UNIT

12

s-Block Elements

SYLLABUS

General introduction to s-block elements—abundance, occurrence, anomalous properties of the first elements in each group, diagonal relationship.

Alkali metals—occurrence, electronic configuration, trends in atomic and physical properties (including IE, atomic and ionic radii), reactivity and electrode potential, reactions with oxygen, hydrogen, halogens and liquid ammonia. Basic nature of oxides and hydroxides, halides. Li and Na—occurrence, extraction, properties and uses, Na_2CO_3.

The alkaline earth metals—occurrence, electronic configuration, trends in atomic and physical properties (including IE, atomic and ionic radii), reactivity and electrode potential, reactions with non-metals. Oxides, hydroxides and halides, solubility and thermal stability of their oxo salts. Magnesium—occurrence, extraction, properties and uses. Compounds of alkaline earth metals—CaO, $Ca(OH)_2$, Plaster of Paris and $MgSO_4$. Industrial uses of lime, lime stone, cement.

12.1. General Introduction

Depending upon the type of the orbital which receives the last electron, the element in the long form of the periodic table have been divided into four blocks, *viz.*, *s*, *p*, *d* and *f*-blocks. Since *s*-subshell has only one orbital which can accommodate only two electrons, there are only two groups of *s*-block elements. Thus, elements of group 1 or IA (alkali metals) and group 2 or IIA (alkaline earth metals) constitute *s*-block elements. The elements of these groups contain one or two electrons in their outermost *s*-orbital while all the inner shells are completely filled. Thus, the electronic configuration of group 1 (alkali metals) may be represented as [Noble gas] ns^1 while that of group 2 (alkaline earth metals) may be represented as [Noble gas] ns^2 where *n* is the number of outermost shell. Although hydrogen which has one electron in the *s*-orbital and helium (inert gas) which has two electrons in the *s*-orbital may also be regarded as *s*-block elements but they are usually discussed separately because of their peculiar behaviour. Therefore, in this unit, we shall discuss the chemistry of alkali and alkaline earth metals only.

12.1.1. Occurrence and Abundance.

Both alkali and alkaline earth metals are highly reactive and hence do not occur in the *free state* but are widely distributed in nature in the combined state. Whereas alkali metals mostly occur as halides oxides, silicates, borates and nitrates, alkaline earth metals mainly occur as silicates, carbonates, sulphates and phosphates.

Although alkali metals have similar chemical properties yet they do not occur together mainly because their ions are of different sizes. Similarly, alkaline earth metals usually do not occur together except dolomite which is a double carbonate of calcium and magnesium [$MgCO_3 . CaCO_3$]. Likewise some double salts of alkali and alkaline earth metals such as carnallite ($KCl.MgCl_2 . 6\,H_2O$) are also known to occur in nature.

Some alkali and alkaline earth metals occur abundantly in nature. For example, *calcium is the* **fifth**, *magnesium is the* **sixth**, *sodium is the* **seventh** and *potassium is the* **eighth**, *barium is the* **fourteenth** and *strontium is the* **fifteenth** most abundant element by weight in the earth's crust. Sodium and magnesium are also present in relatively large amounts in sea water, brine wells and a few salt lakes. Calcium and potassium also occur in sea water but to smaller extents.

It is interesting to note that although sodium and potassium are almost equally abundant (2·83% Na and 2·59% K) in the earth's crust, yet sea water contains 2·8% NaCl but only 0·8% KCl. This is due to the reason that much of potassium appearing in ground water from dissolved minerals in taken up preferentially by plants while sodium ion goes to the sea water.

The remaining elements are much less abundant, *i.e., rubidium is the* **twenty-third**, *caesium is the* **forty-sixth** *and beryllium is the* **fifty-first** most abundant element by weight in the earth's crust while both *francium* (alkali metal) and *radium* (alkaline earth metal) are extremely scare and are also *radioactive.* Radium was isolated by Pierre and Marie Curie by processing many tons of the uranium ore pitchblende. It was used for radiotherapy treatment of cancer at one time but now ^{60}Co is used. Marie Curie was awarded the Nobel Prize for chemistry in 1911 for isolating and studying radium and polonium.

The element francium was discovered later in 1939 by Pierre at the Curie Institute, Paris. Its longest lived isotope ^{223}Fr has a half-life period of 21 minutes. As a result, not much is known about its chemistry. Nevertheless, whatever little knowledge we have about this element clearly shows that in its physical and chemical properties, it closely resembles alkali metals.

12.1.2. Anomalous behaviour of first element of a group.

The first element of a group differs considerably from the rest of the elements (heavier elements) of the same group. This anomalous behaviour is due to *(i) small atomic and ionic radii (ii) high electronegativity and ionization enthalpy, (iii) high polarising power* of its cation* and *(iv) absence of d-electrons in its valence shell.* Thus, Li differs from rest of the alkali metals (Na, K, Rb and Cs) and Be differs from rest of the alkaline earth metals (Mg, Ca, Sr and Ba).

12.1.3. Diagonal relationship.

Some elements of certain groups in the second period resemble with the certain elements of the next higher group in the third period. This is called *diagonal relationship.* These are usually weaker than the similarities within a group but are quite pronounced in the following pairs of elements.

$$\begin{tikzcd}
 & \text{Group 1} & \text{Group 2} & \text{Group 13} & \text{Group 14} \\
\textit{2nd period:} & \text{Li} \arrow[dr] & \text{Be} \arrow[dr] & \text{B} \arrow[dr] & \text{C} \\
\textit{3rd period:} & \text{Na} & \text{Mg} & \text{Al} & \text{Si}
\end{tikzcd}$$

Thus lithium resembles magnesium, beryllium resembles aluminium and boron resembles silicon. *It may, however, be noted that these similarities are much weaker than similarities found within the group.* The main reason for the diagonal relationship are :

(i) Similarity in electropositive character.

We know that electronegativity increases along a period but decreases down a group. Conversely, electropositive character decreases along a period but increases down a group. Evidently on removing diagonally these two opposing trends partly cancel out. As a result, diagonally related elements have similar electropositive character (Fig. 12.1) and hence exhibit similar properties.

(ii) Similarity in atomic or ionic radii. We know that atomic and ionic radii decrease across a period but increase down a group. Evidently, on removing diagonally, these two trends partly cancel out. As a result, diagonally related elements have similar atomic and ionic radii (Fig. 12.1) and hence have similar properties.

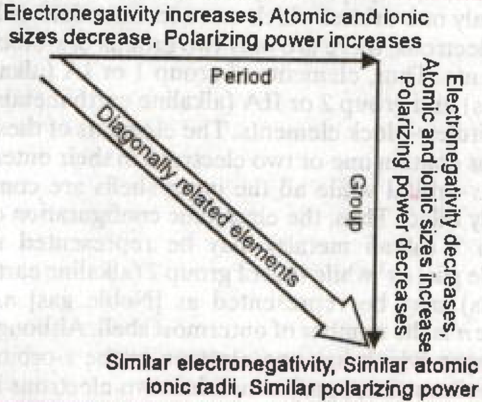

FIGURE 12.1. Illustration of diagonal relationship.

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*When a cation and an anion approach each other, they attract the electron clouds of each other, but the effect of a small cation on a large anion is more pronounced than that of the large anion on the small cation. *This distortion of the electron cloud of an anion by a cation is called* **polarization** *and the capacity of a cation to polarize an anion is known as its* **polarizing power.** Generally, the polarizing power increases as the charge on the cation increases and the size decreases. It is expressed in terms of charge/size ratio or (ionic charge)/(ionic size). Polarising power is also sometimes measured in terms of charge per unit area, i.e., $\dfrac{\text{ionic charge}}{\frac{4}{3}\pi\,(\text{ionic radius})^2}$.

(iii) Similarity in polarising power. On moving across a period, the charge on the ions increases and size decreases, causing the polarizing power to increase. On moving down a group, the size increases and the polarizing power decreases. On moving diagonally, these two trends partly cancel out. As a result, diagonally related elements have similar polarizing power and hence have similar properties.

SECTION—I

ALKALI METALS

The group 1 of the periodic table contains six elements, namely lithium (Li), sodium (Na), potassium (K), rubidum (Rb), caesium (Cs) and francicium (Fr). All these elements are typical metals. These are usually referred to as *alkali metals* since their hydroxides from strong bases or alkalies.

12.2 Occurrence

Alkali metals are highly reactive and hence do not occur in the *free state* but are widely distributed in nature in the *combined state* in form of halides, oxides, silicates, borates and nitrates.

Lithium is the *thirty-fifth* most abundance element by weight in the earth's crust (lithosphere) and mainly occurs in form of silicate minerals, *i.e.* (*i*) *spodumene*, $LiAl(SiO_3)_2$, and (*ii*) *lepidolite*, $Li_2Al_2(SiO_3)(FOH)_2$. Sodium and potassium are the *seventh* and *eighth* most abundant elements by weight in the earth's crust. NaCl and KCl occur in large amounts in sea water. The largest source of sodium is rock salt (NaCl). Other important minerals of sodium are : $Na_2B_4O_7 . 10\,H_2O$ (*borax*), $Na_2CO_3 . NaHCO_3 . 2\,H_2O$ (*trona*), $NaNO_3$ (*chile salt petre*) and sodium sulphate (*mirabilite*).

Potassium mainly occurs as KCl (*sylvite*), a mixture of KCl and NaCl (*sylvinite*) and the double salt, $KCl.MgCl_2 . 6\,H_2O$ (*carnallite*) and as $K_2O . Al_2O_3 . 6\,SiO_2$ (*felspar*).

12.3. Electronic Configuration

Alkali metals are *s*-block elements, because last electron in them enters the *s*-orbital. They contain only one *s*-electron outside the noble gas core. Therefore, their general electronic configuration is [noble gas] ns^1 where n = 2 to 7. Since all these elements have similar valence shell or outer electronic configuration, they have similar physical and chemical properties. The electronic configurations of alkali metals are given in Table 12.1.

TABLE 12.1. Electronic configuration of alkali metals

Elements	Atomic Number	Electronic Configuration	
		Complete	With Inert gas core
Lithium (Li)	3	$1s^2\,2s^1$	[He] $2s^1$
Sodium (Na)	11	$1s^2\,2s^2\,2p^6\,3s^1$	[Ne] $3s^1$
Potassium (K)	19	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$	[Ar] $4s^1$
Rubidium (Rb)	37	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,5s^1$	[Kr] $5s^1$
Caesium (Cs)	55	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6\,6s^1$	[Xe] $6s^1$
Francium (Fr)	87	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,4f^{14}\,5s^2\,5p^6\,5d^{10}\,6s^2\,6p^6\,7s^1$	[Rn] $7s^1$

12.4. Trends in Atomic and Physical Properties

Some important physical properties by alkali metals are given in Table 12.2.

TABLE 12.2. Some physical properties of group 1 elements (alkali metals)

Property	Elements					
	Li	Na	K	Rb	Cs	Fr (Radioactive)
Atomic number	3	11	19	37	55	87
Atomic mass	6·94	22·99	39·10	85·47	132·91	223
Metallic radius (pm)	152	186	227	248	265	375
Ionic radius (M^+/pm)	76	102	138	152	167	180
Ionization enthalpy I	520	496	419	403	376	
(kJ mol^{-1}) II	7298	4562	3051	2633	2230	
Eletronegativity (Pauling scale)	0·98	0·93	0·82	0·82	0·79	—
Density/g cm^{-3} (at 293 K)	0·53	0·97	0·86	1·53	1·90	—
Melting point/K	454	371	336	312	302	—
Boiling point/K	1615	1156	1032	961	944	—
E° (V) at 298 K for $M^+ (aq) + e^- \longrightarrow M (s)$	−3·04	−2·714	−2·925	−2·930	−2·927	—
Occurrence in Lithosphere	18*	227**	1·84**	78·12*	2·6*	—

These proprties are briefly discussed below :

1. Large atomic radii. *The atomic radii of alkali metals are the largest in their respective periods. These increase as we travel down the group from Li to Cs as shown in Table 12.2*

Explanation. This is due to the reason that as the atomic number increases, the number of energy shells increases by one with each succeeding element. As a result, the screening effect of the inner filled shells on the valence *s*-electron increases and the electron cloud tends to expand. In other words, the distance betweeen the nucleus and the last shell increases and thus the atomic radius increases with increase in atomic number. It may, however, be stated here that as the atomic number increases, the nuclear charge also goes up. This tends to decrease the atomic radii by attracting the electron cloud inward more forcibly. But the screening effect is so large that it overcomes the contractive effect of the increased nuclear charge. Hence *the increase in atomic radius as we move down the group from Li to Cs is primarily due to the predominant screening effect (addition of a new energy shell) of inner filled shells on the valence s- electron.*

2. Large ionic radii. *The ionic radii of the cations formed by them are smaller in size than the corresponding atoms*. However like atomic radii, these are the largest in their respective periods.

Explanation. When the valence *s*-electron is lost from the alkali metal atom, the monovalent cation formed has one shell less than the corresponding metal atom. Further,with the loss of one electron, the effective nuclear charge increases and thus the remaining electrons are pulled closer to the nucleus thereby decreasing the size of each individual energy shell. Hence, it can be concluded that *due to contractive effect of the increased nuclear charge and lesser number of energy shells, the radii of cations are much smaller than the corresponding atoms.*

Trend in the group. Like atomic radii, *the ionic radii increase we move down the group from Li to Cs* primarily due to the addition of a new energy shell with each succeeding element as shown in Table 10.1.

3. Low ionization enthalpies. *The ionization enthalpies of the alkali metals are the lowest as compared to the elements in the other groups.*

Explanation. This is mainly because of the fact that noble gas core shields the lone *s*-electron in the valence shell from the direct attraction of the

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*ppm (parts per million **percentage by weight.

positive charge on the atomic nucleus. As a result, the valence *s*-electron is loosely held by the nucleus and can be easily knocked off by supplying only a small amount of energy.

Trend in the group. *The ionization enthalpies of alkali metals decrease progressiely as we move down the group from Li to Cs.*

Explanation. This is due to the fact that the *s*-electron to be removed becomes farther and farther away from the nucleus because of the addition of a new shell with each succeeding element (Li, $2s^1$; Na, $3s^1$; K, $4s^1$; Rb, $5s^1$; Cs, $6s^1$ and Fr, $7s^1$). Due to an increase in the number of inner shells, the screening effect also increases. As a result, the attraction of the nucleus for the valence *s*-electron decreases and hence the ionization enthalpies decrease as we travel down the group from Li to Cs.

4. +1 Oxidation state – Unipositive ions. *The alkali metals exhibit oxidation state of +1 in their compounds and are strongly electropositive in character. The electropositive character increases from lithium down to caesium in the group.*

Explanation. As the alkali metals have low ionization energies, they have a strong tendency to lose the single valence *s*- electron to form the unipositive ions. Thus they show an oxidation state of +1 and are strongly electropositive.

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

The second ionization energies of these elements are fairly high and thus the loss of second electron is quite difficult. This is due to the fact that the second electron has to be lost from the most stable noble gas core , *i.e.* $ns^2\,np^6$. Thus, we may conclude that the *chemistry of alkali metals is essentially the chemistry of unipositive ions.*

As we go down the group, the atomic size increases and the ionisation energy of the elements decreases, *i.e.* the tendency of the elements to lose electrons increases. Consequently the electropositive character increases.

5. Metallic character. *The elements of this group are typical metals and are soft.* These can be easily cut with a knife. When freshly cut, they are silvery white and on exposure to air they are tarnished (*i.e.* become dull.) The metallic character increases down the group.

Explanation. The tendency of an element to lose valence electrons to from positive ions determines its metallic character. As alkali metals have low ionization energies, they have high tendency to lose valence electrons and are, therefore, typical metals. The metallic character increases down the group because ionization energy decreases down the group.

The bigger the kernel or smaller the number of valence electrons, the weaker is the metallic bond.

Since the atoms of alkali metals have bigger kernels and smaller number of valence electrons, the metallic bonds in them are very weak. Hence they are soft and can be cut with a knife.

6. Melting and boiling points. ***The melting and boiling points of alkali metals are very low and decrease with increase in atomic number.***

Explanation. As alkali metals have large size, the intermetallic bonds in them are quite weak. Hence they have low melting and boiling points which decrease down the group with the increase in the atomic size.

7. Nature of bonds formed. ***All the alkali metals form ionic (electrovalent) compounds. The ionic character increases from Li to Cs as we move down in the group.***

Explanation. This is because alkali metals have low ionization energies which decrease down the group.

8. Density. ***The density of alkali metals are quite low as compared to other metals. Li, Na and K are even lighter than water. These densities increase from Li to Cs.***

Explanation. Because of their large size, their atoms are less closely packed. Consequently they have low densities. Further as we move down the goup from Li to Cs, both the atomic size and atomic mass increase. But the increase in atomic mass more than compensates the bigger atomic size. As a result, the densities of alkali metals increase from Li to Cs. ***Potassium is, however, lighter than sodium.*** **This is probably due to an abnormal increase in atomic size of potassium.**

9. Flame colouration. ***All the alkali metals impart a characteristic colour to the flame.***

Metal	Li	Na	K	Rb	Cs
Colour	Crimson	Yellow	Pale violet	Red violet	Blue
λ/nm	670·8	589·2	766·5	780·0	455·5

Explanation. On heating an alkali metal or its salt especially chloride due to its more volatile nature in a flame, the electrons are excited easily to higher energy levels because of absorption of energy. When these excited electrons return to their ground states, they emit extra energy in form of electromagnetic radiations which fall in the visible region thereby imparting a characteristic colour to the flame.

The colour actually arises from electronic transitions in short lived species which are formed momentarily in the flame. The flame is a rich source of electrons, and in case of sodium, the ions are temporarily reduced to atoms

$$Na^+ + e^- \longrightarrow Na$$

The yellow flame of sodium commonly called **sodium D-line** (actually consists of a doublet centred at 589·0 nm and 589·6 nm) arises from the electronic transition $3s^1 \longrightarrow 3p^1$ in sodium atoms formed in the flame. It may be noted here that *the colours from different elements do not all arise from the same transition, or from the same species.* For example, crimson colour of lithium arises from a short lived LiOH species formed in the flame.

10. Photoelectric effect. *Alkali metals (except Li) exhibit photoelectric effect. Photoelectric effect is the phenomenon of ejection or emission of electrons from the metal surfaces when electromagnetic radiations are made to strike against them.*

Explanation. Due to low ionization energies, alkali metals, specially potassium and caseium, eject electrons when exposed to light. It may be noted that lithium which has the highest ionization energy amongst the alkali metals cannot be used in photoelectric cells because it does not release electrons when exposed to light.

12.5. Chemical Properties

Some important chemical properties of alkali metals are discussed below :

12.5.1. Reactivity and Electrode Potential.

All the alkali metals are highly reactive elements since they have a strong tendency to lose the single valence *s*-electron to form unipositive ions having inert gas configuration. This reactivity arises due to their low ionization enthalpies and high negative values of their standard electrode potentials (Table 12.2). Further due to their *strong tendency to lose electron, alkali metals also act as strong reducing agents. In other words, reactivity of an element is measured in terms of its* **reducing character.**

Reducing character. Ionization enthalpy is a measure of the tendency of an atom to lose electrons in the gaseous state. Thus, lower the ionization enthalpy, greater is the tendency of an element to lose electrons and hence stronger is the reducing character or higher is the reactivity of the element. Since the ionization enthalpies of alkali metals decrease down the group, therefore, *their reducing character or reactivity in the gaseous state increases from Li to Cs, i.e., Li < Na < K < Rb < Cs.*

However, in aqueous solutions, it has been observed that the reducing character of alkali metals follows the sequence : Na < K < Rb < Cs < Li. In other words, Li is the *strongest while sodium is the least powerful reducing agent in aqueous solution.* This may be explained in terms of electrode potentials (E°) of alkali metals.

Electrode potential is a measure of the tendency of an element to lose electrons in the aqueous solution. Thus, *more negative is the electrode potential, higher is the tendency of the element to lose electrons and hence stronger is the reducing agent.*

Since the standard electrode potentials (E°) of alkali metals become more and more negative as we move down the group from Na to Cs, therefore, reducing character of these elements increases in the same order, *i.e.*, Na to Cs. However, standard electrode potential of lithium, is the lowest, *i.e.*, −3·04 volts. In other words, *lithium is the strongest reducing agent in the aqueous solution.* This may be explained as follows.

Electrode potential, among other things, depends upon : *(i) enthalpy of sublimation, (ii) ionization enthalpy and (iii) enthalpy of hydration* as shown below :

$$(i)\ \mathrm{Li}\,(s) \xrightarrow{\text{Sublimation enthalpy}} \mathrm{Li}\,(g)$$

$$(ii)\ \mathrm{Li}\,(g) \xrightarrow{\text{Ionization enthalpy}} \mathrm{Li}^+\,(g)$$

$$(iii)\ \mathrm{Li}^+\,(g) + aq \longrightarrow \mathrm{Li}^+\,(aq) + \text{enthalpy of hydration}$$

The sublimation enthalpies of alkali metals are almost similar. Since lithium has the smallest ionic size among alkali metals, its enthalpy of hydration is the highest. Although ionization enthalpy of lithium is the highest among alkali metals, it is more than compensated by the large hydration enthalpy released in **step (iii)**. Thus, among alkali metals, lithium has the most negative standard electrode potential (E° = −3·04 V) *and hence is the strongest reducing agent in the aqueous solution.* Since, in general, stronger reducing agents have higher reactivity, therefore, Li should also be most reactive in aqueous solution. This is, however, not correct as discussed below :

12.5.2. Reaction with water.

Alkali metals react with water, liberating H_2 and forming their hydroxides. *The reaction becomes more and more violent as we move down the group.* Thus, lithium reacts gently, sodium melts on the surface of water and the molten metal moves around vigorously and may sometimes catch fire, potassium melts and always catches fire and so are Rb and Cs.

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

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

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

Because of their large negative reduction potentials alkali metals are better reducing agents than hydrogen. Hence they react with compounds containing acidic hydrogen atoms such as water, alcohol and acetylene liberating hydrogen gas.

$$\underset{\text{(Alkali metals)}}{2\,M} + 2\,H_2O \longrightarrow \underset{\substack{\text{Alkali metal}\\\text{hydroxide}}}{2\,MOH} + H_2$$

$$2\,M + 2\,C_2H_5OH \longrightarrow \underset{\substack{\text{Alkali metal}\\\text{ethoxide}}}{2\,C_2H_5OM} + H_2$$

$$2\,M + HC \equiv CH \longrightarrow \underset{\text{Alkali metal acetylide}}{M^+\ {}^-C \equiv C^-\ M^+} + H_2$$

Thus, *lithium is the least reactive while the reactivity of other alkali metals towards water and other acidic hydrogen containing compounds increases on moving down the group from Na to Cs.*

Cause for low reactivity of lithium. The low reactivity of lithium may be explained as follows :

Standard electrode potential (E°) and Gibbs free energy ($\Delta G°$) are related by the equation,

$$\Delta G° = -\,nFE°$$

where n is the number of electrons lost by the metal and F is the faraday constant.

Since E° for the reaction, $Li^+\,(aq) + e^- \longrightarrow Li\,(s)$ has the lowest negative value, *i.e.* $-3{\cdot}04$ V, therefore, $\Delta G°$ of the reaction has the largest positive value. *In other words, this reaction does not occur.* However, the reverse reaction, $Li\,(s) \longrightarrow Li^+\,(aq) + e^-$ has a large negative value of $\Delta G°$, so Li liberates more energy than any other alkali metal when it reacts with H_2O. In view of this, at first sight, it appears surprising why Li reacts with H_2O gently, whereas Na, which liberates less energy, reacts more vigorously and the hydrogen produced catches fire. The explanation for this observation lies in the kinetics (*i.e.*, the rate at which the reaction proceeds) and not in the thermodynamics (*i.e.*, the total amount of energy liberated).

Sodium has a low melting point, and the heat of the reaction is sufficient to make it melt or even vaporize. The molten metal thus spreads out thereby exposing a larger surface to water. As a result, it reacts even faster, gets even hotter and catches fire. Lithium, on the other hand, has high melting point. Although the heat of the reaction is high, it is still not sufficient to melt the metal and the hence the reaction proceeds gently. Other metals of this group with lower melting points react explosively with water.

From the above discussion, we learn that we should be cautious while predicting the chemical behaviour of elements on the basis of one single fundamental property of atoms since in many cases it may depend upon many other factors.

12.5.3. Reaction with oxygen.

The alkali metals tarnish in air due to the formation of an oxide or hydroxide on the surface. When heated in excess of air, alkali metals form different types of oxides depending upon the nature of the metal, *e.g.*,

Lithium when heated in oxygen forms lithium monoxide (and some lithium peroxide).

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

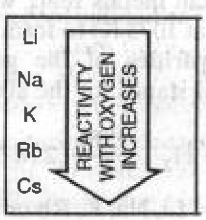
Sodium when heated with oxygen at about 575 K forms mainly sodium peroxide (and some sodium oxide).

$$2\,Na + O_2 \xrightarrow{575\ K} \underset{\text{Sodium peroxide}}{Na_2O_2}$$

Other alkali metals, i.e., K, Rb and Cs react with oxygen to form superoxides of the general formula, MO_2 where M = K, Rb and Cs, *e.g.*

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

Thus the reactivity of alkali metals with oxygen increases down the group. Further, the increasing stability of peroxide or superoxide, as the size of the metal ion increases, is due to the stabilization of larger anions by larger cations through higher lattice energies.



Explanation. Because of the small size, Li^+ has a *strong positive field* around it which attracts the negative charge so strongly that it *does not permit the oxide anion, O^{2-} to combine with another oxygen atom to form peroxide ion, O_2^{2-}*. On the other hand, Na^+ ion because of its larger size than Li^+ ion has comparatively weaker positive field around it which cannot prevent O^{2-} ion to combine with another oxygen atom to form peroxide ion, O_2^{2-}.

The larger, K^+, Rb^+ and Cs^+ ions have still weaker positive fields around them which cannot prevent even peroxide ion, O_2^{2-} to combine with another oxygen atom to form superoxide, O_2^-.

$$\underset{\text{Oxide}}{O^{2-}} \xrightarrow{1/2\,O_2} \underset{\text{Peroxide}}{O_2^{2-}} \xrightarrow{O_2} \underset{\text{Superoxide}}{2\,O_2^-}$$

It may be pointed out here that superoxide ion $[:\ddot{O} \doteq \ddot{O}:]^-$ has a *three electron bond, i.e., it has one unpaired electron which makes it coloured* (LiO_2, NaO_2 are yellow, KO_2 is orange, RbO_2 is brown and CsO_2 is orange) *and paramagnetic.* Sodium peroxide is yellow in colour probably due to the presence of a small amount of superoxide in it. The normal oxides of alkali metals are however, *colourless and diamagnetic.*

12.5.4. Action of air and moisture.

All the alkali metals on exposure to atmosphere (air and moisture) get converted into oxides, hydroxides and finally to carbonates. Thus alkali metals get tarnished when exposed to air and moisture.

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

$$M_2O + H_2O \longrightarrow 2\,MOH$$

$$2\,MOH + CO_2 \longrightarrow M_2CO_3 + H_2O$$

It is because of these reactions that *alkali metals are stored in inert hydrocarbon solvents like petroleum ether and kerosene oil* which prevent them from coming in contact with air and moisture.

12.5.5. Reaction with hydrogen.

All the alkali metals react with hydrogen at 673 K (Lithium at 1073 K) to form colourless crystalline **ionic hydrides** of the general formula, M^+H^- where M stands for the alkali metals

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

where M = Li, Na, K, Rb or Cs

The order of reactivity of the alkali metals towards hydrogen decreases as we move down the group from Li to Cs. This is due to the reason that the lattice energies of these hydrides decrease progressively as the size of the metal cation increases and thus the stability of these hydrides decreases from LiH to CsH.

$$2\,Li + H_2 \xrightarrow{1073\text{ K}} \underset{\text{Lithium hydride}}{2\,LiH}$$

$$2\,Na + H_2 \xrightarrow{673\text{ K}} \underset{\text{Sodium hydride}}{2\,NaH}$$

All the alkali metal hydrides are ionic solids with high melting points.

Since these hydrides contain the hydride ion (H^-), therefore, they liberate hydrogen at the anode on electrolysis.

All these hydrides react with proton donors such as water, alcohols, gaseous ammonia and alkynes liberating H_2 gas.

$$LiH\,(s) + H_2O\,(l) \longrightarrow LiOH\,(aq) + H_2\,(g)$$

$$NaH\,(s) + ROH\,(l) \longrightarrow RONa\,(s) + H_2\,(g)$$

$$NaH\,(s) + NH_3\,(g) \xrightarrow{\text{Heat}} NaNH_2\,(s) + H_2\,(g)$$

$$2KH\,(s) + HC{\equiv}CH\,(g) \xrightarrow{\text{Heat}} KC{\equiv}CK\,(s) + 2H_2\,(g)$$

Lithium hydride is used as a source of hydrogen for military purposes and for filling metrological balloons since it has a low molecular weight and on reacting with H_2O, it evolves highest percentage of hydrogen by weight.

12.5.6. Reaction with halogens.

Alkali metals react vigorously with halogens to form metal halides of the general formula, M^+X^- where M stands for the metal and X for the halogen.

$$2\,M + X_2 \longrightarrow 2\,M^+X^-$$

where M = Li, Na, K, Rb or Cs and

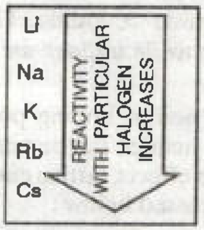
X = F, Cl, Br or I.

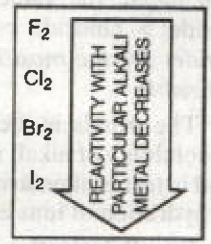
The reactivity of alkali metals towards a particular halogen increases as we move down the group from Li to Cs. For example, potassium reacts with chlorine more vigorously than sodium.

On the other hand, reactivity of halogens towards a particular alkali metal decreases form F_2 to I_2, *i.e.,*

$$F_2 > Cl_2 > Br_2 > I_2$$

12.5.7. Solubility in liquid ammonia.





All alkali metals dissolve in liquid ammonia (solubility may be as high as 5 M) giving highly conducting deep blue solutions.

Explanation. These solutions contain ammoniated cations and ammoniated electrons as shown below :

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

When ordinary light falls on these ammoniated electrons, they get excited to higher levels by absorbing energy corresponding to red region of the visible light. As a result, transmitted light is blue which imparts blue colour to the solution. Some important properties of blue solutions of alkali metals in liquid ammonia are as under :

(*i*) Dilute solutions of alkali metals in liquid ammonia are dark blue in colour but as the concentration increases above 3 M, the colour changes to copper-bronze and the solutions acquire metallic lustre due to formation of metal ion clusters.

(*ii*) The blue coloured solutions are *paramagnetic* due to the presence of large number of unpaired electrons but bronze solutions are *diamagnetic* due to formation of electron clusters in which ammoniated electrons with opposite spin group together, *i.e.*,

$$2\, e^-(NH_3)_y \longrightarrow [\uparrow e^-(NH_3)_y][\downarrow e^-(NH_3)_y]$$

(*iii*) The solutions of alkali metals in liquid ammonia are good conductors of electricity due to the presence of ammoniated cations and ammoniated electrons. However, the conductivity decreases as the concentration increases since the *ammoniated metal cations are bound by the free unpaired* electrons *which have been described as* expanded metals.

(*iv*) These solutions are stronger reducing agents than hydrogen and hence will react with water to liberate hydrogen.

(*v*) In presence of inpurities or catalyst such as Fe, the blue coloured solutions decompose to form metal amides with the liberation of H_2.

$$2\, M^+(NH_3)_x + 2\, e^-(NH_3)_y \longrightarrow 2\, M^+ NH_2^- + H_2 + (x + y - 2)\, NH_3$$

However, under anhydrous conditions and in the absence of catalytic impurities such as transition metal ions, these solutions can be stored for several days.

12.6. General Characteristics of the Compounds of the Alkali Metals

All the compounds of alkali metals are predominantly ionic. Some of the general characteristics of these compounds are discussed below :

12.6.1. Oxides and Hydroxides

All the alkali metals, their oxides, peroxides and superoxides readily dissolve in water to produce corresponding hydroxides which are strong alkalies, *e.g.*,

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

$$Na_2O + H_2O \longrightarrow 2\,NaOH$$

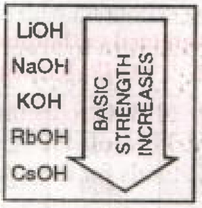
$$Na_2O_2 + 2\,H_2O \longrightarrow 2\,NaOH + H_2O_2$$

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

Thus, peroxides and superoxides also act as *oxidising agents* since they react with H_2O forming H_2O_2 and O_2 respectively.

The hydroxides of all the alkali metals are white crystalline solids. They are strongest of all bases and readily dissolve in water with the evolution of much heat. A number of hydrates of the heavier alkali metal hydroxides *e.g.*, $NaOH.n\,H_2O$ (where $n = 1, 2, 3, 4, 5$ and 7) have been prepared from their aqueous solutions but little is known about their structures.

(*i*) ***Basic strength.*** The basic strength of these hydroxides increases as we move down the group from Li to Cs. Thus, NaOH is a stronger alkali than LiOH ; KOH is a stronger alkali than NaOH and so on.



Explanation. *The hydroxides of alkali metals behave as strong bases due to their low ionization energies.* Due to low ionization energies, the M – O bond in M – O – H can easily break giving M^+ and OH^- ions.

$$MOH \longrightarrow M^+ + OH^- \text{ (basic nature)}$$

As we move down the group, the ionization energy decreases. As a result, the M – OH bond is more and more easily cleaved and hence the basic strength increases down the group from LiOH to CsOH.

(*ii*) *Solubiliity and stability.* All these hydroxides are highly soluble in water and thermally stable except lithium hydroxide.

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

(*iii*) *Formation of salts with acids.* Alkali metal hydroxides being strongly basic react with all acids forming salts.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

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

The salts are colourless ionic solids which are soluble in water.

12.6.2. Halides

The alkali metals combine directly with halogens under appropriate conditions forming halides of the general formula, MX. These halides can also be prepared by the action of aqueous halogen acids (HX) on metal oxides, hydroxides or carbonates.

$$M_2O + 2\,HX \longrightarrow 2\,MX + H_2O$$

$$MOH + HX \longrightarrow MX + H_2O$$

$$M_2CO_3 + 2\,HX \longrightarrow 2\,MX + CO_2 + H_2O$$

(where M = Li, Na, K, Rb or Cs and X = F, Cl, Br or I)

All these halides are colourless, high melting crystalline solids having high negative enthalpies of formation. However, the ΔH_f° values for fluorides become less and less negative as we move down the group while for chlorides, bromides and iodides, these values become more and more negative (Table 12.3).

TABLE 12.3. Standard enthalpies of formation (in kJ mol^{-1}) of alkali metal halides.

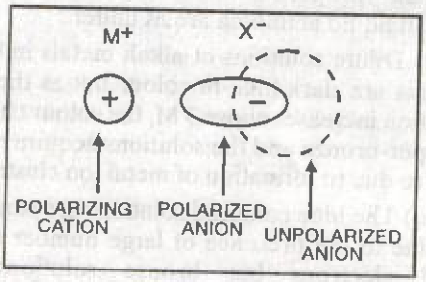
Element	MF	MCl	MBr	MI
Li	–612	–398	–350	–271
Na	–569	–400	–360	–288
K	–563	–428	–392	–328
Rb	–549	–423	–389	–329
Cs	–531	–424	–395	–337

From the above table it is evident that for any given metal, the values decrease in the order : fluoride > chloride > bromide > iodide. Thus, *fluorides are the most stable while iodides are the least stable.*

The trends in melting points, boiling points and solubility of alkali metal halides can be understood in terms of polarization effects, lattice energy and hydration of ions as discussed below :

(*a*) **Polarization effects – Comparison of ionic and covalent character of alkali metal halides.**

When a cation approaches an anion, the electron cloud of the anion is attracted towards the cation and hence gets distorted. This effect is called **polarization.** The power of the cation to polarize the anion is called its **polarizing power** and the tendency of the anion to get polarized is called its **polarizability.** The greater the polarization produced more is the concentration of electrons between the two atoms thereby decreasing the ionic character or increasing the covalent character of the bond.



The covalent character of any compound, in general, depends upon the following factors.

(*i*) **Size of the cation.** *Smaller the cation, greater is its polarizing power and hence larger is the covalent character.* For example, the covalent character decreases as the size of the cation increases :

LiCl > NaCl > KCl > RbCl > CsCl. Thus, LiCl is more covalent than KCl.

(*ii*) **Size of the anion.** *Larger the anion, greater is its polarizability.* This explains why covalent character of lithium halides is in the order

LiI > LiBr > LiCl > LiF

For the same reason, dipole moment of LiI (6·25 D) is much less than the theoretically expected value of 11·5 D if it were 100% ionic.

(*iii*) **Charge on the ion.** *Greater the charge on the cation, greater is its polarizing power* and hence larger is the covalent character. That is why the covalent character of some of the halides increases in the order $Na^+Cl^- < Mg^{2+}Cl_2 < Al^{3+}Cl_3$.

Similarly, greater the charge on the anion, more easily it gets polarized thereby imparting more covalent character to the compound formed. For example, covalent character increases in the order : $NaCl < Na_2SO_4 < Na_3PO_4$ as the size of the anion increases *and hence larger is the covalent character. Thus, the covalent character decreases as the size of the anion decreases.*

(*iv*) **Electronic configuration of the cation.** If two cations have the same charge and size, the one with a *pseudo noble gas configuration, i.e.*, having 18 electrons in the outermost shell has greater polarizing power than a cation with noble gas configuration, *i.e.*, having 8 electrons in the outermost shell. For this reaction, CuCl is more covalent that NaCl (although Na^+ and Cu^+ have same charge *viz.* +1 and nearly the same size *viz.* Na^+ (1·02 Å) and Cu^+(0·96 Å).

(*b*) **Lattice enthalpies.** Lattice enthalpy is defined as the amount of energy required to separate one mole of solid ionic compound into its gaseous ions. *Evidently greater the lattice enthalpy, higher is the melting point of the alkali metal halide and lower is its (Table 12.4) solubility in water.*

TABLE 12.4. Lattice enthalpies, hydration enthalpies (in kJ mol^{-1}), (solubilities (in g/100 g H_2O)) and melting points (in K) of some alkali metal halides.

Compound	Lattice enthalpy	Hydration* enthalpy	Solubility	Melting point
LiCl	–845	–876	63·7	887
NaCl	–770	–776	35·7	1084
KCl	–703	–700	34·7	1039
RbCl	–674	–680	77·0	988
CsCl	–644	–646	162	925
NaF	–893	–919	4·22	1261
NaCl	–770	–776	35·7	1084
NaBr	–730	–745	116	1028
NaI	–685	–685	184	944
LiF	–1005	–1019	0·27	1115
CsI	–582	–670	44·0	

(*c*) **Hydration enthalpy.** It is the amount of enthalpy released when one mole of gaseous ions combine with water to form hydrated ions.

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

$X^-(g) + aq \longrightarrow X^-(aq)$ + hydration enthalpy

*Higher the hydration enthalpy of the ions**, greater is the solubility of the enthalpy in water.*

Further, the extent of hydration depends upon the size of the ion. Smaller the size of the ion, more highly it is hydrated and hence greater is its hydrated ionic radius and less is its ionic mobility (conductance). Thus the order of their radii and mobility are

Ionic radius : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(in pm) 76 102 138 152 167

*Hydration number**** 25·3 16·6 10·5 10·0 9·9

Hydrated radius : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

(in pm) 340 276 232 228 228

Ionic mobility : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(at infinite dilution) 33·5 43·5 64·5 67·5 68

In the light of above arguments, let us now explain the melting points of alkali metal halides and their solubility in water or organic solvents. Thus,

(*i*) A delicate balance between lattice enthalpy and hydration enthalpy determines the ultimate solubility of a compound in water. For example, low *solubility of LiF (0·27 g/100 g H_2O) is due to its high lattice energy (–1005 kJ mol^{-1}) whereas the low solubility of CsI (44 g/100 g H_2O) is due to smaller hydration energy of the two ions (–670 kJ mol^{-1}).*

(*ii*) *The solubility of most of the alkali metal halides except those of fluorides decreases on descending the group* since the decrease in hydration enthalpy is more than the corresponding decrease in the lattice enthalpy. For example, difference in lattice enthalpy between NaCl and KCl is 67 kJ mol^{-1} but difference in hydration enthalpy of Na^+ and K^+ ion is 76 kJ mol^{-1}. Thus *KCl is less soluble in H_2O than NaCl.*

(*iii*) Because of the small size and higher electronegativity, *lithium halides except LiF are predominantly covalent and hence are soluble in*

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*Sum of the hydration enthalpies of cations and anions.

**The hydration enthalpy of the alkali metal cations and halides (in kJ mol^{-1}) respectively are :

Li^+ (–506), Na^+ (–406), K^+ (–330), Rb^+ (–310), Cs^+ (–276) and F^- (–513), Cl^- (–370), Br^- (–339), I^- (–394).

***The hydration number is the average number of water molecules associated with the metal ion.

organic solvents such as alcohol, acetone, ethyl acetate ; LiCl is also soluble in pyridine. In contrast, NaCl being ionic is insoluble in organic solvents.

(*iv*) Due to high hydration enthalpy of Li^+ ion, *lithium halides are soluble in water except LiF which is sparingly soluble due to its high lattice enthalpy.* However, as we move down the group, the solubility of alkali metal fluorides increases regularly as we move from LiF to CsF since the decrease in lattice enthalpy more than compensates the decrease in hydration enthalpy.

(*v*) **For the same alkali metal,** *the melting points decrease in the order : fluoride > chloride > bromide > iodide.*

Explanation. For the same alkali metal ion, the lattice energies decrease as the size of the halide ion increases. For example, lattice enthalpies of NaF, NaCl, NaBr and NaI are 919, 776, 745 and 685 kJ mol^{-1}. As the *lattice enthalpies decrease, energy required to break the lattice (melting point) decreases and hence the melting points of sodium halides decrease from NaF (1261 K) ⟶ NaCl (1084 K) ⟶ NaBr (1028 K) ⟶ NaI (944 K).*

(*vi*) **For the same halide ion,** *the melting points of lithium halides are lower than those of the corresponding sodium halides and thereafter they decrease as we move down the group from Na to Cs.*

Explanation. *The low melting point of LiCl (887 K) as compared to that of NaCl is probably because LiCl is covalent in nature while NaCl is ionic* (because Li atom is smaller in size than Na atom). Thereafter, the melting points decrease as we move from NaCl (1084 K) ⟶ KCl (1039 K) ⟶ RbCl (988 K) ⟶ CsCl (925 K) because the lattice enthalpies decrease as the size of the alkali metal atom increases.

12.6.3. Salts of Oxoacids

Since the alkali metals are highly electropositive, therefore, their hydroxides are very strong bases and hence they form salts with all oxoacids (H_2CO_3, H_3PO_4, H_2SO_4, HNO_3, HNO_2 etc.). They are generally soluble in water and stable towards heat. Here, we shall discuss only carbonates and bicarbonates.

The carbonates (M_2CO_3) of alkali metals are remarkably stable upto 1273 K, above which they first melt and then eventually decompose to form oxides. Li_2CO_3, however, is considerably less stable and decomposes readily.

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

Being strongly basic, alkali metals also form solid bicarbonates. No other metals form solid bicarbonates, though NH_4HCO_3 also exists as a solid. Lithium, however, does not form solid bicarbonate though it does exist in solution. All the bicarbonates on gentle heating undergo decomposition to form carbonates with the evolution of CO_2.

$$2\,MHCO_3 \xrightarrow{\Delta} M_2CO_3 + CO_2 + H_2O$$

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

All the carbonates and bicarbonates are soluble in water and their solubilities increase rapidly on descending the group. This is due to the reason that their lattice energies decrease more rapidly than their hydration energies on moving down the group.

12.7. Anomalous behaviour of Lithium

Lithium – the first element of group I (alkali metals) differs from rest of the elements of this group in many respects contrary to the expectations. This anomalous behaviour of lithium is due to the following reasons :

(*i*) very small size of lithium atom and its ion.

(*ii*) higher polarizing power of Li^+ (*i.e.* charge/size ratio) resulting in increased covalent character of its compounds which is responsible for their solubility in organic solvents.

(*iii*) comparatively high ionization energy and low electropositive character of lithium as compared to other alkali metals.

(*iv*) non-availability of *d*-orbitals in its valence shell.

(*v*) strong intermetallic bonding.

Some of the properties in which lithium differs from the other members of its group illustrating its anomalous behaviour are as follows :-

(*i*) Lithium is harder while all other alkali metals are soft.

(*ii*) The melting and boiling points of lithium are comparitively high.

(*iii*) Lithium forms monoxide with oxygen while other alkali metals form peroxides (M_2O_2) as well as superoxides (MO_2).

(*iv*) Lithium combines with nitrogen to form nitride while other alkali metals do not

$$6\,Li + N_2 \longrightarrow 2\,Li_3N$$

(*v*) LiOH is a weak base while the hydroxides of other alkali metals are strong bases.

(*vi*) Lithium hydroxide on heating decomposes to form lithium oxide while other alkali metal hydroxides do not

$$2\,LiOH \longrightarrow Li_2O + H_2O$$

(*vii*) Lithium carbonate* on heating decomposes to give CO_2 while other alkali metal carbonates do not

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

(*viii*) Lithium bicarbonate does not form a solid though it exists in solution while all other alkali metals form solid bicarbonates.

(*ix*) Lithium does not react with ethyne (acetylene) to form lithium acetylide while all other alkali metals react to form the corresponding acetylides.

$$2\,Na + HC \equiv CH \xrightarrow[196\,K]{Liq.\ NH_3} \underset{\text{Disodium acetylide}}{Na^+\ {}^-C \equiv C^-\ Na^+} + H_2$$

However, when Li is heated with carbon, it forms lithium acetylide (or lithium carbide) while other alkali metals do not react with carbon directly

$$2\,Li + 2C \xrightarrow{\Delta} \underset{\text{Dilithium acetylide}}{Li^+\ {}^-C \equiv C^-\ Li^+}$$

(*x*) Lithium nitrate on heating decomposes to give Li_2O, NO_2 and O_2 while other alkali metal nitrates decompose to give the corresponding nitrite and oxygen

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

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

(*xi*) The oxide, hydroxide, carbonate, phosphate and fluoride of lithium are sparingly soluble in water whereas the corresponding salts of other alkali metals are soluble in water

(*xii*) Because of covalent character, halides of lithium (like LiCl) are soluble in organic solvents while those of other alkali metals are insoluble.

(*xiii*) LiCl is deliquescent and crystallizes as a hydrate, $LiCl.2H_2O$, whereas other alkali metal chlorides do not form hydrates.

(*xiv*) Lithium ion, being very small in size, is very strongly hydrated in aqueous solution than other alkali metals ions that is why effective size of Li^+ ion in aqueous solution is the largest.

12.8. Diagonal relationship of Lithium with Magnesium

Lithium resembles magnesium mainly due to the similarity in sizes of their atoms (Li = 152 pm, Mg = 160 pm) and ions (Li^+ = 76 pm, Mg^{2+} = 72 pm). The main points of similarity are :

(*i*) Both LiOH and $Mg(OH)_2$ are weak bases.

(*ii*) Both form ionic nitrides when heated in an atmosphere of nitrogen.

$$6\,Li + N_2 \xrightarrow{\Delta} 2\,Li_3N$$

$$3\,Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$$

(*iii*) The hydroxides and carbonates of both Li and Mg decompose upon heating.

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

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

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

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

(*iv*) Both Lithium and magnesium do not form solid bicarbonates.

(*v*) Li_2O and MgO do not combine with excess of oxygen to give a peroxide or a superoxide.

(*vi*) Both lithium and magnesium nitrates decompose on heating producing nitrogen dioxide.

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

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

(*vii*) The hydroxides, carbonates and fluorides of both lithium and magnesium are sparingly soluble in water.

(*viii*) Because of covalent character LiCl and $MgCl_2$ are soluble in ethanol.

(*ix*) Both lithium perchlorate and magnesium perchlorate are highly soluble in ethanol.

(*x*) LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl.2\,H_2O$ and $MgCl_2.6\,H_2O$.

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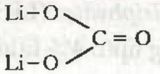
*Structure of Li_2CO_3 is



ADD TO YOUR KNOWLEDGE

1. **Monoxides, peroxides and superoxides of alkali metals.** All the five alkali metals can be induced to form normal oxides (*i.e.* monoxides), peroxides and superoxides by dissolving the metal in liquid ammonia and bubbling in the appropriate amount of oxygen.
2. **Crystal structures of monoxides of alkali metals.** Except Cs_2O which has anti-$CdCl_2$ layer structure, all other monoxides, *i.e.*, Li_2O, Na_2O, K_2O and Rb_2O have anti-fluorite structures.
3. **Potassium superoxide (KO_2)** is used as a source of oxygen in submarines, space shuttles and in emergency breathing apparatus such as *oxygen masks*. Such masks are used in rescue work in mines and in other areas where the air is so deficient in oxygen that an artificial atmosphere must be generated. The moisture of the breath reacts with superoxide to liberate oxygen, and at the same time the potassium hydroxide formed removes carbon dioxide as it is exhaled thereby allowing the atmosphere in the mask to be continuously regenerated.

$$4\,KO_2\,(s) + 2\,H_2O\,(g) \longrightarrow 4\,KOH\,(aq) + 3\,O_2\,(g)\ ;\ KOH\,(aq) + CO_2\,(g) \longrightarrow KHCO_3\,(s)$$

KO_2 also combines directly with CO_2 forming K_2CO_3 and with CO_2 and the moisture forming $KHCO_3$.

$$4\,KO_2 + 2\,CO_2 \longrightarrow 2\,K_2CO_3 + 3\,O_2\ ;\ 4\,KO_2 + 4\,CO_2 + 2\,H_2O \longrightarrow 4\,KHCO_3 + 3\,O_2$$

4. **Potassium ozonide (KO_3)** is formed when ozone is passed through KOH.

$$2\,KOH + 5\,O_3 \longrightarrow 2\,KO_3 + 5\,O_2 + H_2O$$

It is an orange coloured solid and contains the paramagnetic O_3^- ion.

5. **Lithium hydroxide (LiOH)** is used to remove CO_2 from exhaled air in confined quarters like submarines and space vehicles.
6. The alkali metals react with *halogens* and *interhalogen* compounds forming **ionic polyhalide compounds.**

$$KI + I_2 \longrightarrow K\,[I_3]$$
$$KBr + ICl \longrightarrow K\,[BrICl]$$
$$KF + BrF_3 \longrightarrow K\,[BrF_4]$$

7. The solution of alkali metals such as Li, Na or K in liquid ammonia is used for reduction of ethylenic double bonds, acetylenic triple bonds to double bonds and aromatic compounds under the name **Birch reduction.**
8. Lithium is the lightest known metal, having density = 0·534 g/cc. Therefore, it cannot be, stored in kerosene oil because it floats on the surface. It is kept wrapped in paraffin wax.
9. Cs is the most electropositive element due to its lowest ionization energy.
10. Lithium cannot be used in making photoelectric cells because out of all the alkali metals, it has highest ionization energy and cannot emit electrons when exposed to light.
11. The compounds of alkali metals are colourless (unless the anion is coloured like permanganate or dichromate) and diamagnetic. This is because they have noble gas configuration with no unpaired electron.
12. The peroxides of alkali metals are colourless and diamagnetic while superoxides are paramagnetic and coloured.
13. All alkali metals exist as body-centred cubic lattice with a coordination number of 8.
14. Due to small size, lithium does not form alums.
15. Alkali metals combine with mercury to form compounds known as Amalgams. This reaction is highly exothermic.

12.9. Lithium

Lithium is the first member of alkali metals. It is the lightest metal known.

12.9.1. Occurrence.

Lithium is the thirty-fifth most abundant element by weight in the earth's crust. It mainly occurs as silicate minerals but the amount present in any mineral is always small and thus extraction of the metal is not so easy. Some important minerals of lithium are :

Minerals of lithium

(*i*) *Spodumene*, $LiAl(SiO_3)_2$ containing 4–6% lithium.

(*ii*) *Triphylite*, $(Li, Na)_2PO_4.(Fe, Mn)_3(PO_4)_2$ containing upto 4% lithium.

(*iii*) *Petalite*, $LiAl(Si_2O_5)_4$ containing 2·7–3·7% lithium.

(*iv*) *Lepidolite*, $(Li, Na, K)_2\ (SiO_3)_3\ (FOH)_2$ containing 1·5% lithium.

(*v*) *Amblygonite*, $LiAl(PO_4)F$.

Lithium also occurs in certain spring waters and in some plants such as tobacco, beat and sugarcane. In India, lithium is mainly found as lepidolite in Bihar, Rajasthan, Karnatka and Kashmir.

12.9.2. Difficulties encountered during extraction of alkali metals.

Alkali metals, cannot be extracted from their ores by the usual methods of extraction of metals because of the following difficulties :

(*i*) *Alkali metals are strong reducing agents and hence cannot be extracted by reduction of their oxides or chlorides.*

(*ii*) *Alkali metals being highly electropositive cannot be displaced from the aqueous solutions of their salts by other metals.*

(*iii*) *Alkali metals cannot be isolated by electrolysis of the aqueous solution of their salts since hydrogen is liberated at the cathode instead of the alkali metal because the discharge potentials of alkali metals are much higher than that of the hydrogen.* However, by using mercury as cathode, the alkali metals can be deposited at the cathode but the alkali metal so deposited readily combines with mercury to form an amalgam from which its recovery is very difficult.

Therefore, in view of the above difficulties, *the only successful method is the electrolysis of their molten (fused) salts usually chlorides.*

But the melting point.. of these chlorides are very high which are normally difficult to attain. This difficulty can, however, be overcome to some extent by lowering the melting points of these chlorides by the addition of suitable salts such as $CaCl_2$, KF etc.

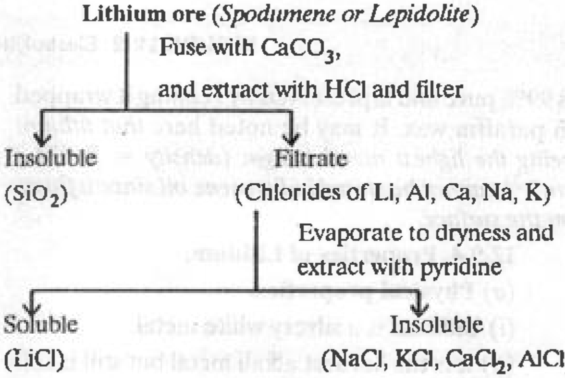
12.9.3. Extraction of Lithium.

It involves the following steps :

1. Preparation of lithium chloride. The minerals are first of all converted into lithium chloride by any one of the following methods :

(*i*) *Acid treatment method.* The finely powdered silicate ore is first heated to about 1373 K to make it more friable and then with H_2SO_4 at 523 K. The $Li_2SO_4.H_2O$ thus formed is cooled, leached with water and then filtered to remove silica (SiO_2). The filtrate thus obtained is treated with a calculated amount of Na_2CO_3 to precipitate aluminium and iron as carbonates which are filtered off. Excess of Na_2CO_3 is then added to the filtrate to precipitate Li_2CO_3. This is filtered and dissolved in HCl to obtain LiCl which is purified by extraction with alcohol.

(*ii*) **Fusion method.** The powdered silicate mineral is fused with $CaCO_3$ and the fused mass is extracted with HCl and filtered. The filtrate contains chlorides of Li, Al, Ca, Na and K whereas silicon is removed as insoluble residue. The filtrate is evaporated to dryness and the residue is extracted with pyridine in which only LiCl dissolves. Pyridine is distilled off while LiCl is left behind. The method discussed above may be summed up in the following flow-sheet.



2. Electrolysis of lithium chloride. A mixture of dry lithium chloride (55%) and potassium chloride (45%) is fused and electrolysed in an electrolytic cell shown in Fig. 12.2.

Potassium chloride is added to *increase the conductivity* of lithium chloride and to lower the *fusion temperature.* The cell is operated at a temperature of about 723 K and voltage of 8-9 volts is applied.

As a result of electrolysis, the following reactions take place :

$$LiCl \rightleftharpoons Li^+ + Cl^-$$

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

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

Chlorine gas, a valuable by product, liberated at the anode leaves the cell through the exist while molten lithium rises to the surface of the fused electrolyte and collects in the cast iron enclosure surrounding the cathode. The metal thus obtained

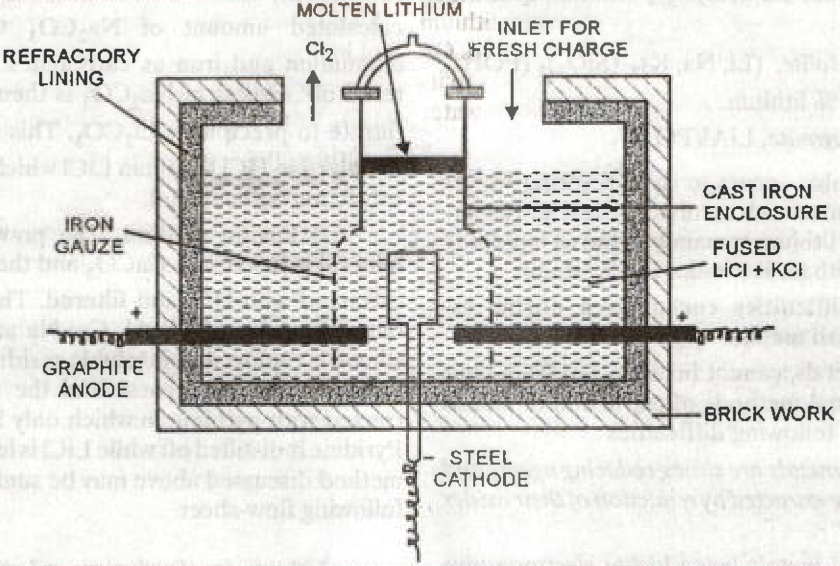


FIGURE 12.2. Electrolytic cell for extraction of lithium.

is 99% pure and is preserved by keeping it wrapped in paraffin wax. It may be noted here *that lithium being the lighest metal known (density = 0·534 g cm^{-3}) cannot be stored in kerosene oil since it floats on the surface.*

12.9.4. Properties of Lithium.

(a) Physical properties.

(*i*) Lithium is a silvery white metal.

(*ii*) It is the hardest alkali metal but still is soft enough to be cut with a knife.

(*iii*) Atomic and ionic radii of lithium are the lowest amongst alkali metals.

(*iv*) It is the lighest element known (density 5·34 *g* cm^{-3}).

(*v*) Being the first member of alkali metals, it has the highest electronegativity (0·98), highest ionization enthalpy (520 kJ mol^{-1}), highest melting point (453·5 K) and highest heat of atomization (1603 K).

(*vi*) When voltatilized, it imparts a crimson red colour to the flame.

(*b*) **Chemical properties.** Lithium like other alkali metals, is a monovalent electropositive element. It a highly reactive element. However, amongst alkali metals, it is the least reactive. Some important chemical properties of lithium are :

(*i*) *Action of air.* Lithium tarnishes slowly in moist air while dry air has no effect. When heated in air or oxygen at about 375 K, it burns with a brilliant white light forming lithium monoxide, Li_2O

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

(*ii*) *Action of water.* Lithium reacts slowly with water evolving H_2 gas. However, the reaction is much less vigorous than in case of Na or K.

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

(*iii*) *Action of acids.* Lithium being a strongly electropositive metal, readily reacts with dilute acids evolving H_2 gas.

$$2\,Li + H_2SO_4 \longrightarrow Li_2SO_4 + H_2$$

$$2\,Li + 2\,HNO_3 \longrightarrow 2\,LiNO_3 + H_2$$

(*iv*) *Reaction with non-metals.* Lithium on heating combines readily with number of non-metals forming their corresponding compounds.

$$2\,Li + H_2 \xrightarrow{\Delta} 2\,LiH \text{ (\textit{Lithium hydride})}$$

$$6\,Li + N_2 \xrightarrow{\Delta} 2\,Li_3N \text{ (\textit{Lithium nitride})}$$

$$2\,Li + Cl_2 \xrightarrow{\Delta} 2\,LiCl \text{ (\textit{Lithium chloride})}$$

$$16\,Li + S_8 \xrightarrow{\Delta} 8\,Li_2S \text{ (\textit{Lithium sulphide})}$$

$$12\,Li + P_4 \xrightarrow{\Delta} 4\,Li_3P \text{ (\textit{Lithium phosphide})}$$

In fact, lithium is the only alkali metal which combines directly with nitrogen to form lithium nitride. Lithium nitride is ionic and is ruby red. On heating to a high temperature, it decomposes to its constitutent elements. It also reacts with water evolving ammonia

$$2\,Li_3N \xrightarrow{\Delta} 6\,Li + N_2$$

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

(*v*) *Reaction with ammonia.* Like other alkali metals, lithium dissolves in liquid ammonia to form a deep blue solution due to the formation of ammoniated electrons.

$$Li + (x + y)\,NH_3 \xrightarrow{196-200\ K} Li\,(NH_3)_x + e^-\,(NH_3)_y$$

However, when NH_3 gas is passed over molten lithium, lithium amide is formed.

$$2\,Li + 2\,NH_3 \xrightarrow{\Delta} 2\,LiNH_2 + H_2$$

12.9.5. Uses of Lithium.

(*i*) It is used in the manufacture of alloys : (*a*) *lithium-lead alloy* (0·05% Li) which is used for making toughened bearings and sheats for cables.

(*b*) *Lithium-aluminium alloy* has great tensile strength and elasticity like that of mild steel. It is used for aircraft construction.

(*c*) *Lithium-magnesium alloy* (with 14% Li) is extremely tough and corrosion-resistant which is used for armour plate and aerospace components.

(*ii*) It is used for producing thermonuclear energy required for propelling rockets and guided missiles.

(*iii*) Lithium is used as a **getter or scavenger** since it combiens readily with oxygen and nitrogen. Thus it is used for removing last fraces of oxygen and nitrogen during refining of metals such as copper and nickel.

(*iv*) *Lithium carbonate* is used in making a special variety of glass which is very strong and is weather proof.

(*v*) *Lithium chloride* is used in air-conditioning plants to regulate the humidity. It is also used in Ni-Fe accumulators.

(*vi*) *Lithium brimide* is used in medicine as sedative.

(*vii*) *Lithium bicarbonate* and *lithium salicylate* have been used for treatment of rheumatism since the resulting lithium urate is soluble in water.

(*viii*) *Lithium hydride* is used as source of hydrogen for meterological purposes and for filling of balloons.

(*ix*) *Lithium hydroxide* is used for removing CO_2 from exhaled air in closed quarters like submarines and space vehicles.

(*x*) *Lithium aluminium hydride* ($LiAlH_4$) is used as a reducing agent in synthetic organic chemistry.

12.10. Sodium

Sodium is the seventh most abundant element by weight found in the earth's crust.

Minerals of sodium

(*i*) *Albite or soda feldspar* $Na_2O.Al_2O_3.6SiO_2$ or $NaAlSi_3O_8$

(*ii*) *Rock salt or sodium chloride* NaCl

(*iii*) *Chile salt petre or sodium nitrate* $NaNO_3$

(*iv*) *Glauber's salt or sodium sulphate* $Na_2SO_4.10H_2O$

(*v*) *Borax or sodium borate* $Na_2[B_4O_5(OH)_4].\,8H_2O$ or $Na_2B_4O_7.10H_2O$

Out of these minerals only NaCl has been used economically to extract the metal and *hence NaCl is the ore of sodium.*

12.10.2. Extraction of Sodium

Sodium is extracted by the electrolysis of fused sodium chloride by a process called **Down's process.**

Difficulties encountered Although sodium chloride is very cheap and is abundantly available yet the development of *Down's process* for the extraction of sodium from fused sodium chloride was delayed because of the following reasons :

(*i*) *Sodium chloride melts at 1074 K and it is difficult to attain and maintain this high temperature.*

(*ii*) *Sodium boils at about 1156 K and hence at the temperature of electrolysis, the metal liberated will vaporise.*

(*iii*) *Molten sodium forms a metallic fog (colloidal solution) with fused sodium chloride.*

(*iv*) *The products of electrolysis, sodium and chlorine, corrode the material of the cell at this high temperature.*

In 1924, J.C. Down overcame all these difficulties. He observed that the addition of calcium chloride and potassium fluoride lower the melting point of sodium chloride to 850 – 875 K.

Further at this low temperature : (*i*) the vapour pressure of sodium is low and hence does not allow sodium to ignite in air (*ii*) the liberated sodium metal does not dissolve in the melt. Had it dissolved, it would short-circuit the electrodes and thus prevent further electrolysis. (*iii*) the products of electrolysis, *i.e.*, sodium metal and chlorine do not corrode the material of the cell appreciably.

Actually during electrolysis both sodium and calcium are liberated at the cathode. These rise through a cooled collecting pipe which allows calcium to solidify and fall back into the melt or the eutectic mixture.

Details of the process. The electrolysis of a fused mixture of sodium chloride (40%) and calcium chloride (60%) is carried out in Down's cell at 873 K (Fig. 12.3). The cell consists of an iron tank lined inside with fire bricks. In the centre, there is a circular graphite anode surrounded by a hood shaped iron cathode. These two electrodes are separated by a wire gauze connected to the lower end of the iron hood so that sodium and chlorine produced during electrolysis do not come in contact with each other. The cathode compartment is provided with a pipe through which the molten sodium produced as a result of electrolysis rises and collects in the receiver.

Reactions. The chemical reactions taking place during electrolysis are :

$$NaCl \xrightarrow{\text{Dissociation}} Na^+ + Cl^-$$

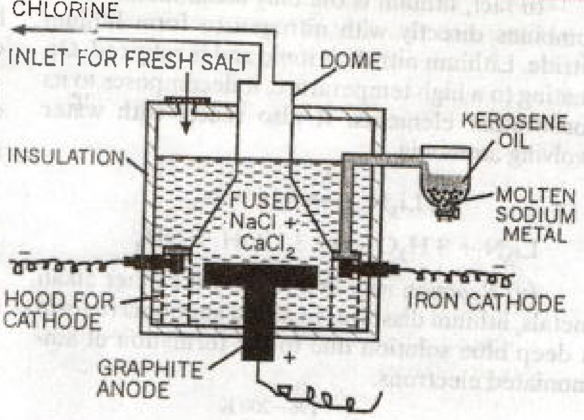


FIGURE 12.3. Down's cell for extraction of Sodium.

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

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

$Cl + Cl \longrightarrow Cl_2$

Advantages of Down's Process.

(*i*) Sodium metal obtained is of high purity (about 99.5%).

(*ii*) The starting material, *i.e.*, sodium chloride is very cheap.

(*iii*) Chlorine is obtained as a valuable by product.

(*iv*) This process is cheaper than *Castner's process* involving electrolysis of fused sodium hydroxide.

ADD TO YOUR KNOWLEDGE

Extration of Potassium. Since K metal is more soluble in KCl (than Na metal is soluble in NaCl), potassium cannot be obtained by electrolysis of a fused solution of KCl. It can, however, be obtained by the following two methods :

1. By electrolysis of fused KOH

$KOH \longrightarrow K^+ + OH^-$

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

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

2. Reduction of KCl with sodium.

Potassium can also be obtained by reduction of KCl with Na vapours at about 1125 K in a large fractionating column.

$KCl + Na \longrightarrow NaCl + K$

Potassium thus obtained is about 99·5% pure

12.10.3. Properties of Sodium

(a) Physical properties

(*i*) Sodium is a soft, silvery white metal.

(*ii*) It is lighter than water, its density being $0{\cdot}97\,g\ \text{cm}^{-3}$.

(*iii*) It is sufficiently malleable and ductile.

(*iv*) It imparts golden yellow flame when introduced into bunsen flame.

(*v*) Like other metals, it is a good conductor of heat and electricity.

(*b*) **Chemical properties.** Sodium is more reactive than lithium. Some important chemical properties of sodium are :

(*i*) *Action of air and moisture.* Sodium is a highly reactive metal. It is tarnished rapidly on exposure to moist air. At first a thin film of sodium monoxide, Na_2O is formed which changes readily into sodium hydroxide by the action of moisture and finally into sodium carbonate by the action of carbon dioxide present in air.

$$4\,Na + O_2 \longrightarrow 2\,Na_2O$$

$$Na_2O + H_2O \longrightarrow 2\,NaOH$$

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

$$\text{or } Na_2O + CO_2 \longrightarrow Na_2CO_3$$

(*ii*) *Action of oxygen.* When heated in a current of air or oxygen, it burns forming a mixture of sodium monoxide and sodium peroxide.

$$4\,Na + O_2 \longrightarrow 2\,Na_2O$$

$$2\,Na_2O + O_2 \longrightarrow 2\,Na_2O_2$$

(*iii*) *Action of water.* It reacts with water more vigorously than lithium producing H_2 gas.

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

Since ionization energy of Na is lower than that of Li, therefore, NaOH is a stronger base than LiOH.

(*iv*) *Action of alcohol.* It reacts slowly with alcohol evolving H_2 gas.

$$2\,C_2H_5OH + 2\,Na \longrightarrow \underset{\text{Sod. ethoxide}}{2\,C_2H_5ONa} + H_2$$

This reaction is widely used for removing excess of sodium from various reactions involving sodium.

(*v*) *Action of acids.* Sodium being more electropositive than lithium reacts with dilute acids and liberates H_2 gas.

$$2\,Na + 2\,HCl \longrightarrow 2\,NaCl + H_2$$

(*vi*) *Action of hydrogen.* When heated with hydrogen, it forms sodium hydride.

$$2\,Na + H_2 \xrightarrow{\Delta} 2\,Na^+H^-$$

(*vii*) *Action of other non-metals.* It combines readily with chlorine, sulphur and phosphorus forming sodium chloride, sulphide and phosphide respectively.

$$2\,Na + Cl_2 \xrightarrow{\Delta} 2\,NaCl$$

$$16\,Na + S_8 \xrightarrow{\Delta} 8\,Na_2S$$

$$12\,Na + P_4 \xrightarrow{\Delta} 4\,Na_3P$$

(*viii*) *Action of ammonia.* Sodium dissolves in liquid ammonia to form a blue solution which is *a good conductor of electricity.*

The blue colour of the solution is due to the formation of ammoniated electrons.

$$Na + (x + y)\,NH_3 \xrightarrow{196\ K} \underset{\text{Ammoniated sodium}}{Na^+(NH_3)_x} + \underset{\text{Ammoniated electrons (blue)}}{e^-(NH_3)_y}$$

However, when ammonia is passed through molten sodium, it yields sodamide evolving H_2 gas.

$$2\,Na + 2\,NH_3 \xrightarrow{475\ K} 2\,NaNH_2 + H_2$$

(*ix*) *Reducing action.* Sodium is a strong reducing agent. It reduces many chlorides and oxides.

$$BeCl_2 + 2\,Na \xrightarrow{\Delta} Be + 2\,NaCl$$

$$AlCl_3 + 3\,Na \xrightarrow{\Delta} Al + 3\,NaCl$$

$$Al_2O_3 + 6\,Na \xrightarrow{\Delta} 2\,Al + 3\,Na_2O$$

12.10.4. Uses of Sodium.

(*i*) Sodium is used as *a reducing agent* in the extraction of boron and silicon.

(*ii*) In the laboratory it is employed as a reducing agent in form of sodium amalgam and as a reagent in *Wurtz reaction* and in the synthesis of many organic compounds.

(*iii*) It is also used in Lassaigne's test for the detection of N, S and halogens in organic compounds.

(*iv*) About 60% of world production of sodium is used to make tetraethyl lead,

$Pb(C_2H_5)_4$ which is used as an *anti-knocking agent* for gasoline.

(*v*) Liquid Na or its alloy with potassium is used as a coolant in nuclear reactors.

(*vi*) It is used in the manufacture of number of chemicals such as Na_2O_2, NaCN and $NaNH_2$.

(*vii*) Sodium is used in sodium vapour lamps.

(*viii*) Sodium is largely used in industry for the production of artificial rubber, dyes, drugs etc.

(*ix*) Because of its lightness and high thermal conductivity, it is used for filling exhaust valves of aeroplane engines.

12.11. Sodium Carbonate, Soda Ash, Na_2CO_3*

Sodium carbonate commonly known as *washing soda* is manufactured by *Solvay ammonia process*.

(a) Principle. The process is based upon the principle that when carbon dioxide is passed through brine (sodium chloride) solution saturated with ammonia, the following ions are present in the solution.

Na^+, NH_4^+, Cl and HCO_3^-

Out of the various compounds possible, sodium bicarbonate being sparingly soluble crystallizes out. This is finally calcined to form sodium carbonate.

(b) Theory. When carbon dioxide is passed through brine solution saturated with ammonia, sodium bicarbonate is formed :

$$NH_3 + H_2O \longrightarrow NH_3.H_2O \longrightarrow NH_4^+ + OH^-$$

$$Na^+ + Cl^- + NH_4^+ + OH^- + CO_2 \longrightarrow Na^+ + HCO_3^- + NH_4^+ + Cl^-$$

$$Na^+ + HCO_3^- \longrightarrow NaHCO_3 \text{ (as precipitate)}$$

$$NH_4^+ + Cl^- \longrightarrow NH_4Cl \quad \text{(in solution)} \quad ...(i)$$

Because of the common ion effect due to the presence of Na^+ ions of sodium chloride, sodium bicarbonate precipitates out. It is filtered and then ignited to get sodium carbonate.

$$2\,NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + CO_2 + H_2O \quad ...(ii)$$

Sodium carbonate as obtained above is contaminated with ammonium salts. It is purified by passing CO_2 through its aqueous solution. The sodium bicarbonate thus formed is filtered and heated to give pure sodium carbonate. **Recrystallization from water produces washing soda, $Na_2CO_3.10\,H_2O$.**

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2\,NaHCO_3$$

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Function of ammonia. CO_2 is only slightly soluble in water. As a result, the concentration of H_2CO_3 is very low. Further since H_2CO_3 is a very weak acid, the concentration of HCO_3^- in the reaction mixture is extremely low.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad ...(i)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad ...(ii)$$

To shift the equilibrium in the forward direction, a base such as NH_3 is used which combines with H^+ to form NH_4^+ ion.

$$H^+ + NH_3 \longrightarrow NH_4^+$$

Thus the function of NH_3 is to produce a sufficient amount of HCO_3^- ion which enables sparingly soluble $NaHCO_3$ to precipitate out of the reaction mixture.

(c) Details of the process. The manufacturing details of the Solvay ammonia process are described below :

(i) Ammoniation tower. A saturated solution of brine (30%) is introduced into the top of the iron tower while gaseous ammonia from ammonia recovery tower is passed from below (Fig. 12.4). As a result of this counter current process, brine gets saturated with ammonia while impurities of calcium and magnesium present as impurities in commercial sodium chloride get precipitated as their corresponding insoluble carbonates.

$$2\,NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

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

$$MgCl_2 + (NH_4)_2CO_3 \longrightarrow 2\,NH_4Cl + MgCO_3\downarrow$$

The ammoniated brine thus obtained is passed through filters to remove precipitated calcium and magnesium carbonates and then passed through the carbonation tower.

(ii) Carbonation tower. It is made up of iron and is fitted with a number of perforated horizontal partitions. The clear ammoniated brine solution is made to trickle down from the top of the tower

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*Non-evaluative.

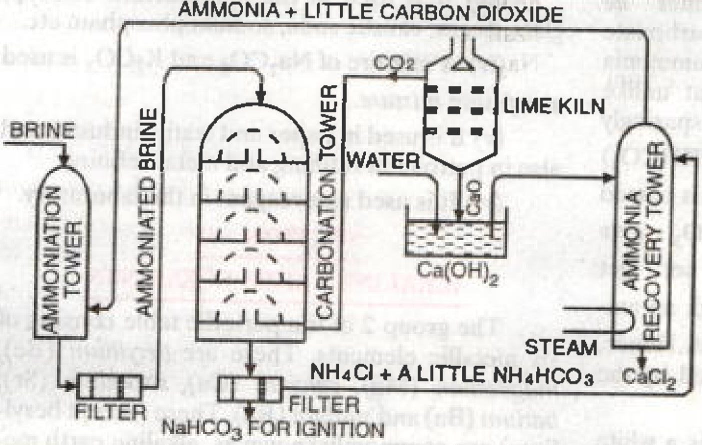

FIGURE 12.4. Solvay-Ammonia process for the manufacture of sodium carbonate.

while carbon dioxide from lime kiln is introduced from the bottom at a pressure of 1 – 2 atmospheres. Carbon dioxide rises through the small holes and reacts with ammoniated brine to form sodium bicarbonate.

$$NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3(s) + NH_4Cl\ (aq)$$

Throughout the process, a temperature of 300 – 310 K is maintained.

(iii) Filtration. The solution flowing out of the carbonation tower contains tiny crystals of sodium bicarbonate. These are filtered by passing through vacuum filters.

(iv) Calcination of sodium bicarbonates. The sodium bicarbonate obtained above is heated strongly or calcined in a kiln when sodium carbonate is formed.

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

(v) Ammonia recovery tower. The filtrate from the carbonation tower contains ammonium chloride and a little ammonium bicarbonate. It is made to flow down the ammonia recovery tower while a current of steam is made to go up. Milk of lime is introduced at a point little above the middle of the tower. Ammonium bicarbonate is decomposed by steam and ammonium chloride by milk of lime as follows :

$$NH_4HCO_3 \xrightarrow{\text{Heat}} NH_3 + CO_2 + H_2O$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

This recovered ammonia mixed with little carbon dioxide is used for saturation of brine in the ammoniation tower as discussed above. Calcium chloride is obtained as a by product.

(vi) Lime kiln. Here, carbon dioxide is generated by heating limestone to about 1273 K

$$CaCO_3 \xrightarrow{1273\text{ K}} CaO + CO_2 \quad ...(iii)$$

The carbon dioxide is brought to the carbonation tower while lime is slaked with water in a tank known as slaker to form milk of lime which is pumped to the ammonia recovery tower.

Raw Materials. The solvay-ammonia process is very economical since except NaCl and $CaCO_3$ all other raw materials used are not consumed in the process. For example,

(*a*) Quick lime (CaO) left in the lime kiln and ammonium chloride (NH_4Cl) left in the mother liquor after removal of $NaHCO_3$ are reacted to produce NH_3. Therefore, except for small losses, no additional NH_3 is required.

(*b*) CO_2 produced during conversion of $NaHCO_3$ to Na_2CO_3 according to reaction (*iii*) is reintroduced in the carbonation lower.

Thus, NaCl and $CaCO_3$ are the only raw materials used which are quite cheap. At the same time $CaCl_2$ is produced as a bye product which, of course, has no large scale industrial applications. Thus, solay ammonia process is economical, continuous and self-contained as shown in Fig. 12.5.

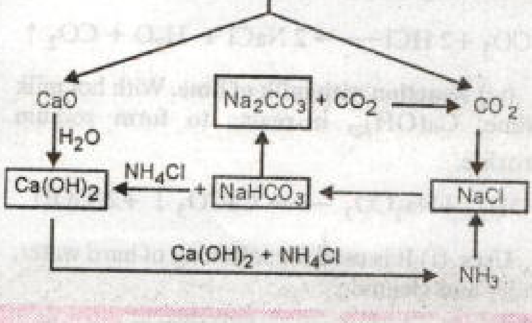

FIGURE 12.5. Flow-sheet for Solvay-Ammonia process.

Why potassium carbonate cannot be prepared by Solvay process ? Potassium carbonate cannot be prepared by the Solvay-ammonia process. This is due to the reason that unlike sodium bicarbonate ($NaHCO_3$) which is sparingly soluble in water, potassium bicarbonate ($KHCO_3$) is fairly soluble in water. Thus, when CO_2 is passed through ammoniated brine, $NaHCO_3$ gets precipitated while $KHCO_3$ does not get precipitated when CO_2 is passed through an ammoniated solution of potassium chloride. Hence, potassium carbonate cannot be prepared by the Solvay-ammonia process.

Properties. (*i*) Sodium carbonate is a white crystalline solid which crystallizes as decahydrate ($Na_2CO_3.10H_2O$).

(*ii*) It is readily soluble in water.

(*iii*) **Action of heat.** On heating below 373 K, it loses 9 molecules of water of crystallization to form monohydrate ($Na_2CO_3.H_2O$). On heating above 373 K, the monohydrate changes to an anhydrous white powder called **soda ash** but does not decompose further.

$$Na_2CO_3.10H_2O \xrightarrow{\text{Below 373 K}} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{\text{Above 373 K}} Na_2CO_3 + H_2O$$

(*iv*) **Hydrolysis.** Being a salt of a strong base (NaOH) and weak acid (H_2CO_3), when dissolved in water, sodium carbonate undergoes hydrolysis to form an *alkaline solution*.

$$Na_2CO_3 + 2H_2O \longrightarrow \underset{\textit{(Weakly ionized)}}{H_2CO_3} + \underset{\textit{(Strongly ionized)}}{2NaOH}$$

(*v*) **Action of acids.** It reacts with dil. mineral acids evolving CO_2 gas.

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

(*vi*) **Reaction with milk of lime.** With hot milk of lime, $Ca(OH)_2$, it reacts to form sodium hydroxide.

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

Uses. (*i*) It is used for softening of hard water, laundry and cleaning.

(*ii*) It is used in paints and dyes.

(*iii*) It is used in the manufacture of soap, glass, borax, caustic soda, sodium phosphate etc.

(*iv*) A mixture of Na_2CO_3 and K_2CO_3 is used as a *fusion mixture*.

(*v*) It is used in paper and textile industry and also in petroleum refining and metal refining.

(*vi*) It is used as a reagent in the laboratory.

SECTION—II

ALKALINE EARTH ELEMENTS

The group 2 of the periodic table consists of six metallic elements. These are *beryllium* (Be), *magnesium* (Mg), *calcium* (Ca), *strontium* (Sr), *barium* (Ba) and *radium* (Ra). These (except beryllium) are commonly known as alkaline earth metals or simply *alkaline earths*. The name alkaline earths was initially given only to magnesium, calcium, barium and strontium since their oxides* were alkaline in nature and these oxides remained unaffected by heat or fire and *existed in earth*. The term has now been extended to include all the elements of group 2.

12.12. Occurrence

Like alkali metals, alkaline earth metals are also highly reactive and hence do not occur in the free state but are widely distributed in nature in the combined state as silicates, carbonates, sulphates and phosphates.

Beryllium is the *fifty-first* most abundant element by weight found in the earth's crust. It is found in small quantities as silicate minerals *beryl* $Be_3Al_2Si_6O_{18}$ and *phenacite*, Be_2SiO_4.

Magnesium is the *sixth* most abundant element by weight found in the earth's crust as carbonate, sulphate and silicate. It also occurs to about 0·13% in sea water as chloride and sulphate.

Calcium is the *fifth* most abundant element by weight found in the earth's crust. It mainly occurs as $CaCO_3$ in form of limestone, marble and chalk. Other important minerals of calcium are *fluoropatite* $[3\,(Ca_3(PO_4)_2)\,.\,CaF_2]$, *gypsum* $CaSO_4\,.\,2\,H_2O$ and *anhydrite* $CaSO_4$.

Strontium and barium are much less abundant. Whereas strontium is mined as *celestite* $SrSO_4$ and *strontianite* $SrCO_3$ and barium is mined as barytes, $BaSO_4$. Radium is extremely scrare and is radioactive.

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*Magnesia (MgO), lime (CaO), strontia (SrO) and baryta (BaO).

12.13. Electronic Configuration

The atoms of all the alkaline earth metals have two *s*-electrons in their outermost shell (ns^2) as shown in Table 12.5.

TABLE 12.5. ELectronic configuration of alkaline earth metals

Element	Atomic Number	Electronic Configuration	
		Complete	With Inert gas core
Beryllium (Be)	4	$1s^2\ 2s^2$	[He] $2s^2$
Magnesium (Mg)	12	$1s^2\ 2s^2\ 2p^6 3s^2$	[Ne] $3s^2$
Calcium (Ca)	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	[Ar] $4s^2$
Strontium (Sr)	38	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$	[Kr] $5s^2$
Barium (Ba)	56	$1s^2\ 2s^2\ 2p^6 3s^2 3p^6 3d^{10} 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2$	[Xe] $6s^2$
Radium (Ra)	88	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4s^{10}\ 4f^{14}$ $5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2$	[Rn] $7s^2$

As these elements have similar valence shell eletronic configuration , they show similar physical and chemical properties.

Some important physical properties of alkaline earth metals are given in Table 12.6.

TABLE 12.6. Physical properties of group 2 elements (alkaline earth metals)

Property	Elements					
	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic mass	9·01	24·31	40·08	87·62	137·33	226·03
Metallic radius/pm	112	160	197	215	222	—
Ionic radius/pm	51	72	100	118	135	148
Ionisation enthalpy (kJ mol^{-1}) I	899	737	590	549	503	509
II	1757	1450	1146	1064	965	979
Enthalpy of hydration of M^{2+} ions (kJ mol^{-1})	−2494	−1921	−1577	−1443	−1305	—
Electronegativity (Pauling scale)	1·57	1·31	1·00	0·95	0·89	0·9
Density/g mol^{-1} at 293 K	1·85	1·74	1·55	2·63	3·62	5·5
Melting point /K	1562	924	1124	1062	1002	973
Boiling point /K	2745	1363	1767	1655	2078	(1973) (uncertain)
E° (V) at 298 K for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$	−1·97	−2·37	−2·87	−2·89	−2·90	−2·92
Occurence in lithosphere	2*	2·76**	4·6**	384*	390*	10^{-10}**

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

12.14. Trends in Physical Properties

1. Atomic radii *The atomic radii of alkaline earth metals are fairly large though smaller than the corresponding alkali metals and they increase down the group.*

Explanation. This is due to higher nuclear charge of these atoms which tends to pull the orbital electrons inwards *i.e.* towards the nucleus.

On moving down the group, atomic radii increase primarily due to addition of an extra shell of electrons in each succeeding element.

2. Ionic radii. *The atoms of these elements form divalent ions which show the same trend of increase in their size down the group.*

3. Ionisation enthalpy. *The alkaline earth metals have fairly low ionization enthalpies though greater than those of the corresponding elements of group 1 and they decrease down the group.*

Explanation. The low ionisation enthalpy of the alkaline earth metals is because of their strong tendency to lose electrons due to their smaller nuclear charge and comparatively larger atomic size which results in weaker forces of attraction between the valence electrons (ns^2) and the nucleus. But the values of the first ionization enthalpy of elements of group 2 are greater than those of the elements of group 1 because the atoms of the alkaline earth metals have smaller size and higher nuclear charge than those of alkali metals.

On moving down the group, ionization enthalpy values go on decreasing because of the increase in atomic size due to addition of new shells and screening effect of the electrons in the inner shells which overweigh the effect of increased nuclear charge.

It is of interest to note that the second ionization enthalpies IE_2 of the elements of group I are higher than those of the elements of group 2. The IE_1 and IE_2 values of sodium (alkali metal) and magnesium (alkaline earth metals) are given below :

Element	IE_1 (kJ mol^{-1})	IE_2 (kJ mol^{-1})
Na (Group 1)	496	4562
Mg (Group 2)	737	1450

Explanation. The second electron in case of alkali metals (*e.g.* Na) is to be removed from a cation (unipositive ion) which has already acquired a noble gas configuration whereas in case of alkaline earth metals (*e.g.* Mg), the second electron is to be removed from a cation (unipositive ion) which is yet to acquire the stable noble gas configuartion. Therefore, removal of second electron in case of alkaline earth metals requires much less energy than that in case of alkali metals.

4. Dipositive oxidation state (M^{2+}). *The chemistry of alkaline earth metals is dominated by the dipositive (M^{2+}) oxidation state just as unipositive (M^+) oxidation state is the predominant oxidation state of group 1 elements. Alkaline eath metals always form divalent cations.*

Explanation. In view of lower value of first ionisation enthalpy, it would appear that the alkaline earth metals should prefer to form +1 ions (M^+) rather than +2 ions (M^{2+}). However in actual practice, these give only +2 ions *e.g.* Mg^{2+}, Ca^{2+}, etc. If ionisation enthalpy were the only factor involved, we would have got the monovalent ions. *i.e.* Mg^+, Ca^+ etc. rather than the divalent ions *i.e.* Mg^{2+}, Ca^{2+} etc. But actually we get divalent ions. This anomaly is explained as follows :

(*i*) The divalent cations of alkaline earth metals acquire stable inert gas configuration.

(*ii*) The existence of divalent ions in the solid state is due to *greater enthalpy of formation* of MX_2 rather than MX compounds. For example, the enthalpy of formation of hypothetical MgCl is -125 kJ mol^{-1} and the corresponding value for $MgCl_2$ is -642 kJ mol^{-1}. Thus, the enthalpy of disproportionation reaction,

$$2\,MgCl \longrightarrow MgCl_2 + Mg$$

$$\text{is } -642 - 2(-125) = -392 \text{ kJ mol}^{-1}$$

This implies that any method used to prepare MX would always result in the formation of MX_2 compounds. Similarly, we can show that in case of alkaline earth metals. MX_3 compounds are not formed. In other words, *alkaline earth metals uniformally form dipositive ions.*

(*iii*) The existence of divalent ions in the **aqueous solution** is due to *greater enthalpy of hydration of* the divalent ions which counterbalances the higher value of second ionisation enthalpy. For example, enthalpy of hydration of divalent alkaline earth metal ions are about 4-5 times higher than those of alkali metal ions of comparable size [*e.g.*, ΔHyd for Li^+ (size 76 pm) = $-$ 506 kJ mol^{-1}, ΔHyd for Mg^{2+} (size 72 pm) = $-$ 1921 kJ mol^{-1}]

while those of monovalent alkaline earth metals are lower [*e.g.* ΔHyd for $Mg^+ = -365$ kJ mol^{-1}] than the corresponding alkali metal ions. Larger hydration enthalpy is due to the fact that the alkaline earth metals ions, because of their much larger charge to size ratio, exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.

As a result, the enthalpy of hydration of $MgCl_2$ is much higher [$-1921\ (Mg^{2+}) - 2 \times 370\ (2\ Cl^-) = -2661$ kJ mol^{-1}] than that of MgCl [$-365\ (Mg^+) - 370\ (Cl^-) = -765$ kJ mol^{-1}] and this higher enthalpy of hydration more than compensates the higher value of IE_2. Consequently, the net energy change accompanying the formation of $MgCl_2$ (*aq*) is much higher (*i.e.* 774 kJ mol^{-1}) than that of MgCl (*aq*) *i.e.* 74 kJ mol^{-1} as calculated below. Therefore, *alkaline earth metals prefer to form divalent ions rather than monovalent ions.*

Comparison of energy changes in the formation of MgCl (aq) and $MgCl_2$ (aq)

MgCl (*aq*)	ΔH (kJ mol^{-1})	$MgCl_2$ (*aq*)	ΔH (kJ mol^{-1})
$Mg(s) \longrightarrow Mg(g)$	150	$Mg(s) \longrightarrow Mg(g)$	150
$Mg(g) \longrightarrow Mg^+(g) + e^-$	737	$Mg(s) \longrightarrow Mg^{2+}(g) + 2e^-$	2187
$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	122	$Cl_2(g) \longrightarrow 2\,Cl(g)$	244
$Cl(g) + e^- \longrightarrow Cl^-(g)$	–348	$2\,Cl(g) + 2e^- \longrightarrow 2\,Cl^-(g)$	– 696
$Mg^+(g) + Cl^-(g) + aq \longrightarrow Mg^+(aq) + Cl^-(aq)$	– 735	$Mg^{2+}(g) + 2\,Cl^-(g) + aq \longrightarrow Mg^{2+}(aq) + 2\,Cl^-(aq)$	– 2661
Net energy change = –74		Net energy change = –774	

5. Electropositive or Metallic character *The alkaline earth metals are highly electropositive and hence metallic and their eletropositive or metallic character increases down the group. However they are less electropositive or metallic than the alkali metals.*

Explanation. On account of their relatively low ionization energies, the alkaline earth metals have a strong tendency to lose both the valence electrons to form dipositive cations. Thus, these elements show strong eletropositive or metallic character.

On moving down the group, the atomic radii increase and ionization energies decrease. Consequently, the electropositive or metallic character increases.

Further since the atoms of the alkaline earth metals have smaller size and higher ionization energies as compared to corresponding alkali metals, their tendency to lose valence electrons is lesser than those of alkali metals. Consequenctly, alkaline earth metals have less electropositive or metallic character as compared to alkali metals.

Due to smaller size of the kernels and greater number of valence eletrons, the metallic bonding in alkaline earth metals is stronger as compared to alkali metals. Because of this reason, these metals are less soft (*i.e.* they are harder) than alkali metals.

6. Melting and boiling points. *The alkaline earth metals have higher melting and boiling points as compared to those of alkali metals. However, down the group, there is no regular trend in their melting and boiling points.*

Explanation. Because of their smaller size and more close packed crystal lattice as compared to alkali metals, their melting and boiling points are higher than those of group I elements.

7. Nature of bonds formed *Like alkali metals, alkaline earth metals predominantly form ionic compounds which are, however, less ionic than the correponding alkali metal compounds. The tendency to form ionic compounds increases down the group. The first member, Be forms covalent compounds. Mg also shows some tendency for covalency. All other elemments form ionic compounds.*

Explanation. They form ionic compounds becaue they have low ionization energies. Their compounds are less ionic because their ionization energies are higher than those of the corresponding alkali metals. The tendency to form ionic compounds increases down the group because ionization energy decreases. Beryllium forms covalent compounds because it has smaller size and high ionization energy.

8. Density *The alkaline earth metals are denser than the alkali metals. However the densities of alkaline earth metals do not show any regular trend with increasing atomic number. The density of these metals first decreases from Be to Ca and then increases from Ca to Ba.*

Explanation. Because of their smaller size and hence better packing as compared to alkali metals, they are denser than alkali metals. The decrease in density from Be to Ca may be due to decrease in the packing of atoms in their solid lattice.

9. Flame colouration *Alkaline earth metals impart a characteristic colour to the flame.*

Calcium	Strontium	Barium	Radium
Brick red	*Crimson*	*Apple green*	*Crimson.*

Explanation. When alkaline earth elements or their compounds are put into a flame, the electrons absorb energy and are excited to higher levels. When they return to their ground state (normal state), the absorbed energy is emitted in form of visible light of particular wavelength.

Beryllium and magnesium atoms are smaller in size and their electrons are strongly bound to the nucleus. They need large amounts of energy for excitation to higher energy levels which is not available in the bunsen flame. So they do not impart colour to the flame.

12.5. Reactivity and Electrode Potential

All the alkaline earth metals are highly reactive elements since they have a strong tendency to lose the two valence *s*-electrons to form the corresponding dipositive ions having inert gas configuration.

This reactivity arises due to their low ionization energies and high negative values of their standard electrode potentials (Table 12.6). Further, the chemical reactivity of alkaline earth metals increases on moving down the group from Be to Ba because the ionization energies decrease and electrode potentials become more and more negative with increasing atomic number from Be to Ra. Thus, *beryllium is the least reactive while Ba (or Ra) is the most reactive element.*

Further since the ionization energies of alkaline earth metals are higher and their electrode potentials less negative than the corresponding alkali metals, therefore, *alkaline earth metals are less reactive than corresponding alkali metals.*

12.15.1. Reducing character.

The alkaline earth metals are weaker reducing agents than the alkali metals. Like alkali metals, their reducing character also increases down the group.

Explanation. Except beryllium, the alkaline earth metals have a fairly strong tendency to lose two electrons to form dipositive ions ($M \longrightarrow M^{2+} + 2e$) because of their low ionisation energies and high negative values of standard electrode potentials. Therefore, *they act as reducing agents.*

The reducing character of alkaline earth metals however, increases as we move down the group from Be to Ba because the ionization energies increase and electrode potentials become more and more negative with increasing atomic number from Be to Ba.

Further since the ionization energies of alkaline earth metals are higher and their electrode potentials are less negative than the corresponding alkali metals, therefore, *alkaline earth metals are weaker reducing agents than alkali metals.*

12.15.2. Reaction with water – Formation of hydroxides.

The electrode potential of beryllium ($Be^{2+}/Be = -1 \cdot 97$ 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 at red heat.

The electrode potential of Mg ($Mg^{2+}/Mg = -2 \cdot 37$ V), although more negative than that of Be, yet is still less negative than those of alkali metals and hence it does not react with cold water but reacts with boiling water or steam.

$$Mg + H_2O \longrightarrow MgO + H_2$$

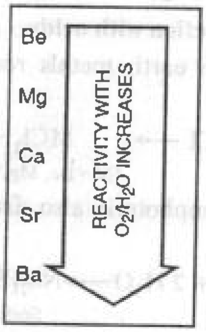
$$\text{or } Mg + 2\,H_2O \longrightarrow Mg(OH)_2 + 2\,H_2.$$

Mg, in fact, forms a protective layer of oxide on its surface. therefore, despite its favourable electrode potential, it does not react readily with water unless the oxide layer is removed by amalgamating it with mercury. In the formation of oxide film, Mg resembles Al.

Ca, Sr and Ba have more negative electrode potentials similar to those of the corresponding group 1 alkali metals and hence react with increasing vigour even with cold water, liberating H_2 and forming the corresponding metal hydroxides

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

This means that reactivity of alkaline earth metals increases as we move down the group. However, the reaction of alkaline earth metals is less vigorous as compared to alkali metals.



12.15.3. Reaction with air (nitrogen and oxygen)

(*a*) **Formation of oxides and nitrides.** Beryllium metal is relatively unreactive in the massive form and hence does not react below 873 K. However, powdered beryllium is more reactive and burns brilliantly on ignition to give a mixture of beryllium oxide (BeO) and beryllium nitride (Be_3N_2)

$$2\,Be + O_2\,(air) \xrightarrow{\Delta} 2\,BeO$$

$$3\,Be + N_2\,(air) \xrightarrow{\Delta} Be_3N_2$$

Magnesium is more electropositive than beryllium and hence burns with dazzling brilliance in air to form a mixture of magnesium oxide and magnesium nitride

$$Mg + air \xrightarrow{\Delta} MgO + Mg_3N_2$$

Calcium, strontium and barium being even more electropositive react with air readily to form a mixture of their respective oxides and nitrides.

Thus, reactivity towards oxygen increases as the go down the group. Thus, Ca, Ba and Sr are stored in paraffin but Be and Mg are not because they form a protective layer of oxide on their surface.

(*b*) **Formation of nitrides.** All the alkaline earth metals burn in dinitrogen to form ionic nitrides of the formula, M_3N_2. This is in contrast to alkali metals where only Li forms Li_3N.

$$3\,M + N_2 \xrightarrow{\Delta} M_3N_2$$

Be_3N_2 being covalent is volatile while the nitrites of all other elements are crystalline solids.

All these nitrides decompose on heating and react with water liberating NH_3

$$Be_3N_2 \xrightarrow{\Delta} 3\,Be + N_2$$

$$Ca_3N_2 + 6\,H_2O \longrightarrow 3\,Ca(OH)_2 + 2\,NH_3$$

(*c*) **Formation of peroxides.** Since larger cations stabilize larger anions, therefore, tendency to form peroxide increases as the size of the metal ion becomes larger. Thus barium peroxide (BaO_2) is formed by passing air over heated BaO at 773 K but

$$2\,BaO + O_2 \xrightarrow{773\ K} 2\,BaO_2$$

$$2\,SrO + O_2 \xrightarrow[\text{high pressure}]{773\ K} SrO_2$$

SrO_2 is prepared in a similar way but under high pressure and temperature. CaO_2 is not formed this way but can be prepared as the hydrate by treating $Ca(OH)_2$ with H_2O_2 and then dehydrating the product.

$$Ca(OH)_2 + H_2O_2 \longrightarrow CaO_2.2H_2O$$

Crude MgO_2 has been made using H_2O_2 but peroxide of beryllium is not known.

All peroxides are white crystalline ionic solids containing the peroxide ion, O_2^{2-}. Treatment of peroxides with acids liberates hydrogen peroxide.

$$BaO_2 + 2\,HCl \longrightarrow BaCl_2 + H_2O_2$$

12.15.4. Reaction with hydrogen – Formation of hydrides.

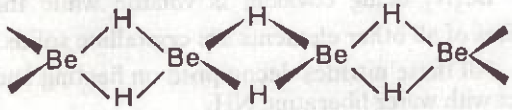
All the alkaline earth metals except berryllium combine with hydrogen directly on heating to form metal hydrides of the formula MH_2.

$$M + H_2 \xrightarrow{\text{Heat}} \underset{\text{Metal hydride}}{MH_2}$$

The hydride of beryllium can also be obtained by the reduction of $BeCl_2$ with $LiAlH_4$

$$2\,BeCl_2 + LiAlH_4 \longrightarrow 2\,BeH_2 + LiCl + AlCl_3$$

Both beryllium hydride (BeH_2) and magnesium hydride (MgH_2) are covalent *compounds having polymeric structures* in which H-atoms between beryllium atoms are held together by three centre-two electron $(3c-2e)$ bonds as shown below :



The hydrides of other elements of this group, *i.e.*, CaH_2, SrH_2 and BaH_2 are *ionic* and *contain the* H^- *ions.* All the hydrides of alkaline earth metals react with water liberating H_2 gas and thus act as *reducing agents*

$$MH_2 + 2\,H_2O \longrightarrow M(OH)_2 + 2\,H_2$$

CaH_2 is called **hydrolith** and is used for production of H_2 by action of water on it.

12.15.5. Reaction with carbon – Formation of carbides.

When beryllium oxide is heated with carbon at 2175 – 2275 K, a brick red coloured carbide of *the formula,* Be_2C *is formed.*

$$2\,BeO + 2\,C \xrightarrow{2175-2275\ K} Be_2C + 2\,CO$$

It is an *ionic* compound and reacts with water forming methane

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

The rest of the alkaline earth metals (Mg, Ca, Sr and Ba) form carbides of the general formula, MC_2 either when the metal is heated with carbon in an electric furnance or when their oxides are heated with carbon.

$$Ca + 2\,C \xrightarrow{1375\ K} CaC_2$$

$$CaO + 3\,C \xrightarrow{2275\ K} CaC_2 + CO$$

All these carbides react with water producing acetylene gas.

$$\underset{\text{Cal. carbide}}{CaC_2} + 2\,H_2O \longrightarrow \underset{\text{Acetylene}}{HC \equiv CH} + Ca(OH)_2$$

It may be noted here that MgC_2 on heating gives Mg_2C_3. This carbide contains C_3^{4-} units and reacts with water to form propyne (*i.e.* methylacetylene)

$$Mg_2C_3 + 4\,H_2O \longrightarrow \underset{\text{Propyne}}{CH_3C \equiv CH} + 2\,Mg(OH)_2$$

Calcium carbide is an important chemical intermediate. When CaC_2 is heated in an electric furnace with atmospheric dinitrogen at 1375 K, it forms calcium cyanamide, CaNCN

$$CaC_2 + N_2 \xrightarrow{1375\ K} \underset{\text{Cal. cyanamide}}{CaNCN} + C$$

The mixture of calcium cyanamide and carbon is called *nitrolim* and is used as a slow acting nitrogenous fertilizer as it hydrolysis slowly over a period of months evolving NH_3 gas

$$CaNCN + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3$$

12.15.6. Reaction with acids.

All alkaline earth metals react with acids liberating H_2.

$$M + 2\,HCl \longrightarrow MCl_2 + H_2$$

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

Be being amphoteric also dissolves is alkali liberating H_2.

$$Be + 2\,NaOH + 2\,H_2O \longrightarrow \underset{\text{Sod. berylate}}{Na_2[Be(OH)_4]} + H_2$$

12.15.7. Reaction with Liquid Ammonia

Like alkali metals, all alkaline earth metals dissolve in liquid ammonia. The dilute solutions are bright blue in colour due to solvated electrons but concentrated solutions are bronze coloured due to the formation of metal clusters.

These solutions decompose very slowly forming amides and evolving H_2, but the reaction is accelerated by many transition metals and their compounds.

$$M + (x+2y)\,NH_3 \longrightarrow M^{2+}(NH_3)_x + 2\,e^-(NH_3)_y$$

$$e^-(NH_3)_y \longrightarrow NH_2^- + \frac{1}{2}H_2 + (y-1)\,NH_3$$

Whereas evaporation of ammonia from solutions of alkali metals gives the metal, evaporation of ammonia from solutions of alkaline earth metals gives hexammoniates which slowly decompose to give the corresponding metal amides.

$$M(NH_3)_6 \longrightarrow M(NH_2)_2 + 4\,NH_3 + H_2$$

12.16. General Characteristics of Compounds of the Alkaline Earth Metals

As discussed above, due to higher enthalpy of formation in the solid state and due to higher hydration enthalpy in the aqueous solution, alkaline earth metals unformally form dipositive ions.

Further due to increased nuclear charge and smaller size, alkaline earth metals form compounds which are less ionic than the corresponding compounds of the alkali metals. Usually the oxides and other salts of Be and Mg are more covalent than those formed by the heavier and larger members (Ca, Sr, Ba). A general survey of some of their compounds is presented below.

12.16.1. Oxides and Hydroxides

Oxides. The oxides of alkaline earth metals MO, are obtained either by heating the metals in dioxygen or by thermal decomposition of their carbonates.

$$2\,M + O_2 \xrightarrow{\Delta} 2\,MO \qquad (M = Be, Mg, Ca)$$

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

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

Except BeO, all the oxides have rock-salt structures. Further, the enthalpies of formation of these oxides are quite high and consequently they are very stable.

Metal oxide	BeO	MgO	CaO	SrO	BaO
$\Delta_f H^\circ$ (kJ mol^{-1})	550	590	623	590	545

These have high melting points, have very low vapour pressures, are very good conductors of heat, are chemically inert and act as electrical insulators. Because of these properties, these oxides are used for lining furnances and hence are used as refractory materials. Due to small size of beryllium ion, BeO is *covalent* but still has high melting point because of its *polymeric* nature. Each Be atom is tetrahedrally coordinated to four other oxygen atoms. Therefore, like other metal oxides, BeO is also used as a refractory.

Hydroxides. The hydroxides of Ca, Sr and Ba are obtained either by treating the metal with cold water or by reacting the corresponding oxides with water. The reaction of these oxides with H_2O is also sometimes called as **slaking.**

$$M + 2\,H_2O \longrightarrow M(OH)_2 + H_2$$

$$(M = Ca, Sr, Ba)$$

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

$$(M = Ca, Sr, Ba$$

$Be(OH)_2$ and $Mg(OH)_2$ being insoluble are obtained from suitable metal ion solutions by precipitation with OH^- ions.

$$BeCl_2 + 2\,NaOH \longrightarrow Be(OH)_2\downarrow + 2\,NaCl$$

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

Properties of hydroxides. (*i*) *Basic character.* Due to small size and high ionization enthalpy, $Be(OH)_2$ is amphoteric. It, therefore, dissolves both in acids and bases.

$$Be(OH)_2 + 2\,HCl \longrightarrow BeCl_2 + 2\,H_2O$$

$$Be(OH)_2 + 2\,NaOH \longrightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2} + 2\,H_2O$$

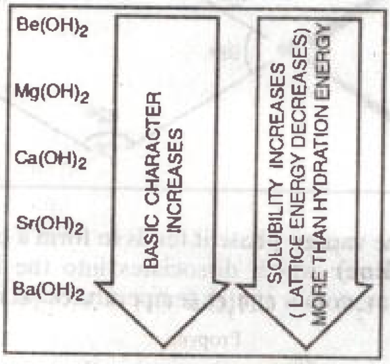
$$\text{or } Be(OH)_2 + 2\,OH^- \longrightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

The hydroxides of Mg, Ca, Sr and Ba are basic. Their basic strength increases as we move down the group. This is because increase in their sizes and decrease of their ionization energies weaken the strength of M–O bonds in MOH which ultimately breaks to give OH^- ions and thus increase the basic strength.

However, these hydroxides are less basic than the corresponding alkali metal hydroxides because of higher ionization energies, smaller ionic sizes and greater lattice energies.

(*ii*) *Solubility in water**. Alkaline earth metal hydroxides are less soluble in water as compared to the alkali metal hydroxides.

The solubility of the alkaline earth metal hydroxides in water increases with increase in atomic number down the group. This is due to the reason that *both lattice energy and hydration energy decrease down the group as the size of the cation increases but lattice energy decreases more rapidly than the hydration energy* and hence *their solubility increases down the group.*



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*The solubility of a salt in water depends upon : (*i*) Lattice energy and (*ii*) Hydration energy.

In general, If hydration energy > lattice energy, *salt dissolves.*

If hydration energy < lattice energy, *salt does not dissolve.*

12.16.2. Halides

The alkaline earth metals combine directly with halogens at appropriate temperatures forming halides, MX_2.

These halides can also be prepared by the action of halogen acids (HX) on metals, metal oxides, hydroxides and carbonates.

$$M + 2\,HX \longrightarrow MX_2 + H_2$$

$$MO + 2\,HX \longrightarrow MX_2 + H_2O$$

$$M(OH)_2 + 2\,HX \longrightarrow MX_2 + 2\,H_2O$$

$$MCO_3 + 2\,HX \longrightarrow MX_2 + CO_2 + H_2O$$

Properties of halides

1. All beryllium halides are essentially covalent and are soluble in organic solvents. They are hydroscopic, and fume in air due to hydrolysis. On hydrolysis, they produce acidic solution.

$$BeCl_2 + 2\,H_2O \longrightarrow Be(OH)_2 + 2\,HCl.$$

2. The halides of all other alkaline earth metals are ionic. Their ionic character, however, increases as the size of the metal ion increases.

3. Except $BeCl_2$, all other chlorides of group 2 form hydrates but their tendency to form hydrates decreases. For example, $MgCl_2.6\,H_2O$, $CaCl_2.6\,H_2O$, $SrCl_2.6\,H_2O$ and $BaCl_2.2\,H_2O$.

4. The hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be dehydrated on heating but those of Be and Mg undergo hydrolysis.

Anhydrous beryllium halides are best prepared by the following methods :

$$Be + 2\,NH_3 + 4\,HF \longrightarrow (NH_4)_2[BeF_4] \xrightarrow{\Delta} BeF_2 + 2\,NH_4F$$

$$BeO + C + Cl_2 \xrightarrow{873\text{ K}} BeCl_2 + CO$$

$$2\,BeO + CCl_4 \xrightarrow{973\text{ K}} 2\,BeCl_2 + CO_2$$

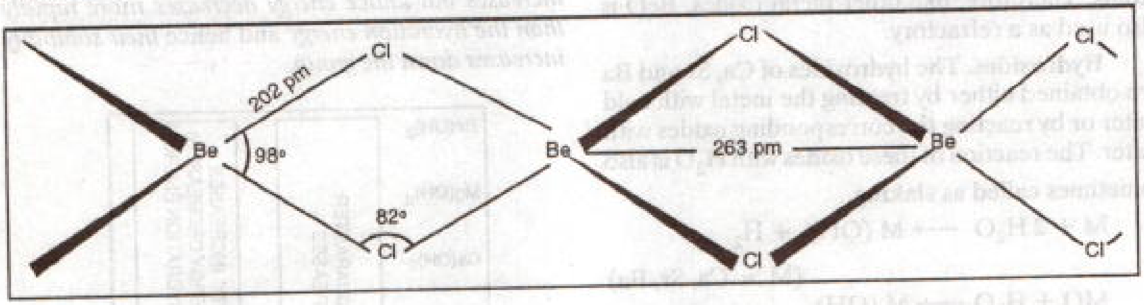
5. BeF_2 is very soluble in water due to the high hydration energy of the small Be^{2+} ion. The other fluorides (MgF_2, CaF_2, SrF_2 and BaF_2) are almost insoluble in water. Since on descending the group, lattice energy decreases more rapidly than the hydration energy, therefore, whatever little solubility these fluorides, have much that increases down the group.

The chlorides, bromides and iodides of all other elements, *i.e.*, Mg, Ca, Sr, Ba are ionic, have lower melting points than the fluorides, and are readily soluble in water. The solubility, decreases somewhat with increasing atomic number.

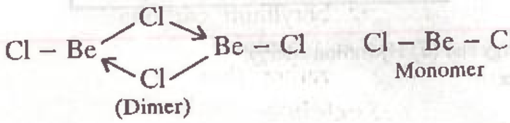
6. Except $BeCl_2$ and $MgCl_2$, the other chlorides of alkaline earth metals impart characteristic colours to flame.

$CaCl_2$	$SrCl_2$	$BaCl_2$
Brick red colour	Crimson colour	Grassy green colour

Structure of $BeCl_2$. In the solid phase, $BeCl_2$ has polymeric structure with halogen bridges in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a coordinate bond to another beryllium atom as shown below :



In the vapour phase it tends to form a chloro bridged dimer which dissociates into the linear triatomic monomer at high temperatures (at nearly 1200 K).



$$Cl-Be\begin{matrix}Cl\\ Cl\end{matrix}Be-Cl \qquad Cl-Be-Cl$$

(Dimer) Monomer

Uses. (*i*) Calcium fluoride or fluorospar (CaF_2) is by far the most important of all the fluorides of the alkaline earth metals since it is the only large scale source of fluorine.

(*ii*) $CaCl_2$ is widely used for melting ice on roads, particularly in very cold countries because 30% eutectic mixture of $CaCl_2$/ice freezes at 218 K compared to NaCl/ice at 255 K. It is also used as a desiccant (drying agent in the laboratory).

(*iii*) Anhydrous $MgCl_2$ is used in the electrolyte extraction of magnesium.

12.17. Solubility and Thermal Stability of Oxo Salts

The salts containing one or more atoms of oxygen such as oxides, hydroxides, carbonates, bicarbonates, nitrites, nitrates, sulphates oxalates and phosphates are called oxo salts. Let us now discuss the solubility and thermal stability of some of the oxo salts of alkaline earth metals.

12.17.1. Sulphates.

The sulphates of alkaline earth metals (MSO_4) are prepared by the action of sulphuric acid on metals, metal oxides, hydroxides and carbonates.

$$M + H_2SO_4 \longrightarrow MSO_4 + H_2$$

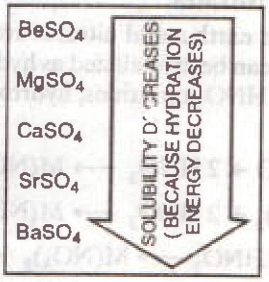
$$MO + H_2SO_4 \longrightarrow MSO_4 + H_2O$$

$$M(OH)_2 + H_2SO_4 \longrightarrow MSO_4 + 2\,H_2O$$

$$MCO_3 + H_2SO_4 \longrightarrow MSO_4 + CO_2 + H_2O$$

Properties of sulphates.

(*i*) The sulphates of alkaline earth metals are all white solids. Beryllium, magnesium and calcium sulphates crystallise in the hydrated form, *i.e.*, $BeSO_4.4H_2O$, $MgSO_4.7H_2O$, $CaSO_4.2H_2O$ but sulphates of stronium and barium crystallise without water of crystallization.



(*ii*) *Solubility.* The solubility of the sulphates in water decreases down the group, *i.e.* Be > Mg >> Ca > Sr > Ba. Thus, $BeSO_4$ and $MgSO_4$ are highly soluble, $CaSO_4$ is sparingly soluble but the sulphates of Sr, Ba and Ra are virtually insoluble.

Explanation. The magnitude of the lattice energy remains almost constant as the sulphate is so big that small increase in the size of the cations from Be to Ba does not make any difference. However the hydration energy decreases from Be^{2+} to Ba^{2+} appreciably as the size of the cation increases down the group. *Hence, the solubilities of sulphates of alkaline earth metals decrease down the group mainly due to the decreasing hydration energies from* Be^{2+} *to* Ba^{2+}. *The high solubility of* $BeSO_4$ *and* $MgSO_4$ *is due to the high hydration energies due to smaller* Be^{2+} *and* Mg^{2+} *ions.*

(*iii*) *Stability.* The sulphates of alkaline earth metals decompose on heating giving the oxides and SO_3.

$$MSO_4 \xrightarrow{\Delta} MO + SO_3$$

The temperature of decomposition of these sulphates increases as the basicity of the hydroxide of the corresponding metal increases down the group. For example,

Compounds :	$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
Temp. of decomposition :	773 K	1168 K	1422 K	1647 K

Uses. (*i*) The almost negligible solubility of $BaSO_4$ in water is used in the detection and estimation of SO_4^{2-} ions.

(*ii*) $BaSO_4$ is both insoluble in H_2O and opaque to X-rays. Therefore, *'barium meal'* is used to obtain a shadow of the stomach on an X-ray film which is useful in diagnosing stomach ulcers.

12.17.2. Carbonates and Bicarbonates.

Alkaline earth metal carbonates are obtained as white precipitates when

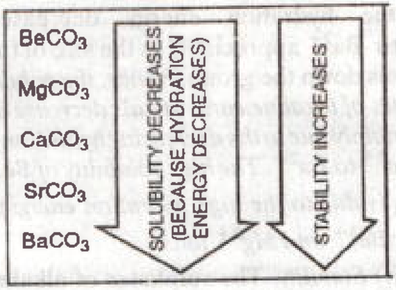
(*i*) calculated amount of carbon dioxide is passed through the solution of the alkaline metal hydroxides

$$M(OH)_2(aq) + CO_2\,(g) \longrightarrow MCO_3(s) + H_2O(l)$$

and (*ii*) sodium or ammonium carbonate is added to the solution of the alkaline earth metal salt such as $CaCl_2$

$$CaCl_2\,(aq) + Na_2CO_3\,(aq) \longrightarrow CaCO_3\,(s) + 2\,NaCl\,(aq)$$

Properties of carbonates. (*i*) All carbonates are ionic but beryllium carbonate is prone to hydrolysis. It contains the hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+} and hence is precipitated only in an atmosphere of CO_2.



$$BeCO_3 + 4\,H_2O \underset{\text{Presence of } CO_2}{\overset{\text{Absence of } CO_2}{\rightleftharpoons}} [Be(H_2O)_4]^{2+} + CO_3^{2-}$$

(*ii*) *Solubility*. The carbonates of magnesium and other alkaline earth metals are sparingly soluble in water and their solubility decreases down the group from Be to Ba. For example, $MgCO_3$ is slightly soluble in water but $BaCO_3$ is almost insoluble.

As we move down the group, the lattice energies of carbonates remain approximately the same. The reason being that carbonate ion is so large that relatively small changes in the sizes of the cations from Be^{2+} to Ba^{2+} do not make any material difference. However, the *hydration energies* of the metal cations decrease from Be^{2+} to Ba^{2+}. Hence, *the solubilities of carbonates of the alkaline earth metals decrease down the group mainly due to decreasing hydration energies of the cations from* Be^{2+} *to* Ba^{2+}.

All the carbonates of alkaline earth metals are, however, more soluble in the presence of CO_2 due to the formation of corresponding bicarbonates. For example,

$$CaCO_3\,(s) + CO_2\,(g) + H_2O\,(g) \longrightarrow Ca(HCO_3)_2\,(aq)$$

(*ii*) *Stability*. The carbonates of all alkaline earth metals decompose on heating to form the corresponding metal oxide and CO_2.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

The temperature of decomposition, i.e., thermal stability of these carbonates, however, increases down the group as the basicity of metal hydroxide increases from $Be(OH)_2$ *to* $Ba(OH)_2$. For example,

$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
<373 K	813 K	1173 K	1563 K	1633 K

$BeCO_3$ is thus unstable and can be kept only in an atmosphere of CO_2.

Bicarbonates. The bicarbonates of alkaline earth metals are prepared by passing CO_2 through a suspension of metal carbonates in water.

$$\underset{(Insoluble)}{M_2CO_3} + H_2O + CO_2 \longrightarrow \underset{(Soluble)}{M(HCO_3)_2}$$

All the bicarbonates of alkaline earth metals are *stable only in solution* and have not been isolated in the pure state.

Uses. The extremely low solubility of alkaline earth carbonates in water is made use of in qualitative analysis. For example,

(*i*) The cations of group V (Ba^{+}, Sr^{2+}, Ca^{2+}) of qualitative analysis are precipitated as their insoluble carbonates from the solution of their soluble salts by adding $(NH_4)_2CO_3$ in presence of NH_4Cl and excess of NH_4OH.

(*ii*) The soluble carbonates, *i.e.*, carbonates of alkali metals and NH_4^+ ion are detected by precipitation as insoluble magnesium carbonate.

(*iii*) $CaCO_3$ is used in solvay-ammonia process for manufacture of Na_2CO_3, in glass making and in cement manufacture.

12.17.3. Nitrates

Alkaline earth metal nitrates are prepared in solution and can be crystallized as hydrated salts by the action of HNO_3 on oxides, hydroxides and carbonates.

$$MO + 2\,HNO_3 \longrightarrow M(NO_3)_2 + H_2O$$

$$M(OH)_2 + 2\,HNO_3 \longrightarrow M(NO_3)_2 + 2\,H_2O$$

$$MCO_3 + 2\,HNO_3 \longrightarrow M(NO_3)_2 + CO_2 + H_2O$$

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

Magnesium nitrate crystallizes as $Mg(NO_3)_2.6H_2O$ while $Ba(NO_3)_2$ *crystallises as anhydrous salt.*

Beryllium nitrate is unusual because it forms basic nitrate, *i.e.*, $[Be_4O(NO_3)_6]$ in addition to the normal salt.

All nitrates on heating give the corresponding oxides.

$$2\,M(NO_3)_2 \longrightarrow 2\,MO + 4\,NO_2 + O_2$$

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

Strontium and barium nitrates are used in pyrotechnics for giving red and green flames respectively.

From the above discussion, it follows that calcium, strontium and barium are the three elements of group 2 whose physical and chemical properties are closely related and change systematically with increasing atomic size. Thus, Ca, Sr and Ba are highly electropositive, have high negative electrode potentials (*i.e.* E°) and show systematic trends in the solubility of their oxo salts.

12.18. Anomalous behaviour of Beryllium

Beryllium, the first member of alkaline earth metals, shows an anomalous behaviour, *i.e.*, differs from the rest of the members of its family. The main reasons for this difference are as follows:

(*a*) exceptionally small atomic and ionic size

(*b*) high ionization energy

(*c*) absence of *d*-orbitals in its valence shell.

Some important properties in which beryllium differs from the rest of the members of its group (especially the next member, Mg) are as follows :

(*i*) Beryllium is harder than other members of its group.

(*ii*) It has higher melting and boiling points than the other members.

(*iii*) Beryllium does not react with water even at high temperatures while other metals do, *e.g.*,

$$\underset{(Boiling)}{Mg + H_2O} \longrightarrow MgO + H_2$$

(*iv*) Beryllium forms covalent compounds (because of high charge density and hence greater polarizing power) whereas other members form ionic compounds.

Because of covalent character, salts of beryllium are easily hydrolysed. For example,

$$BeCO_3 + 4\,H_2O \longrightarrow [Be(H_2O)_4]^{2+} + CO_3^{2-}$$

(*v*) Beryllium oxide and hydroxide are amphoteric whereas oxides of other alkaline earth metals are basic.

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

$$BeO + 2\,NaOH \longrightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2} + H_2O$$

(*vi*) Carbides of Be(Be_2C and BeC_2) are covalent (*e.g.*, Be = C = Be) whereas carbides of other members are ionic *e.g.*, CaC_2 is $Ca^{2+}(C \equiv C)^{2-}$

(*vii*) Beryllium carbide reacts with water to produce methane gas whereas carbides of other alkaline earth metals give acetylene gas. Thus

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

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

(*viii*) Beryllium does not exhibit coordination number of more than four since its valence shell (n = 2) has only four orbitals. The remaining elements of this group can show a coordination number of six by making use of *d*-orbitals in addition to *s*- and *p*-orbitals.

(*ix*) Beryllium forms fluoro complex anion (BeF_4^{2-}) whereas other members of the group do not form fluoro complex anions.

12.19. Resemblance between Beryllium and Aluminium (Diagonal Relationship)

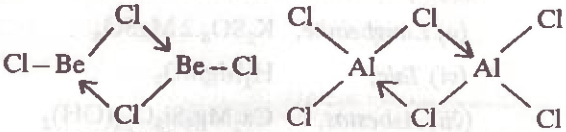
Just as lithium shows resemblance with its diagonally opposite element magnesium, in a similar way beryllium shows resemblance with its diagonally opposite element aluminium. This is due to the reason that these two elements have the same electronegativity (Be = 1·5, Al = 1·5) and the polarising power *i.e.* charge/radius ratio, (Be^{2+} = 2/31 = 0·064 and Al^{3+} = 3/50 = 0·060) of their ions are very similar.

Some points of similarity are given below :

(*i*) Both metals have a tendency to form covalent compounds, *e.g.*, the chlorides of both (*i.e.* $BeCl_2$ and $AlCl_3$) being covalent are soluble in organic solvents.

(*ii*) Both $BeCl_2$ and $AlCl_3$ act as strong Lewis acids.

(*iii*) Both $BeCl_2$ and $AlCl_3$ have bridged chloride structures in the vapour phase.



(*iv*) Both the metals dissolve in strong alkalies to form soluble complexes : beryllates $[Be(OH)_4]^{2-}$ and aluminates $[Al(OH)_4]^-$

(*v*) The oxides of both beryllium (BeO) and aluminium (Al_2O_3) are hard high melting insoluble solids.

(*vi*) The oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide solution as well as in hydrochloric acid.

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

$$BeO + 2\,NaOH \longrightarrow Na_2BeO_2 + H_2O$$

$$Al_2O_3 + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2O$$

$$Al_2O_3 + 2\,NaOH \longrightarrow \underset{\text{Sod. meta-aluminate}}{2\,NaAlO_2} + H_2O$$

(*vii*) Carbides of both the metals react with water liberating methane gas.

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

$$Al_4C_3 + 12\,H_2O \longrightarrow 4\,Al(OH)_3 + 3\,CH_4$$

(*viii*) Salts of both these elements form hydrated ions *e.g.*, $[Be(OH_2)_4]^{2+}$ and $[Al(OH_2)_6]^{3+}$ in aqueous solutions.

(*ix*) Because of similar polarising power both beryllium and aluminium forms complexes. For example, beryllium forms tetrahedral complexes such as $[BeF_4]^{2-}$ and $[Be(C_2O_4)_2]^{2-}$ and aluminium forms octahedral complexes like $[AlF_6]^{3-}$ and $[Al(C_2O_4)_3]^{3-}$.

ADD TO YOUR KNOWLEDGE

1. The compounds of alkaline earth metals in which the metal is divalent are diamagnetic and colourless unless the anion is coloured. This is because they have noble gas configuration with no unpaired electrons.
2. Reduction of sulphates with carbon gives sulphides. Therefore, most of the barium compounds are made from barium sulphate.

$$BaSO_4 + 4\,C \xrightarrow{\Delta} BaS + 4\,CO$$

3. Magnesium perchlorate $(MgClO_4)$ is used as a drying agent called anhydrone.

12.20. Magnesium

12.20.1. Minerals of Magnesium.

Magnesium is the *sixth* most abundant element by weight in the earth's crust. Its chief minerals are :

(*i*) *Carnallite*,	$KCl.MgCl_2.6\,H_2O$
(*ii*) *Magnesite*,	$MgCO_3$
(*iii*) *Dolomite*,	$CaCO_3.MgCO_3$
(*iv*) *Epsomite*,	$MgSO_4.7\,H_2O$.
(*v*) *Langbeinite*,	$K_2SO_4.2\,MgSO_4$
(*vi*) *Talc*,	H_2MgSiO_3
(*vii*) *Asbestos*,	$Ca_2Mg_5Si_8O_{22}(OH)_2$

Magnesium is also present in sea water up to an extent of 0·13% as $MgCl_2$ and $MgSO_4$ from which it is being extracted on an increasing scale. India has a good reserve (approx. 250 million tonnes of magnesite ore, mostly in U.P., Tamil Nadu and Rajasthan.

Besides these minerals, magnesium is the essential constituent of chlorophyll, the green colouring matter of the plants.

12.20.2. Extraction of Magnesium

1. From Magnesite or Dolomite. The ore is calcined to form the oxide.

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

$$MgCO_3.CaCO_3 \xrightarrow{\Delta} MgO.CaO + 2\,CO_2$$

The mineral is obtained from the oxide or the mixed oxides as follows :

(*a*) **From MgO.** The oxide is mixed with carbon and heated in a current of Cl_2 gas.

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

The anhydrous $MgCl_2$ thus obtained is subjected to electrolysis (discussed below).

(*b*) **From mixed oxides, MgO.CaO.** The mixed oxides obtained above is reduced with ferrosilicon under reduced pressure above 1273 K.

$$2\,MgO.CaO + FeSi \xrightarrow{> 1273\,K} 2\,Mg + Fe + Ca_2SiO_4$$

2. From sea water. The sea water containing magnesium chloride and magnesium sulphate is concentrated under the sun and is treated with slaked lime, $Ca(OH)_2$.

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

Magnesium hydroxide being almost insoluble thus precipitated is filtered and heated to give the oxide.

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

The oxide so obtained is converted into $MgCl_2$ as described under 1 (*a*) above and then subjected to electrolysis as described below :

Electrolysis of anhydrous magnesium chloride. The anhydrous $MgCl_2$ obtained above is added to a molten mixture of NaCl and $CaCl_2$ (973 – 1023 K) and electrolysed. The electrolysis is carried out in an iron vessel which serves as the cathode (Fig. 12.6). A graphite rod which dips in the molten electrolyte ($MgCl_2 + NaCl + CaCl_2$) acts as the anode. The anode is surrounded by a porcelain tube which prevents the intermixing of the products of electrolysis (Mg and Cl_2). The electrolytic tank is heated to 923 – 1023 K to melt the electrolyte. A stream of some inert gas such as coal gas is passed through the tank to expel air in order to protect the molten magnesium from oxidation. On passing electric current, fused $MgCl_2$ undergoes electrolysis as follows :

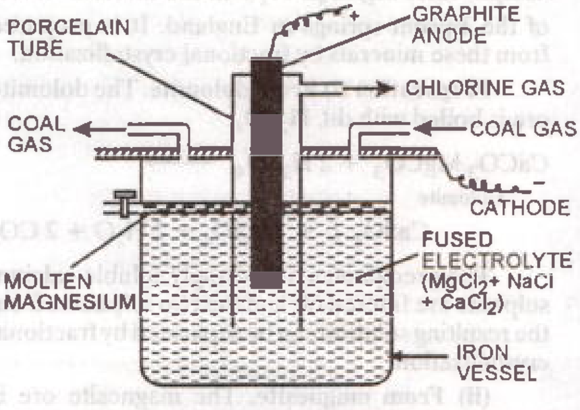


FIGURE 12.6. Extraction of Magnesium.

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$

At cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$

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

$$Cl + Cl \longrightarrow Cl_2.$$

Chlorine liberated at the anode passes out from the exist provided in the porcelain tube while the magnesium liberated at the cathode is in the molten state (m.p. 924 K). It being lighter rises to the surface of the molten electrolyte from where it is removed from time to time by means of perforated laddles. Magnesium thus obtained is about 99% pure. It is refined further by subliming at 873 K under a pressure of 1 mm mercury.

3. From carnallite, 2 KCl.MgCl₂.6H₂O. Carnallite is heated to 625 K in an atmosphere of hydrogen chloride gas to make it anhydrous. *Excess of HCl gas prevents the hydrolysis of magnesium chloride by its own water of crystallisation.*

$$MgCl_2 + H_2O \longrightarrow MgO + 2\,HCl$$

The anhydrous carnallite thus obtained is fused with anhydrous $CaCl_2$ and NaCl. The electrolysis of the fused mixture is then carried out as described above.

12.20.3. Properties of Magnesium

(*a*) **Physical properties.** (*i*) Magnesium is a silvery white metal which soon becomes dull in air

(*ii*) It is a light metal with a density of $1 \cdot 74\,g\,cm^{-3}$.

(*iii*) It is fairly malleable and ductile.

(*b*) **Chemical properties.** Magnesium is a fairly active metal although much less reactive than calcium, strontium and barium. Some important chemical properties of magnesium are :

(*i*) *Action of oxygen or air.* Magnesium does not react with dry air but slowly gets tarnished in moist air due to the formation of a thin film of the oxide, MgO. It burns in oxygen or air with a dazzling light.

$$2\,Mg + O_2 \xrightarrow{\Delta} 2\,MgO$$

(*ii*) *Action of carbon dioxide and sulphur dioxide.* Because of its great affinity for oxygen, magnesium keeps on burning even in CO_2 or SO_2.

$$2\,Mg + CO_2 \xrightarrow{\Delta} 2\,MgO + C$$

$$2\,Mg + SO_2 \xrightarrow{\Delta} 2\,MgO + S$$

(*iii*) *Action of nitrogen.* On heating, magnesium combines with nitrogen to form magnesium nitride.

$$3\,Mg + N_2 \longrightarrow Mg_3N_2$$

Thus when magnesium burns in air both the oxide and the nitride are formed.

(*iv*) *Action of halogens.* Magnesium on heating with halogens readily forms the halides, *e.g.*,

$$\mathrm{Mg + Cl_2 \xrightarrow{\Delta} MgCl_2}$$

(*v*) *Action of water.* Magnesium does not decompose water in cold but decomposes boiling water or steam.

$$\mathrm{Mg + H_2O\ (\mathit{steam}) \longrightarrow MgO + H_2}$$

Magnesium amalgam, however, liberates H_2 from cold water.

(*vi*) *Action of acids.* Dilute acids including nitric acid react with magnesium to produce dihydrogen.

$$\mathrm{Mg + 2\,HCl \longrightarrow MgCl_2 + H_2}$$

$$\mathrm{Mg + Dil.\ H_2SO_4 \longrightarrow MgSO_4 + H_2}$$

$$\mathrm{Mg + 2\,HNO_3 \longrightarrow Mg(NO_3)_2 + H_2}$$

However with conc. H_2SO_4, SO_2 is produced

$$\mathrm{Mg + \underset{(\mathit{conc.})}{H_2SO_4} \longrightarrow MgSO_4 + SO_2 + 2\,H_2O}$$

(*vii*) *Reaction with alkyl and aryl halides.* Magnesium reacts with alkyl and aryl halides in dry ether to form covalent compounds called *Grignard reagents.*

$$\mathrm{Mg + C_2H_5I \xrightarrow{\text{Dry ether}} \underset{\text{Ethylmag. iodide}}{C_2H_5MgI}}$$

$$\mathrm{Mg + C_6H_5Br \xrightarrow{\text{Dry ether}} \underset{\text{Phenylmag. bromide}}{C_6H_5MgBr}}$$

12.20.4. Uses of Magnesium.

(*i*) Magnesium is the lightest structural metal having density two-thirds of aluminium. It is therefore, widely used in the preparation of alloys. Some of the magnesium alloys contain more than 90% Mg together with 2-9% Al and 1% Zn. *Duralumin* (Al = 95%, Cu = 4%, Mn = 0.5% and Mg = 0.5%) being light tough and resistant to corrosion is used for the manufacture of airplanes and automobile parts. *Magnalium* (Al = 90% and Mg = 10%) being light, tough and hard is used for making balance beams.

(*ii*) Magnesium burns with an intense light. Therefore, magnesium (as powder or ribbon) is used in flash bulbs for photography, fireworks and signal fires.

(*iii*) Magnesium is also used in cathodic protection of metals and as an oxygen scavenger in metallurgy.

(*iv*) Being a reducing agent, magnesium is used in the extraction of boron and silicon from their respective oxides.

$$\mathrm{B_2O_3 + 3\,Mg \longrightarrow 3\,MgO + 2\,B}$$

$$\mathrm{SiO_2 + 2\,Mg \longrightarrow 2\,MgO + Si}$$

It is also used in the extraction of other metals such as Ti, Zr and Hf.

(*v*) Magnesium is used in the preparation of *Grignard reagents* which are widely used in organic synthesis.

(*vi*) Magnesium is used for ignition of thermite charge in aluminothermy.

(*vii*) A suspension of magnesium hydroxide known as *milk of magnesia* is used as an antacid for patients suffering from acidity.

(*viii*) Magnesium carbonate is one of the components of tooth paste.

SECTION—III

12.21. Compounds of Alkaline Earth Metals

Alkaline earth metals form many comopounds. Some of these are discussed below :

12.21.1. Magnesium sulphate, Epsom salt, $MgSO_4.7H_2O$.

Magnesium sulphate occurs as *Kieserite*, $MgSO_4.2\,H_2O$ in Stassfurt (Germany) deposits or as *Epsomite*, $MgSO_4.7\,H_2O$ in the mineral waters of the Epsom springs in England. It is prepared from these minerals by fractional crystallization.

Preparation (i) From dolomite. The dolomite ore is boiled with dil. H_2SO_4.

$$\mathrm{\underset{\text{Dolomite}}{CaCO_3.MgCO_3} + 2\,H_2SO_4 \longrightarrow CaSO_4\downarrow + MgSO_4 + 2\,H_2O + 2\,CO_2}$$

The precipitates of sparingly soluble calcium sulphate are filtered off and the two sulphates from the resulting solution can be separated by fractional crystallization.

(ii) From magnesite. The magnesite ore is powdered and dissolved in dil. H_2SO_4. The resulting solution is concentrated and crystallized in the temperature range 275-320 K when crystals of $MgSO_4.7\,H_2O$ separate out.

$$\mathrm{MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + CO_2 + H_2O}$$

(iii) From kieserite. The mineral kieserite ($MgSO_4.H_2O$) is powdered and dissolved in water. The resulting solution upon concentration and crystallization is the temperature range 275-320 K gives crystals of $MgSO_4.7H_2O$.

(iv) Laboratory preparation. In the laboratory, magnesium sulphate is prepared by dissolving magnesium metal or magnesium oxide or magnesium carbonate with dil. H_2SO_4.

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$

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

The resulting solution upon concentration and cooling (275-320 K) gives crystals of $MgSO_4.7\,H_2O$.

Properties. (*i*) Magnesium sulphate is a colourless efforescent (loses water of crystallization slowly) crystaline solid highly soluble in water.

Its extract formula is $[Mg(H_2O)_6]SO_4.H_2O$.

(*ii*) **Isomorphism*.** $MgSO_4.7H_2O$ shows isomorphism since it exists in two crystalline forms ; one isomorphous with $ZnSO_4.7H_2O$ and the other isomorphous with $FeSO_4.\ 7H_2O$.

(*iii*) It forms double salts with alkali metal sulphates. The double salt, $K_2SO_4.MgSO_4.6H_2O$ is sold as a fertilizer under the name *potash magnesis.*

(*iv*) **Action of heat.** When heated to 423 K, it loses six molecules of water of crystallisation and changes into magnesium sulphate monohydrate. The monohydrate becomes anhydrous when heated to 503 K and on further strong heating, it decomposes to give MgO and SO_3 gas.

$$MgSO_4.7\,H_2O \xrightarrow[-6H_2O]{423\text{ K}} MgSO_4.H_2O$$

$$\xrightarrow[-H_2O]{503\text{ K}} MgSO_4 \xrightarrow[\text{heating}]{\text{Strong}} MgO + SO_3$$

Uses. Magnesium sulphate is used :

(*i*) in weighting, sizing and fire-proofing of paper and cloth.

(*ii*) as a mordant for dyeing and tanning.

(*iii*) in the preparation of paints and soaps.

(*iv*) as a purgative in medicine.

(*v*) Anhydrous magnesium sulphate is used as a drying agent in Organic Chemistry.

12.21.2. Calcium oxide**, Quick lime, CaO

Preparation. Calcium oxide is called quick lime. It is prepared by heating limestone in a rotatory kiln at 1273 K.

$$CaCO_3 \overset{1273\text{ K}}{\rightleftharpoons} CaO + CO_2\ ;$$

$$\Delta H = +\ 179{\cdot}9\text{ kJ}$$

It is only above 1100 K that CO_2 escapes freely and hence a temperature of 1273 is maintained.

The necessary conditions for obtaining a good yield of quick lime are :

(*i*) Since the reaction is reversible, *carbon dioxide should be removed as soon as it is formed* in order to shift the equilibrium in the forward direction in accordance with *Le Chatelier's Principle*.

(*ii*) The temperature should not be allowed to rise above 1273 K otherwise silica present as impurity in lime will combine with calcium oxide to form infusible calcium silicate.

$$CaO + SiO_2 \xrightarrow{\text{Above 1273 K}} CaSiO_3\ \textit{(calcium silicate)}$$

Properties. (*i*) It is a white amorphous solid with a *m.p.* of 2273 K.

(*ii*) It is usually obtained in form of hard lumps. When heated is oxyhydrogen flame, it emits brilliant white light called **limelight.**

(*iii*) When exposed to atmosphere, it absorbs moisture and carbon dioxide forming slaked lime and calcium carbonate respectively.

$$\underset{(moisture)}{CaO + H_2O} \longrightarrow \underset{(calcium\ silicate)}{Ca(OH)_2}$$

$$CaO + CO_2 \longrightarrow CaCO_3\ \textit{(calcium carbonate)}$$

(*iv*) On adding water, it produces a hissing sound and a large amount of heat is evolved which converts water into steam. This process is called *slaking of lime* and the fine powder thus obtained is called *slaked lime.*

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

$$\Delta H = -64{\cdot}5\text{ kJ mol}^{-1}$$

(*v*) **Action of acids and acidic oxides. It is a** *basic oxide* **and hence combines with acids and acidic oxides forming salts.**

***Compounds having same crystal structure are called Isomorphous and the phenomenon is called Isomorphism.**

**Non-evaluative.

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

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$6\,CaO + P_4O_{10} \longrightarrow 2\,Ca_3(PO_4)_2$$

$$CaO + SO_2 \longrightarrow CaSO_3$$

(vi) **Reaction with coke.** When heated with coke in an electric furnace at 2273-3273 K, it forms calcium carbide.

$$CaO + 3C \xrightarrow{2273-3273\,K} CaC_2 + CO$$

(vii) **Reaction with ammonium salts.** On heating with ammonium salts, it liberates ammonia gas.

$$CaO + 2\,NH_4Cl \longrightarrow CaCl_2 + 2\,NH_3 + H_2O$$

Uses. *(i)* As a constituent of mortar, it is used on a very large scale in building constructions.

(ii) In the preparation of cement, glass, calcium carbide and sodium carbonate (from caustic soda).

(iv) It is used in the preparation of ammonia and soda-lime (CaO + NaOH).

(v) It is used for drying alcohols and non-acidic gases.

(vi) It is used as a basic lining in furnaces.

12.21.3. Calcium hydroxide,* Slaked lime, $Ca(OH)_2$

Preparation. *(i)* **From quick lime.** Calcium hydroxide is prepared on a commercial scale by adding water to quick lime. This process is called *slaking of lime.*

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

During the process of slaking, lumps of quick lime crumble to a fine powder.

(ii) From calcium chloride. It is also obtained by treating calcium chloride with caustic soda.

$$CaCl_2 + 2\,NaOH \longrightarrow Ca(OH)_2 + 2\,NaCl$$

Properties. *(i)* It is a white amorphous powder sparingly soluble in water, the solubility decreasing further with rise in temperature. *An aqueous solution is known as lime water and a suspension of slaked lime in water is called* **milk of lime.**

(ii) **Action of heat.** On heating, slaked lime loses water only at temperatures greater than 700 K

$$Ca(OH)_2 \xrightarrow{700\,K} CaO + H_2O.$$

(iii) **Reaction with chlorine.** Slaked lime reacts with chlorine to form calcium hypochlorite, a constituent of bleaching powder

$$2\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + 2\,H_2O.$$

(iv) **Reaction with carbon dioxide.** When carbon dioxide is passed through lime water, it turns milky due to the formation of insoluble calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{(Milkiness)}{CaCO_3\downarrow} + H_2O$$

On passing excess of carbon dioxide, the precipitates of calcium carbonate dissolve to form soluble calcium bicarbonate and hence *the milkiness disappears*.

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{(Soluble)}{Ca(HCO_3)_2}$$

If this clear solution of calcium bicarbonate is heated, the solution again turns milky due to the decomposition of calcium bicarbonate back to calcium carbonate.

$$Ca(HCO_3)_2(aq) \xrightarrow{Heat} CaCO_3(s) + CO_2(g) + H_2O(l)$$

(v) **Reaction with acids.** Slaked lime being a strong base reacts with acids and acidic gases forming salts.

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

$$Ca(OH)_2 + SO_3 \longrightarrow CaSO_4 + H_2O$$

However, $Ca(OH)_2$ does not dissolve in dil. H_2SO_4 because the calcium sulphate formed is sparingly soluble in water.

Uses. *(i)* Calcium hydroxide is used

(i) for absorbing acidic gases such as CO_2, NO_2, SO_2, SO_3 etc.

(ii) for preparing ammonia from ammonium salts.

(iii) in the production of mortar which is used as a building material.

(iv) in white washing due to its disinfectant properties.

(v) for softening of hard water.

(vi) in the manufacture of bleaching powder.

(vii) in the laboratory, as *lime water* for detection of carbon dioxide.

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*Non-evaluative.

(*viii*) It is also used in making glass, in tanning industry, as a cheap alkali for neutralising acids and in the purification of sugar and coal gas.

12.21.4. Plaster of Paris*, $CaSO_4.1/2\,H_2O$ or $(CaSO_4)_2.H_2O$.

Plaster of Paris is calcium sulphate hemihydrate $CaSO_4.1/2\,H_2O$.

Preparation. It is prepared by heating gypsum to 393.

$$\underset{\text{Gypsum}}{2\,CaSO_4.2\,H_2O} \xrightarrow{393\text{ K}} \underset{\text{Plaster of Paris}}{2\,CaSO_4.1/2H_2O} + 3\,H_2O$$

The following conditions are necessary :

(*i*) The temperature should not be allowed to rise above 393 K because above this temperature the whole of water of crystallisation is lost. The resulting anhydrous $CaSO_4$ is called *dead burnt plaster* because it loses the properties of setting with water.

(*ii*) The gypsum should not be allowed to come in contact with carbon containing fuel otherwise some of it will be reduced to calcium sulphite.

Properties. (*i*) It is a white powder.

(*ii*) On mixing with one-third its weight of water, it forms a plastic mass which sets into a hard mass of interlocking crystals of gypsum within 5 to 15 minutes. It is due to this reason that it is called plaster. The addition of common salt accelerates the rate of setting, while a little borax or alum reduces it. The setting of Plaster of Paris is believed to be due to rehydration and its reconversion into gypsum.

$$\underset{\text{Plaster of Pairs}}{2\,CaSO_4.1/2\,H_2O} + 3\,H_2O \longrightarrow \underset{\text{Gypsum}}{2\,CaSO_4.2\,H_2O}$$

During the process of setting, slight expansion (1%) in volume occurs. As a result, it can take the shape and impression of the mould in which it is put.

Uses. (*i*) Plaster of Paris is used for producing moulds for pottery and ceramics and casts of statues and busts.

(*ii*) It is used for making statues, models and other decorative materials.

(*iii*) It is used in surgical bandages used for plastering broken or fractured bones of the body and for preparing black board chalks.

(*iv*) It is also used in dentistry.

12.22. Industrial Uses of Lime and Limestone

Uses of lime. Calcium oxide is called lime or quicklime. Its main industrial uses are :

(*i*) It is used in steel industry to remove phosphates and silicates as *slag*.

(*ii*) It is used to make cement by mixing it with silica, alumina or clay.

(*iii*) It is used in making glass.

(*iv*) **In chlor alkali industry** (includes the production of three main chemicals : NaOH, Cl_2, Na_2CO_3), it is used in the lime-soda process for the conversion of Na_2CO_3 to NaOH and vice-versa.

(*v*) It is used for softening water, for making slaked lime, $Ca(OH)_2$ by treatment with water and calcium carbide.

Uses of slaked lime. Calcium hydroxide is called slaked lime. Its main industrial uses are :

(*i*) Slaked lime is used as a building material in form of **mortar.** It is prepared by mixing slaked lime with 3-4 times its weight of sand. The mixture is made into a thick paste with gradual addition of water. The paste is called *mortar* and is used in building construction. It sets into a hard mass by loss of H_2O and gradual absorption of CO_2 from the air. Sometimes coal ash is mixed with lime instead of sand.

(*ii*) It is used in the manufacture of bleaching powder by passing Cl_2 gas.

(*iii*) It is used in making glass and in the purification of sugar and coal gas.

(*iv*) It is used in softening of hard water.

Uses of limestone. Limestone rock is the common form of calcium carbonate. It occurs as chalk, marble, corals, calcite, aragonite etc. Mixed with magnesium carbonate, it occurs as dolomite. Its main uses are :

(*i*) It is used as a building material in form of marble.

(*ii*) It is used in the manufacture of quick lime.

(*iii*) It is also used in the manufacture of quick lime.

(*iv*) It is used as a raw amterial for the manufacture of sodium carbonate is Solvay-ammonia process.

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*Non-evaluative.

(*v*) Commercial limestone contains iron oxide, alumina, magnesia, silica and sulphur, with a CaO content of 22 – 56%, and MgO content upto 21%. It is used as such as a fertilizer.

12.23. Cement*

It is one of the most important building materials of modern times. Its use was discovered in 1824 by *Joseph Aspdin*, a mason of Leeds (U.K.). He found that when a strongly heated mixture of limestone and clay was mixed with water and allowed to stand for some time, it hardened to a stone like mass resembling Portland rock which was a popular building stone in England those days. He, therefore, named it as **portland cement.**

Cement is essentially a finely powdered mixture of calcium silicates and aluminates along with small quantities of gypsum which sets into a hard stone like mass when treated with water.

The chief components of cement are tricalcium silicate, $3CaO.SiO_2$, dicalcium silicate, $2CaO.SiO_2$ and tricalcium aluminate $3CaO.Al_2O_3$. Out of all these, tricalcium silicate is the most important since it has property of setting quickly and acquiring considerable strength within a few days. It usually constitutes 50% of the cement.

12.23.1. Composition of Portland Cement

The average composition of portland cement is

Lime (CaO)	50 – 60%
Magnesium oxide (MgO)	2 – 3%
Silica (SiO_2)	20 – 25%
Ferric oxide (Fe_2O_3)	1 – 2%
Alumina (Al_2O_3)	5 – 10%
Sulphur trioxide (SO_3)	1 – 2%

For a good quality cement, the ratio of alumina (Al_2O_3) to silica (SiO_2) should lie between 2·5 and 4 while that of lime (CaO) to silica + alumina + ferric oxide should be as close to 2 as possible.

12.23.2. Raw Materials

The essential raw materials required for the manufacture of cement are : (*i*) *limestone* $CaCO_3$, (*ii*) *clay* which provides both silica and alumina and (*iii*) *gypsum*, $CaSO_4.2H_2O$. Besides these, small amounts of magnesia (MgO) and iron oxide (Fe_2O_3) are also required for imparting suitable colour to cement.

12.23.3. Manufacture of Cement

Portland cement is chiefly manufactured by the following two processes :

(*i*) *Wet Process* (*ii*) *Dry Process*.

The wet process is preferred when the raw materials *i.e.* lime stone and clay are soft, climate is humid and the fuel is cheap. The dry process is preferred when the raw materials are hard.

The main raw materials are *lime stone* and *clay* whereas the former supplies lime while the latter is a source of silica, alumina and iron oxide. The raw materials are first crushed separately in a suitable machine. They are then mixed in the required proportions (3 parts lime stone + one part clay) and ground together finely. This grinding is done either by the *dry process* or by the *wet process*.

In the **wet process**, the clay is washed with water in a wash mill to remove flint and other foreign substances. It is then mixed with requisite quantity of limestone and pulverised in a special mill. The resulting pasty mass is then thoroughly homogenised to get 'raw slurry' containing about 40% water.

In the **dry process**, the raw materials are dried and mixed in desired proportions. The mixture is then finely powdered and passed through 300 mesh sieves and homogenised with the help of compressed air. The homogeneous mass is called *'raw meal'*.

The slurry or the raw meal is introduced into the upper end of a rotary kiln (Fig. 12.7) by means of screw conveyer. The kiln consists of an inclined steel rotating cylinder, 150 – 200 ft long and about 10 ft in diameter lined inside with firebricks. The charge travels downwards slowly due to the rotatory motiong given to the kiln and is heated by burning coal dust which is blown in from the lower end. The charge takes about 2 – 3 hours to cover the entire journey in the kiln. In the kiln, the following changes occur :

(*i*) *In the upper part of the kiln*, the temperature is around 1000 – 1100 K. Here, the charge loses all its water due to evaporation by hot gases.

(*ii*) *In the middle of the kiln*, the temperature is around 1100-1200 K. Here, limestone decomposes to form calcium oxide and carbon dioxide.

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*Non-evaluative.

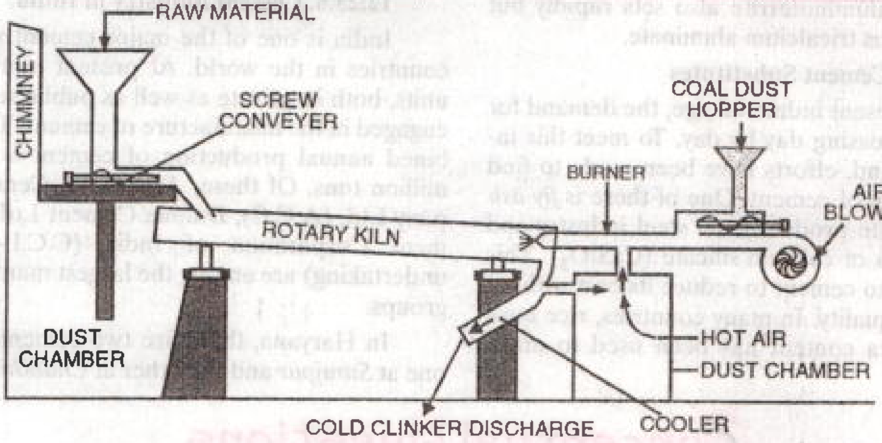


FIGURE 12.7. Manufacture of Portland Cement.

(*iii*) *The lower part of the kiln*, from where coal dust is blown in is the hottest with the temperature ranging between 1770 – 1870 K. As the charge reaches here, chemical combination takes place between lime, alumina and silica to form calcium silicates and aluminates :

$$2\,CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate}}{2\,CaO.SiO_2}$$

$$3\,CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate}}{3\,CaO.SiO_2}$$

$$3\,CaO + Al_2O_3 \longrightarrow \underset{\text{Tricalcium aluminate}}{3\,CaO.Al_2O_3}$$

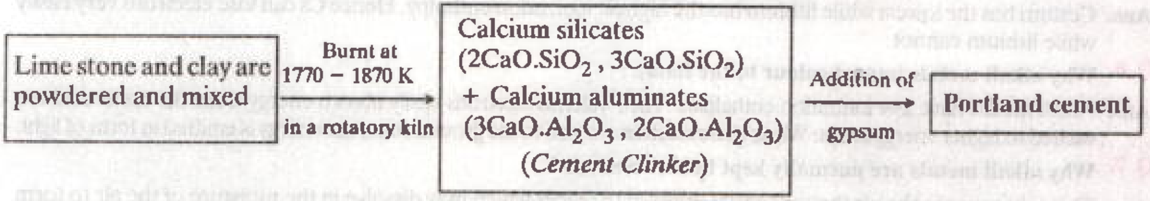
$$2\,CaO + Al_2O_3 \longrightarrow \underset{\text{Dicalcium aluminate}}{2\,CaO.Al_2O_3}$$

$$4\,CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tetracalcium aluminoferrite}}{4\,CaO.\,Al_2O_3.Fe_2O_3}$$

Due to very high temperature in this zone, about 20 – 30% mass melts and combines with solid mass to form grey coloured balls (ranging in size from a pea to that of an egg) called **cement clinkers**.

The hot clinkers are cooled by cold air and are mixed with 2 – 3% gypsum (to slow down the process of setting of cement and thereby imparting greater strength to it) and finely powdered to 325 mesh size in grinding machines. The fine powder called the *'Portland cement'* is sieved and packed in bags.

The flow sheet diagram of the entire manufacturing process is given below :



12.23.4. Setting of Cement

The important constituents 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%.

When water is added to cement, an *exothermic reaction* occurs. During this process, the cement reacts with water to form a gelatinous mass which slowly sets into a hard mass having three-dimensional net work structure involving – Si – O – Si – and – Si – O – Al – chains.

Out of the various constituents of cement, the most important is tricalcium silicate. It sets quickly and develops considerable strength within a few days. Dicalcium silicate sets slowly and develops appreciable strength after a month or so. Tricalcium aluminate sets instantaneously in presence of water. The internal strength acquired by cement is primarily due to the setting of tricalcium aluminate.

Tetracalcium aluminoferrite also sets rapidly but not as quickly as tricalcium aluminate.

12.23.5. Cement Substitutes

In the present industrial age, the demand for cement is increasing day by day. To meet this increasing demand, efforts have been made to find some substitute of cement. One of these is *fly ash* which is a waste product from steel industry and mainly consists of calcium silicate ($CaSiO_3$). This can be added to cement to reduce its cost without affecting the quality. In many countries, rice husk with high silica content has been used to make cement.

12.23.6. Cement industry in India

India is one of the major cement producing countries in the world. At present more than 60 units, both in private as well as public sectors, are engaged in the manufacture of cement. Their combined annual production of cement is about 21 million tons. Of these, Associated Cement Company Ltd, (A.C.C), Dalmia Cement Ltd., and Cement Corporation of India (C.C.I – a Govt. undertaking) are among the largest manufacturing groups.

In Haryana, there are two cement factories, one at *Surajpur* and the other at *Charkhi Dadri*.

Conceptual Questions

Q. 1. Sodium fire in the laboratory should not be extinguished by pouring water. Why ?

Ans. Sodium reacts violently with water producing H_2 gas which also catches fire. As a result, the fire spreads rather than being extinguished. Therefore, H_2O should not be used for extinguishing sodium fire. Instead pyrene (CCl_4) should be used.

Q. 2. Why does table salt get wet in rainy season ?

Ans. Pure NaCl is not hygroscopic but table salt is impure NaCl containing impurities of Na_2SO_4, $CaSO_4$, $MgCl_2$ and $CaCl_2$. All of these being hygroscopic absorb moisture from air in rainy season. As a result, table salt gets wet.

Q. 3. Alkali metals are paramagnetic but their salts are diamagnetic. Explain.

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

Q. 4. Which out of sodium or potassium has higher melting point ?

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

Q. 5. Why cesium can be used in photoelectric cell while lithium cannot be ?

Ans. Cesium has the lowest while lithium has the highest ionization enthalpy. Hence Cs can lose electrons very easily while lithium cannot.

Q. 6. Why alkali metals impart colour to the flame ?

Ans. Alkali metals have low ionization enthalpies. Their valence electrons easily absorb energy from the flame and are excited to higher energy levels. When these electrons return to the ground state, the energy is emitted in form of light.

Q. 7. Why alkali metals are normally kept in kerosene oil ?

Ans. This is because in the air they are easily oxidized to oxides which may dissolve in the moisture of the air to form hydroxides or they also combine directly with water vapours present in moisture to form hydroxides.

Q. 8. Among alkali metals in aqueous solution, Li^+ ion has the lowest mobility. Why ?

Ans. Because of smallest size among alkali metals, Li^+ ions are most highly hydrated in aqueous solution. As a result, among alkali metals, mass of hydrated lithium ion is the highest and thus has lowest ionic mobility.

Q. 9. Lithium has highest ionization enthalpy in group I elements, yet it is the strongest reducing agent. Why ?

Ans. This is because lithium has the highest oxidation potential.

Q. 10. Give reasons for the following :

(*i*) LiCl is more covalent that KCl. **(*ii*) LiI has lower melting point than LiF.**
(*iii*) $MgCl_2$ is more covalent than NaCl. **(*iv*) CuCl is more covalent than NaCl.**

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

(*ii*) Due to bigger size, I^- is more polarizable than F^- and hence LiI is more covalent than LiF.

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

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

Q. 11. **What makes lithium to show properties uncommon to the rest of the alkali metals ?** *(N.C.E.R.T.)*

Ans. The unusual properties of lithium as compared to other alkali metals is due to (*i*) the exceptionally small size of its atom and ion and (*ii*) high polarising power (charge/size ratio).

Q. 12. **When is a cation highly polarising ? Which alkali metal has the highest polarising power ?** *(N.C.E.R.T.)*

Ans. A cation is highly polarising if its charge/size ratio is very high. Li^+ ion has the highest polarising power among the alkali metal ions.

Q. 13. **The enthalpy of formation of hypothetical CaCl(*s*) is theoretically found to be -188 kJ mol^{-1} and $\Delta_f H°$ for $CaCl_2(s)$ is -795 kJ mol^{-1}. Calculate $\Delta_f H°$ for the disproportionation reaction.**

$$2\,CaCl(s) \longrightarrow CaCl_2(s) + Ca(s)$$

(N.C.E.R.T.)

Ans. $\Delta_f H°$ for the above reaction $= \Delta_f H°\,(\text{products}) - \Delta_f H°\,(\text{reactants})$

$$= \Delta_f H°\,(CaCl_2) + \Delta_f H°\,(Ca) - 2\,\Delta_f H°\,(CaCl)$$

$$= -795 + 0 - 2 \times -188 \text{ kJ mol}^{-1} = -419 \text{ kJ mol}^{-1}$$

Q. 14. **Why does the reaction $>C{-}Cl + MF \longrightarrow\ >C{-}F + MCl$ proceed better with KF than with NaF ?** *(N.C.E.R.T.)*

Ans. The standard enthalpies of formation of alkali metal chlorides become more and more negative as we move down the group, *i.e.* $\Delta_f H°$ of KCl is more negative (-428 kJ mol^{-1}) than that of NaCl (-400 kJ mol^{-1}). Therefore, the above reaction proceeds better with KF than with NaF.

Q. 15. **Why is it that on being heated in excess supply of air, K, Rb and Cs form superoxides in preference to oxides** and peroxides ? *(N.C.E.R.T.)*

Ans. K^+, Rb^+ and Cs^+ are large cations and superoxide (O_2^-) is larger than oxide (O^{2-}) and peroxide (O_2^{2-}) ion. Since a large cation stabilizes a large anion, therefore, these metals form superoxides in preference to oxides and peroxides.

Q. 16. **Why solutions of alkali metals in liquid ammonia are conducting, paramagnetic and blue in colour ?** *(P.S.B. 1991 S)*

Ans. Refer to Sec. 12.5.7 on page 12/9.

Q. 17. **Magnesium metal burns in air to give a white ash. When this ash is treated with water, the odour of ammonia can be detected. Explain.**

Ans. Mg burns in air to form MgO and Mg_3N_2.

$$2\,Mg + O_2 \longrightarrow 2\,MgO \quad ; \quad 3\,Mg + N_2 \longrightarrow Mg_3N_2$$

Magnesium nitride on hydrolysis with H_2O gives NH_3.

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

Q. 18. **Why is calcium preferred over sodium to remove last traces of moisture from alcohol ?**

Ans. Both Na and Ca react with water to form their respective hydroxides. But Na readily reacts with alcohol to form sodium ethoxide but Ca reacts only very slowly.

$$2\,C_2H_5OH + 2\,Na \longrightarrow 2\,C_2H_5ONa + H_2$$

Therefore, Ca is preferred over Na to remove the last traces of moisture from alcohol.

Q. 19. **What is the difference between milk of lime and lime water ?**

Ans. A suspension of slaked lime, *i.e.*, $Ca(OH)_2$ in water is called milk of lime but a clear decanted solution of slaked lime in water is called lime water.

Q. 20. **A piece of burning magnesium ribbon continues to burn in sulphur dioxide. Explain.**

Ans. A piece of magnesium ribbon continues to burn in SO_2 since it reacts to form MgO and S.

$$2\,Mg + SO_2 \xrightarrow{\text{Heat}} 2\,MgO + S$$

This reaction is so much exothermic that heat evolved keeps the magnesium ribbon burning.

Q. 21. Alkaline earth metals always form divalent cations even though their second ionization enthalpies are almost double than their first ionization enthalpies. Explain.

Ans. The higher enthalpy of lattice formation by M^{2+} ions more than compensates the higher second ionization enthalpies of metals.

Q. 22. Halides of Be dissolve in organic solvents while those of Ba do not. Why is it so ?

Ans. Halides of Be are covalent because of high IE of Be while those of Ba are ionic due to low IE of Ba.

Q. 23. Explain why halides of beryllium fume in moist air but other alkaline earth metal halides do not. ***(P.S.B. 1992)***

Ans. $BeCl_2$ being a salt of a weak base, $Be(OH)_2$ and a strong acid, HCl undergoes hydrolysis by water to form HCl which fumes in air. $BaCl_2$, on the other hand, being a salt of a strong base, $Ba(OH)_2$ and strong acid, HCl does not undergo hydrolysis by water to form HCl and hence does not fume in air.

$BeCl_2 + 2\,H_2O \longrightarrow Be(OH)_2 + 2\,HCl$; $BaCl_2 + H_2O \not\longrightarrow Ba(OH)_2 + 2\,HCl$

Q. 24. Why Be and Mg do not give characteristic colour to the flame whereas other alkaline earth metals do give. ***(H.P.S.B. 1993)***

Ans. Be and Mg have high ionization enthalpies and hence their valence electrons are not easily excited.

Q. 25. Why superoxides of alkali metals are paramagnetic while normal oxides are diamagnetic ?

Ans. Superoxides contain the ion O_2^- which has the structure $(:\ddot{O} \overset{\cdot\cdot}{\cdot\cdot\cdot} \ddot{O}:)^{-}$ containing a three electron bond, *i.e.*, it has one unpaired electron and hence is paramagnetic. Normal oxides containing the ion O^{2-} do not have any unpaired electrons and hence are diamagnetic.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Name the alkali metals which form superoxides when heated in excess of air ? *(N.C.E.R.T.)*

Ans. K, Rb and Cs.

Q. 2. Name the metal which floats on water without any apparent reaction with it. *(N.C.E.R.T.)*

Ans. Li.

Q. 3. Name the chief factor responsible for the anomalous behaviour of lithium. *(N.C.E.R.T.)*

Ans. Small size, high electronegativity and high ionization enthalpy.

Q. 4. Name the element which is invariably bivalent and whose oxide is soluble in excess of NaOH and its dipositive ion has noble gas core. *(N.C.E.R.T.)*

Ans. Be ; BeO dissolves in alkali to form beryllates.

Q. 5. Mention the main constituents of Portland cement ? *(N.C.E.R.T.)*

Ans. Dicalcium silicate, tricalcium silicate and tricalcium aluminate.

Q. 6. Draw the structure of (*i*) $BeCl_2$ (vapour) (*ii*) $BeCl_2$ (*s*). *(N.C.E.R.T.)*

Ans. Refer to the text.

Q. 7. What happens when KO_2 reacts with water ? Write the balance chemical equation for the reaction. *(N.C.E.R.T.)*

Ans. $2\,KO_2 + 2\,H_2O \longrightarrow 2\,KOH + H_2O_2 + O_2$.

Q. 8. Predict giving reason the outcome of the reaction, *(N.C.E.R.T.)*

$LiI + KF \longrightarrow$

Ans. $LiI + KF \longrightarrow LiF + KI$; larger cation stabilizes larger anion.

Q. 9. Name one reagent or one operation to distinguish between
(*i*) $BeSO_4$ and $BaSO_4$ (*ii*) $Be(OH)_2$ and $Ba(OH)_2$ (N.C.E.R.T.)

Ans. (*i*) $BeSO_4$ is soluble in H_2O while $BaSO_4$ is not (*ii*) $Be(OH)_2$ dissolves in alkali but $Ba(OH)_2$ does not.

Q. 10. Why does beryllium show similarities with aluminium ? (N.C.E.R.T.)

Ans. Due to same electronegativity $(1\cdot5)$ and very similar polarizing power ($Be^{2+} = 0\cdot064$ and $Al^{3+} = 0\cdot060$) of their ions.

Q. 11. Arrange the following in order of the increasing covalent character : MCl, MBr, MF, MI (where M = alkali metal). (N.C.E.R.T.)

Ans. As the size of the anion increases, covalent character increases and hence the order is $MF < MCl < MBr < MI$.

Q. 12. What is the general name for elements of group I ?

Ans. Alkali metals.

Q. 13. Which alkali metal is radioactive ? Give its atomic number also. (H.P.S.B. 2004)

Ans. Fr, Z = 87.

Q. 14. Name the alkali metal which shows diagonal relationship with magnesium.

Ans. Li.

Q. 15. Which alkali metal acts as the strongest reducing agent in aqueous solution ?

Ans. Li.

Q. 16. Name the alkaline earth metal which forms covalent compounds.

Ans. Be.

Q. 17. Which alkaline earth metal is radioactive ?

Ans. Ra.

Q. 18. Name the alkaline earth metal hydroxide which is amphoteric.

Ans. $Be(OH)_2$.

Q. 19. Why the elements of second row (first short period) show a number of differences in properties from other members of their respective families.

Ans. The difference in the properties of the first member of a group from those of the other members is due to (*i*) smaller size of the atom (*ii*) presence of one inner shell of only two electrons and (*iii*) absence of *d*-orbitals.

Q. 20. What is diagonal relationship due to ?

Ans. Similar size of atoms or ions, similar electronegativity or similar polarising power.

Q. 21. Why alkaline earth metals have a greater tendency to form complexes than the alkali metals.

Ans. Due to higher nuclear charge.

Q. 22. Alkali and alkaline earth metals cannot be obtained by chemical reduction method. Explain.

Ans. Since they are themselves stronger reducing agents than majority of the common reducing agents.

Q. 23. Why does table salt get wet in rainy season ?

Ans. Table salt contains impurities of $CaCl_2$ and $MgCl_2$ which being deliquescent compounds absorb moisture from the air in rainy season.

Q. 24. Why is sodium metal kept under kerosene oil ?

Ans. Na metal is highly reactive and combines with moisture, O_2 and CO_2 of the air forming NaOH, Na_2O and Na_2CO_3 etc. Therefore, to protect Na from moisture and air, it is kept under kerosene oil.

Q. 25. What are the raw materials used for the manufacture of washing soda by Solvay process ?

Ans. NaCl, $CaCO_3$ and NH_3.

Q. 26. Why is calcium preferred over sodium to remove last traces of moisture from alcohol ?

Ans. Both Na and Ca react with water forming their respective hydroxides. In contrast, Na reacts with alcohol to form sodium alkoxide but Ca does not.

Q. 27. Bones contain calcium ions. What do you think would be the anion associated with them ?

Ans. PO_4^{3-} ion.

Q. 28. Give one important ore of each of sodium and potassium.

Ans. Na : NaCl and K : KCl.

Q. 29. Give two ores of magnesium.

Ans. Carnallite ($KCl.MgCl_2.6H_2O$) and magnesium chloride ($MgCl_2$).

Q. 30. The second ionization enthalpy of calcium is more than that of the first and yet calcium forms $CaCl_2$ and not CaCl. Why? *(N.C.E.R.T.)*

Ans. The higher enthalpy of lattice formation by Ca^{2+} ions more than compensates the higher ionization enthalpy of calcium.

Q. 31. Give the chemical formula of dolomite and carnallite.

Ans. $CaCO_3.MgCO_3$ and $KCl.MgCl_2.6H_2O$.

Q. 32. What is the formula of gypsum ? What happens when it is heated ?

Ans. $CaSO_4.2H_2O$. When heated to 393 K, it gives Plaster of Paris ($CaSO_4.1/2H_2O$) but at 473 K it gives dead burnt plaster ($CaSO_4$).

Q. 33. What is quick lime ? What happens when we add water to it ?

Ans. CaO, slaked lime, $Ca(OH)_2$ is formed.

Q. 34. What is the formula of Plaster of Paris ?

Ans. $CaSO_4.\frac{1}{2}H_2O$.

Q. 35. What is dead burnt plaster ?

Ans. Anhydrous $CaSO_4$ which has no tendency to absorb H_2O is called dead burnt plaster.

Q. 36. What is Epsom salt ? What is the action of heat on it ?

Ans. $MgSO_4.7\,H_2O$; $MgSO_4.7\,H_2O \xrightarrow[-6H_2O]{423K} MgSO_4\,.\,H_2O \xrightarrow[-H_2O]{573K} MgSO_4 \xrightarrow{Heat} MgO+SO_3$.

Q. 37. Why is it necessary to add gypsum in the final stage of preparation of cement ?

Ans. Gypsum is added to slow down the process of setting of cement and thus imparting greater strength to it.

Q. 38. What is fly ash ?

Ans. It is a waste product from steel industry and has properties similar to that of cement. It mainly consists of calcium silicate.

Q. 39. Why cannot sodium and potassium be prepared by the electrolysis of their aqueous solutions ?

Ans. The electrode potential i.e. reduction potential of Na (– 2·71 V) or K (– 2·92) is much lower than that of H_2O (– 0·83 V), therefore, upon electrolysis, water gets reduced in preference to Na^+ or K^+ ions. In other words, sodium and potassium cannot be obtained by electrolytic reduction of Na^+ or K^+ ions in aqueous solution.

Q. 40. Amongst alkali metals, why is lithium regarded as most apt reducing agent in aqueous solutions ? *(D.S.B. 2001)*

Ans. Amongst alkali metals, Li^+ has the smallest size and hence has the highest hydration energy. In other words, it has the lowest electrode potential ($E° = —3·04$ V), *i.e.*, it has the maximum tendency to lose electrons and hence is *the strongest* (most apt) *reducing* agent amongst alkali metals.

Q. 41. State any one reason for alkaline earth metals having a greater tendency to form complexes than alkali metals. *(D.S.B. 2001)*

Ans. Because of smaller size and higher charge on alkaline earth metal cations as compared to the corresponding alkali metal cations, alkaline earth metal cations have a greater tendency to form complexes.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 12.1.

1. What are *s*-block elements ?
2. Comment on the statement, "The first element of a group shows anomalous behaviour with respect to the rest of the members of the group."
3. What is meant by diagonal relationship in the periodic table ? What is it due to ? *(N.C.E.R.T.)*
4. What is the cause of diagonal similarity ? *(A.I.S.B. 1992)*

Sec. 12.2. to 12.8.

5. Why are the elements of group 1 called the alkali metals ?
6. Name the alkali metals in order of increasing atomic masses and write their electronic configurations.
7. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information ? *(N.C.E.R.T.)*
8. Account for the following :
   (*i*) Alkali metals show only +1 oxidation state.
   (*ii*) The hydroxides of alkali metals are strong bases. *(P.S.B. 2000)*
   (*iii*) Na and K impart colour to the flame but Mg does not.
   (*iv*) Li is the best reducing agent in aqueous solution. *(H.S.B. 2004)*
9. Discuss the diagonal relationship of lithium with magnesium.
10. List three properties of lithium in which it differs from rest of the alkali metals. *(N.C.E.R.T.)*
11. Discuss the anomalous behaviour of lithium in its group. Compare the properties of lithium with those of magnesium. *(H.S.B. 2004 C)*
12. Alkali metals have low ionization energies. Why is it so ? *(A.I.S.B. 1993)*
13. Account for the following
    (*i*) There is a striking similarity between Li and Mg. *(A.I.S.B. 1994)*
    (*ii*) Alkali metals are difficult to reduce. *(H.P.S.B. 1994)*
14. Why alkali metals and their salts give characteristic colour to the flame ? *(H.S.B. 2001)*
15. When an alkali metal dissolves in liquid ammonia, the solution acquires different colours. Explain the reasons for this type of colour change. *(N.C.E.R.T.)*
16. What happens when
    (*i*) sodium metal is dropped in water ?
    (*ii*) sodium metal is heated in a free supply of air ?
    (*iii*) sodium peroxide dissolves in water *(N.C.E.R.T.)*
17. Explain what happens when
    (*i*) sodium hydrogen carbonate is heated
    (*ii*) sodium amalgam reacts with water
    (*iii*) fused sodium metal reacts with ammonia. *(N.C.E.R.T.)*
18. Write balanced equations for reactions between
    (*a*) Na_2O_2 and water
    (*b*) KO_2 and water
    (*c*) Na_2O and CO_2. *(N.C.E.R.T.)*
19. Comment on each of the following observations :
    (*a*) The mobilities of alkali metal ions in aqueous solution are : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(*b*) Lithium is the only alkali metal to form a nitride directly

(*c*) LiF is least soluble among the fluorides of alkali metals

(*d*) LiF is more soluble than KF in ethanol.

(*e*) LiI is more soluble than KI in ethanol. *(N.C.E.R.T.)*

20. State as to why

(*a*) lithium on being heated in air mainly forms the monoxide and not the peroxide *(N.C.E.R.T.)*

(*b*) sodium is stored in kerosene oil.

Sec. 12.9. to 12.11.

21. List some important minerals of lithium and sodium.

22. Enumerate the main difficulties encountered in the extraction of alkali metals by usual methods.

23. Sodium metal cannot be obtained by the electrolysis of aqueous sodium chloride solution. Why ?

24. Describe the extraction of sodium by Down's process. What precautions are taken for collecting sodium ?

25. Enlist some important uses of sodium and potassium metals.

26. Write equations for the reactions involved in making sodium bicarbonate from sodium chloride.

27. Discuss briefly the function of ammonia in solvay- ammonia process for manufacture of sodium carbonate.

28. Starting with sodium chloride how will you proceed to prepare (state the steps only)

(*i*) sodium metal

(*ii*) sodium hydroxide

(*iii*) sodium peroxide

(*iv*) sodium carbonate. *(N.C.E.R.T.)*

29. State as to why

(*a*) A solution of Na_2CO_3 is alkaline

(*b*) Alkali metals are prepared by electrolysis of their fused chlorides

(*c*) Sodium is found more useful than potassium.

30. Give reasons for the following :

(*i*) Sodium carbonate is prepared indirectly through sodium bicarbonate in Solvay-ammonia process.

(*ii*) Potassium carbonate cannot be prepared by Solvay- ammonia process. *(N.C.E.R.T.)*

31. What happens when :

(*i*) Carbon dioxide is passed through ammoniacal brine solution.

(*ii*) Carbon dioxide is passed through an aqueous solution of sodium carbonate.

(*iii*) Sodium hydrogen carbonate is heated

Sec. 12.12. to 12.22.

32. Why are elements of group 2 known as alkaline earth metals ?

33. Name the alkaline earth metals and give their electronic configurations.

34. Why are alkaline earth metals good reducing agents ?

35. Alkaline earth metals form ionic salts having bivalent cations. Justify the statement by giving reasons in favour of your answer. *(H.S.B. Sample Paper 1991)*

36. In what respects does $BeCl_2$ differ from the halides of other group 2 elements ?

37. What is diagonal relationship ? Discuss the diagonal relationship between Be and Al. Give the points of resemblance between Be and Al. *(J. & K. 1997; H.S.B. 2004)*

38. Explain the trend of solubility of carbonates, sulphates and hydroxides of alkaline earth metals down the group. *(P.S.B. 1992)*

39. The second ionization energy of an alkaline earth metal is higher than its first ionization energy. Why is it so ? *(A.I.S.B. 1993)*

40. Why do alkaline earth metals not occur in the free state ? Name some important minerals of magnesium.

41. How does magnesium occur in nature ? How is the magnesium metal obtained by the electrolysis method ?

42. Why alkaline earth metals cannot be obtained by reduction of their oxides with carbon ?

43. Give reasons for the following ?

(*i*) Alkaline earth metals do not occur free in nature.

(*ii*) Magnesium does not impart colour to the flame while calcium does.

(*iii*) Alkaline earth metals always form divalent cations even though the second ionization energies of these metals are almost double their first ionization energies.

(*iv*) A piece of burning magnesium ribbon continues to burn in SO_2.

(*v*) Be and Mg do not impart colour to the flame. *(H.S.B. 2004)*

44. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

45. Give three important uses of each of calcium and magnesium.

46. What happens when

(*i*) magnesium is burnt in air

(*ii*) quicklime is heated with silica

(*iii*) chlorine reacts with slaked lime

(*iv*) calcium nitrate is heated. *(N.C.E.R.T.)*

47. Commercial aluminium always contains some magnesium. Name two such alloys of aluminium. What properties are imparted by the addition of magnesium to these alloys ? *(N.C.E.R.T.)*

48. Beryllium exhibits some similarities with aluminium. Point out three such properties. *(N.C.E.R.T.)*

49. Like lithium in Group 1, beryllium shows anomalous behaviour in Group 2. Write three such properties of beryllium which make it anomalous in the group. *(N.C.E.R.T.)*

50. Complete the following equations for the reaction between

(*i*) $Ca + H_2O$

(*ii*) $BeOH + NaOH$

(*iii*) $Ca(OH)_2 + Cl_2$

(*iv*) $BaO_2 + H_2SO_4$. *(N.C.E.R.T.)*

51. Contrast the action of heat on the following and explain your answer :

(*i*) Na_2CO_3 and $CaCO_3$

(*ii*) $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$

(*iii*) $Ca(NO_3)_2$ and $NaNO_3$ *(N.C.E.R.T.)*

52. How will you explain ?

(*i*) BeO is insoluble but $BeSO_4$ is soluble in water

(*ii*) BaO is soluble but $BaSO_4$ is insoluble in water

(*iii*) E° for $M^{2+}\ (aq) + 2\ e^- \longrightarrow M\ (s)$ (where M = Ca, Sr or Ba) is nearly constant.

(*iv*) $NaHCO_3$ is known in solid state but $Ca(HCO_3)_2$ is not isolated in solid state. *(N.C.E.R.T.)*

53. Give one method of preparing quick lime. What happens when rain water falls on it ?

54. What is Epsom salt ? How is it prepared ? Enlist its important uses.

55. How is Plaster of Paris prepared ? Describe its chief property due to which it is widely used. *(N.C.E.R.T.)*

56. Differentiate between
(*a*) quick lime
(*b*) lime water
(*c*) slaked lime. (*N.C.E.R.T.*)

57. Describe two important uses of each of the following :
(*i*) quicklime
(*ii*) gypsum
(*iii*) calcium carbide
(*iv*) magnesium sulphate.

58. Describe the importance of the following :
(*i*) limestone
(*ii*) cement
(*iii*) Plaster of Paris. (*N.C.E.R.T.*)

Sec. 12.52. **59.** List the raw materials required for the manufacture of Portland cement ? What is the role of gypsum in it. (*N.C.E.R.T.*)

60. What is the effect of heat on the following compounds ? (Write equations for the reactions).
(*i*) Calcium carbonate
(*ii*) Magnesium chloride hexahydrate ?
(*iii*) Gypsum
(*iv*) Magnesium sulphate heptahydrate.

Long Answer Questions CARRYING 5 or more MARKS

Sec. 12.1. to 12.20. **1.** Discuss the position of lithium in the periodic table. How does it differ from other members of the family ? To what other elements in the periodic table does it resemble ? Justify your answer with suitable examples. (*A.I.S.B. 1990 C*)

2. Give general characteristics of alkali metals. Discuss the anomalous behaviour of lithium. Mention similarities shown by lithium towards magnesium ? (*A.I.S.B. 1992*)

3. List some importance ores of lithium. Discuss the various difficulties encountered in the extraction of alkali metals. Describe briefly the extraction of lithium from a silicate ore.

4. How is sodium obtained by the Down's process ? Write equations for the reactions involved. Why sodium cannot be obtained by electrolysis of an aqueous solution of sodium chloride ?

5. Describe in detail manufacture of sodium carbonate by the solvay process. State the principles involved in this process. (*N.C.E.R.T.*)

6. Why is it that *s*-block elements never occur free in nature ? What are their usual modes of occurrence and how are they generally prepared ? (*N.C.E.R.T.*)

7. Write three general characteristics of the elements of *s*-block of the periodic table which distinguish them from the elements of the other blocks. (*N.C.E.R.T.*)

8. Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals.
(*a*) nitrates (*c*) carbonates (*c*) sulphates (*N.C.E.R.T.*)

9. Mention the general trends in Group 1 and Group 2 with increasing atomic number with respect to (*i*) density (*ii*) melting point (*iii*) atomic size (*iv*) ionization enthalpy. (*N.C.E.R.T.*)

10. How do the following properties change on moving from Group 1 to Group 2 in the periodic table ?
(*i*) Atomic size
(*ii*) Ionization enthalpy
(*iii*) Density
(*iv*) Melting points. (*N.C.E.R.T.*)

11. Compare and contrast the chemistry of Group 1 metals with those of Group 2 metals with respect to
(*i*) nature of oxides
(*ii*) solubility and thermal stability of carbonates
(*iii*) polarizing power of cations
(*iv*) reactivity and reducing power. (*N.C.E.R.T.*)

12. The chemistry of beryllium is not essentially ionic. Justify the statement by making a reference to the nature of oxide, chloride, fluoride of beryllium. (*N.C.E.R.T.*)

13. Give any three points of similarity between beryllium and aluminium and two points of dissimilarity between beryllium and barium.

14. Describe three industrial uses of caustic soda. Describe one method of manufacture of sodium hydroxide. What happens when sodium hydroxide reacts with (*i*) aluminium metal (*ii*) CO_2 (*iii*) SiO_2 ? (*N.C.E.R.T.*)

Sec. 12.21 to 12.23.

15. Name chief forms of occurrence of magnesium in nature. How is magnesium extracted from one of its ores ? (*N.C.E.R.T.*)

16. Describe the manufacture of Portland cement., What is its approximate composition ?

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Sodium peroxide

Manufacture. It is manufactured by heating sodium metal on aluminium trays in CO_2 free air.

$$2\,Na + O_2\,(air) \longrightarrow Na_2O_2$$

Properties. (*i*) Pure Na_2O_2 is colourless. The faint yellow colour of the ordinary sodium peroxide is due to the presence of a small amount of sodium superoxide (NaO_2) as an impurity. The yellow colour, however, disappears when it comes in contact with moist air due to the formation of NaOH and Na_2CO_3. Thus,

$$4\,NaO_2 + 2CO_2 \longrightarrow 2\,Na_2CO_3 + 3\,O_2$$
$$2\,Na_2O_2 + 2H_2O \longrightarrow 4\,NaOH + O_2$$
$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

(*ii*) Sodium peroxide is a powerful oxidising agent. It oxidises

(*i*) Chromium (III) hydroxide to chromate ion

$$O_2^{2-} + 2\,H_2O + 2\,e^- \longrightarrow 4\,OH^- \quad] \times 3$$
$$Cr(OH)_3 + 5\,OH^- \longrightarrow CrO_4^{2-} + 4\,H_2O + 3\,e^- \quad] \times 2$$

$$2\,Cr(OH)_3 + 2\,O_2^{2-} \longrightarrow 2\,CrO_4^{2-} + 2\,OH^- + 2\,H_2O$$

(*ii*) *Manganese sulphate to sodium manganate*

$$MnSO_4 + 2\,Na_2O_2 \longrightarrow Na_2MnO_4 + Na_2SO_4$$

(*iii*) *Sulphides to sulphates*

$$S^{2-} + 3\,O_2^{2-} + 2\,H_2O \longrightarrow SO_4^{2-} + 4\,OH^-$$

Uses. (*i*) It is used for the purification of air in confined spaces such a submarines since it combines with CO_2 to form sodium carbonate and oxygen.

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

(*ii*) Because of its oxidising property, it is used as a bleaching agent.

(*iii*) Na_2O_2 is widely used in the manufacture of dyes and many chemicals such as benzoyl peroxide, sodium perborate etc.

2. Sodium hydroxide, Caustic soda, NaOH

Caustic soda is manufactured by the electrolysis of an aqueous solution of sodium chloride. The following two types of cells are used.

ADDITIONAL USEFUL INFORMATION contd.

(*a*) **The mercury cathode cell-(Castner-Kellner cell).** It consists of a large rectangular iron tank in which mercury flows at the bottom of the cell and is made the cathode. The brine solution flows in the same direction. The anode consists of a number of graphite blocks. When electricity is passed, electrolysis of brine occurs. Since hydrogen has a high over voltage at mercury cathode, sodium is preferentially discharged at the cathode which forms amalgam with mercury.

The sodium amalgam flows out and is reacted with water to give NaOH.

$$2\,Na.Hg + 2\,H_2O \longrightarrow 2\,NaOH + 2\,Hg + H_2$$

Hydrogen and chlorine are the two bye-products of this process.

(*b*) **Diaphragm cell-Nelson Cell.** In this cell, NaOH and Cl_2 are kept separate by the use of a diaphragm. It consists of a U-shaped perforated steel cathode lined on the inside with asbestos diaphragm and is suspended in a rectangular iron tank. The anode consists of a graphite rod and is suspended in the solution. On passing electricity, electrolysis begins ; Cl_2 is liberated at the graphite anode and NaOH is formed at the outside edges of the cathode.

(*c*) **Using Nafion Membrane Cell.** The natural brine is now electrolysed in a membrane cell in which cathode and anode are separated by NAFION membrane. Nafion is a copolymer of tetrafluoroethylene and perfluorosulphonylethoxy ether. The copolymer is supported on a teflon mesh. Plastic membranes (*e.g.* Nafion) are increasingly being used in diaphragm cells these days because of their lower resistance than asbestos.

Properties. (*i*) Sodium hydroxide is a deliquescent solid and absorbs moisture and carbon dioxide forming a hydrated solid carbonate.

$$2\,NaOH + CO_2 + 9\,H_2O \longrightarrow Na_2CO_3.10\,H_2O$$

(*ii*) Its aqueous solution contains a high concentration of OH^- ions and thus precipitates insoluble metal hydroxides from their aqueous solutions containing these cations :

$$Fe^{3+} + 3\,OH^- \longrightarrow \underset{\substack{\textbf{Ferric hydroxide}\\ \textit{(Reddish brown ppt.)}}}{Fe(OH)_3\downarrow}\;;$$

$$Cr^{3+} + 3\,OH^- \longrightarrow \underset{\substack{\textbf{Chrominium hydroxide}\\ \textit{(Green ppt.)}}}{Cr(OH)_3\downarrow}$$

The hydroxides of Al, Zn, Pb and Sn being amphoteric dissolve in excess of NaOH giving clear solutions.

$$Zn(OH)_2 + 2\,OH^- \longrightarrow \underset{\textbf{Zincate ion}}{[Zn(OH)_4]^{2-}}$$

or $$Zn + 2\,OH^- + 2\,H_2O \longrightarrow [Zn(OH)_4]^{2-} + H_2$$

$$Al(OH)_3 + 3\,OH^- \longrightarrow \underset{\textbf{Aluminate ion}}{[Al(OH)_6]^{3-}}$$

or $$2\,Al + 6\,OH^- + 6\,H_2O \longrightarrow 2\,[Al(OH)_6]^{3-} + 3\,H_2$$

These metals also dissolve in NaOH liberating H_2 gas.

Uses. NaOH is widely used in (*a*) soap, paper, textile and petroleum industry (*b*) the preparation of pure fats and oils and artificial silk.

C.B.S.E.-P.M.T. (MAINS) SPECIAL

Q. 1. **How is anhydrous magnesium chloride prepared from magnesium chloride hexahydrate ?**

Ans. Anhydrous $MgCl_2$ cannot be prepared by simply heating $MgCl_2 . 6\,H_2O$ because it gets hydrolysed by its own water of crystallization.

$$MgCl_2 . 6\,H_2O \longrightarrow MgO + 2\,HCl + 5\,H_2O$$

However, if hydrated magnesium chloride is heated in an atmosphere of HCl gas at 650 K, it checks the above hydrolysis reaction and the hydrated magnesium chloride now loses water of crystallization to form anhydrous magnesium chloride

$$MgCl_2 . 6\,H_2O \xrightarrow[650\,K]{HCl\ gas} MgCl_2 + 6\,H_2O.$$

Q. 2. **Account for the following :**

(*i*) $Be(OH)_2$ is insoluble but $Ba(OH)_2$ is fairly soluble in water.

(*ii*) $Be(OH)_2$ is amphoteric while $Mg(OH)_2$ is basic.

Ans. (*i*) This is because with increase in size (from Be to Ba) the lattice enthalpy decreases significantly but hydration enthalpy remains almost constant.

(*ii*) Because of higher sum of $IE_1 + IE_2$ of Be than that of Mg, the M—OH bond can break less easily in $Be(OH)_2$ than in $Mg(OH)_2$. In other words, *$Be(OH)_2$ acts as a weak base even weaker than $Mg(OH)_2$.*

Further because of smaller size and higher electronegativity than that of Mg, $Be(OH)_2$ can accept OH^- ions from alkalies to form beryllate ion but $Mg(OH)_2$ does not.

$$Be(OH)_2 + 2\,OH^- \longrightarrow Be(OH)_4^{2-} \longrightarrow \underset{\text{Beryllate ion}}{BeO_2^{2-}} + 2\,H_2O$$

$$Mg(OH)_2 + 2\,OH^- \not\longrightarrow Mg(OH)_4^{2-}$$

Thus, $Be(OH)_2$ acts as a weak acid but $Mg(OH)_2$ does not. Combining both the facts, we conclude that $Be(OH)_2$ is amphoteric but $Mg(OH)_2$ is basic.

Q. 3. **It is necessry to add gypsum in the final stages of preparation of cement. Explain why ?**

Ans. Gypsum ($CaSO_4.2H_2O$) is added in the final stages of preparation of cement since when H_2O is added to cement it slows down the process of setting of cement so that it gets sufficiently hardened thereby imparting greater strength to it.

Q. 4. **What is fly ash ?**

Ans. It is a waste product from iron industry and has properties similar to that of cement. It mainly consists calcium silicate ($CaSiO_3$).

Q. 5. **Give briefly the isolation of magnesium from sea water by the Dow process. Give equations for the steps involved.** *(I.I.T. 1993)*

Ans. See pages 12/30.

Q. 6. **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.** *(I.I.T. 1995)*

Ans. Mg_3N_2 is a salt of a strong base, $Mg(OH)_2$ and a weak acid (NH_3) and hence gets hydrolysed to give NH_3. In contrast, $MgCl_2$ is a salt of a strong base, $Mg(OH)_2$ and a strong acid, HCl and hence does not undergo hydrolysis to give HCl.

Q. 7. **The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why ?** *(I.I.T. 1997)*

Ans. Due to smaller size and higher nuclear charge, alkaline earth metals have a higher tendency than alkali metals to attract H_2O molecules and thus contain more water of crystallization than alkali metals. For example, $LiCl.2H_2O$ and $MgCl_2.6H_2O$.

Q. 8. **Chlorination of calcium hydroxide produces bleaching powder. Write its chemical equation.** *(I.I.T. 1998)*

Ans. Bleaching powder is obtained by passing Cl_2 into $Ca(OH)_2$. Though bleaching powder is often written as $Ca(OCl)_2$, it is actually a mixture.

$$3\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{Ca(OCl)_2 . Ca\,(OH)_2 . CaCl_2 . 2\,H_2O}$$

I.I.T. (MAINS) SPECIAL

Q. 1. **Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B.** *(I.I.T. 1996)*

Ans. Ca burns in air to form CaO and Ca_3N_2.

$$2\,Ca + O_2 \longrightarrow 2\,CaO$$

$$3\,Ca + N_2 \longrightarrow Ca_3N_2$$

Calcium nitride on hydrolysis with H_2O gives ammonia (A)

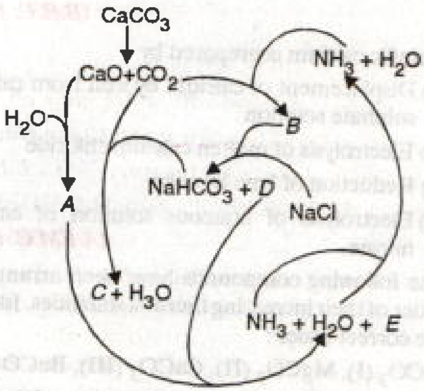
$$Ca_3N_2 + 6\,H_2O \longrightarrow 3\,Ca(OH)_2 + \underset{A}{2\,NH_3}$$

The alkaline solution of $Ca(OH)_2$ thus formed reacts with CO_2 present in the air to form $CaCO_3$(B).

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{B}{CaCO_3} + H_2O$$

Thus, A=NH_3 and B=$CaCO_3$] (white powder)

Q. 2. The Haber-process can be represented by the following scheme.



Identify A, B, C, D and E. *(I.I.T. 1999)*

Ans. (*i*) $CaO + H_2O \longrightarrow \underset{(A)}{Ca(OH)_2}$

(*ii*) $NH_3 + H_2O + CO_2 \longrightarrow \underset{(B)}{NH_4HCO_3}$

(*iii*) $2\,NaHCO_3 \longrightarrow \underset{(C)}{Na_2CO_3} + CO_2 + H_2O$

(*iv*) $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + \underset{(D)}{NH_4Cl}$

(*v*) $2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3 + 2\,H_2O + \underset{(E)}{CaCl_2}$

Thus, $A = Ca\,(OH)_2$,

$B = NH_4HCO_3$,

$C = Na_2CO_3$,

$D = NH_4Cl$

and $E = CaCl_2$.

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. The raw materials used in the manufacture of sodium carbonate by Solvay's process are :
   (*a*) Ammonia and carbon dioxide
   (*b*) Sodium chloride and carbon dioxide
   (*c*) Sodium chloride, limestone and carbon dioxide
   (*d*) Sodium chloride, limestone and ammonia.

2. Glauber's salt is
   (*a*) $FeSO_4.7H_2O$ (*b*) $MgSO_4.7H_2O$
   (*c*) $Na_2CO_3.10H_2O$ (*d*) $Na_2SO_4.10H_2O$.

3. Plaster of Paris is
   (*a*) $(CaSO_4)_2.H_2O$ (*b*) $CaSO_4.2H_2O$
   (*c*) $CaSO_4.H_2O$ (*d*) $CaSO_4$.

4. Which of the following is not present in cement ?
   (*a*) Gypsum (*b*) Clay
   (*c*) Alumina (*d*) Alum.

5. Which of the following has the lowest melting point?
   (*a*) LiCl (*b*) NaCl
   (*c*) KCl (*d*) RbCl.

6. Which of the following alkaline earth metal sulphates is least soluble in water ?
   (*a*) $BaSO_4$ (*b*) $MgSO_4$
   (*c*) $SrSO_4$ (*d*) $CaSO_4$.

7. The basic character of the oxides, MgO, SrO, K_2O, NiO and Cs_2O increases in the order :

A N S W E R S

1. *d* **2.** *d* **3.** *a* **4.** *d* **5.** *a* **6.** *a*

(*a*) $MgO > SrO > K_2O > NiO > Cs_2O$
(*b*) $Cs_2O < K_2O < MgO < SrO < NiO$
(*c*) $NiO < MgO < SrO < K_2O < Cs_2O$
(*d*) $K_2O < NiO < MgO < SrO < Cs_2O$.

8. Which of the following are arranged in increasing order of solubilities ?
(*a*) $CaCO_3 < KHCO_3 < NaHCO_3$
(*b*) $NaHCO_3 < KHCO_3 < CaCO_3$
(*c*) $KHCO_3 < NaHCO_3 < CaCO_3$
(*d*) $CaCO_3 < NaHCO_3 < KHCO_3$.

9. The thermal stability of alkaline earth metal carbonates decreases in the order :
(*a*) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
(*b*) $BaCO_3 > SrCO_3 > MgCO_3 > CaCO_3$
(*c*) $CaCO_3 > SrCO_3 > MgCO_3 > BaCO_3$
(*d*) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$.

10. Which of the following alkali metal halides has the lowest lattice energy ?
(*a*) LiF (*b*) NaCl
(*c*) KBr (*d*) CsI.

11. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of
(*a*) sodium atoms (*b*) sodium hydride
(*c*) sodium amide (*d*) solvated electrons.
(I.I.T. 1981)

12. Sodium reacts with water more vigorously than lithium because, it
(*a*) has higher atomic weight
(*b*) is a metal
(*c*) is more electropositive
(*d*) more electronegative *(I.I.T. 1981)*

13. The hydration energy of Mg^{2+} is greater than that of
(*a*) Al^{3+} (*b*) Na^+
(*c*) Be^{2+} (*d*) Mg^{3+} *(I.I.T. 1984)*

14. The compound insoluble in acetic acid is
(*a*) calcium oxide (*b*) calcium carbonate
(*c*) calcium oxalate (*d*) calcium hydroxide.
(I.I.T. 1986)

15. The metallic lustre exhibited by sodium is explained by
(*a*) diffusion of sodium ions
(*b*) oscillation of loose electrons
(*c*) excitation of free electrons
(*d*) existence of body centred cubic lattice.
(I.I.T. 1989)

16. Gypsum on heating to 390 K gives
(*a*) $CaSO_4.2H_2O$ (*b*) $CaSO_4$
(*c*) $CaSO_4. 1/2\,H_2O$ (*d*) SO_3 and CaO.
(C.P.M.T. 1993)

17. The by-product of Solvay ammonia process is
(*a*) Carbon dioxide (*b*) Ammonia
(*c*) Calcium chloride (*d*) Calcium carbonate.
(A.F.M.C. 1994)

18. The drying agent which absorbs carbon dioxide and reacts violently with water is
(*a*) Sodium carbonate (*b*) Alcohol
(*c*) Conc. H_2SO_4 (*d*) Calcium oxide.
(B.H.U. 1994)

19. Metallic calcium is prepared by
(*a*) Displacement of calcium by iron from calcium sulphate solution
(*b*) Electrolysis of molten calcium chloride
(*c*) Reduction of lime by coke
(*d*) Electrolysis of aqueous solution of calcium nitrate. *(A.F.M.C. 1994)*

20. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order :
K_2CO_3 (I), $MgCO_3$ (II), $CaCO_3$ (III), $BeCO_3$ (IV)
(*a*) I < II < III < IV (*b*) IV < II < III < I
(*c*) IV < II < I < III (*d*) II < IV < III < I
(I.I.T. 1996)

21. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in
(*a*) NO_2^+ and BaO_2 (*b*) KO_2 and AlO_2^-
(*c*) KO_2 only (*d*) BaO_2 only.
(I.I.T. 1997)

22. Property of alkaline earth metals that increases with their atomic number is
(*a*) ionization energy
(*b*) solubility of their hydroxides
(*c*) solubility of their sulphates
(*d*) electronegativity *(I.I.T. 1997)*

23. Calcium is obtained by the
(*a*) Roasting of limestone
(*b*) Electrolysis of a solution of calcium chloride in H_2O

ANSWERS

7. *c* **8.** *d* **9.** *a* **10.** *d* **11.** *d* **12.** *c* **13.** *b* **14.** *c* **15.** *b* **16.** *c*
17. *c* **18.** *d* **19.** *b* **20.** *b* **21.** *c* **22.** *b*

(*c*) Reduction of calcium chloride with carbon

(*d*) Electrolysis of molten anhydrous calcium chloride. *(C.B.S.E. P.M.T. 1997)*

24. For two ionic solids CaO and KI, identify the *wrong* statement among the following ?

(*a*) Lattice energy of CaO is much higher than that of KI

(*b*) KI is soluble in benzene

(*c*) CaO has high m.p.

(*d*) KI has high m.p. *(C.B.S.E. P.M.T. 1997)*

25. The compounds of alkaline earth metals have the following magnetic nature

(*a*) Diamagnetic (*b*) Paramagnetic

(*c*) Ferromagnetic (*d*) Antiferromagnetic *(M.P.P.M.T. 1998)*

26. The stability of the following alkali metal chlorides follows the order :

(*a*) LiCl > KCl > NaCl > CsCl

(*b*) CsCl > KCl > NaCl > LiCl

(*c*) NaCl > KCl > LiCl > CsCl

(*d*) KCl > CsCl > NaCl > LiCl *(M.P.P.M.T. 1998)*

27. Which of the following substances can be used for drying gases ?

(*a*) Calcium carbonate (*b*) Sodium carbonate

(*c*) Sodium bicarbonate (*d*) Calcium oxide. *(M.P.C.E.E. 1999)*

28. Epsom salt is

(*a*) $MgSO_4.7\ H_2O$ (*b*) $CaSO_4.H_2O$

(*c*) $MgSO_4.2\ H_2O$ (*d*) $BaSO_4.2\ H_2O$. *(M.P.C.E.E. 1999)*

29. Among the alkaline earth metals, the element forming predominantly covalent compound is

(*a*) Barium (*b*) Strontium

(*c*) Calcium (*d*) Beryllium. *(M.P.C.E.E. 1999)*

30. The solubility in water of sulphates down the Be group is : Be > Mg > Ca > Sr > Ba. This is due to

(*a*) Increase in melting point

(*b*) High ionization energy

(*c*) Higher coordination number

(*d*) All of these. *(A.I.I.M.S. 1999)*

31. Which of the following is the correct order of gradually decreasing basic nature of the oxides ?

(*a*) Al_2O_3, MgO, Cl_2O_7, SO_3

(*b*) Cl_2O_7, SO_3, Al_2O_3, MgO

(*c*) SO_3, Cl_2O_7, MgO, Al_2O_3

(*d*) MgO, Al_2O_3, SO_3, Cl_2O_7. *(D.C.E. 1999)*

32. Which one is used as an air purifier in space craft ?

(*a*) Quick lime (*b*) Slaked lime

(*c*) Potassium superoxide

(*d*) Anhydrous $CaCl_2$. *(D.C.E. 2000)*

33. The active constituent of bleaching powder is

(*a*) $Ca(OCl)_2$ (*b*) Ca(OCl)Cl

(*c*) $Ca(ClO_2)_2$ (*d*) $Ca(ClO_2)Cl$. *(A.F.M.C. 2000)*

34. Bleaching powder loses its power on keeping for a long time because

(*a*) it changes into calcium hypochlorate

(*b*) it changes into calcium chloride and calcium hydroxide

(*c*) it absorbs moisture

(*d*) it changes into calcium chloride and calcium chlorate. *(Karnatka C.E.T. 2000)*

35. The correct order of increasing ionic character is

(*a*) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$

(*b*) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$

(*c*) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$

(*d*) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$ *(A.F.M.C. 2000)*

36. KO_2 (potassium superoxide) is used in oxygen cylinders in space and submarines because it

(*a*) absorbs CO_2 and increases O_2 content

(*b*) eliminates moisture

(*c*) absorbs CO_2

(*d*) produces ozone *(A.I.E.E.E. 2002)*

37. A metal M readily forms water soluble sulphate MSO_4, water insoluble hydroxide $M(OH)_2$ and oxide MO which becomes inert on heating. The hydroxide is soluble in NaOH. The metal M is

(*a*) Be (*b*) Mg

(*c*) Ca (*d*) Sr *(A.I.E.E.E. 2002)*

38. Which of the following process is used in the extractive metallurgy of magnesium ?

(*a*) fused salt electrolysis

(*b*) self reduction

(*c*) aqueous solution electrolysis

(*d*) thermite reduction *(I.I.T. 2002)*

39. Identify the correct order of acidic strengths of CO_2, CuO, CaO, H_2O

ANSWERS

23. *d* **24.** *d* **25.** *a* **26.** *d* **27.** *d* **28.** *a* **29.** *d* **30.** *c* **31.** *d* **32.** *c*

33. *b* **34.** *d* **35.** *a* **36.** *a* **37.** *a* **38.** *a*

(*a*) $CaO < CuO < H_2O < CO_2$
(*b*) $H_2O < CuO < CaO < CO_2$
(*c*) $CaO < H_2O < CuO < CO_2$
(*d*) $H_2O < CO_2 < CaO < CuO$ *(I.I.T. 2002)*

40. The paramagnetic species is
(*a*) KO_2 (*b*) SiO_2
(*c*) TiO_2 (*d*) BaO_2
(A.I.I.M.S. 2003)

41. On dissolving moderate amount of sodium metal in liquid NH_3 at low temperature, which one of the following does not occur ?
(*a*) Blue coloured solution is obtained
(*b*) Na^+ ions are formed in the solution
(*c*) Liquid ammonia becomes good conductor of electricity
(*d*) Liquid ammonia remains diamagnetic.
(A.I.I.M.S. 2003)

42. The substance not likely to contain $CaCO_3$ is
(*a*) dolomite (*b*) a marble statue
(*c*) calcined gypsum (*d*) sea shells
(A.I.E.E.E. 2003)

43. Solubilities of carbonates decrease down the magnesium group due to decrease in
(*a*) entropy of solution formation
(*b*) lattice energies of solids
(*c*) hydration energy of cations
(*d*) inter-ionic attraction *(A.I.E.E.E. 2003)*

44. In curing cement plasters, water is sprinkled from time to time. This helps in
(*a*) converting sand into silicic acid
(*b*) keeping it cool
(*c*) developing interlocking needle like crystals of hydrated silicates
(*d*) hydrating sand and gravel mixed with cement
(A.I.E.E.E. 2003)

45. Mg and Li are similar in their properties due to
(*a*) same e/m ratio (*b*) same electron affinity
(*c*) same group (*d*) same ionic potential
(A.F.M.C. 2004)

46. Photoelectric effect is maximum in
(*a*) Cs (*b*) Na
(*c*) K (*d*) Li *(A.F.M.C. 2004)*

47. Which of the following metal has stable carbonates ?
(*a*) Na (*b*) Mg
(*c*) Al (*d*) Si *(A.F.M.C. 2004)*

48. A sodium salt of unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is
(*a*) SO_4^{2-} (*b*) HCO_3^-
(*c*) CO_3^{2-} (*d*) NO_3^- *(I.I.T. 2004)*

49. A solid compound 'X' on heating gives CO_2 gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of CO_2 through 'Y' in water, a clear solution 'Z' is obtained. On boiling 'Z', compound 'X' is reformed. The compound 'X' is
(*a*) $Ca(HCO_3)_2$ (*b*) $CaCO_3$
(*c*) Na_2CO_3 (*d*) K_2CO_3
(C.B.S.E. P.M.T. 2004)

50. One mole of magnesium nitride on reaction with an excess of water gives
(*a*) one mole of ammonia
(*b*) one mole of nitric acid
(*c*) two moles of ammonia
(*d*) two moles of nitric acid *(A.I.E.E.E. 2004)*

51. Which of the following is not a Mg ore ?
(*a*) Gypsum (*b*) Magnesite
(*c*) Dolomite (*d*) Carnallite
(C.P.M.T. 2004)

HINTS/EXPLANATIONS to Multiple Choice Questions

5. LiCl being covalent has the lowest m.p.

7. Alkali metal oxides are most basic followed by alkaline earth metal oxides while transition metal oxides are least basic. Amongst alkali and alkaline earth metal oxides, basicity increases down the group. Thus, Cs_2O is more basic than K_2O and SrO is more basic than MgO. Therefore, the overall order is $NiO < MgO < SrO < K_2O < Cs_2O$.

8. The solubility of bicarbonates of alkali metals increases down the group. But alkaline earth metal carbonates are insoluble in H_2O.

10. Bigger the size of the ions, larger is the distance (r) between their centres and lower is the lattice energy ($q_1 q_2 / r^2$).

13. Na^+ has +1 unit charge, Mg^{2+} and Be^{2+} have +2 unit charge while Mg^{3+} and Al^{3+} have +3 unit charge, therefore, hydration energy of Al^{3+} and Mg^{3+} is expected to be higher than those of Mg^{2+} and Be^{2+}, which in turn, are expected to be higher than that of Na^+. Further the hydration

ANSWERS

39. *a* **40.** *a* **41.** *d* **42.** *c* **43.** *c* **44.** *c* **45.** *d* **46.** *a* **47.** *a* **48.** *b*
49. *b* **50.** *c* **51.** *a*

energy of Be^{2+} is higher than that of Mg^{2+} due to its smaller size. In other words, hydration energy of Mg^{2+} is expected to be higher than that of Na^{+}.

14. CaO, $CaCO_3$ and $Ca(OH)_2$ are all bases and hence must dissolve in acetic acid to form calcium acetate. Only calcium oxalate does not dissolve in CH_3COOH.

21. Only KO_2 has an unpaired electron,

$$K^{+}\quad {}^{-}:\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot\cdot}{\dot{O}}:$$

24. Due to lower lattice energy of KI as compared to that of CaO, the m.p. of KI is much lower than that of CaO.

26. The stability of a compound depends upon its enthalpy of formation, $\Delta H°_f$. Evidently more negative the value of $\Delta H°_f$, more stable is the compound. (Refer to Table 12.3 on page 12/10). Thus, option (*d*) is correct, *i.e.*, KCl (—428) > CsCl (—424) > NaCl (—400) > LiCl (—399). The values given in parentheses are in kJ mol^{-1}.

30. As the size increases, the extent of hydration, *i.e.*, coordination number decreases and hence the solubility decreases accordingly.

31. MgO is basic, Al_2O_3 is amphoteric SO_3 and Cl_2O_7 both are acidic but Cl_2O_7 is more acidic than SO_3. Therefore, option (*d*) is correct.

35. As the size of the cation increases, electronegativity decreases and hence the electronegativity difference increases and hence ionic character increases accordingly.

36. $4\,KO_2 + 2\,CO_2 \longrightarrow 2\,K_2CO_3 + 3\,O_2$

Although KO_2 also reacts with moisture of the breath but does not completely eliminate it.

$4\,KO_2 + 2\,H_2O \longrightarrow 4\,KOH + 3\,O_2$

For further explanation, refer to page 12/14.

37. BeO being amphoteric dissolves in NaOH.

39. H_2O is a neutral oxide. Non-metallic oxides, (*i.e.* CO_2) are acidic white metallic oxides (*i.e.* CaO and CuO) are basic. However, oxides of alkaline earth metals are more basic than oxides of transition metals. Thus, the overall acid strength decreases in the order : CaO < CuO < H_2O < CO_2.

45. Li^{+} and Mg^{2+} ions have similar polarising power or ionic potential.

48. Bicarbonates on heating form insoluble carbonates

$$MgCl_2 + 2\,NaHCO_3 \longrightarrow NaCl + Mg(HCO_3)_2$$

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

49. $\underset{(X)}{CaCO_3} \xrightarrow{\Delta} CO_2 + CaO$

$$CaO + H_2O \longrightarrow \underset{(Y)}{Ca(OH)_2}$$

$$Ca(OH)_2 + \underset{(excess)}{2\,CO_2} \longrightarrow \underset{Z}{Ca(HCO_3)_2}$$

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

50. $Mg_3H_2 + 3\,H_2O \longrightarrow 3\,Mg(CH)_2 + 2\,NH_3$

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT, but reason is CORRECT.

	Assertion (Column 1)	Reason (Column 2)
1.	Magnesium can be obtained by the electrolysis of aqueous $MgCl_2$.	The reduction potential of Mg^{2+} is far lower than that of H^+.
2.	Common salt becomes damp after some time on keeping in air.	Common salt is NaCl which is hygroscopic in nature.
3.	Magnesium keeps on burning in CO_2.	Magnesium reduces CO_2 to C.
4.	Calcium and magnesium oxides are not reduced by carbon.	Calcium and magnesium oxides react with carbon to form their respective carbides.
5.	Li^+ (*aq*) has larger ionic radius than that of Na^+ (*aq*).	Li^+ (*aq*) is relatively more extensively hydrated as composed to Na^+ (*aq*).
6.	Potassium can be obtained by the electrolysis of fused KCl in molten $CaCl_2$.	Metallic potassium is soluble in melt (molten $CaCl_2$). Thus, the cell for electrolysis gets short circuited.
7.	The alkali metals are strong reducing agents.	They have only one electron to be lost from their valence shells.
8.	Potassium carbonate cannot be manufactured by a process similar to the Solvay's soda ammonia process.	Potassium hydrogen carbonate is less soluble in water than sodium hydrogen carbonate.
9.	Li resembles Mg.	Li^+ has same size as Mg^{2+} *(A.I.I.M.S. 1997)*
10..	Na_2SO_4 is soluble in water while $BaSO_4$ is insoluble.	Lattice energy of barium sulphate exceeds its hydration energy. *(A.I.I.M.S. 1997)*
11.	The alkali metals can form ionic hydrides which contain the hydride ion, H^-.	The alkali metals have low electronegativity ; their hydrides conduct electricity when fused and liberate hydrogen at the anode. *(I.I.T. 1995)*
12.	Sodium ions are discharged in preference to hydrogen ions at a mercury cathode.	The nature of cathode can affect the order of discharge of cations. *(A.I.I.M.S. 1996)*
13.	Alkali metals impart colour to the flame.	Their ionizaton energies are low. *(A.I.I.M.S. 1998)*
14.	Sulphur is estimated as $BaSO_4$ and not as $MgSO_4$.	The ionic radius of Mg^{2+} is smaller than that of Ba^{2+}. *(I.I.T. 1998)*
15.	LiCl is predominantly covalent compound.	Electronegativity difference between Li and Cl is too small. *(I.I.T. 1998)*
16.	$Al(OH)_3$ is amphoteric in nature.	Al—O and O—H bonds can be broken with equal ease in $Al(OH)_3$. *(I.I.T. 1998)*
17.	Barium is not required for normal biological function in human.	Barium does not show variable oxidation state. *(A.I.I.M.S. 2003)*
18.	Barium carbonate is more soluble in HNO_3 than in plain water.	Carbonate is a weak base and reacts with the H^+ from the strong acid causing the barium salt to dissociate. *(A.I.I.M.S. 2003)*
19.	Mg is not present in enamel of human teeth.	Mg is an essential element for biological functions of human. *(A.I.I.M.S. 2004)*

True/False Statements

Which of the following statements are true and which are false ?

1. Elements found in the combined state are often present as oxides, carbonates, sulphides and silicates.
2. All alkali metal hydroxides are strong bases.
3. Sodium carbonate is called soda ash.
4. Magnesium imparts pink colour to the flame.
5. Dead burnt plaster can be used as a desiccant.
6. Calcium is present in the bones of animals and human beings as phosphates.
7. Mg and Ca form dipositive ions due to their high hydration energies.
8. Solvay-ammonia process is used for the manufacture of caustic soda.

9. Lithium resembles magnesium since their electronegativities are almost the same.

10. Lithium burns in nitrogen to give lithium nitride.

11. Beryllium is more electropositive than magnesium.

12. Alkaline earth metals are better reducing agents than alkali metals.

13. Beryllium resembles aluminium closely in its properties though it belongs to a different group.

14. Magnesium is an essential constituent of chlorophyll, the green colouring matter of plants.

15. Sodium when burnt in excess of oxygen gives sodium oxide. *(I.I.T. 1987)*

16. In group 1 of alkali metals, the ionization potential decreases down the group. Therefore, Lithium is a powerful reducing agents.

Fill In The Blanks

1. Highly electropositive metals like alkali metals are obtained by .... .
2. Magnesium burns in air to give......and....... .
3. Lithium resembles more with......than with sodium.
4. Be(OH)$_2$ is.......and thus dissolves in alkalies as well as acids.
5. Lithium nitrate on heating gives........and........ .
6. Na$_2$CO$_3$ is........in water but BaCO$_3$ is........ .
7. In Solvay process, excess of........is passed through sodium chloride solution which has been previously saturated with........ .
8. Sodium is obtained by the electrolysis of .... as well as .... in their molten state.
9. During electrolytic extraction of Mg from MgCl$_2$, ... is added to lower the melting point of the electrolyte.
10. Calcium oxide is commonly known ..... while calcium hydroxide is called ..... .
11. The.......of Be is highest among the alkali metals.
12. The alkali metal hydroxides are......and the basicity of the hydroxide with increase in size of the cation.
13. Among alkaline earth metals, ... salts impart red colour while ..... salts do not impart any colour to the flame.
14. Ca is extracted by the electrolysis of a fused mixture of ..... and ..... .
15. Ca^{2+} has a smaller ionic radius than K^{+} because it has ..... . *(I.I.T. 1993)*
16. On heating, Rb(ICl$_2$) will decompose giving......... and......... *(I.I.T. 1997)*
17. A solution of sodium in liquid ammonia at –33°C conducts electricity. On cooling, the conductivity of this solution........

Matching Type Questions

Match items given in Column A against those given in Column B.

Column A	**Column B**
1. Alkali metals are extracted by	(*a*) Flame test
2. Sodium chloride	(*b*) *s*-Block elements
3. Sodium bicarbonate is used in	(*c*) Fire extinguishers
4. Alkali metals are	(*d*) Reducing agents
5. Alkaline earth metals are	(*e*) Electrolytic method
6. Magnesium does not ive	(*f*) An ore of sodium

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*d*) **2.** (*c*) **3.** (*a*) **4.** (*a*) **5.** (*a*) **6.** (*d*) **7.** (*a*) **8.** (*c*) **9.** (*a*) **10.** (*a*) **11.** (*a*) **12.** (*a*) **13.** (*a*) **14.** (*b*) **15.** (*c*) **16.** (*a*) **17.** (*b*) **18.** (*a*) **19.** (*b*).

TRUE/FALSE STATEMENTS

1. True **2.** True **3.** True **4.** False, does not impart any colour **5.** False **6.** True **7.** True **8.** False, washing soda **9.** True **10.** True **11.** False, Mg is more electropositive than Be **12.** False, alkali metals because of their more electronegative standard electrode potentials are better reducing agents than alkaline earth metals. **13.** True, diagonal relationship. **14.** True **15.** False, Na_2O_2 **16.** False, electrode potential of Li in the most negative amongst the alkali metals and hence it is the strongest reducing agent.

FILL IN THE BLANKS

1. electrolytic reduction **2.** MgO, Mg_3N_2 **3.** magnesium **4.** amphoteric **5.** NO_2, Li_2O and O_2 **6.** soluble, insoluble **7.** carbon dioxide, ammonia **8.** sodium chloride, sodium hydroxide **9.** NaCl and $CaCl_2$ **10.** quick lime, slaked lime **11.** ionization energy or electronegativity. **12.** strong bases, increases. **13.** Ca^{2+}, Mg^{2+} **14.** $CaCl_2$, CaF_2 **15.** higher effective nuclear charge **16.** RbCl and ICl **17.** increases.

MATCHING TYPE QUESTIONS

1. (*e*) **2.** (*f*) **3.** (*c*) **4.** (*d*) **5.** (*b*) **6.** (*a*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

1. *Correct assertion* : Mg can be obtained by the electrolysis of fused $MgCl_2$.

2. *Correct reason* : NaCl contains impurities of $MgCl_2$, $CaCl_2$, $MgSO_4$, $CaSO_4$ etc. which are hygroscopic.

6. *Correct assertion* : K cannot be obtained by the electrolysis of fused KCl in molten $CaCl_2$.

8. *Correct reason* : $KHCO_3$ is more soluble in H_2O than $NaHCO_3$.

14. *Correct explanation.* $BaSO_4$ is insoluble while $MgSO_4$ is soluble.

15. *Correct reason.* Because of small size Li prefers to share rather than donating electrons.