CHAPTER 2

(For Board & Competitive Exams)

Some Basic Concepts of Chemistry

Chapter Contents

INTRODUCTION

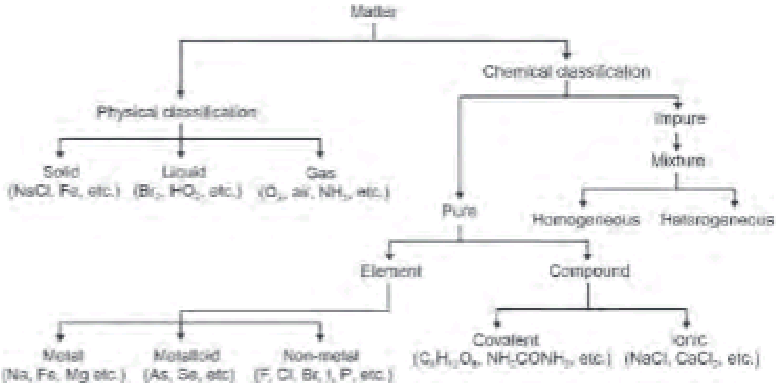
All developments in chemistry are based on scientific approach. A scientist is always very keen to perform experiments, make observations and draw inferences from the observations. In order to achieve correct results, he has to rely upon the various skills connected with the measurements.

Chemistry is the science of molecules and their transformations which deals with the study of matter, its composition, the changes that matter undergoes and the relation between changes in composition and changes in energy. Chemistry plays a central role in science and is often intertwined with other branches of science. Chemistry plays an important role in meeting human needs for food, health care products.

The term "Stoichiometry" refers to calculations based on chemical equations. A chemical equation is a symbolic representation of chemical reaction. It indicates the number of moles, molecules, mass and volume (in case of gases) of reactants and their respective products formed.

MATTER

Matter is anything that occupies space, has mass, offer *resistance* and can be perceived of directly by our senses.



ELEMENT

Element is the purest form of matter. It is made up of only one type of atoms.
Ex.- carbon, iron, copper, oxygen etc.

Symbol

Symbol of an element is either the 1st alphabet or first alphabet along with one other alphabet of the Latin name.

Element	Symbols	Latin Name
Magnesium	Mg	Magnesia
Potassium	K	Kalium
Sodium	Na	Natrium

COMPOUND

Compound is the substance which is made up of two or more elements combined together in a fixed ratio by their weight *e.g.*, carbon dioxide.

Try Yourself

1. Identify the elements and compounds among the substances given below.
   - (a) Water
   - (b) Sodium chloride
   - (c) Sodium metal
   - (d) Carbon dioxide gas
   - (e) Ammonia gas

MIXTURE

Mixture is the substance which is made up of two or more substances in any ratio.

e.g., Sugar + Water, Sodium Chloride + Water, Sand + Water

On the basis of composition, mixtures are of following type :

1. **Homogeneous mixture :** The mixture which has uniform composition throughout.
   e.g., sugar solution.
2. **Heterogeneous mixture :** The mixtures which do not have uniform composition throughout.
   e.g. sand in water.

ATOM

Atom is the smallest particle which may or may not exist free but takes part in chemical reaction. Atom word means not to be cut.

The International System of Units (S.I.)

The international system of units (in French *Le Systeme International d' Unités* - abbreviated as SI) was established in 1960 by the 11th general conference on weights and measures (CGPM from *Conference Generale des Poids at Measures*). The CGPM is one of the inter governmental treaty organization created by a diplomatic treaty known as Meter Convention which was signed in Paris in 1875.

SI system is a modification of metric system and has seven base units pertaining to the seven fundamental scientific quantities.

CHAPTER 13

(For Board & Competitive Exams)

The *s*-Block Elements

Chapter Contents

INTRODUCTION

In this chapter, we will study the general characteristics of the alkali and alkaline earth metals and their compounds. We will also study the compounds of *s*-block elements, their uses and importance, commercially and industrially. The biological significance of sodium, potassium, calcium and magnesium will also be discussed in this chapter.

THE *s*-BLOCK ELEMENTS

s-block is located at extreme left-hand side of the periodic table. Since *s*-orbital can accommodate only two electrons, the elements having one electron in their outermost *s*-orbital is grouped into group-1 and those having two electrons are grouped into group-2 of periodic table.

Group-1 of periodic table contains : Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs) and Francium (Fr). Together these elements are called **alkali metals** because they form hydroxides on reaction with water, which are strongly alkaline in nature. Sodium and Potassium are abundant in nature while Lithium, Rubidium and Caesium have lower abundance. Francium, the last element of group-1, is radioactive.

The group-2 includes Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). Except Beryllium, rest of the elements of group-2 are called the **alkaline earth metals**. These are called so because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth crust.

Beryllium is not considered alkaline earth metal because its oxide *i.e.*, BeO is amphoteric is nature, which can be explained by its reaction with acids as well as alkalies.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium beryllate}}{Na_2[Be(OH)_4]}$$

Out of alkaline earth metals, calcium and magnesium are ranked 5th and 6th respectively as per their abundance in the Earth's crust, Strontium and Barium have comparatively lower abundance, Beryllium is rare and Radium is the rarest of all alkaline earth metals.

General electronic configuration for alkali metals is [noble gas] ns^1 and that for alkaline earth metals is [noble gas] ns^2.

The first element in each group shows some anomalous behaviour or properties as compared to other members of the respective group due to

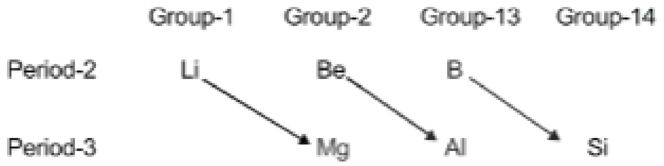
(i) Smaller size of the atom

(ii) Their higher ionization enthalpies

(iii) Their higher electronegativities

(iv) Absence of vacant *d*-orbitals in their valence shells

In these anomalous properties they resemble the second element of the next group. Thus lithium shows similarities to magnesium and beryllium to aluminium in many of their properties, and this similarity is known as diagonal relationship.



Cause of diagonal relationship

In moving along the period from left to right the electropositive character decreases while in descending a group, electropositivity of the elements increases. These two effects tend to cancel each other in moving diagonally from top left to bottom right. Therefore, the elements diagonally related in this way tend to have similar properties or we can say that diagonal relationship is due to the similarity in ionic sizes.

Biological fluids contain large amount of Na^+, K^+, Mg^{2+} and Ca^{2+} ions. These ions are also important in maintaining ion balance and nerve impulse conduction.

GROUP-1 ELEMENTS : ALKALI METALS

The alkali metals show a regular trend in their physical and chemical properties with the increasing atomic number.

Electronic Configuration

The alkali metals have one valence electron, outside the noble gas core.

[Noble gas] ns^1 ; where $n = 2$ to 7

Since the outermost electron is loosely held, alkali metals readily lose electron to give monovalent M^+ ions, that is why they are most electropositive metals and are never found in free state in nature.

The electronic configurations of alkali metals are given below in table

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2 2s^1$ or $[He]2s^1$
Sodium	Na	$1s^2 2s^2 2p^6 3s^1$ or $[Ne]3s^1$
Potassium	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $[Ar]4s^1$
Rubidium	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ or $[Kr]5s^1$
Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[Xe]6s^1$
Francium	Fr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$ or $[Rn]7s^1$

Atomic and Ionic Radii

The atoms of alkali metals have the largest size in their respective periods. The atomic radius increases on moving down the group.

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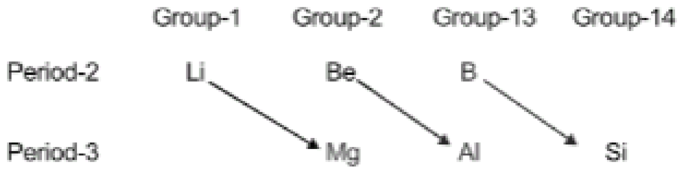

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Caesium	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[Xe]6s^1$
Francium	Fr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$ or $[Rn]7s^1$

Atomic and Ionic Radii

The atoms of alkali metals have the largest size in their respective periods. The atomic radius increases on moving down the group.

Reason : On moving down the group there is a progressive addition of new energy shells. Although, the nuclear charge also increases down the group but the effect of addition of new shells is more dominant and hence atomic radii of alkali metals increases on going down the group from top to bottom.

Alkali metal change itself into positively charged ions by losing their one valence electron. The monovalent ions (M^+) are smaller than of the parent atom. Within the group, the ionic radii increase with increase in atomic number.

Ionization Enthalpy

The first ionisation enthalpies of alkali metals are low as compared to the elements of other groups belonging to the same period. However, within the group the ionization enthalpies of the alkali metals decrease down the group.

The radii of atoms of alkali metals are the largest in their respective periods, therefore, the outermost electrons which are far away from the nucleus experience a less force of attraction from the nucleus and hence can be easily removed.

Decrease in ionization enthalpy on moving down the group is due to increase in size of the atoms of alkali metals and increase in the magnitude of screening effect due to increase in the number of intervening electrons.

Hydration Enthalpy

The alkali metal ions are extensively hydrated in aqueous solutions. Smaller the ion more is the extent of hydration. The hydration enthalpies of alkali metal ions decrease with increase in ionic size.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ (hydration energy decreases)

Li^+ has maximum degree of hydration and for this reason many lithium salts exist as hydrated salts. For example, $LiCl.\ 2H_2O$.

Physical Properties

Alkali metals are silvery white in colour and are generally soft and light metals. Softness of alkali metals is due to weak metallic bonding in them because of large size of the atoms. As we move down the group metallic bonding weakens and hence, softness increases. Potassium is softer than sodium. The densities of alkali metals are low and increase down the group. Potassium, however, is lighter than sodium. Lithium is the lightest metal having a density of 0.534 g/cm^3. It cannot be stored in kerosene oil because it floats on the surface. It is kept wrapped in paraffin wax. The low density of alkali metals is attributed to their large atomic size and weak metallic bond. However, going down the group, atomic size as well as atomic mass increases but the corresponding increase in atomic mass is not neutralised by the increase in atomic volume : Thus, the ratio, mass/volume, *i.e.*, density gradually increases.

Alkali metals have low melting and boiling point. The low melting point are attributed to their larger atomic size, due to which the binding energies of their atoms in the crystal lattice are low. Further, in moving down the group, their atomic size increase and the strength of metallic bond decreases which causes decrease in melting points. The boiling points of the members of this group also follow the same order due to same reasons.

(i) **Flame colouration**

When alkali metals and their salts are heated in the oxidizing flame of a Bunsen burner, they impart characteristic colours to the flame. This happens because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

This particular property of alkali metals is helpful in detecting them by respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.

(ii) Photoelectric Effect

Alkali metals (except Li) exhibit photoelectric effect (a phenomenon of emission of electrons from surface by exposing it to visible light). These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron. This property makes caesium and potassium useful as electrodes in photoelectric cells.

Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol^{-1})	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Ionization enthalpy/kJ mol^{-1}	520	496	419	403	376	~375
Hydration enthalpy/kJ mol^{-1}	–506	–406	–330	–310	–276	–
Metallic radius / pm	152	186	227	248	265	–
Ionic radius M^+ / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	–
b.p./ K	1615	1156	1032	961	944	–
Density / g cm^{-3}	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^\ominus$ / V for (M^+ / M)	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere†	18*	2.27**	1.84**	78-12*	2-6*	~10^{-18}*

* ppm (part per million), ** percentage by weight; † Lithosphere : The Earth's outer layer : its crust and part of the upper mantle

EXAMPLE 1 : *Why does alkali metals impart characteristic colour to the flame?*

Solution : This happens because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region.

Chemical Properties

The alkali metals are highly reactive elements. The cause for their high chemical reactivity is (i) low value of first ionisation enthalpy (ii) large size (iii) low heat of atomisation. The reactivity of these metals increases down the group.

(i) Reactivity towards air

You might have seen that alkali metals tarnish in dry air because of formation of their oxides and when these oxides react with moisture they form hydroxides.

Alkali metals burn very fast in oxygen and form different kind of oxides like monoxides, peroxides and superoxides. Lithium forms monoxide, sodium forms peroxide and other metals form superoxides. The superoxide O_2^- ion generally remain stable only in the presence of large cations like K, Rb, Cs. This stability is related to the compatibility of size and higher lattice energy

$4Li + O_2 \longrightarrow 2Li_2O$ (oxide)

$2Na + O_2 \longrightarrow Na_2O_2$ (peroxide)

$M + O_2 \longrightarrow MO_2$ (superoxide)

(M = K, Rb, Cs)

In all the compounds formed by alkali metals with oxygen, their oxidation state is +1.

Due to diagonal relationship with magnesium, lithium like magnesium forms its nitride, Li_3N on heating with N_2. Rest of the alkali metals do not behave in this way.

$6Li + N_2 \longrightarrow 2Li_3N$

Alkali metals are generally kept immersed in kerosene oil because they are highly reactive towards air and water.

(ii) Reactivity towards water

The alkali metals on reaction with water from their respective hydroxide and dihydrogen.

$2M + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2$

(M = an alkali metal)

This tendency of forming hydroxide with water depends upon their electrode potential (E^o) and this electrode potential is a measure of the tendency of an element to lose electron in the aqueous solution. Thus, more negative is the electrode potential, higher is the tendency of the element to lose electron and hence stronger is the reducing agent. Lithium has most negative E^o value therefore its reaction with water is less vigorous than that of sodium which has the least negative E^o value among the alkali metals. Rest of the members of the alkali metal react vigorously with water and may sometimes catch fire, they also react with proton donors or acidic hydrogen such as alcohol, gaseous ammonia, hydrogen halide and alkynes.

$2M + 2C_2H_5OH \longrightarrow 2C_2H_5OM + H_2$

$2M + HC = CH \longrightarrow M^+ \, {}^-C = C^-M^+ + H_2$

$2M + 2HX \longrightarrow 2\,MX + H_2$

Knowledge Cloud

However, magnitude of $\Delta_{hydration}H^{\ominus}$ of Li^+ is maximum but reaction of sodium with water is most violent as m.pt. of sodium is achieved by the heat evolved in the process of hydration of sodium, so it sublimates and now its surface area increases manifold, therefore, reaction becomes violent.

(iii) Reactivity towards dihydrogen

Alkali metal react with dry di-hydrogen at about 673 K (lithium at 1073 K) to form crystalline hydrides which are ionic in nature and have high melting points.

$2M + H_2 \xrightarrow{Heat} 2M^+H^-$

(iv) Reactivity towards halogens

The alkali metals react vigorously with halogens and form halides which are ionic in nature, M^+X^-. But the halides of lithium are a bit covalent in nature, this is due to the fact that lithium ion has high polarisation capability (The distortion of electron cloud of the anion by the cation is called polarisation). Since the Li^+ ion is very small in size, it has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) Reducing nature

The alkali metals have strong tendency to get oxidised, that is why they act as strong reducing agents, among these lithium is the strongest and sodium is the least powerful reducing agent. The standard electrode potential (E°) measures the reducing power and represents the changes.

$M(s) \longrightarrow M(g)$ Sublimation enthalpy

$M(g) \longrightarrow M^+(g) + e^-$ ionization enthalpy

$M^+(g) + H_2O \longrightarrow M^+(aq)$ hydration enthalpy

Since lithium ion has small size, it has the highest hydration enthalpy which gives an explanation for its high negative E° value and its high reducing power.

Higher the negative value of E° value more reducing will be the ionic species.

(vi) Solutions in liquid ammonia

All alkali metals dissolve in liquid ammonia and give deep blue colour solution which are conducting in nature. These solutions contain ammoniated cations and ammoniated electrons as shown below :

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

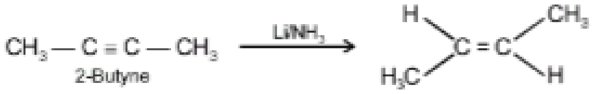
The blue colour of the solution is considered to be due to ammoniated electrons which absorb energy corresponding to red region of visible light for their excitation to higher energy levels. The transmitted light thus, imparts blue colour to the solution. **The electrical conductivity of the solution is due to both ammoniated cations and ammoniated electrons.** The blue solution on standing slowly liberates hydrogen resulting in the formation of amide.

$$M^+_{(am)} + e^- + NH_3(l) \longrightarrow \underset{\text{(Metal amide)}}{MNH_2(am)} + \frac{1}{2}H_2(g)$$

(where 'am' denotes solution in ammonia). At concentrations above 3M, the solution of alkali metals in liquid ammonia are copper bronze-coloured. These solutions contain cluster of metal ions and hence possess metallic lustre. The blue solutions are paramagnetic whereas bronze coloured solutions are diamagnetic.

Reducing Property

The free ammoniated electrons make the solution a very powerful reducing agent. The ammoniacal solution of an alkali metal is favoured as a reducing agent than its aqueous solution because in aqueous solution, the alkali metal being highly electropositive evolves hydrogen from water while its solution in ammonia is quite stable, provided no catalyst is present.



(Birch reduction)

Note : *Terminal alkynes do not give this test. Terminal alkynes give alkynide ions.*

Reaction with sulphur and phosphorous : All metals form sulphides and phosphides

$$3Na + P \longrightarrow \underset{\text{Sodium phosphide}}{Na_3P}$$

$$2Na + S \longrightarrow \underset{\text{Sodium sulphide}}{Na_2S}$$

Reaction with mercury : Alkali metals combine with mercury to form amalgams. The reaction is highly exothermic in nature

$$\mathrm{Na + Hg \longrightarrow \underset{Sodium\ Amalgam}{Na[Hg]}}$$

USES

1. Lithium is used as a metal in a number of alloys. Its alloys with magnesium, containing about 14% lithium is extremely tough and corrosion resistant which is used for armour plate and aerospace components; with lead to make white metal with aluminium to make aircraft parts.
2. Lithium hydroxides is used in the ventilation systems of space crafts and submarines to absorb carbon dioxide.
3. Lithium aluminium hydride ($LiAlH_4$) is a powerful reducing agent which is commonly used in organic synthesis.
4. Liquid sodium or its alloys with potassium is used as a coolant in nuclear reactors.
5. Sodium-lead alloy is used for the preparation of tetraethyl lead, $Pb(C_2H_5)_4$, which is used as an antiknocking agent in petrol.

   $$\underset{\text{Lead-sodium alloy}}{(Pb + 4Na)} + 4C_2H_5Cl \longrightarrow \underset{\text{Tetraethyl lead}}{(C_2H_5)_4Pb} + 4NaCl$$

6. Sodium is used in the production of sodium vapour lamps.
7. Potassium chloride is used as fertilizer.
8. Potassium hydroxide is used in the manufacture of soft soaps and also as absorbent of carbon dioxide.
9. Potassium ions play a vital role in biological systems.
10. Caesium is used in photoelectric cells.

GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature

(i) Oxides and hydroxides

Alkali metals when burnt in air form different kinds of oxides. For example, the alkali metals on reaction with limited quantity of oxygen form normal oxides of the formula, M_2O.

$$4M + O_2 \longrightarrow 2M_2O$$

(where M = Li, Na, K, Rb, Cs)

However, when heated with excess of air lithium forms normal oxide, (Li_2O) and some peroxide Li_2O_2 sodium forms peroxide, Na_2O_2 and some superoxide NaO_2 whereas potassium, rubidium and caesium form superoxide having general formula MO_2.

$$4Li + O_2 \rightarrow \underset{\text{Lithium oxide}}{2Li_2O}$$

$$2Na + O_2 \rightarrow \underset{\text{Sodium peroxide}}{Na_2O_2}$$

$$K + O_2 \rightarrow \underset{\text{Potassium superoxide}}{KO_2}$$

The temperature required for the reaction to take place decrease on descending the group.

The stability of peroxide or superoxide increases as the size of the alkali metal increases. This is due to stabilization of large anions by large cations through lattice energy effects.

The oxides and the peroxides are colourless when pure but superoxides are yellow or orange in colour, peroxides are diamagnetic whereas superoxide are paramagnetic in nature.

The normal oxides of alkali metal dissolve readily in water to form hydroxides and a large amount of heat is produced.

$$M_2O(s) + H_2O(l) \longrightarrow 2MOH(aq) + \text{Heat} \longrightarrow 2M^+ + 2OH^-$$

The peroxides and superoxides are also readily hydrolysed by water as shown below:

$$M_2O_2 + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2$$

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

$$2MO_2 + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

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

The higher oxides generally act as good oxidising agent, sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

The hydroxides which are obtained by reaction of the oxides with water are all white crystalline solids. The hydroxides of alkali metals are strong bases. The basic character of alkali metal hydroxides increases in going down the group.

$LiOH < NaOH < KOH < RbOH < CsOH$ (Basic character increases)

Alkali metal hydroxides are freely soluble in water and their dissolution in water is accompanied by evolution of much heat due to intense hydration.

(ii) Halides

The alkali metals combine with halogens to form metal halides, which are ionic colourless, crystalline solids having high melting point and general formula MX.

(X = F, Cl, Br, I)

$$2M + X_2 \longrightarrow 2\,MX$$

$$2Na + Cl_2 \longrightarrow 2NaCl$$

Reactivity with particular alkali metal M follow the order

$$F_2 > Cl_2 > Br_2 > I_2$$

The alkali metal halides can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^\ominus$ value for fluorides become less negative as we go down the group, while the reverse is true for $\Delta_f H^\ominus$ for chlorides, bromides and iodides. For a given metal, $\Delta_f H^\ominus$ always becomes less negative from fluoride to iodide. The melting and boiling points always follow the trend, fluoride > chloride > bromide > iodide.

All halides of the alkali metals except lithium fluoride (LiF) are freely soluble in water. The low solubility of lithium fluoride is attributed to greater force of attraction between lithium ions and fluoride ions in the crystal lattice or high lattice enthalpy. Caesium iodide (CsI) also has relatively low solubility in water. This is attributed to smaller hydration energy of its large sized ions. LiCl, LiBr and LiI are soluble in ethanol, acetone and other solvents of low polarity. This is due to predominant covalent character of these halides. The predominant covalent character of lithium halides is due to greater polarizing power of Li^+ ion. Among lithium halides LiI has maximum covalent character due to large polarizability of iodide ion. LiCl is soluble in pyridine also.

(iii) Salts of oxo-acids

Oxo-acids are those acids in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom, *e.g.*, carbonic acid, $H_2CO_3[OC(OH)_2]$, sulphuric acid, $H_2SO_4[O_2S(OH)_2]$. The alkali metals form salts with all the oxo-acids.

The salts of oxo-acids are generally soluble in water and thermally stable.

The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) of alkali metals are quite stable towards heat. Li_2CO_3, however, is considerably less stable and decomposes readily on heating. Lithium being very small in size polarises a large CO_3^{2-} ions leading to the formation of stable Li_2O and CO_2 on heating.

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

As the electropositive character increases down the group, the stability of the carbonates and hydrogen carbonates increases.

EXAMPLE 2 : *The main oxides formed on combustion of Li, Na and K in excess of air are, respectively*

(1) LiO_2, Na_2O_2 and K_2O (2) Li_2O_2, Na_2O_2 and KO_2

(3) Li_2O, Na_2O_2 and KO_2 (4) Li_2O, Na_2O and KO_2

Solution : Li mainly gives oxide, Na gives peroxide and K gives superoxide.

ANOMALOUS PROPERTIES OF LITHIUM

Lithium shows properties which are very different from the other members of its group. This is due to the (i) exceptionally small size of its atom and ion and (ii) greater polarizing power of lithium ion (*i.e.*, charge/radius ratio). Due to these factors, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

Points of difference between Lithium and other Alkali Metals

(i) As compared to other alkali metals, lithium is harder and its melting point and boiling point are higher.

(ii) Among all the alkali metals lithium is least reactive but the strongest reducing agent. When burnt in air it forms mainly monoxide, Li_2O and the nitride, Li_3N unlike other alkali metals.

(iii) LiCl is deliquescent and crystallises as a hydrate, $LiCl\cdot 2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(iv) Except for lithium, rest of alkali metal's hydrogen carbonates are obtained in the solid form.

(v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.

(vi) Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

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

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

(vii) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

Points of similarities between Lithium and Magnesium

The similarity between lithium and magnesium is because of their similar sizes; comparable atomic radii and electronegativities.

Li = 152 pm

Mg = 160 pm

Ionic radii : Li^+ = 76 pm

Mg^{2+} = 72 pm

The major similarities are

(i) Both lithium and magnesium are harder and lighter than other elements of the respective groups.

(ii) Both lithium and magnesium react slowly with water. Their oxides and hydroxides are less soluble and their hydroxides decompose on heating. Both lithium and magnesium form nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) Their oxides like Li_2O and MgO do not combine with excess oxygen to give their superoxide.

(iv) The carbonates of both decompose easily on heating and form oxides and CO_2 and both do not form solid hydrogen carbonates.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol, are deliquescent and crystallise from aqueous solution as hydrates, $LiCl\cdot 2H_2O$ and $MgCl_2\cdot 8H_2O$.

EXAMPLE 3 : *The products obtained on heating $LiNO_3$ will be*

(1) $Li_2O + NO + O_2$ (2) $LiNO_2 + O_2$

(3) $Li_2O + NO_2 + O_2$ (4) $Li_3N + O_2$

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

EXAMPLE 4 : *Both lithium and magnesium display several similar properties due to the diagonal relationship, however, the one which is incorrect, is*

(1) *Both form nitrides*

(2) *Nitrates of both Li and Mg yield NO_2 and O_2 on heating*

(3) *Both form basic carbonates*

(4) *Both form soluble bicarbonates*

Solution : Mg forms basic carbonate

$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ but no such basic carbonate is formed by Li.

EXAMPLE 5 : *An excess of KO_2 is placed in a closed container of CO_2 (g). After reaction is completed, will the gas pressure be same, greater or less than initial value. Explain.*

Solution : $2KO_2(s) + CO_2(g) \longrightarrow K_2CO_3(s) + 3/2\, O_2(g)$

The gas pressure will increase as number of moles of gaseous product is 3/2 while that of gaseous reactant was one.

EXERCISE

[Group-1 elements, Properties of group-1 elements]

1. Which is a correct statement regarding alkali metals?

(1) Cation is larger in size than atom (2) Sizes of cation and atom are same

(3) Cation is smaller in size than atom (4) Cation is less stable than atom

2. Which alkali metal has highest tendency for half reaction; $M(g) \rightarrow M^+(aq) + 1e^-$?

(1) Li (2) Na (3) Cs (4) K

3. Sequence of ionic mobility in aqueous solution is

(1) $Rb^+ > K^+ > Cs^+ > Na^+$ (2) $Na^+ > K^+ > Rb^+ > Cs^+$

(3) $K^+ > Na^+ > Rb^+ > Cs^+$ (4) $Cs^+ > Rb^+ > K^+ > Na^+$

4. Which alkali metal is most metallic in nature?

(1) K (2) Cs (3) Na (4) Li

5. The colour imparted by sodium to the flame is

(1) Crimson red (2) Brick red (3) Apple green (4) Golden yellow

6. Elements of group IA provide a colour to the Bunsen burner flame due to

(1) Low ionisation potential (2) Low melting point

(3) Softness (4) Presence of one e^- in outermost orbit

7. With the increase in atomic weights, melting points of alkali metals

(1) Increase (2) Decrease

(3) Remain constant (4) Don't show definite trend

8. Which of the following mainly form metal oxide on heating in air?

(1) Na (2) K (3) Cs (4) Li

9. When sodium reacts with excess of oxygen. Oxidation number of oxygen changes from

(1) 0 to –1 (2) 0 to –2 (3) –1 to –2 (4) +1 to –1

10. Thermal stability of hydrides of first group elements follows the order
    (1) LiH > KH > RbH > NaH (2) LiH > NaH > KH > RbH
    (3) LiH > RbH > KH > NaH (4) RbH > KH > NaH > LiH
11. Alkali metals are strong reducing agents because
    (1) These are monovalent
    (2) Their ionisation potentials are very high
    (3) Their standard electrode potentials are very much negative
    (4) They are metals
12. Solution of sodium metal in liquid ammonia is strongly reducing due to the presence in solution of the following
    (1) Sodium hydride (2) Sodium atom (3) Solvated electrons (4) Sodium hydroxide
13. The alkali metal that reacts with nitrogen directly to form nitride is
    (1) Li (2) Na (3) K (4) Rb
14. Which of the following gives CO_2 on heating?
    (1) Li_2CO_3 (2) Na_2CO_3 (3) K_2CO_3 (4) Rb_2CO_3
15. Which salt of heating does not give brown coloured gas?
    (1) $LiNO_3$ (2) KNO_3 (3) $PbNO_3$ (4) $AgNO_3$
16. Lithium shows diagonal relationship with
    (1) Mg (2) Be (3) Al (4) B
17. Lithium shows similarities to Mg in its chemical behaviour because of
    (1) Similar size, greater electronegativity and similar polarising power
    (2) Similar size, same E.N and lower polarising power
    (3) Similar high polarising power of their cations
    (4) None of these
18. Which of the following does not illustrate the anomalous properties of lithium?
    (1) Li forms Li_3N, unlike group I metals
    (2) Li is much softer than other alkali metals
    (3) M.P. and B.P. of Li are comparatively high
    (4) The ion of Li and its compounds are more heavily hydrated than those of rest of the group.

COMPOUNDS OF SODIUM AND POTASSIUM

Sodium (Na)

Sodium is highly reactive and always found in combined state.
The isotope of sodium (Na) is used in detection of leukemia.

Compounds of Sodium

1. **Sodium Oxide (Na_2O) :**
   Preparation :
   (i) $2NaNO_3 + 10Na \xrightarrow{\Delta} 6Na_2O + N_2$
   (ii) $2NaNO_2 + 6Na \xrightarrow{\Delta} 4Na_2O + N_2$
   (iii) $3NaN_3 + NaNO_2 \xrightarrow{\Delta} 2Na_2O + 5N_2$
   (iv) $Na_2O_2 + 2Na \xrightarrow{\Delta} 2Na_2O$

Properties :

(i) Sodium oxide is a colourless ionic solid.

(ii) Aqueous solution of sodium oxide is strongly basic.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

(iii) $2Na_2O \xrightarrow{400°C} Na_2O_2 + 2Na$ (Disproportionation reaction)

(iv) Sodium oxide on reaction with liquid ammonia forms sodamide.

$$Na_2O + NH_3 \longrightarrow NaNH_2 + NaOH$$

EXAMPLE 6 : *What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water?*

(1) Oxidation number of oxygen increases

(2) Oxidation number of sodium decreases

(3) Oxide ion accepts sharing in a pair of electrons

(4) Oxide ion donates a pair of electrons

Solution : Answer (4)

$$:\ddot{\underset{\cdot\cdot}{O}}{}^{-2}\curvearrowright H^{+} \longrightarrow \bar{O}-H$$

2. Sodium Peroxide (Na_2O_2) :

Preparation :

Sodium when heated in excess of air (free from moisture and carbon dioxide) or when heated in excess of pure oxygen gives sodium peroxide.

$$2Na + O_2\text{ (excess)} \xrightarrow{350°C} Na_2O_2$$

Properties :

(i) Sodium peroxide is a pale-yellow diamagnetic compound.

(ii) Sodium peroxide is a powerful oxidising agent.

(iii) Sodium peroxide combines with CO and CO_2 to give carbonate.

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

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

(iv) At low temperature, when sodium peroxide is reacted with water or acids, H_2O_2 is formed.

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

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

(v) At high temperature, oxygen is formed.

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

$$2Na_2O_2 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + 2H_2O + O_2$$

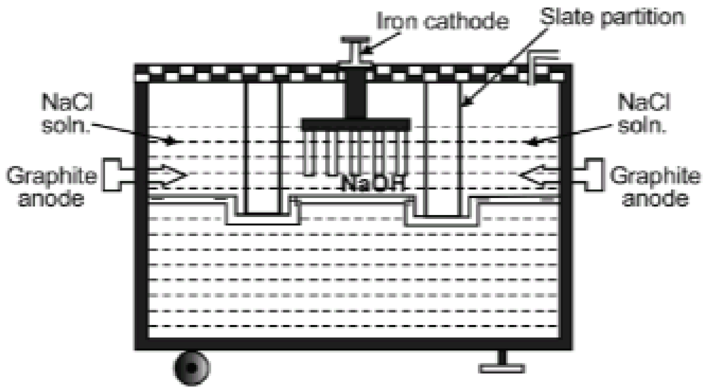
3. Sodium Hydroxide (Caustic Soda) (NaOH) :

Preparation :

(a) Gossage process : When sodium carbonate is treated with calcium hydroxide it give calcium carbonate along with sodium hydroxide. Also known as lime caustic soda process. It is a reversible reaction.

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

(b) Electrolysis of NaCl : Castner - Kellner Cell.



(i) The cell consists of a large rectangular trough divided into three compartments which do not touch the bottom of cell. Middle of cell is with mercury which is used as cathode.

(ii) The mercury can flow from one compartment to other, but solution in each compartment can't flow.

(iii) In two outer compartments NaCl solution is taken and dilute sodium hydroxide in middle compartment.

(iv) Mercury in two outer compartments act as cathode and mercury in touch with middle compartment acts as anode by induction.

(v) The outer compartment on electrolysis gives Cl_2 gas and sodium at Hg cathode.

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

At anode : $2Cl^- \rightarrow 2Cl + 2e^-$

$2Cl \rightarrow Cl_2$

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

$Na + Hg \rightarrow \text{Amalgam}$

(vi) The sodium amalgam thus formed moves in inner middle compartment where it itself acts as anode and iron acts as cathode.

At anode : $Na\ (\text{amalgam}) \rightarrow Na^+ + Hg + e^-$

At cathode : $2H_2O + 2e^- \rightarrow H_2\uparrow + OH^-$

Thus, NaOH is taken out from inner compartment and evaporated to give solid NaOH.

Properties of Sodium Hydroxide :

(i) Sodium hydroxide is a white crystalline deliquescent solid.

(ii) Sodium hydroxide is corrosive in nature.

(iii) Sodium hydroxide is highly soluble in water.

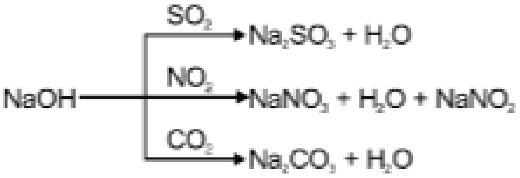
(iv) Sodium hydroxide reacts with acid forming corresponding salts.

$NaOH + HCl \longrightarrow NaCl + H_2O$

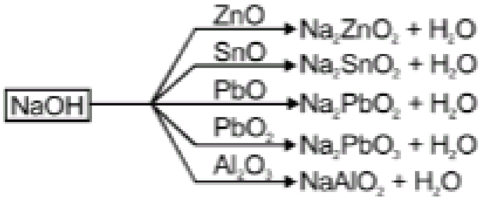
$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

$3NaOH + H_3PO_4 \longrightarrow Na_3PO_4 + 3H_2O$

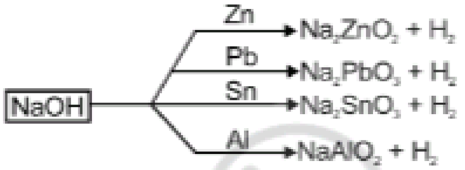
(v) Sodium hydroxide combines with acidic oxide like SO_2, NO_2, CO_2 to form respective salt.



(vi) Sodium hydroxide combine with oxides of Zn, Sn, Pb, Al to give salts.



(vii) Sodium hydroxides reacts with metals like Zn, Pb, Sn, Al to evolve hydrogen.



(viii) Sodium hydroxide attacks on non-metals like halogens, yellow phosphorous, Sulphur, Silicon.

(a) $Cl_2 + 2NaOH \text{ (cold and dilute)} \longrightarrow NaCl + NaClO + H_2O$

(b) $Br_2 + 2NaOH \text{ (cold and dilute)} \longrightarrow NaBr + NaBrO + H_2O$

(c) $I_2 + 2NaOH \text{ (cold and dilute)} \longrightarrow NaIO + NaI + H_2O$

(d) $3X_2 + 6NaOH \text{ (hot and conc.)} \longrightarrow 5NaX + NaXO_3 + 3H_2O$
(X = Cl, Br, I)

(e) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

(f) $4S + 6NaOH \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

(g) $Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$

(ix) Some salts of transition metals give insoluble hydroxide with sodium hydroxide.

(a) $FeCl_3 + NaOH \longrightarrow Fe(OH)_3\downarrow$

(b) $CrCl_3 + NaOH \longrightarrow Cr(OH)_3\downarrow$

(c) $CuSO_4 + NaOH \longrightarrow Cu(OH)_2\downarrow$

(x) Sodium hydroxides when treated with ammonium salts decompose to give NH_3.

(a) $NH_4Cl + NaOH \longrightarrow NH_3\uparrow + NaCl + H_2O$

(b) $(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3\uparrow + Na_2SO_4 + 2H_2O$

4. Sodium Carbonate (Na_2CO_3) :

Preparation :

(a) Trona, *i.e.*, sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) on decomposition gives sodium carbonate.

$$2(Na_2CO_3.NaHCO_3.2H_2O) \xrightarrow{\Delta} 3Na_2CO_3 + CO_2 + 5H_2O$$

(b) Le-Blanc process :

(i) Conversion of NaCl into Na_2SO_4 (salt cake)

$NaCl + \text{conc. } H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HCl$

$NaHSO_4 + NaCl \xrightarrow{\Delta} Na_2SO_4 + HCl$

(ii) Conversion of salt cake (Na_2SO_4) into black ash

$Na_2SO_4 + CaCO_3 + 4C \longrightarrow Na_2CO_3 + 4CaS + CO$

Black ash is a solid residue with 45% of Na_2CO_3

(iii) Recovery of Na_2CO_3 from black ash is done with help of H_2O where sodium carbonate dissolve in it leaving behind insoluble impurities. The soluble solution is evaporated to get solid Na_2CO_3.

(c) Solvay ammonia soda process : The reactions involved in Solvay process are

$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$

$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$

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

Note : *NH_4Cl is treated with $Ca(OH)_2$ to get back NH_3 in ammonia recovery tower.*

Properties :

(i) Sodium carbonate is a white crystalline solid.

(ii) $Na_2CO_3.10H_2O$ is known as washing soda.

$Na_2CO_3.H_2O$ is known as crystal carbonate

Na_2CO_3 is known as light ash or soda ash.

(iii) Na_2CO_3 is a thermally stable compound.

(iv) Sodium carbonate reacts with acids to give carbon dioxide.

$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

(v) Sodium carbonate on reaction with CO_2 gives sodium bicarbonate.

$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

(vi) Sodium carbonate on reaction with sulphur dioxide gives sodium sulphite which on further reaction gives sodium thiosulphate.

$Na_2CO_3 + SO_2 \xrightarrow{H_2O} Na_2SO_3 + CO_2$

$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$

(vii) Sodium carbonate reacts with metal salts (except alkali metals) to give carbonates.

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 + 2NaCl$

$2AgNO_3 + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaNO_3$

5. Sodium Bicarbonate (Baking Soda) ($NaHCO_3$) :

Preparation :

1. In Solvay's process, it is obtained as an intermediate.

   $NaCl + NH_3 + CO_2 + H_2 \longrightarrow NaHCO_3 + NH_4Cl$

2. When NaOH is treated with CO_2 in presence of H_2O it gives sodium bicarbonate.

   $NaOH + CO_2 + H_2O \longrightarrow NaHCO_3$

Properties :

On heating sodium bicarbonate loses CO_2 and H_2O forming Na_2CO_3.

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

6. **Sodium Chloride (NaCl) :**

Manufacture of sodium chloride is done from sea water. Sea water is allowed to dry up under summer heat in small tanks and solid crust so formed is collected.

Properties :

(1) Sodium chloride is a white crystalline solid.

(2) It is slightly hygroscopic.

(3) It is soluble in water and insoluble in alcohol.

7. **Sodium Sulphate (Na_2SO_4) :**

Preparation :

Sodium sulphate is obtained by heating NaCl with $NaHSO_4$.

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

Properties :

(1) Anhydrous sodium sulphate is known as salt cake. Sodium sulphate is hygroscopic in nature.

(2) Aqueous solution of Na_2SO_4 when cooled below 32°C, Glauber's salt ($Na_2SO_4.10H_2O$) separates out and if cooling is done below 12°C, $Na_2SO_4.7H_2O$ crystals are formed.

Potassium (K)

Potassium is the eighth most abundant Alkali metal in earth crust.

All plants contain considerable amounts of potassium compounds which they receive from soil.

Compounds of Potassium

1. **Oxides :**

When potassium is heated in presence of oxygen it can form potassium monoxide, K_2O; potassium tetra oxide, K_2O_4; potassium superoxide, KO_2; potassium sesquioxide, K_2O_3; out of these oxides the stable oxide is KO_2.

Preparation :

(a) $K + O_2 \longrightarrow KO_2$

(b) $2KOH + O_3 \longrightarrow 2KO_2 + H_2O$

Properties :

(a) Potassium superoxide (KO_2) is a chrome yellow powder. It can act as oxidising agent.

(b) Potassium superoxide (KO_2) reacts directly with carbon monoxide and carbon dioxide.

$$2KO_2 + CO \longrightarrow K_2CO_3 + O_2$$

$$2KO_2 + CO_2 \longrightarrow K_2CO_3 + \frac{3}{2}O_2$$

(c) Potassium superoxide reacts with sulphur to give potassium sulphate.

$$2KO_2 + S \longrightarrow K_2SO_4$$

2. **Potassium Hydroxide (KOH) :**

Potassium hydroxide is manufactured by electrolysis of KCl solution.

Properties :

Potassium hydroxide is used in adsorption of CO_2, SO_2 etc.

3. **Potassium Carbonate (K_2CO_3) :**

Preparation :

Le-Blanc Process : KCl is reacted with H_2SO_4, which gives K_2SO_4. This K_2SO_4 is further reacted with $CaCO_3$ and carbon, which finally converts it into K_2CO_3.

$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl\uparrow$

$KHSO_4 + KCl \longrightarrow K_2SO_4 + HCl\uparrow$

$K_2SO_4 + CaCO_3 + 2C \longrightarrow K_2CO_3 + CaS + 2CO_2$

Properties :

(i) Potassium carbonate is white powder.

(ii) Potassium carbonate is deliquescent in nature and is highly soluble in water.

(iii) Potassium carbonate on hydrolysis gives KOH and H_2CO_3.

$K_2CO_3 + 2H_2O \longrightarrow 2KOH + H_2CO_3$

(iv) Potassium carbonate on reaction with hot steam gives KOH and CO_2.

$K_2CO_3 + H_2O\ (steam) \xrightarrow{\Delta} 2KOH + CO_2\uparrow$

4. **Potassium Chloride (KCl) :**

Potassium chloride is prepared by the electrolysis of carnallite *i.e.*, $KCl.MgCl_2.6H_2O$.

5. **Potassium Sulphate :**

(i) The mineral – $K_2SO_4.MgSO_4.6H_2O$ (Schonite) when treated with KCl in aqueous solution, K_2SO_4 separates out.

$K_2SO_4.MgSO_4.6H_2O + 2KCl \longrightarrow 2K_2SO_4 + MgCl_2 + 6H_2O$

(ii) Potassium when heated with excess of oxygen followed by S gives K_2SO_4.

Properties :

(i) K_2SO_4 is highly soluble in water and can form double salts to form potash alum

$K_2SO_4 + Al_2(SO_4)_3 + (aq) \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$

(ii) K_2SO_4 when heated with carbon gives CO and K_2S

$K_2SO_4 + 4C \xrightarrow{\Delta} K_2S + 4CO\uparrow$

(iii) K_2SO_4 when treated with $BaCl_2$ gives Barium sulphate.

Try Yourself

1. NaH is an example of
   - (1) Metallic hydride
   - (2) Electron-rich hydride
   - (3) Molecular hydride
   - (4) Saline hydride
2. The metal mainly used in devising photoelectric cells is
   - (1) Na
   - (2) Rb
   - (3) Li
   - (4) Cs
3. Metallic sodium does not react normally with:
   - (1) Ethyne
   - (2) Gaseous ammonia
   - (3) But-2-yne
   - (4) Tert-butyl alcohol
4. Which one of the following compounds is used as a chemical in certain type of fire extinguishers?
   - (1) Baking soda
   - (2) Soda ash
   - (3) Washing soda
   - (4) Caustic Soda

EXAMPLE 7 : *Why potassium carbonate cannot be prepared by Solvay process?*

Solution : This is due to the reason that potassium bicarbonate ($KHCO_3$) formed as an intermediate (When CO_2 is passed through ammoniated solution of potassium chloride) is highly soluble in water and cannot be separated by filtration.

EXAMPLE 8 : *Following statement are given.*

Statement - I *Ionic mobility in aqueous solution is in order*

$Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus}$

Statement - II *Stability for the following superoxide is* $CsO_2 > RbO_2 > KO_2$

Statement - III *Thermal stability order*

$K_2CO_3 > CaCO_3 > MgCO_3 > BeCO_3$

Which of following are correct statement(s)

(A) I, II *(B) II, III*

(C) I, II, III *(D) IV only*

Solution : All orders given are correct.

EXAMPLE 9 : *The correct statement for the molecule,* CsI_3*, is*

(1) It is a covalent molecule

(2) It contains Cs^+ *and* I_3^- *ions*

(3) It contains Cs^{3+} *and* I^- *ions*

(4) It contains Cs^+, I^- *and lattice* I_2 *molecule*

Solution : It contains Cs^+ and I_3^- ions.

EXERCISE

[Compounds of group-1 elements]

19. The electronic configuration of metal M is $1s^2, 2s^2, 2p^6, 3s^1$. The formula of its oxide would be

(1) MO (2) M_2O (3) M_2O_3 (4) MO_2

20. Sodium carbonate is prepared by

(1) Solvay's process (2) Kolbe's process (3) Contact process (4) Haber's process

21. Aqueous solution of Na_2CO_3 is basic in nature due to

(1) Hydrolysis of Na^+ (2) Hydrolysis of CO_3^{2-}

(3) Hydrolysis of both Na^+ and CO_3^{2-} (4) Hydrolysis of both Na^+ and HCO_3^-

22. A mixture of KCl and KF is added to sodium chloride

(1) To increase the conductivity of NaCl

(2) To decreases Melting point of NaCl

(3) To supress the degree of dissociation of NaCl

(4) To decrease the volatility of NaCl

23. Which one of the following salts gives aqueous solution, which is weakly basic?

(1) NH_4HCO_3 (2) $NaHSO_4$ (3) $NaHCO_3$ (4) NaCl

24. Sodium peroxide which is a yellow solid, when exposed to air becomes white due to the formation of?

(1) H_2O_2 (2) Na_2O (3) Na_2O and O_3 (4) NaOH and Na_2CO_3

25. $A + Na_2CO_3 \rightarrow B + C$

$\xrightarrow{CO_2}$ Milky cloud, C

(1) $Ca(OH)_2$, NaOH, $CaCO_3$ (2) NaOH, $Ca(OH)_2$, $CaCO_3$

(3) $Ca(OH)_2$, $CaCO_3$ and NaOH (4) CaO, NaOH, $Ca(OH)_2$

26. During electrolysis of fused sodium chloride, the anodic reaction is

(1) Reduction of Na^+ to Na (2) Oxidation of Na to Na^+

(3) Reduction of chloride ions (4) Oxidation of chloride ions

27. Which of the following is paramagnetic?

(1) KO_2 (2) Na_2O_2 (3) BaO_2 (4) NaCl

28. Solubility of alkali metal carbonates
    (1) Increases first and then decreases
    (2) Does not show regular variation
    (3) Increases as we go down the group
    (4) Decreases as we go down the group

29. RbO_2 is
    (1) Peroxide and paramagnetic
    (2) Peroxide and diamagnetic
    (3) Superoxide and paramagnetic
    (4) Superoxide and diamagnetic

30. Which one of the following on heating will not give CO_2?
    (1) Li_2CO_3
    (2) $PbCO_3$
    (3) $CaCO_3$
    (4) Na_2CO_3

GROUP-2 ELEMENTS : ALKALINE EARTH METALS

The elements of group-2 are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). Except for Be, rest are known as alkaline earth metals, because they were alkaline in nature and existed in the earth. Be differs from rest of the members and show diagonal relationship with aluminium.

Atomic and Physical Properties of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol^{-1})	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I)/kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II)/kJ mol^{-1}	1757	1450	1145	1064	965	979
Hydration enthalpy kJ mol^{-1}	–2494	–1921	–1577	–1443	–1305	–
Metallic radius / pm	111	160	197	215	222	–
Ionic radius M^{2+} / pm	31	72	100	118	135	148
m.p. / K	1560	924	1124	1062	1002	973
b.p./ K	2745	1363	1767	1655	2078	(1973)
Density / g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potentials E / V for (M^{2+}/ M)	–1.97	–2.36	–2.84	–2.89	–2.92	–2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390*	10^{-6}*

**ppm (parts per million); ** percentage by weight*

Electronic Configuration

The alkaline earth metals have 2 electrons in the *s*-orbital of the valence shell. Their general electronic configuration may be represented as

[Noble gas]ns^2; where n = 2 to 7

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$ or [He]$2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$ or [Ne]$3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or [Ar]$4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ or [Kr]$5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe]$6s^2$
Radium	Ra	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$ or [Rn] $7s^2$

Atomic and Ionic Radii

The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding members of alkali metals. This is due to the fact that the alkaline earth metals have a higher nuclear charge due to which the electrons are more strongly attached towards the nucleus causing a decrease in atomic size. Within the group, the atomic and ionic radii increase with increase in atomic number.

Ionization Enthalpies

The alkaline earth metals owing to their large size of atoms have fairly low values of ionization enthalpies. Within the group, the ionization enthalpy decreases as the atomic number increases. It is because of increase in atomic size due to addition of new shells and increase in the magnitude of screening effect of the electrons in inner shells.

The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding group 1 metals. This is due to their small size as compared to the corresponding alkali metals. It is interesting to note that the second ionization enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metal.

Hydration Enthalpies

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Therefore, compounds of alkaline earth metals are more extensively hydrated, for example, magnesium chloride and calcium chloride exists as hexahydrates ($MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$) whereas sodium chloride and potassium chloride do not form such hydrates.

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

Physical Properties

The alkaline earth metals are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. But this trend is not systematic, because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.

Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. Ca, Sr and Ba give flame test which helps in their detection in qualitative analysis and estimation by flame photometry. The alkaline earth metals just like those of alkali metals have high electrical and thermal conductivities which are a typical characteristics of metals.

EXAMPLE 10 : *Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?*

(1) $CaSO_4$ (2) $BeSO_4$

(3) $BaSO_4$ (4) $SrSO_4$

Solution : $BeSO_4$ has hydration energy greater than its lattice energy.

Chemical Properties

As compared to alkali metals, alkaline earth metals are less reactive due to their relatively higher ionization enthalpies. The reactivity of alkaline earth metals increases on going down the group because their ionization enthalpies decreases and electropositive character increases.

Chemical Properties of Group-2 Elements

(i) **Reaction with water :** Ca Sr, and Ba have reduction potentials similar to those of corresponding group Ist metals and are quite high in the electrochemical series. They react with cold water readily, liberating hydrogen forming metal hydroxides.

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

Magnesium has an intermediate value and it does not react with cold water but it decomposes hot water. Be($Be^{+2}/Be = -1.97$ V) is least negative amongst all the alkaline earth metals. This means that Be is much less electropositive than other alkaline earth metals and hence does not react with water or steam even when red hot.

Knowledge Cloud

The alkaline earth metals react with water with increasing vigour even in cold to form hydroxide. All the alkaline earth metal hydroxides are bases except $Be(OH)_2$ which is amphoteric.

The solubilities of hydroxide of alkaline-earth metals increase markedly on moving down the group as shown below.

Hydroxide	**Solubility in water at 298 K (gL^{-1})**
$Be(OH)_2$	Insoluble
$Mg(OH)_2$	0.03
$Ca(OH)_2$	1.3
$Sr(OH)_2$	8
$Ba(OH)_2$	380

Solubility in water increases

Basic strength increases

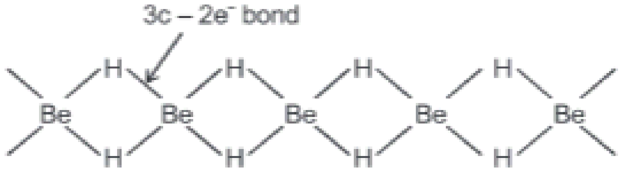
Among the hydroxides of this group, it is observed that the magnitude of hydration enthalpy remains almost unaltered whereas the magnitude of lattice enthalpy decreases significantly down the group due to increase in size. Thus, the net effect of the two factors, ($\Delta H_{lattice} - \Delta H_{hydration} = \Delta H_{solution}$); $\Delta H_{solution}$ becomes more negative from Be to Ba accounting for increase in solubility.

(ii) **Reaction with Air :** Except Be these metals are easily tarnished in air as a layer of oxide is formed on their surface. The effect of atmosphere increases as the atomic number increases. Ba in powdered form bursts into flame on exposure to air.

(iii) **Reaction with hydrogen :** The elements Mg, Ca, Sr and Ba all react with hydrogen to form hydrides MH_2. Beryllium hydride is difficult to prepare and less stable than others. BeH_2, however, can be prepared by reaction of $BeCl_2$ with $LiAlH_4$.

$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$

It is polymeric as $(BeH_2)_n$ possesses hydrogen bridges. Three centre two electron bonds are present in which a banana shaped molecular orbital covers three atoms Be-----H------Be and contains 2 electrons. The stability of hydrides decreases with increasing atomic number because metallic nature of elements increases.



(iv) Reaction with oxygen : Except Ba and Ra the elements when burnt in oxygen form oxides of the type MO. Beryllium metal is relatively unreactive and does not react below 600°C but the powdered form is much more reactive and burns brilliantly. The element Mg, burns with dazzling brilliance evolving a considerable amount of heat. Barium and radium being highly electropositive form peroxides.

$$\text{Ba} \xrightarrow{O_2} \underset{\text{Barium oxide}}{\text{BaO}} \xrightarrow[\text{High temperature}]{O_2} \underset{\text{(Barium peroxide)}}{\text{BaO}_2}$$

Knowledge Cloud

Beryllium, magnesium and calcium form monoxides while strontium and barium form peroxides.

$2M + O_2 \rightarrow \underset{\text{(Monoxide)}}{2MO}$ (M = Be, Mg or Ca)

$M + O_2 \rightarrow \underset{\text{(Peroxide)}}{MO_2}$ (M = Ba or Sr)

The monoxide can also be prepared by decomposition of their respective carbonates.

$MCO_3 \rightarrow MO + CO_2$

(M = Be, Mg, Ca, Sr or Ba)

The reactivity of alkaline earth metals towards oxygen increases as we move down the group.

(v) Reaction with halogens : When heated with halogens the alkaline earth metals directly combine with them.

$$\text{Ca} + \text{Cl}_2 \xrightarrow{\text{heated}} \text{CaCl}_2$$

Beryllium halides are covalent in nature. This is due to small size and high charge of Be^{+2} ions, that is, it has high polarising power. The glassy forms of halide are known to have chain of …X_2 Be X_2 Be ....

The halides of the type MX_2 of other metals are ionic solids.

(vi) Reaction with nitrogen : All alkaline earth metals react with N_2 to form nitrides.

$$3Mg + N_2 \rightarrow Mg_3N_2$$

N_2 molecule is very stable and it requires a lot of energy to convert N_2 into N^{3-}, nitride ions. The large amount of energy required comes from the very large amount of lattice energy evolved when the crystalline solid is formed. The lattice energy is particularly high because of high charges on the ions M^{+2} and N^{-3}. Be_3N_2 is volatile but the other nitrides are not volatile, they are ionic crystalline solids. The nitrides are hydrolysed with water and liberate ammonia.

(vii) Reaction with carbon : With the exception of Be, other metals when heated with carbon in an electric furnace form carbides. These carbides are called acetylides.

$$Ca + 2C \rightarrow CaC_2$$

On hydrolysis, these carbides evolve acetylene, when BeO is heated with carbon at about 2000°C a brick red coloured carbide of formula Be_2C is formed. On hydrolysis it evolves methane and is thus called methanide. MgC_2 on heating changes to Mg_2C_3. Mg_2C_3 on hydrolysis evolves propyne.

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

$$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3 - C \equiv CH$$

$$BaC_2 + N_2 \xrightarrow{\Delta} Ba(CN)_2$$

$$CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$$

(viii) Reaction with acids and bases : All metals react with acids and liberate H_2 although Be reacts slowly

$Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow$

Be is amphoteric as it also reacts with NaOH giving H_2 and sodium beryllate

$$Be + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2 \cdot 2H_2O} + H_2$$

(ix) Formation of amalgams : Alkaline earth metals combine with mercury to form amalgams.

(x) Complex formation : Alkaline earth metal cations do not have large size and their ionic charge is slightly more than those of alkali metals, so they are capable of forming complexes, but the tendency of M^{+2} ions to form complexes decreases with the increase in size of M^{+2} ion. Be, being smallest in size has maximum tendency to form complexes such as $[BeF_3]^-$, $[BeF_4]^{2-}$ and so on while Ba^{+2} has the least tendency to form complexes.

Uses of alkaline earth metals

1. Beryllium is used in the manufacture of alloys. Copper-Beryllium alloys are used in the making of high strength springs.
2. Metallic beryllium is used for making windows of X-rays tubes.
3. Magnesium, being a light metal, forms many light alloys with aluminium, zinc, manganese and tin.
4. Magnesium (Powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals).
5. Magnesium-aluminium alloys are used in aircraft construction.
6. Magnesium is used as sacrificial anode for the prevention of corrosion of iron.
7. A suspension of magnesium hydroxide in water (called milk of magnesia) is used as an ant-acid to control excess acidity in stomach.
8. Magnesium carbonate is an ingredient of tooth-paste.
9. Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon.
10. Calcium and barium metals are used to remove air from vacuum tubes, due to their tendency to react with oxygen and nitrogen at high temperature.
11. Radium salts are used for radio therapy of cancer.

Comparison of group1 and 2 metals

(i) Li < K < Na < Rb < Ca < Mg < Be < Cs < Sr < Ba (Density)
(ii) Cs < Rb < K < Na < Li < Mg < Ba < Sr < Ca < Be (Melting point)
(iii) Cs < Rb < K < Na < Mg < Li < Sr < Ca < Ba < Be (Boiling point)
(iv) Li > Cs > Rb > K > Ba > Sr > Ca > Na > Mg > Be (S.O.P. ($E^0_{M/M^{n+}}$); n = 1or 2)

GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The most common valence of group 2 element is 2+, *i.e.*, dipositive oxidation state.

The alkaline earth metals commonly form ionic compounds but ionic character of their compounds is lesser than that of the alkali metals. This is due to high ionization energy due to increased nuclear charge and smaller size.

The tendency to form ionic compounds increases down the group, that is the reason why the oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and larger sized members (Ca, Sr, Ba).

The general characteristics of some of the compounds of the alkaline earth metals are described below.

(i) **Oxides and hydroxides :** The alkaline earth metals being less electro positive than alkali metals react with air or oxygen slowly upon heating to form monoxides, MO and except for BeO, all alkaline earth metals have rock-salt structure.

The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat.

BeO is amphoteric in nature and oxides of other elements are ionic and basic in nature, and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

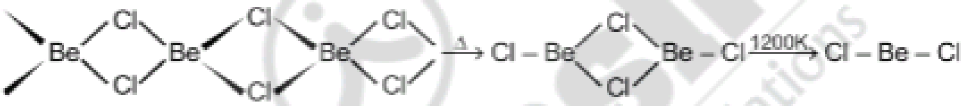
The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. The hydroxides of alkaline earth metals are less basic and less stable when compared with that of the alkali metals. Beryllium hydroxide is amphoteric in nature.

$$Be(OH)_2 + 2OH^- \rightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

$$Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(H_2O)_4]Cl_2$$

(ii) **Halides :** Beryllium forms covalent halides, all other members forms ionic halides. Beryllium halides are soluble in organic solvents.

Beryllium chloride has a chain structure



$BeCl_2$ in vapour phase form a chloro-bridged dimer which at high temperatures of the order of 1200 K dissociates into linear monomer. The tendency to form halide hydrates gradually decreases, (for example, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) down the group. The hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be dehydrated by heating but the corresponding hydrated halides of Be and Mg on heating undergoes hydrolysis. The fluorides of alkaline earth metals are less soluble than chlorides due to their high lattice energies.

Nature of bicarbonates and carbonates : All the bicarbonates of alkaline earth metals are known in solution only. On heating, these are decomposed with evolution of CO_2.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$$

Carbonates of alkaline earth metals are solids. These dissolve in water in the presence of CO_2. On heating, the carbonates decomposes to give CO_2 and metal oxide.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

The temperature of decomposition increases from Mg to Ba. $BeCO_3$ is kept in atmosphere of CO_2 to prevent its decomposition.

	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Decomposition temp. (°C)	<100°C	540°C	900°C	1290°C	1360°C

$BeCO_3$ have unusual low thermal stability because it exist as $[Be(H_2O)_4]^{+2}CO_3^{-2}$

Nature of sulphates : The solubility of sulphates decreases on moving down the group. $CaSO_4$ is sparingly soluble, while $SrSO_4$, $BaSO_4$ and $RaSO_4$ are almost insoluble. The solubilities of $BeSO_4$ and $MgSO_4$ are due to high energy of solvation of smaller Be^{+2} and Mg^{+2} ions. The sulphates decompose on heating to give corresponding oxide (MO)

$$2MSO_4 \rightarrow 2MO + 2SO_2 + O_2$$

Nitrates : All the nitrates on heating give the mixture of NO_2 and O_2. Beryllium forms a basic nitrate in addition to the normal salt. Basic nitrate is a covalent compound.

$$Be(NO_3)_2 \xrightarrow{\Delta} [Be_4O(NO_3)_6] + N_2O_5$$

ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium shows different behaviour from the rest members of its group and shows diagonal relationship to aluminium due to reasons discussed below.

(i) Beryllium has exceptionally small atomic and ionic sizes and therefore does not compare well with other members of the group, because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell, there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.

(iii) The oxides and hydroxide of beryllium unlike the hydroxide of other elements in the group, are amphoteric in nature.

Diagonal relationship between Beryllium and Aluminium

The ionic radius of Be^{2+} is approx. 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Similarities between Al and Be is given below.

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ions, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have Cl^- bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel-Crafts catalysts.

(iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.

EXAMPLE 11 : *Why beryllium is different from other members of its group in some properties?*

Solution : (i) It is due to small atomic and ionic size.

(ii) Absence of *d*-orbitals.

COMPOUNDS OF MAGNESIUM AND CALCIUM

Magnesium (Mg)

Magnesium salts occur in sea water.

Magnesium has closed packed hexagonal lattice. Magnesium ion is the essential element in human body and is the important constituent of chlorophyll.

Compounds of Magnesium

1. **Magnesium Oxide (MgO) :**

Preparation :

(i) Magnesium Ribbon when burnt in air (oxygen) give magnesium oxide (MgO).

$$2Mg + O_2 \longrightarrow 2MgO$$

(ii) When magnesium hydroxide is strongly heated, it gives magnesium oxide.

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

(iii) When magnesium carbonate is strongly heated, it gives magnesium oxide.

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

(iv) When magnesium nitrate is strongly heated, it gives magnesium oxide.

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

Properties :

(i) Magnesium oxide is a white powder.

(ii) Magnesium oxide is a basic oxide, which is soluble in water.

(iii) Magnesium oxide and magnesium chloride is together known as magnesia cement or Sorel's cement, *i.e.*, $MgCl_2.5MgO.H_2O$, used for dental fillings.

(iv) Magnesium oxide when reacted with HCl or H_2SO_4 gives respective salts.

$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$

2. **Magnesium Hydroxide ($Mg(OH)_2$) :**

Preparation :

(i) When magnesium chloride is reacted with calcium hydroxide or sodium hydroxide, magnesium hydroxide is formed.

$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$

$MgCl_2 + NaOH \longrightarrow Mg(OH)_2 + 2NaCl$

(ii) When magnesium oxide is reacted with water it gives magnesium hydroxide.

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

Properties :

(i) Magnesium hydroxide is a white powder.

(ii) Magnesium hydroxide is basic in nature.

(iii) Magnesium hydroxide on decomposition gives magnesium oxide.

(iv) Magnesium hydroxide on reaction with NH_4Cl gives magnesium chloride.

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

3. **Magnesium Carbonate ($MgCO_3$) :**

Preparation :

(i) Magnesium carbonate is prepared by adding sodium bicarbonate to a hot solution of magnesium salt.

$MgSO_4 + 2NaHCO_3 \longrightarrow MgCO_3 + Na_2SO_4 + H_2O + CO_2$

(ii) Magnesium sulphate when reacted with sodium carbonate gives white precipitate of a basic carbonate which when suspended in water and CO_2 passed, magnesium bicarbonate is formed which when further boiled gives magnesium carbonate.

$2MgSO_4 + 2Na_2CO_3 + H_2O \longrightarrow MgCO_3.Mg(OH)_2 + 2Na_2SO_4 + CO_2$

$MgCO_3.Mg(OH)_2 + 3CO_2 + H_2O \longrightarrow 2Mg(HCO_3)_2$

$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + CO_2 + H_2O$

4. **Magnesium Chloride ($MgCl_2$) :**

Preparation :

(i) Magnesium chloride is prepared by dissolving Mg or MgO or $Mg(OH)_2$ or $MgCO_3$ in dil. HCl.

$Mg + 2HCl \longrightarrow MgCl_2 + H_2$

$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$

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

(ii) Carnallite ($KCl.MgCl_2.6H_2O$) when fused and cooled to 176°C, KCl is deposited while $MgCl_2.6H_2O$ is obtained in fused state.

Properties :

(i) Magnesium chloride is a colourless crystalline solid, highly soluble in water.

(ii) $MgCl_2.6H_2O$ when reacted with sodium bicarbonate gives magnesium carbonate which on further reaction with H_2SO_4 give magnesium sulphate.

$MgCl_2.6H_2O \xrightarrow{NaHCO_3} MgCO_3 \xrightarrow{H_2SO_4} MgSO_4.7H_2O$

5. **Magnesium Sulphate ($MgSO_4$) :**

Preparation :

(i) When magnesite ($MgCO_3$) is treated with dil. sulphuric acid, magnesium sulphate is formed.

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

(ii) When dolomite ($MgCO_3.CaCO_3$) is treated with dil. sulphuric acid, magnesium sulphate is formed.

$MgCO_3.CaCO_3 + 2H_2SO_4 \longrightarrow MgSO_4 + CaSO_4 + 2CO_2 + 2H_2O$

Properties :

(i) Magnesium sulphate is colourless crystalline compound soluble in water.

(ii) Magnesium sulphate forms double salt with alkali metal sulphates ($K_2SO_4.MgSO_4.6H_2O$).

(iii) Magnesium sulphate on strong heating gives MgO

$$MgSO_4.7H_2O \xrightarrow{150^\circ C} MgSO_4.H_2O \xrightarrow{200^\circ C} MgSO_4 \xrightarrow{\Delta} MgO + SO_2 + \frac{1}{2}O_2$$

Calcium (Ca)

Compounds of Calcium

1. **Calcium Oxide (CaO) :**

Preparation :

Calcium carbonate when decomposed at 800°C gives calcium oxide.

$CaCO_3 \xrightarrow{800^\circ C} CaO + CO_2\uparrow$

Properties :

(i) Calcium oxide is also known as 'Quick lime' or 'Burnt lime', is white amorphous substance.

(ii) Calcium oxide when reacted with SiO_2 and P_2O_5 at high temperature gives calcium silicate ($CaSiO_3$) and Calcium phosphate ($Ca_3(PO_4)_2$) respectively. CaO is used as flux in blast furnace for removal of impurities in the form of slag.

$CaO + SiO_2 \longrightarrow CaSiO_3$

$6CaO + 2P_2O_5 \longrightarrow 2Ca_3(PO_4)_2$

(iii) When water is added to lime a hissing sound is produced along with clouds of steam. The lime forms slaked lime [$Ca(OH)_2$]. The paste of lime in water is called milk of lime ($Ca(OH)_2$).

(iv) Calcium oxide reacts with moist chlorine to form bleaching powder.

$CaO + Cl_2 \longrightarrow CaOCl_2$ [Mixture of $CaCl_2 + Ca(OCl)_2$]

(v) Calcium oxide on reaction with moist SO_2 forms $CaSO_3$ and with moist CO_2 forms $CaCO_3$.

$CaO + SO_2 \longrightarrow CaSO_3$

$CaO + CO_2 \longrightarrow CaCO_3$

(vi) Calcium oxide on reaction with moist HCl gas forms $CaCl_2$.

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

(vii) Calcium oxide on reaction with carbon at around 2000°C forms calcium carbide.

$CaO + 3C \xrightarrow{2000^\circ C} CaC_2 + CO$

2. **Calcium Carbonate ($CaCO_3$) :**

Preparation :

(i) Carbon dioxide when passed through lime water gives calcium carbonate.
$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

(ii) Calcium chloride on reaction with sodium carbonate gives calcium carbonate.
$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

Properties :

(i) Calcium carbonate is a white powder insoluble in water.

(ii) Calcium carbonate dissolves in water in presence of CO_2 due to formation of calciumbicarbonate.

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

3. Calcium Chloride ($CaCl_2$) :

Preparation :

Calcium oxide, calcium hydroxide or calcium carbonate when treated with HCl gives calcium chloride.

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

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

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

$$CaCl_2 \text{ (Solution)} \xrightarrow{\text{Crystallization}} CaCl_2.6H_2O \text{ (Crystal)}$$

Properties :

(i) Calcium chloride is a colourless deliquescent crystalline substance which is soluble in water as well as in alcohol.

(ii) Crystals of calcium chloride when strongly heated gives off water of crystallisation.

Calcium sulphate (Plaster of Paris) [$CaSO_4 \cdot \frac{1}{2} H_2O$]

Preparation : When Gypsum is heated at about 120° - 130°C, Plaster of Paris is formed.

$$\underset{\text{Gypsum}}{2CaSO_4 \cdot 2H_2O} \longrightarrow \underset{\text{Plaster of Paris}}{(CaSO_4)H_2O} + 3H_2O$$

Properties :

(i) It is a white crystalline solid. It is sparingly soluble in water.

(ii) It becomes anhydrous at about 200°C. Anhydrous form is known as dead burnt plaster.

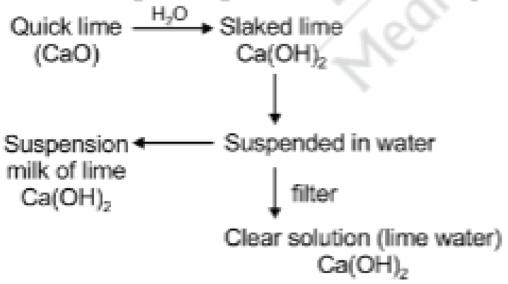
$$\underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow{120^\circ C} \underset{\text{plaster of Paris}}{CaSO_4 \cdot \frac{1}{2} H_2O} \xrightarrow{200^\circ C} \underset{\substack{\text{anhydrous} \\ \text{(dead burnt plaster)}}}{CaSO_4}$$

Calcium hydroxide $Ca(OH)_2$ or slaked lime

Preparation :

(i) **From quick lime :** $CaO + H_2O \rightarrow Ca(OH)_2$

(ii) **From $CaCl_2$:** $CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl$



Properties :

It gives $CaCO_3$ and $Ca(HCO_3)_2$ with CO_2

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3 \downarrow} + H_2O$$

On prolong treatment with CO_2 milkiness disappears due to formation of $Ca(HCO_3)_2$

$$CaCO_3 + H_2O + CO_2 \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)}$$

Try Yourself

5. The amphoteric hydroxide is
   (1) $Mg(OH)_2$ (2) $Be(OH)_2$
   (3) $Sr(OH)_2$ (4) $Ca(OH)_2$
6. The number of water molecules in gypsum, dead burnt plaster and plaster of Paris, respectively
   (1) 2, 0 and 1 (2) 0.5, 0 and 2
   (3) 5, 0 and 0.5 (4) 2, 0 and 0.5
7. *s*-block element which cannot be qualitatively confirmed by the flame test is
   (1) Li (2) Na
   (3) Rb (4) Be

EXAMPLE 12 : *Predict the outcome of the following reactions and write balanced equations.*

(i) $BaO_2(s) + H_2SO_4(aq) \rightarrow$
(ii) $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow$
(iii) $Ca(s) + H_2(g) + Heat \rightarrow$

Solution :
(i) $BaO_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(l)$
(ii) $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$
(iii) $Ca(s) + H_2(g) + Heat \rightarrow CaH_2(s)$

EXAMPLE 13 : *Explain why both $BeCO_3$ and $BeSO_4$ are unstable to heat, while $BaCO_3$ and $BaSO_4$ are stable.*

Solution : The decomposition of a salt is promoted by the formation of a new compound with high lattice energy. From $BeCO_3$ and $BeSO_4$, BeO will be formed by decomposition. The small doubly charged ions will result in very high lattice energy for BeO which will help to drive the reaction. (Reaction is also favoured by an increase in entropy since a gaseous product is formed).

CEMENT

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is : CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe_2O_3, 1-2% and SO_3, 1-2%. **For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO_2) aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close as possible to 2.**

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) to form cement. **Thus, important ingredients present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51% and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.**

Setting of cement : When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses : Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England.

Illustration 1 : *The metal that forms nitride by reacting directly with N_2 of air, is*

(1) Li *(2) Rb*

(3) Cs *(4) K*

Solution : Only lithium react with N_2 among alkali metals. **Answer (1)**

Illustration 2 : *The correct order of hydration enthalpies of alkali metal ions is*

(1) $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$ *(2) $Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$*

(3) $Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$ *(4) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$*

Solution : Smaller is size more is hydration energy.

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ Size

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ Hydration energy **Answer (4)**

Illustration 3 : *The INCORRECT statement is*

(1) Lithium is least reactive with water among the alkali metals

(2) $LiNO_3$ decomposes on heating to give $LiNO_2$ and O_2

(3) Lithium is the strongest reducing agent among the alkali metals

(4) LiCl crystallises from aqueous solution as $LiCl.2H_2O$

Solution : $4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$ **Answer (2)**

Illustration 4 : *A s-block element (M) reacts with oxygen to form an oxide of the formula MO_2. The oxide is pale yellow in colour and paramagnetic. The element (M) is*

(1) K *(2) Na*

(3) Mg *(4) Ca*

Solution : $K + O_2 \rightarrow KO_2$ (Paramagnetic because of O_2^-) **Answer (1)**

Illustration 5 : *Match List-I with List-II :*

	List-I *Elements*		*List-II* *Properties*
(a)	*Li*	*(i)*	*Poor water solubility of I^- salt*
(b)	*Na*	*(ii)*	*Most abundant element in cell fluid*
(c)	*K*	*(iii)*	*Bicarbonate salt used in fire extinguisher*
(d)	*Cs*	*(iv)*	*Carbonate salt decomposes easily on heating*

Choose the correct answer from the options given below :

(1) (a)-(i), (b)-(iii), (c)-(ii), (d)-(iv)

(2) (a)-(i), (b)-(ii), (c)-(iii), (d)-(iv)

(3) (a)-(iv), (b)-(iii), (c)-(ii), (d)-(i)

(4) (a)-(iv), (b)-(ii), (c)-(iii), (d)-(i)

Solution : Among alkali metals and their compounds Li_2CO_3 is thermally least stable and decomposes easily on heating.

$NaHCO_3$ is used as fire extinguisher.

K is most abundant element in cell fluid.

CsI is a covalent compound and has poor water solubility.

∴ Correct answer

(a)-(iv), (b)-(iii), (c)-(ii), (d)-(i) **Answer (3)**

Illustration 6 : ***Statement-I:*** *An alloy of lithium and magnesium is used to make aircraft plates.*

Statement-II: *The magnesium ions are important for cell-membrane integrity.*

In the light of the above statements, choose the correct answer from the options given below:

(1) Both Statement-I and Statement-II are true

(2) Both Statement-I and Statement-II are false

(3) Statement-I is true but Statement-II is false

(4) Statement-I is false but Statement-II is true

Solution : Magnesium alloys are used to make body of aircraft which is lightweight and resistant to corrosion. Calcium is responsible for cell membrane integrity. **Answer (2)**

Illustration 7 : *The structures of beryllium chloride in the solid state and vapour phase, respectively, are*

(1) Chain and dimeric *(2) Dimeric and dimeric*

(3) Dimeric and chain *(4) Chain and chain*

Solution : $BeCl_2$ in vapour phase exist as dimer (below 1200 K temperature).

$BeCl_2$ in solid state has chain structure. **Answer (1)**

Illustration 8 : *The correct sequence of thermal stability of the following carbonates is :*

(1) $MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

(2) $BaCO_3 < SrCO_3 < CaCO_3 < MgCO_3$

(3) $MgCO_3 < SrCO_3 < CaCO_3 < BaCO_3$

(4) $BaCO_3 < CaCO_3 < SrCO_3 < MgCO_3$

Solution : Stability of alkaline earth metal carbonates increases down the group :

$MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$ **Answer (1)**

Illustration 9 : *Match the following compounds (Column-I) with their uses (Column-II).*

S. NO.	***Column-I***	***S. NO.***	***Column-II***
(I)	$Ca(OH)_2$	*(A)*	*casts of statues*
(II)	*NaCl*	*(B)*	*white wash*
(III)	$CaSO_4 \cdot \frac{1}{2}H_2O$	*(C)*	*antacid*
(IV)	$CaCO_3$	*(D)*	*washing soda preparation*

(1) (I)-(B), (II)-(C), (III)-(D), (IV)-(A) *(2) (I)-(B), (II)-(D), (III)-(A), (IV)-(C)*

(3) (I)-(C), (II)-(D), (III)-(B), (IV)-(A) *(4) (I)-(D), (II)-(A), (III)-(C), (IV)-(B)*

Solution :

$Ca(OH)_2$ – Used in white wash

NaCl – Used for the preparation of washing soda (Na_2CO_3)

$CaSO_4 \cdot \frac{1}{2}H_2O$ – Used for making casts of statues

$CaCO_3$ – Used as an antacid **Answer (2)**

Illustration 10 : *The correct order of density is*

(1) Be > Mg > Ca > Sr *(2) Sr > Ca > Mg > Be*

(3) Sr > Be > Mg > Ca *(4) Be > Sr > Mg > Ca*

Solution :

Density of Sr = 2.63 g/cm^3

Density of Be = 1.84 g/cm^3

Density of Mg = 1.74 g/cm^3

Density of Ca = 1.55 g/cm^3 **Answer (3)**

EXERCISE

[Group-2 elements, Properties, Compounds of group-2]

31. Which metal does not impart colour to the flame on heating?

(1) Be (2) Ca

(3) Sr (4) Ba

32. Which of following hydroxide is least soluble in water?

(1) $Mg(OH)_2$ (2) $Ca(OH)_2$

(3) $Sr(OH)_2$ (4) $Ba(OH)_2$

33. Pair of amphoteric hydroxides is

(1) $Be(OH)_2$, $Mg(OH)_2$ (2) $Be(OH)_2$, $Zn(OH)_2$

(3) $Be(OH)_2$, $B(OH)_3$ (4) LiOH, $Be(OH)_2$

34. Which of the following is strongest base?

(1) $Si(OH)_4$ (2) $Al(OH)_3$

(3) $Mg(OH)_2$ (4) $Be(OH)_2$

35. Correct order of covalent character of fluorides of alkaline earth metals is

(1) $BeF_2 > MgF_2 > CaF_2 > SrF_2 > BaF_2$ (2) $BaF_2 > SrF_2 > CaF_2 > MgF_2 > BeF_2$

(3) $MgF_2 > BaF_2 > SrF_2 > CaF_2 > BeF_2$ (4) $BeF_2 > BaF_2 > SrF_2 > CaF_2 > MgF_2$

36. Thermal stability of alkaline earth metal carbonates in decreasing order is

(1) $CaCO_3 > SrCO_3 > MgCO_3 > BaCO_3$ (2) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

(3) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$ (4) $BaCO_3 > SrCO_3 > MgCO_3 > CaCO_3$

37. Which of the following is most soluble in water?

(1) $CaSO_4$ (2) $SrSO_4$ (3) $MgSO_4$ (4) $BaSO_4$

38. Which of the following oxide is amphoteric?

(1) CaO (2) BaO (3) BeO (4) MgO

39. Which of the following elements have the greatest tendency to form covalent compounds?

(1) Ca (2) Mg (3) Sr (4) Be

40. Grignard reagent is an organometallic compound of

(1) Calcium (2) Sodium (3) Magnesium (4) Potassium

41. Silica reacts with magnesium to form a magnesium compound 'x', which reacts with dil. HCl and forms 'y'. Compound y is

(1) $MgSiO_3$ (2) $SiCl_4$ (3) $MgCl_2$ (4) MgO

42. When CO_2 is passed through solution of calcium hydroxide, which one of the following compounds is precipitated?

(1) $Ca(HCO_3)_2$ (2) CaO (3) $CaCO_3$ (4) $Ca(OH)_2$

43. Hydrolith is the common name of

(1) CaH_2 (2) LiH (3) NaF (4) NaH

44. Plaster of Paris in contact with water sets into a hard mass, the composition of hard mass is

(1) $CaSO_4.H_2O$ (2) $CaSO_4.Ca(OH)_2$

(3) $CaSO_4.2H_2O$ (4) $CaSO_4.2Ca(OH)_2$

45. Which of the following pairs can be distinguished by the action of heat?

I. Na_2CO_3 and $CaCO_3$

II. $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$

III. $Ca(NO_3)_2$ and $NaNO_3$

(1) I & II (2) I only

(3) I & III (4) I, II & III

BIOLOGICAL IMPORTANCE OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM

(i) They activate many enzymes.

(ii) Participate in oxidation of glucose to produce ATP (adenosine triphosphate), potassium ions.

(iii) In combination with sodium ions are responsible for transmission of nerve signals.

(iv) These ions participate in the transmission of nerve signals.

(v) They also regulate flow of water across cell membranes and in transport of sugars and amino acids into the cells.

(vi) An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper.

(vii) All enzymes that uses ATP in phosphate transfer require magnesium as the cofactor.

(viii) The chlorophyll contains magnesium

(ix) About 99% of body calcium is present in bones and teeth.

(x) It also plays important roles in neuromuscular function, inter-neuronal transmission, cell membrane integrity and blood coagulation.

(xi) The calcium concentration in plasma is regulated at about 100 mg L^{-1}. Which is maintained by two hormones: calcitonin and parathyroid hormone.

(xii) Bone is continuously solubilised and redeposited to the extent of 400 mg per day in man.

Quick Recap

1. Group-1 (alkali metals) and group-2 (alkaline earth metals) together constitute the *s*-block of the periodic table. They are called so because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one *s*-electron and the alkaline earth metals by two *s*-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive (M^+) and dipositive (M^{2+}) ions respectively. It is seen that there is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic number. The atomic and ionic sizes increase and the ionization enthalpies decrease systematically down the group. The same kind of trends are observed among the properties of the alkaline earth metals. The first element in each of the group, *i.e.*, lithium in group-1 and beryllium in group-2 shows similarities in properties to the second member of the next group. Such similarities are termed as the diagonal relationship in the periodic table.

2. The alkali metals are silvery white, soft and have low melting point. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate. Sodium hydroxide is manufactured by Castner-Kellner process and sodium carbonate by Solvay process.
3. The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some difference arises because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxide.
4. Industrially, important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate (Plaster of paris), calcium carbonate (lime stone) and cement. Portland cement is an important constructional material. It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2 - 3%) to give a fine powder of cement. All these substances find variety of uses in different areas.
5. Ions of sodium, potassium, magnesium and calcium are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

❑ ❑ ❑