solid phase, it has a polymeric structure with chlorobridges in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a coordinate bond and to another atom by a covalent bond.



GENERAL TREND OF DIFFERENT PROPERTIES IN THE PERIOD AND GROUPS