UNIT 4 ALKALI METALS

Structure

4.1 INTRODUCTION

You have studied the classification of the elements and the periodicity in their various atomic properties in Units 1 and 2. You must be well acquainted now with the concept of periodicity observed in the properties of elements. Presuming this, let us start proper group study from the s-block elements. In the previous unit, we discussed hydrogen separately as its properties resemble the Group 1 elements in some respects and the Group 17 elements in others.

The elements of Group 1 and Group 2 are called the s-block elements because the outermost electron(s) in these elements occupy the s-orbital. In this unit, we will take up Group 1 elements, which are some of the most reactive elements. Group 1 consists of the elements Li, Na, K, Rb, Cs and Fr. They are called **alkali metals** because they form hydroxides which are strong alkalies. We will discuss in this unit, the general trends in properties and the comparative behaviour of theGroup 1 elements. One important fact which you will notice here, and later in subsequent groups also, is that the first member in all the groups behaves 'abnormally' which means that the first member of each group is rather different in its properties from the rest of the members of the same group. All the Group 1 elements are metals. Of these, francium is in the form of a short lived radioactive isotope and will not be discussed in detail here.

Objectives

After studying this unit, you should be able to:

- outline the occurrence of Group 1 elements and their isolation,
- list their uses,
- describe the general characteristics of Group 1 elements,
- explain the stability of alkali metal salts,
- explain the solvation phenomenon of the metals,
- describe the complexation tendency of the alkali metals, and
- explain the anomalous nature of lithium.

4.2 OCCURRENCE, EXTRACTION AND USES

Alkali metals are useful as metals as well as in the form of their compounds. Let us see how they occur in nature and also how they are extracted from their compounds. We will also discuss some of their important uses.

Occurrence

Before describing the chemistry of the elements of Group 1, let us first see how they are present in nature. The alkali metals are highly reactive, so they do not occur in the free state in nature. They occur in the combined form in the earth's crust in the following relative abundance: sodium 2.27%, potassium 1.84% and lithium, rubidium and caesium in trace amounts $1.8 \times 10^{-3}\%$, $7.8 \times 10^{-3}\%$ and $0.26 \times 10^{-3}\%$, respectively. Sodium as sodium

Sea water is actually a 3% solution of various salts, out of which 98% is sodium chloride.

chloride is the most abundant metal in sea water (~1.08%). Lithium occurs in alumino-silicate rocks, e.g., spodumene, $LiAl (SiO_3)_2$ and lepidolite, $(Li, Na, K)_2 \cdot l_2 (SiO_3)_3 (F, OH)_2$, sodium in rock salt, $NaCl$, Chile saltpetre, $NaNO_3$ and cryolite, Na_3AlF_6; potassium in carnallite, $KCl.MgCl_2.6H_2O$, saltpetre KNO_3, and kainite, $KCl.MgSO_4.3H_2O$. Rubidium and caesium are rare elements and generally occur in small quantities along with other alkali metals. For example, carnallite contains upto 0.04 per cent rubidium chloride and lepidolite, a lithium ore contains about 0.2 to 0.7 per cent of caesium expressed as caesium oxide. Francium being a radioactive element with a very short half-life period (21.8 minutes) occurs in very minute traces in nature.

Extraction

Lithium and sodium are extracted by electrolysis of their fused (molten) chlorides. Potassium is obtained by the reduction of its chloride with sodium vapour. This reduction by Na appears to be contrary to the normal order of reactivity, K>Na. However, at about 1150 K the following equilibrium is set up:

$$Na (g) + K^+ (l) \rightleftharpoons Na^+ (l) + K(g).$$
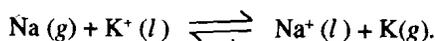
Since potassium is more volatile, it distils off more readily displacing the equilibrium to the right and allowing the forward reaction to proceed. Rubidium and caesium, can be prepared by the reduction of their chlorides with calcium metal at 1000 K under reduced pressure. Rubidium and caesium salts are obtained during the recrystallisation of other naturally occurring alkali metal salts. Francium is produced as a result of α—emission (1%) during the radioactive decay of actinium, as shown in Fig. 4.1.
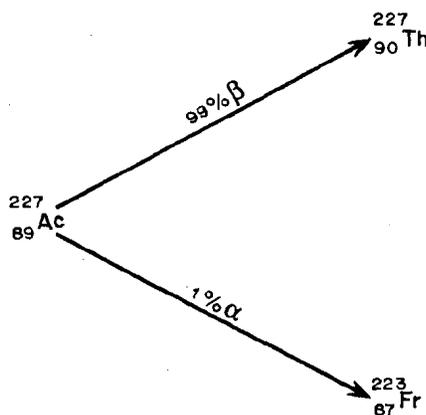

Fig. 4.1 : Production of francium from actinium as a result of α-decay.

Uses

The alkali metals are very good conductors of heat and electricity. But due to their highly reactive nature, they cannot be used for this purpose. Sodium in polyethylene enclosed cables is used in some underground high voltage transmission applications. Because of the high specific heat and thermal conductivity, liquid sodium is used as coolant in nuclear reactors. You must have seen bright yellow lights on the streets and particularly on the highways. These are sodium vapour lamps and the light from them can penetrate the fog well.

Caesium has the distinction of being the metal from which electrons are ejected most easily on exposure to light. This phenomenon is called photoelectric effect. Photocells, which are a device for converting light into electricity are based on this phenomenon.

Besides the above uses as metals, alkali metal compounds have a variety of applications. Lithium in the form of lithium stearate is used for the production of lubricating greases. The hydrides of lithium and sodium, viz., $LiAlH_4$ and $NaBH_4$ are used as reducing agents in synthetic organic chemistry. Lithium and potassium compounds are used in picture tubes of colour televisions.

Can you imagine food without common salt! Apart from being an essential constituent of food, sodium chloride has many other important industrial uses like in the manufacture of NaOH, Na_2CO_3, Cl_2 and H_2 gases. Other compounds of sodium also have many uses. Caustic soda or sodium hydroxide is used in making soaps, sodium carbonate also known as

washing soda, in laundering and in manufacture of glass, sodium bicarbonate as baking soda in baking powder, in medicine and in fire extinguishers.

Baking soda (sodium bicarbonate) puts out fires.

Potassium compounds also have many uses, like potassium hydroxide is used in liquid detergents, potassium superoxide in breathing apparatus, potassium chlorate in matches and explosives, and potassium bromide (KBr) in photography. Potassium nitrate is used along with charcoal and sulphur in gun powder. Potassium is a major component of plant fertilisers also where it is used in the form of chloride and nitrate salts.

4.3 GENERAL CHARACTERISTICS

Now let us study some of the physical and chemical properties of Group 1 elements. All the elements of Group 1 have one electron in their outermost orbital. Because of the similar outer electronic configuration of these elements, many similarities in their chemical behaviour are to be expected. However, lithium shows considerable differences from the rest of the elements of Group 1 about which we will discuss later in Section 4.7.

4.3.1 Physical Properties

Most of the physical properties are directly related to atomic properties of elements. Variation of the physical properties from one element to the other in a group is governed by the trends of the various atomic properties which we have already discussed in Unit 2. Let us apply them to understand the group trends in the various physical properties of the Group 1 elements given in Table 4.1.

Table 4.1: Properties of the Group 1 metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs
Atomic number	3	11	19	37	55
Electronic configuration	$[He]2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$
Atomic weight	6.939	22.898	39.102	85.47	132.905
Covalent radius (pm)	123	156	203	216	235
Ionic radius (pm)	60	95	133	148	169
Boiling point (K)	1620	1154	1038	961	978
Melting point (K)	453	371	337	312	301.5
Density (10^3 x kg m^{-3})	0.53	0.97	0.86	1.53	1.87
Electronegativity (Pauling)	1.0	0.9	0.8	0.8	0.7
Electronegativity (A/R)	1.15	1.0	0.9	0.9	0.85
Ionisation energy (kJ mol^{-1})	520	495	418	403	374

Atomic Size

If you recall Unit 2, you will see that alkali metals are the largest in their corresponding

periods in the periodic table. The size of the atom or its ion increases on descending the group (Table 4.1). This is due to the addition of an extra shell of electrons as we move down the group from one element to the next. The addition of the extra shell of electrons . outweighs the effect of increased nuclear charge and thus there is an increase in size from Li to Cs. This trend is shown in Fig. 4.2.
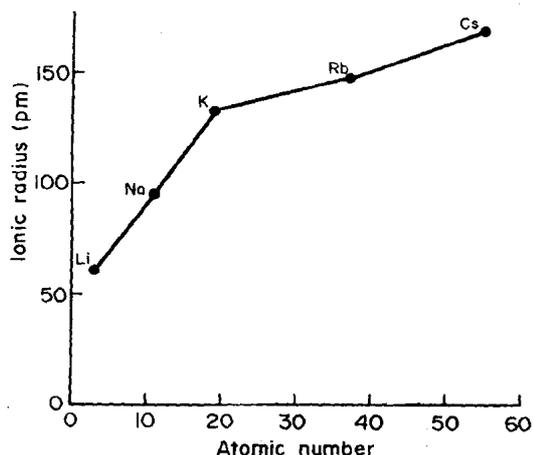
Fig. 4.2: Trend in ionic radii of Group 1 elements.

Density

Related to atomic size is the density of the elements. Density can be defined as mass per unit volume. For solids, the density is a function of atomic weight, size of the atom and the structure of the solid which determines the closeness of the packing of the atoms. There are two general trends observed in the densities of the elements in the periodic table. Along a period there is a general increase in density because of the increase in atomic mass and decrease in the size of the atom. Thus, in a particular period the alkali metals have the lowest density, considering the solid elements only. In a group also, density increases on going down the group. Since the elemental structures are often the same within any group, the factors which determine the density are atomic mass and volume. As you can see from Table 4.1, density increases as we move from Li to Cs. This means that the increase in atomic weight from one element to the next in passing down the group overweighs the effect of increase in the size of the atom. There are, however, some exceptions to this general trend and in this particular group of alkali metals, you can see from Table 4.1 that the density of potassium is less than that of sodium. Thus, potassium is an exception in this trend.

Melting Points and Boiling Points

These metals are soft and can be cut with a knife. As a result of increase in size and repulsion of the non-bonded electrons, their cohesive energy and tendency for metallic bonding decrease down the group and thus softness increases as we go down from Li to Cs. These metals have low melting and boiling points which also reflect the low values of cohesive energy between the atoms. Their melting and boiling points decrease as we go down the group. This trend in their melting points is shown in Fig. 4.3.
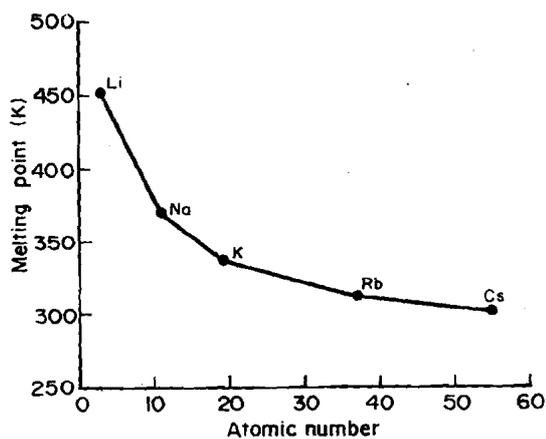
Fig. 4.3: Trend in the melting point of Group 1 elements.

Thermal and Electrical Conductivity

In alkali metals, electrons of the noble gas core efficiently shield the lone valence shell electron from the nuclear charge. Therefore, the effective nuclear charge felt by the electron in the valence shell of an atom of an alkali metal is the least and their atoms are the largest in respective periods. As a consequence, the sole valence electron is very loosely held by the nucleus. It can move freely from one metal ion to the other in the lattice, thereby the alkali metals are good conductors of heat and electricity. This loosely bound electron is also responsible for the silvery lustre of the alkali metals when freshly cut!

Ionisation Energy

By losing the loosely bound solitary outermost electron, these elements can acquire the electronic configuration of the preceding noble gas elements. They have, therefore, a high tendency of giving up this electron to form univalent cations. Their first ionisation energies are the lowest in the respective periods and so, they are the most reactive of all the metals. As we go down the group, their atomic size increases, their ionisation energies decrease, resulting in an increase in their reactivity. The effective nuclear charge felt by the electrons increases after the removal of one electron from the atom of any element and hence, their second ionisation energies are always higher than the first. However, in the case of alkali metals, the unipositively charged ions (Li^+, Na^+, K^+, etc.) have the stable electronic configuration of the preceding noble gases. Removal of an electron from a stable noble gas configuration is extremely difficult. These metals, therefore, form univalent cations only. Fig. 4.4 shows the trend in the first ionisation energies of the alkali metals down the group.
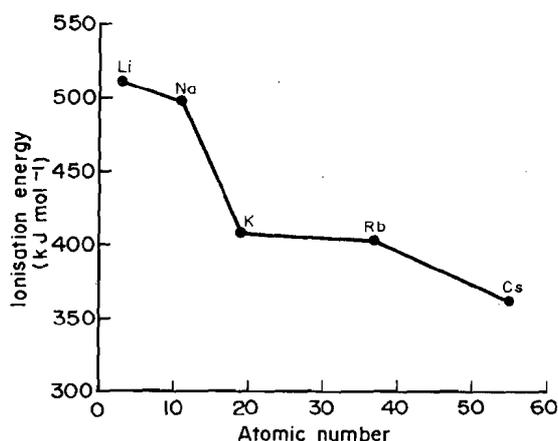

Fig. 4.4: Trend in first ionisation energies of alkali metals.

On account of their low ionisation energies, these elements have a high tendency to form cations. In other words, they have high electropositive or metallic character which increases as we move down in the group from Li to Cs. In fact, Rb and Cs are so highly electropositive that they emit electrons even when exposed to light; that is, they exhibit photoelectric effect.

Electronegativity

Because alkali metals have a tendency to lose electron easily rather than to gain, values of electronegativity of these elements are very small. In fact, alkali metals are the least electronegative elements in the periodic table. As expected the electronegativity decreases on moving down the group.

Ionic Character of Compounds

Compounds formed by alkali metals with highly electronegative elements like halogens and oxygen are largely ionic in nature because of a large electronegativity difference. The trends in ionic character of alkali metal halides are shown in Fig. 4.5. You can see that the trends are as expected; the ionic character increases with increase in cation size and decreases with increase in anion size. Because of the small size of Li^+, it has more polarising power and, therefore, favours covalent bonding.

Solubility, Lattice Energy and Hydration Energy

Alkali metal salts like halides, oxides, hydroxides, carbonates, sulphates, etc. exhibit some interesting trends in their solubility in water. To understand these trends, let us first recapitulate lattice energy and hydration energy which you have studied in Unit 3 of the 'Atoms and Molecules' course. Lattice energy is the driving force for the formation of an ionic compound and its stability. Lattice energy is directly proportional to the charge on the

Lattice energy is the **enthalpy** change when one mole of crystal lattice is formed from the isolated gaseous ions.

Hydration energy is the enthalpy change when one mole of solute is dissolved in water.

ions and inversely proportional to the distance between the cation and anion. This distance is taken as the sum of radii of cation and anion $(r_c + r_a)$. In a group, the charge on cations remains constant. Thus, lattice energy depends mainly on the size of the cation. Similarly, hydration energy also varies with the charge and size of the cation. The higher the charge and the smaller the size of the ion, the more is the hydration energy. In a group, lattice energy and hydration energy decrease as we move down. While the decrease in lattice energy favours the solubility, the decrease in hydration energy makes the compound insoluble.
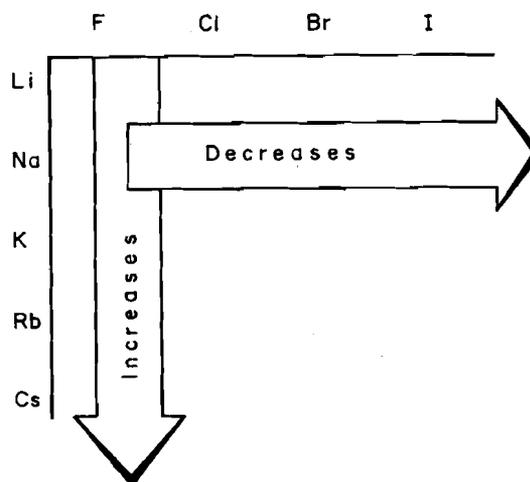

Fig. 4.5: Trend in the ionic character of alkali metal halides.

For the salts of small anions (like F^-, O^{2-}, OH^-, etc.), the lattice energy which is inversely proportional to $r_c + r_a$, is very sensitive to the change in the size of the cation, anion being very small in size has little contribution in the total $(r_c + r_a)$ and decreases sharply as we move down the group. Thus, in these salts, the decrease in lattice energy is greater than the decrease in hydration energy and, therefore, the solubility of these salts increases as we go down the group. For example, in the case of alkali metal fluorides, the solubility increases in the order LiF<NaF<KF<RbF<CsF.

For the salts having large anions (SO_4^{2-}, I^-, NO_3^-, HCO_3^-, CO_3^{2-}, etc.), as $r_a \gg r_c$, the radii of the cation has little effect on $r_a + r_c$ and thus on lattice energy. The main factor for solubility is, therefore, hydration energy which decreases as the size of the cation increases. Thus, in this case, the decrease in hydration energy is more than the decrease in lattice energy and the solubility decreases as we move down the group. For example, in the case of alkali metal carbonates, lithium carbonate is highly soluble while the solubility of caesium carbonate is very little.

Another important factor contributing to the solubility of the compound is the match in the size of the cation and anion. Whenever there is a mismatch, e.g., cation is small, anion is large or *vice-versa*, this will result in the increased solubility of the compound. Let us keep the cation constant say caesium. If we, then, change the anion from fluoride to iodide, then the solubility of the compounds will vary as CsF > CsCl > CsBr > CsI. Thus, caesium fluoride will be most soluble and caesium iodide will be the least. Similarly, from lithium

Table 4.2: The main trends in the properties of alkali metals.

increasing:	decreasing:	
electropositivity	m.p. and b.p.	Li
density*	hardness	Na
atomic radii	ionisation energy	K
atomic volume	conductivity	Rb
reactivity	electronegativity	Cs
reducing power	solubility of salts having large anions	
anion stabilisation		
solubility of salts having small anions		

* The density of K is less than that of Na.

fluoride to lithium iodide, the solubility will increase in the order: $LiF < LiCl < LiBr < LiI$. There can be many more examples which can be explained on the basis of above reasonings. So far we have discussed the periodic trends observed in the physical properties of the alkali metals and their compounds. These trends are summarised in Table 4.2.

SAQ 1

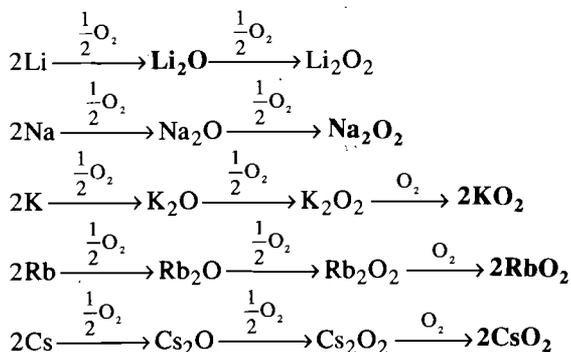Given below are some of the statements about the alkali metals. Write 'T' if true and 'F' if false against them.

i)   Sodium is the most abundant alkali metal in the earth's crust.

ii)   Sodium is the most abundant metallic element in sea water.

iii) Alkali metals occur in the free state in nature.

iv)   Lepidolite is an ore of lithium.

v)   Atomic radii of the alkali metals decrease down the group.

vi)   Ionisation energy increases from lithium to francium.

vii) Melting and boiling points of alkali metals decrease down the group.

viii) Lithium is the lightest of all the metallic elements.

ix)   Solubility of alkali metal fluorides in water increases down the group.

x)   Ionic character of alkali metal halides decreases down the group.
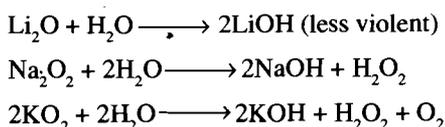
4.3.2 Chemical Properties

In the previous subsection you have studied the important physical properties of the alkali metals. In accordance with their highly electropositive character, these metals are very reactive and are powerful reducing agents reacting with water and most non-metals. They form crystalline ionic salts with high melting and boiling points. These salts are usually soluble in water giving conducting solutions. Now we shall discuss some of the important classes of these salts.

Oxides and Hydroxides

As alkali metals are very reactive, their lustre is lost in air due to the formation of oxide with atmospheric oxygen. Three types of oxides are formed by the alkali metals, viz., normal oxides having O^{2-} ion and the peroxides having O_2^{2-} [$^-O - O^-$] ion, both of which are **diamagnetic** and colourless. The third one which is coloured and **paramagnetic** is superoxide containing O_2^- ion. Controlled oxidations of these metals are shown below:

Materials that are **diamagnetic** experience no attraction for another magnet. **Paramagnetic** substances, on the other hand, are weakly attracted to a magnetic field.

$$2Li \xrightarrow{\frac{1}{2}O_2} Li_2O \xrightarrow{\frac{1}{2}O_2} Li_2O_2$$

$$2Na \xrightarrow{\frac{1}{2}O_2} Na_2O \xrightarrow{\frac{1}{2}O_2} Na_2O_2$$

$$2K \xrightarrow{\frac{1}{2}O_2} K_2O \xrightarrow{\frac{1}{2}O_2} K_2O_2 \xrightarrow{O_2} 2KO_2$$

$$2Rb \xrightarrow{\frac{1}{2}O_2} Rb_2O \xrightarrow{\frac{1}{2}O_2} Rb_2O_2 \xrightarrow{O_2} 2RbO_2$$

$$2Cs \xrightarrow{\frac{1}{2}O_2} Cs_2O \xrightarrow{\frac{1}{2}O_2} Cs_2O_2 \xrightarrow{O_2} 2CsO_2$$

In the above scheme the products in bold letters are the main products when the metals are burnt in a free supply of air. You may notice in the above scheme that **lithium forms normal oxide, sodium forms peroxide while potassium, rubidium and caesium form superoxide as the main product**. All the Group 1 metal oxides are strongly basic and react vigorously giving hydroxide:

$Li_2O + H_2O \longrightarrow 2LiOH$ (less violent)

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

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

As we see, the peroxides and the superoxides on reaction with water give H_2O_2 which in turn is a powerful oxidising agent. Thus, the peroxides and the superoxides are also oxidising in nature.

The basic strength of the hydroxides increases down the group. As the charge density

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(charge/size ratio) of the cation decreases from Li^+ to Cs^+, attraction between M^+ and OH^- also decreases. So, OH^- can be liberated readily into the solution, as we go down the group.

Sulphides

Alkali metals react with sulphur to form two types of sulphides: simple sulphides Na_2S and polysulphides like Na_2S_n where n = 2, 3, 4, 5 or 6. These polysulphides have a zig-zag chain structure of sulphur atoms as shown below:
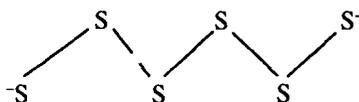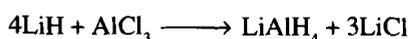

Hydrides

The alkali metals react with hydrogen and form ionic hydrides, M^+H^-. These hydrides on reaction with water liberate hydrogen. Thus, they are a useful source of hydrogen:

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

Lithium hydride on reaction with $AlCl_3$ in ether solution forms lithium aluminium hydride which is a useful reducing agent in organic chemistry.

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

Similarly, sodium hydride forms sodium borohydride which is also used as a reducing agent.

Carbides

Lithium reacts with carbon to form ionic carbide whereas similar carbides of other metals are not formed on reacting them with carbon. They can, however, be formed on heating the metal with acetylene or when acetylene is passed through a solution of the metal in liquid ammonia:

$$Na + C_2H_2 \xrightarrow{\text{Liq·NH}_3} NaHC_2 \longrightarrow Na_2C_2$$
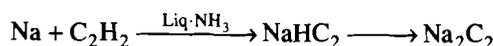
These carbides contain the carbide ion $(C\equiv C)^{2-}$. On hydrolysis they give acetylene. Hence, they are termed as **acetylides**:

$$Na_2C_2 + 2H_2O \longrightarrow 2NaOH + C_2H_2$$

Alkali metals also form covalent compounds such as methyllithium, $LiCH_3$ and ethylsodium, NaC_2H_5. These come under the separate class of organometallic compounds.

The main reactions of Group 1 elements are summarised in Table 4.3.

Table 4.3: The reactions of the Group 1 elements.

Reaction	Description
$2Li + O_2 \xrightarrow{\text{excess}} Li_2O$	The higher metals from Na_2O_2, K_2O_2, KO_2, RbO_2, CsO_2.
$2M + S \longrightarrow M_2S$	Very vigorous reaction. Polysulphides are also formed.
$M + H_2O \longrightarrow MOH + \frac{1}{2}H_2$	With Li fairly slow, whereas K explodes.
$M + ROH \longrightarrow MOR + \frac{1}{2}H_2$	Vigorous (R = alkyl, aryl). With Li fairly slow.
$M + \frac{1}{2}H_2 \longrightarrow MH$	At high temperatures, ionic hydrides. LiH is the most stable.
$M + \frac{1}{2}X_2 \longrightarrow MX$	X = halogen. The higher members can form polyhalides, e.g., KI_3.
$3Li + \frac{1}{2}N_2 \longrightarrow Li_3N$	Slow at room temperature; rapid at elevated temperatures.
$M + NH_3 (l) \longrightarrow [M(NH_3)_n]^+ + e^-(NH_3) \xrightarrow{\text{catalyst}} M^+NH_2^- + \frac{1}{2}H_2$	
$2M + C(\text{or } C_2H_2) \longrightarrow M_2C_2$ (acetylides) $\xrightarrow{H_2O} C_2H_2$	
$M + Hg \longrightarrow$ amalgams	

SAQ 2

Explain briefly in the space given below why do alkali metals act as strong reducing agents.

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*The standard **enthalpy of formation** of a compound is the enthalpy change when one mole of the compound in the standard state is formed from the elements in the standard state.*

Thermal Stability of Salts

The ease of thermal decomposition of a salt is related to the **enthalpy of formation** of the salt. The **enthalpy of formation**, ΔH^o_f of a salt MA (M is the metal, A is anion) is given by

$$\Delta H^o_f = (\Delta H_{atom} + I)_{metal} + (\Delta H_{atom} - E_A)_{anion} - \Delta H_{latt}$$

where ΔH_{atom} is the **enthalpy of atomisation**, I is the ionisation energy and E_A is the electron affinity. Since for any salt in a particular group the terms involving the anion alone remain constant, the value of ΔH_f° for such compounds is dependent upon the sum of the enthalpy terms of the particular metal, $(\Delta H_{atom} + I)_{metal}$ and the lattice energy, ΔH_{latt}. The larger the lattice energy, the more negative the enthalpy of formation and so, more stable is the compound. All these terms become smaller on descending the series from lithium to caesium. The relative stabilities of the salts are, therefore, decided by the parameter which decreases more rapidly — the lattice energy or the sum of the metal enthalpies.

The **enthalpy of atomisation** of an element is the enthalpy change when one mole of gaseous atoms is formed from the element in the standard state, e.g.,

$1/2 Cl_2(g) \longrightarrow Cl(g) + \Delta H_{atom}$ In this equation ΔH_{atom} is the enthalpy of atomisation.
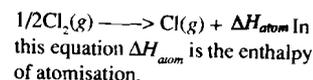
In the salts having small anions of high charge density, e.g., F^-, N^{3-}, OH^-, O^{2-} etc., the change in lattice energy is much dependent on the size of the cation and decreases rapidly on descending the group. Thus, as the size of the cation increases, lattice energy decreases more than the change in the sum of the metal enthalpies. Therefore, as we go down the group, the stability of these salts having small anions decreases. Thus, in alkali metal fluorides, the stability decreases in the order LiF > NaF > KF > RbF > CsF.

The opposite trend is observed in the stability of the salts containing large anions of low charge density, e.g., Br^-, I^-, NO_3^-, etc. In such cases, the lattice energy is relatively insensitive to the change in cation size and there is more rapid decrease in ionisation energy and atomisation enthalpy on descending the group. The lower values of these favour stability of the compounds. Thus, the stability of the compounds having large anions increases as we move down the group from lithium to caesium.

The stability of the compounds can also be explained by using the concept of polarising power. The simple idea is that, as the charge density of the metal ion increases, the thermal stability of the salts of large polarisable anions, relative to some decomposition product decreases. In general, the least polarising metal ions are those of the most electropositive metal ions and these form the most stable salts with large anions. In other words, small cations form stable salts with small anions and large cations form stable salts with large anions. Let us take the example of carbonates of Group 1 metals. The carbonates of sodium, potassium, rubidium and caesium are resistant to the heat of a bunsen burner flame, however, lithium carbonate decomposes to its oxide and carbon dioxide under the same conditions:

$Li_2CO_3 \longrightarrow Li_2O + CO_2$
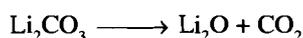
The tendency of Li_2CO_3 to undergo thermal decomposition may be explained in terms of the gain in electrostatic attraction that occurs when extremely small Li^+ ion combines with the smaller oxide ion rather than the much larger carbonate ion. The other carbonates of Group 1(Na - Cs) are more stable because the cations have a lower charge density and are considerably larger in size and so, their decomposition is less favourable energetically.

All the metals except lithium form stable bicarbonates (lithium bicarbonate is formed only in aqueous solutions and has not been isolated). When we heat the alkali metal bicarbonates, they are decomposed to carbonates and simultaneously, carbon dioxide and water are liberated.

$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$
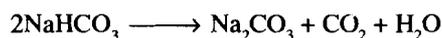
The thermal stability of Group 1 hydroxides also follows a similar trend as that of carbonates. Thus, except LiOH, which on heating decomposes to Li_2O, all other Group 1 hydroxides are stable. Similarly, lithium nitrate also decomposes on heating to give Li_2O, NO_2 and O_2 but all other alkali metal nitrates decompose on strong heating to nitrites liberating oxygen:

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

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$
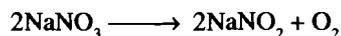
SAQ 3

Tick the correct answer in the boxes provided, from the following choices given:

a) Thermally least stable alkali metal fluoride is:

i) LiF ☐   iii) KF ☐   v) CsF ☐

ii) NaF ☐   iv) RbF ☐

b) Potassium nitrate on heating will give:

i) K_2O, O_2 & K ☐   iii) KNO_2, KO_2 & O_2 ☐

ii) KNO_2 & O_2 ☐   iv) K, KO_2 & O_2 ☐

4.4 SOLVATION OF THE ALKALI METAL IONS

When a metal ion is surrounded by the solvent molecules, the phenomenon is called **solvation** of the metal ion. When the solvent is water it is called **hydration**. The alkali metal ions are highly hydrated. The smaller the size of the ion, the greater is its degree of hydration. This is because the smaller the size, the more will be its charge density and the more will be its attraction for the polar solvent molecules. Thus, Li^+ ion, which is the smallest gets more hydrated than the Na^+ ion and so on. The degree of hydration decreases on moving down the group. As a result of differences in their degree of hydration, the hydrated ionic radii of the alkali metal ions decrease as we go down the group from lithium to caesium. Li^+ ion has the largest hydrated radius while Cs^+ has the smallest hydrated radius in the first group. You will agree that the smaller the size of the ion and the lighter it is, the more will be its mobility and thus conductance. In this regard we should expect the highest conductance for Li^+ which is the smallest of the alkali metals but this is not so. We have explained above that the hydrated radius of Li^+ is the largest of all the alkali metal ions, in solution. Therefore, **Li^+ ion is the least conducting in solution.** The ionic conductance in solution actually decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

SAQ 4
In the space given below, briefly explain how does conductivity vary in solutions of alkali metal salts and why.

. . . .

. . . .
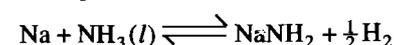

4.5 SOLUTIONS OF ALKALI METALS IN LIQUID AMMONIA

All the alkali metals are highly soluble in liquid ammonia giving deep blue colour. Per 100g of NH_3, the solubilities are: Li, 10g; Na, 25g and K, 49g. The dissolution of the alkali metal is accompanied by its dissociation into the metal ions and the electrons. The metal ion and the electrons then get associated with ammonia solvent molecules. Electrons associated with the solvent are known as **solvated electrons.**

$$Na\ (s) + NH_3(l) \longrightarrow Na^+\ (NH_3)_x + e(NH_3)_y$$
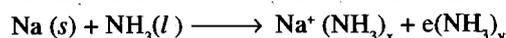
The alkali metal solutions in liquid ammonia are highly conducting and behave almost as metals. Their specific conductivities are almost the same, because the anion, i.e., solvated electron in all the cases is the same. The small difference in the conductivity is due to the nature of the metal itself. The solution of alkali metals in liquid ammonia is blue in colour due to the presence of solvated electrons and, therefore, the solutions are also paramagnetic. With increasing concentration there is a decrease in paramagnetism suggesting that the electron can get associated to form diamagnetic electron pairs. Although, there may be other equilibria also:

$$Na(s)\ (dispersed) \rightleftharpoons Na(in\ solution) \rightleftharpoons Na^+ + e$$

$$2e \rightleftharpoons e_2$$
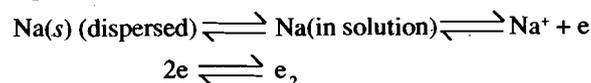
On increasing the concentration above 3M, the colour of the solution changes to copper bronze having metallic luster because the metal ions form clusters. Except lithium, other alkali metals can be recovered unchanged from solution. Lithium in ammonia solution forms a complex of the type $[Li(NH_3)_4]^+$. The blue solutions of alkali metals are moderately stable at temperatures where ammonia is still a liquid, but the reaction to give amide,

$$Na + NH_3(l) \rightleftharpoons NaNH_2 + \tfrac{1}{2}H_2$$

can occur photochemically and is catalysed by transition metal salts. The alkali metal solutions in liquid ammonia are powerful reducing agents and are used for this purpose in inorganic and organic reactions.

SAQ 5

Alkali metals dissolve in ammonia giving blue coloured soluti~~un~~.. ..~~e~~ blue colour of the solution of sodium in liquid ammonia is due to one of the following reasons. Tick the correct answer in the boxes provided along side.

i) ammonia ☐

ii) solvated electron ☐

iii) sodium metal ☐

iv) all of the above ☐

v) none of the above ☐

4.6 COMPLEXATION BEHAVIOUR OF ALKALI METALS

Before discussing the complexation behaviour of alkali metals, let us first define 'what is a complex compound'. A completely satisfactory definition of this is difficult to give at this stage but we can define a complex compound as a compound having a central metal atom/ ion surrounded by a group of ions or molecules called 'ligands'. These ligands are usually bound to the metal by the 'coordinate bond', i.e., the bond formed by the donation of a lone pair of electrons from one atom (of the ligand) to the other (metal atom/ion). Although both metal and the ligand are usually capable of independent existence as stable chemical species, yet when the complex is formed, it generally retains its identity in solution. For example, in solution Fe^{++} and CN^- can exist independently but once the complex $[Fe(CN)_6]^{4-}$ is formed it exists in solution as such, i.e., it does not dissociate appreciably into Fe^{++} and CN^-; as a result it will not give any test for Fe^{++} and CN^-. It is thus a complex species. **The most stable complexes would be formed by the highly polarising cations**, which have a strong tendency of interacting with electron clouds of other anionic or neutral electron rich species (ligands).

A ligand which occupies more than one coordination position, i.e., more than one atom of the ligand is bonded to the central metal is called a **chelating ligand**, e.g., salicylaldehyde, can bind the metal by its both the oxygen atoms. A coordination compound formed with a chelating ligand is called a **chelate**.

According to the above model, a very weak coordinating ability is expected in the Group 1 metals because of their large size and low charge of the cations, M^+. According to this view, stability of the complexes of the alkali metals should decrease in the order Li>Na>K>Rb>Cs and this is the observed trend also. Alkali metals form few complexes, mostly **chelates** with the ligands like β-diketones, nitrophenols, nitrosonaphthols, etc. as shown in Fig. 4.6. They are of low stability.
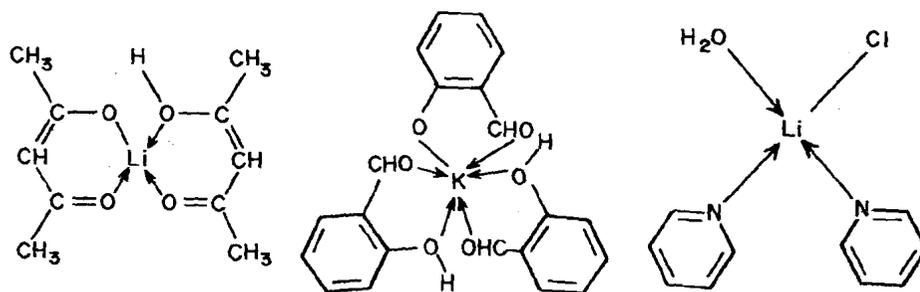

Fig. 4.6 : Some complexes of alkali metal ions

Lithium, being the most polarising cation of all the alkali metals, forms tetrahedral complexes with ligands like NH_3, C_5H_5N, etc. With ammonia it forms the complex of the type $[Li(NH_3)_4]I$, whereas with pyridine, a complex of the type $[LiCl (C_5H_5N)_2 (H_2O)]$ is formed.

SAQ 6

Explain briefly, in the space given below, why alkali metals are poor complexing agents.

....

....

4.7 ANOMALOUS NATURE OF LITHIUM

On descending any group of *s*- or *p*-block elements of the periodic table, there is a general decrease in electronegativity or increase in electropositivity. The difference in electronegativity between the first and the second elements of each group is much greater than that between any two successive elements. This is reflected in the properties of the elements. Thus, not only is the first element more electronegative than the other elements of the group, but it is much more electronegative than expected by simple extrapolations. The differences, therefore, between the first and rest of the Group 1 metals are those between a less electropositive metal and a more electropositive metal. We have discussed most of these properties at the appropriate places in earlier sections. Let us summarise them again.

Due to the very small size of lithium, the metallic bonding between the atoms in the metallic lattice is very strong giving rise to strong cohesive forces. This is shown in its relatively higher melting and boiling points, hardness and homonuclear bond energy.

The relatively higher attraction of lithium for its outer electron results in its relatively higher electronegativity, ionisation energy, hydration energy, electron affinity and of course smaller atomic radii relative to the other homologues.

Similar anomalies are also found in the chemical properties but the differences appear greater.

i) Lithium salts of large polarisable anions are thermally less stable than those of other alkali metals, e.g., lithium carbonate decomposes at 950 K, whereas no decomposition of sodium carbonate takes place below 1050 K.

ii) Lithium forms no solid bicarbonate, triiodide and superoxide as these are unstable at room temperature, whereas those of other alkali metals require a higher temperature to effect their decomposition.

iii) Lithium salts of anions of high charge density are less soluble than those of other alkali metals. The halides of lithium are more covalent than the other halides and are more soluble in organic solvents.

iv) Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For example, in air, lithium forms the normal oxide, whereas the others form higher oxides. Lithium reacts with nitrogen to form nitride, Li_3N, the others do not react. Lithium hydride is more stable than the other hydrides and lithium carbide is formed more easily with acetylene.

v) Lithium reacts slowly with water.

vi) Lithium forms more stable covalent bonds than other alkali metals and, therefore, forms more stable complex compounds (Section 4.6). For example, lithium cannot be recovered unchanged from its liquid ammonia solution, owing to the formation of $[Li(NH_3)_4]^+$.

This correlation of properties with the concepts of electronegativity and electropositivity is only one way of rationalising the data.

Other way of looking at the anomalous nature of lithium is by considering the variation of the ionic radius down the Group 1 metals. This determines the energy of interaction of the alkali metal ions with other (negative) ions and polar molecules and determines such important factors as hydration energies, the complexing power, solubilities, stabilities, electrode potentials, etc.

4.8 SUMMARY

Let us recall what we have discussed in this unit. As far as the main trends in properties of alkali metals are concerned, we have seen that electropositivity, density, atomic radii, atomic volume, reactivity, reducing power and large anion stabilisation increase down the group, whereas m.p., b.p., hardness and ionisation energy decrease down the group. The elements of this group form carbonates, bicarbonates and nitrates, the stability of which increases on descending the group.

Li^+ being the smallest cation is heavily hydrated and is least conducting. Bigger cations are

less solvated. All the alkali metals have good solubility in liquid NH_3 and their ammonia solutions are highly conducting. Since the metal ions are large and have low charge, they form less stable complexes. Some covalent compounds, e.g., methyllithium and ethylsodium have also been prepared.

We have also noticed that lithium behaves quite abnormally in many respects, e.g., it has high cohesive properties, high electronegativity, ionisation energy, electron affinity and small atomic radius.

4.9 TERMINAL QUESTIONS

1 Why the elements of Group 1 are called the alkali metals?

2 Why do alkali metals not occur as free elements in nature?

3 Explain why
   i)   alkali metals are good conductors of electricity.
   ii) lithium has the highest ionisation energy in the group.
   iii) sodium forms +1 ion and not +2 ion.
   iv) Group 1 elements form ionic compounds.

4 Consider the elements Li, Na, K, Rb, Cs and Fr. List them in the order of
   i)   decreasing atomic radius
   ii) decreasing hydrated ionic radius
   iii) increasing density
   iv) decreasing melting and boiling points
   v)   increasing ionisation energy.

5 Explain how does the solubility of salts vary and why do hydroxides become stronger alkalies on descending the group.

6 Explain
   i)   The trend in the solubility of alkali metal iodides.
   ii) Why lithium forms oxide, sodium forms peroxide and potassium, caesium and rubidium form superoxide. [Hint: discuss on the basis of the size of cation and anion.]
   iii) Why stability of carbonates increases down the group.
   iv) Why lithium compounds have more covalent character than potassium compounds.

7 Why do peroxides and superoxides oxidise in aqueous solution?

8 What will be the action of water on
   i)   alkali metal oxides
   ii) alkali metal hydrides
   iii) alkali metal carbides
   Give equations only.

9 What will be the action of the following on lithium? Give equations only.
   i) H_2
   ii) N_2
   iii) O_2
   iv) NH_3
   v) Cl_2

10. Explain why lithium forms more complexes than the other elements of Group 1.
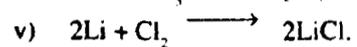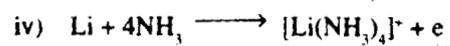
4.10 ANSWERS

Self Assessment Questions
1 i) T   ii) T   iii) F   iv) T   v) F
   vi) F   vii) T   viii) T ix) T   x) F

2 The outermost electron in alkali metals is very loosely bound so it can be removed easily. Thus, alkali metals are strong reducing agents.

3 a. (v)   b. (ii)

4 Conductivity in solution decreases as the hydrated ionic radii of the metal ion

increases. Thus, for alkali metal salts conductivity varies as $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

5   (ii).

6   Because of the large size and low charge on the alkali metal ions, they have poor complexing power.

Terminal Questions

1   Group 1 elements form hydroxides which are strong alkalies so they are called alkali metals.

2   Alkali metals are very reactive, therefore, they do not occur as free elements in nature.

3   i)   The outermost electron in alkali metals is very loosely bound and can go from one metal ion to other easily. Therefore, these metals are good conductors of electricity.

   ii)   Lithium, being the smallest metal in its group, holds its electrons most tightly. So maximum energy is required to remove its outermost electron among Group 1 metals. Thus it has the highest ionisation energy in the group.

   iii)   After losing one electron and forming Na^+ ion, sodium achieves noble gas configuration $1s^2\, 2s^2 2p^6$, from which removing an electron is extremely difficult. Thus, sodium forms +1 ion and not +2.

   iv)   Group 1 elements are large in size and are highly electropositive. They also have low charge to size ratio and thus they form ionic compounds mostly.

4   i) $Fr > Cs > Rb > K > Na > Li$

   ii) $Li > Na > K > Rb > Cs > Fr$

   iii) $Li < Na > K < Rb < Cs < Fr$

   iv) $Li > Na > K > Rb > Cs > Fr$

   v) $Fr < Cs < Rb < K < Na < Li$

5   For salts of alkali metals with the anions of high charge density (F^-, O^{2-}, OH^- etc.), the solubility increases on moving down the group. For salts having anions of low charge density (CO_3^{2-}, HCO_3^-, I^-, NO_3^-), solubility decreases on moving down the group.

   As the hydroxides of the alkali metals which are lower in the group are more soluble, OH^- ions are released more readily. Therefore, the hydroxides become stronger alkalies on moving down the group.

6   i) $LiI > NaI > KI > RbI > CsI$.

   ii)   Small cations form stable compounds with small anions of high charge density and *vice versa*. The charge density of oxide ions varies as $O^{2-} > O_2^{2-} > O_2^-$ and that of alkali metals as $Li > Na > K > Rb > Cs$. Therefore, Li forms stable oxide, Li_2O, sodium forms peroxides, Na_2O_2 and potassium, rubidium and caesium form stable superoxides.

   iii)   The trend in stability of carbonates is $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$. When cations are large, salts with large anions are stable. Thus, stability of carbonates increases down the group. Lithium having high charge density, its carbonate decomposes to oxide which is much more stable.

   iv)   Lithium cation is much smaller than the potassium cation, therefore, the polarising power of lithium cation is much higher than that of potassium cation. So, the lithium compounds are more covalent than the potassium compounds.

7   Peroxides and superoxides in aqueous solution give H_2O_2 which is a strong oxidising agent. Thus, peroxides and superoxides are strong oxidising agents.

8   i) $Li_2O + H_2O \longrightarrow 2LiOH$

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

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

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

   iii) $Na_2C_2 + 2H_2O \longrightarrow 2NaOH + C_2H_2$

9   i) $2Li + H_2 \longrightarrow 2LiH$

   ii) $6Li + N_2 \longrightarrow 2Li_3N$

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

iv) $Li + 4NH_3 \longrightarrow [Li(NH_3)_4]^+ + e$

v) $2Li + Cl_2 \longrightarrow 2LiCl.$

10. The most stable complexes would be formed by the highly polarising cations. Li^+ being the most polarising cation of all the alkali metals, forms larger number of complexes than the other Group 1 metals.

UNIT 5 ALKALINE EARTH METALS

Structure

5.1 INTRODUCTION

In the previous unit, you studied the general characteristics of Group 1 elements, i.e., alkali metals and their compounds. Group 1 and Group 2 elements belong to the s-block of the periodic table, as they have ns^1 and ns^2 outer shell electronic configuration, respectively. s-Block elements are known to be very reactive metals and generally form ionic compounds In this unit you will study the elements of Group 2 consisting of beryllium, magnesium, calcium, strontium, barium and radium. Elements Ca, Sr, Ba and Ra are called **alkaline earth metals** because their earths (earth is the old name for a mineral oxide) are alkaline in nature. However, beryllium is not counted as an alkaline earth metal since its earth is not alkaline. Like the Group 1 elements, they show a distinct group relationship in which similarities between the elements are more pronounced than the differences between them. The first member of the group is 'anomalous' (cf. lithium). In this unit, we will study the general characteristics and chemistry of this group of elements.

Objectives

After studying this unit you should be able to:

● describe the general trend in the properties of the Group 2 elements,
● explain chemistry of the Group 2 elements,
● correlate the complexation behaviour of these elements, and
● explain why and how beryllium differs from the rest of the members of the group.

5.2 OCCURRENCE, EXTRACTION AND USES

The alkaline earth metals, like alkali metals are very reactive, therefore, do not occur free in nature. All of them are found in the form of their salts. These metals are strong reducing agents and, therefore, it is very difficult to obtain them by chemical reduction methods. All of these find some or the other use in industry. Let us now study their occurrence, extraction and uses in this section.

Occurrence

Beryllium, the first member of the group is found in small quantities in the silicate mineral, phenacite, Be_2SiO_4 and beryl, $3BeO.Al_2O_3.6SiO_2$. Magnesium (2.76%) and calcium (4.66%) are among the eight most abundant elements in the earth's crust. Magnesium (0.13%) is the second most abundant metallic element next only to sodium (chloride) in sea water. It occurs as magnesite, $MgCO_3$; dolomite, $MgCa(CO_3)_2$; kieserite, $MgSO_4.H_2O$ and carnallite, $KMgCl_3.6H_2O$ in the earth's crust. Calcium occurs extensively as calcite and lime-stone $(CaCO_3)$ in many mountain ranges. Calcium and magnesium are very important biologically too. Calcium is found in the bones of animals and human beings. Magnesium is found in the green pigment, viz., chlorophyll of the plants. Strontium (0.038%) and barium (0.039%) are much less abundant and occur as carbonates and sulphates. These metals are well known because they occur as concentrated ores and are easy to extract. Radium is extremely scarce $(10^{-10}\%)$ and it is a radioactive element.

The gem stone, emerald, is beryl, the green colour being due to the presence of chromium.