NATIONAL OPEN UNIVERSITY OF NIGERIA

CHM 111

Introduction to Inorganic Chemistry

Module 3

CHM 111 Introductory Inorganic Chemistry Module 3

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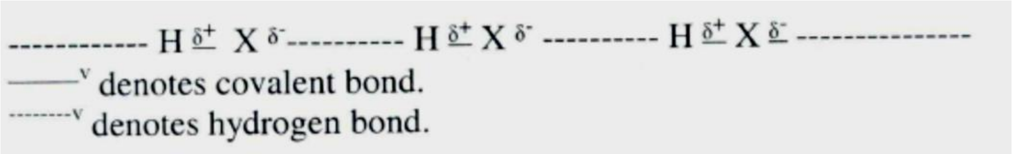
Module 3

Unit 1 Hydrogen Bonding

1.0 Introduction

A very important aspect of the chemistry of hydrogen is its formation of hydrogen bonds. When hydrogen is covalently bonded to a highly electronegative element like F, 0, or N, the electronegative element attracts the electron pair towards itself giving rise to an induced positive charge (5+) on the hydrogen atom and negative charge (S) on the electronegative atom for example:

Ho + Xo where X is the electronegative atom. When this happens the hydrogen, due to its positive character, will attract another electronegative atom of the neighbouring molecule forming a bond. This bond is known as hydrogen bond. This is illustrated below



------------ H $^{\underline{\delta+}}$ X $^{\delta-}$---------- H $^{\underline{\delta+}}$ X $^{\delta-}$ ---------- H $^{\underline{\delta+}}$ X $^{\underline{\delta-}}$ ---------------

——^{v} denotes covalent bond.

--------^{v} denotes hydrogen bond.

In this unit, you will be studying the types of bonding, the effect of hydrogen bonding on boiling and melting points. Also, the effects of hydrogen bonding on water solubility of the compound containing hydrogen bonded elements.

2.0 Objectives

At the end of this unit, you should be able to:

- define hydrogen bonding
- list and discuss the two types of hydrogen bonding
- list and discuss the effect of bonding on boiling and melting points
- discuss the effect of bonding on the solubility of a substance
- discuss giving examples, the polarising power of H+.

3.0 Main Content

3.1 Hydrogen Bonding

Hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same compound.

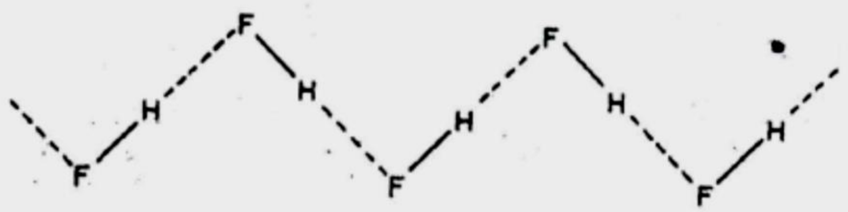
The hydrogen bond energy is only about 7 — 59 kg mol^{-1} compared to the normal covalent bond energy of 389 — 665 kg mol $^{-1}$ for H-N, H-0 and H—F bonds. This hydrogen bond is much weaker than a covalent bond. Obviously, its length is also much more than the covalent bond.

There are two types of hydrogen bonding. These are:

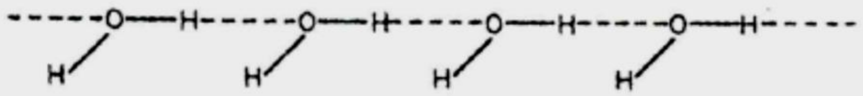
- Intermolecular hydrogen bonding
- Intra-molecular hydrogen bonding.

3.2 Intermolecular Hydrogen Bonding

In this case, two or more molecules of the same element are involved in hydrogen bonding. Some common examples of intermolecular hydrogen bonding occurring between the molecules of the same compound are HF, H_2O, alcohols etc.

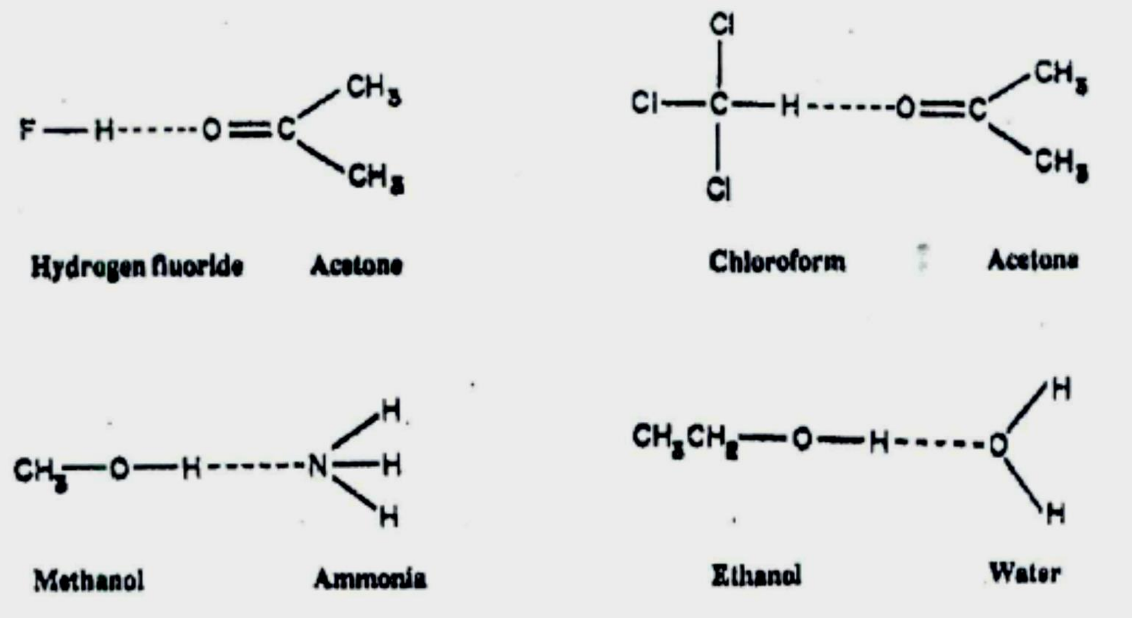


Hydrogen fluoride, $(HF)_n$



Cluster of water molecules, $(H_2O)_n$

Examples of the intermolecular hydrogen bonding between two different kinds of molecules are as following.

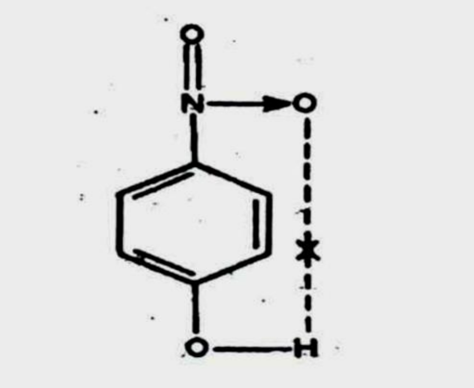


3.3 Intra-Molecular Hydrogen Bonding

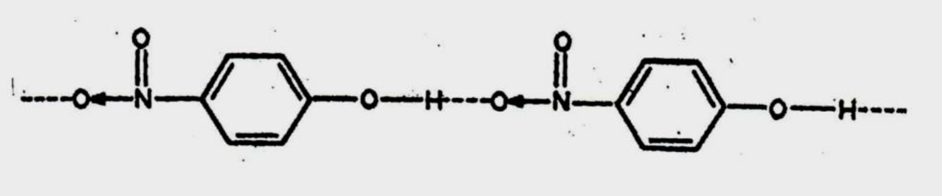
Intramolecular hydrogen bond is formed between two atoms of the same molecule. As a consequence of this, generally a five or six membered ring called chelate ring is formed.

You have seen above, that intramolecular hydrogen bonding takes place in molecules like 6-nitrophenol and salicyladehyde.

Intramolecular hydrogen bonding does not take place in p-nitrophenol because of the large distance between the two groups (NO_2 and QH) in p — nitrophenol



This type of hydrogen bonding is not possible. It does however show the usual intermolecular hydrogen bonding.



It is significant to note that the vast majority of intra-molecular hydrogen bonding occurs where a five or six membered ring can be formed because of the stability associated with such rings.

3.4 Effects of Hydrogen Bonding

Hydrogen bonding plays a very significant role in determining the properties of compounds. In this section we shall discuss its effect on the melting point, boiling point and solubility in water.

3.4.1 Boiling Point and Melting Point

If you examine the values for the melting and boiling points shown in Figure 1.1, you will see that the melting and boiling points of the hydrides of Group 14 elements i.e. CH_4, SiH_4 and GeH_4 and SnH_4 show a general increase with increase in molecular weight. However, NH_3 in Group 15, HF in Group l7 and water have abnormally high melting and boiling points as compared to other hydrides in their respective groups in the periodic table.

This anomaly is explained on the basis of hydrogen bond formation. In compounds where the molecules are linked by hydrogen bonds, some extra energy is required to break the intermolecular hydrogen bond and this is responsible for their higher boiling and melting points.

Intra-molecular hydrogen bond however has the opposite effects. For example, in ortho-nitrophenol the groups present in ortho position are involved in intramolecular hydrogen bonding thus preventing the intermolecular hydrogen bond formation, i.e. association of the molecule. Due to the intramolecular chelated structure, o-nitrophenol is seen to be volatile whereas p-nitrophenol is not.

3.4.2 Water Solubility

Solubility of a substance increases markedly when hydrogen bonding is possible between the solvent and the solute molecules. For example, lower alcohols like, methanol, ethanol etc are highly miscible with water due to the hydrogen bonding with water molecules.

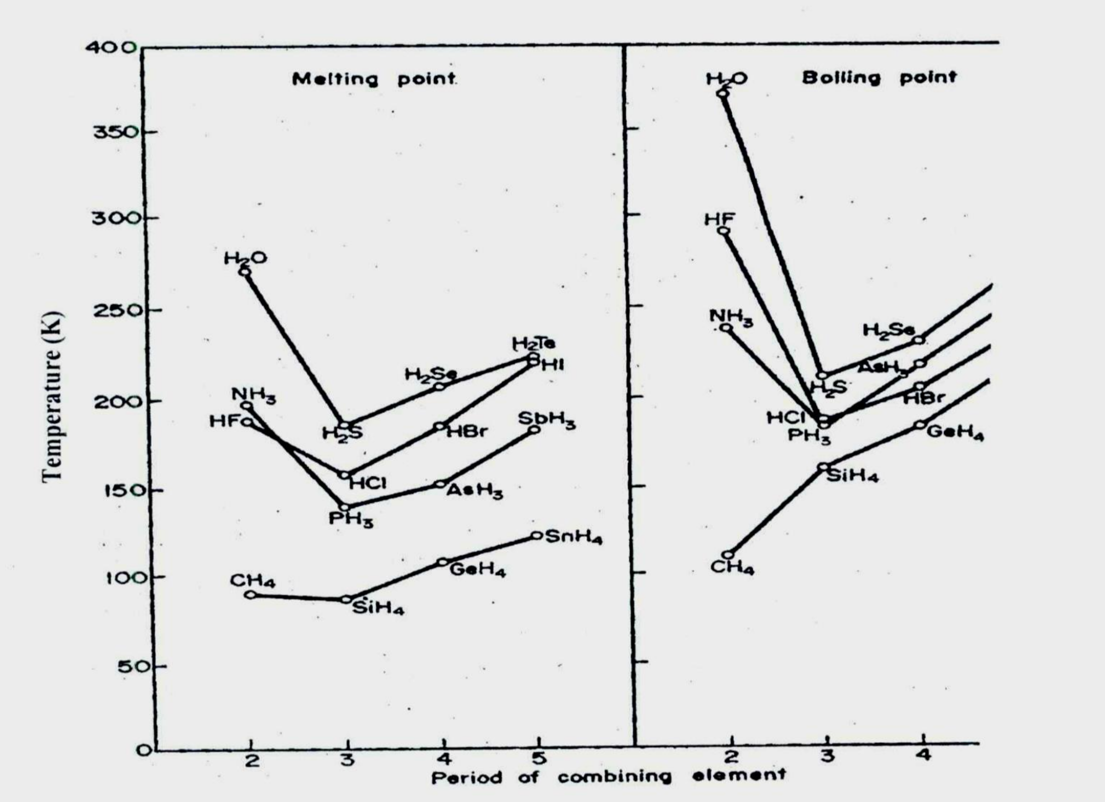


Fig. 1.1: (a) Melting point curves and (b) Boiling point curves of the molecular hydride

3.5 Polarising Power of H^+

We know that the polarising power of a cation, i.e. its ability to distort or polarise an anion is directly proportional to its positive charge and inversely proportional to its size. We can also say that the polarising power of a cation is proportional to the ratio of its charge to its size. This ratio is known as the ionic potential of the cation. As the hydrogen cation, i.e. proton is vanishgly small, it has a very high ionic potential and a vast polarising power.

As result of this polarising power for protons, H^+ hardly exists freely. They are generally found associated with other molecules. For example, with ammonia and water, these form species like NH^{4+}, H_30^+ SO^+, $Hg0^{4+}$ etc. The aquated proton species are represented as H^+. H Enthalpy of formation of these aquated proton species is large (-1075kg mol^{-1}). It is mainly because of this reason that many covalent hydrides (H-X) are acidic in aqueous solution, i.e. they release H^+ ions even though H — X bonds are often very strong in them.

4.0 Conclusion

We can conclude this unit by stating that hydrogen bond formation is a very important phenomenon and it helps in explaining the behaviour of some compounds. Variations in boiling and melting points and solubility of substances are explainable by the existence of hydrogen bonds.

5.0 Summary

In summary, you have studied the following in this unit:

- hydrogen bond is defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom of another molecule, generally of the same compound
- there are two types of hydrogen bonds:
- Intermolecular hydrogen bond
- Intra molecular hydrogen bond
- the hydrogen bonding in substances affect their melting points, boiling points and their solubility in water because of the high polarising power of H^+, it hardly exists freely. It always exists in association with other molecules such as in NH^{4+} H_30^+ H_5O^+ etc.

Self-Assessment Exercise

1. What is the effect of hydrogen bonding on the properties of H_20, HF and NH_3?
2. Why is H_2O a liquid and H_2S a gas at room temperature?
3. Why are Group 2 metals harder and have higher melting points as compared to the Group 1 metals?

6.0 Self-Assessment Exercise

1. Which hydrogen bond do you expect to be stronger and why?
    i. S ---H ------O or (b) O---- N-------S
2. Explain why the boiling points of hydrogen halides follow the trend
3. When a hydrogen bond is symbolised by X-H……….. Y, what do the solid and dotted lines represent? Which distance is shorter?

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry.* Cambridge: Cambridge University Press.

Unit 2 General Physical and Chemical Characteristics of the Alkali Metals

1.0 Introduction

You will no doubt recall that at the beginning of our studies we learnt how the efforts of leading scientists resulted in the formation of the periodic table as we know it today. You recall that the end product of that effort is the arrangement of the elements according to their atomic numbers. You also recall how in the last few units, we discussed that the properties of the elements in a periodic table are indeed a periodic function of their atomic numbers as stated by the periodic law. We also saw that elements belonging to the same groups have the same properties.

In earlier units, you studied hydrogen and learnt about its unique position. Hydrogen, you recall gas properties which resemble the Group 1 elements in some respects and the Group 17 elements in others.

In this unit, you will be studying the elements of Group 1, their occurrence extraction and uses. You will also be studying their physical properties.

The elements of Group 1 and 2 are called the S-block elements because the outermost electron(s) in these elements occupy the S-orbital. Group 1 elements consist of Li, Na, K, Rb, C and Fr. They are called **alkali metals** because they form hydroxides which are strong alkalis.

2.0 Objectives

At the end of this unit, you should be able to:

- list for each member number of the alkali group where they can be land
- give for each member at least one use
- discuss, the atomic size, density, melting and boiling points, ionisation energy and electro negativity of members of the group.

3.0 Main Content

3.1 Alkali Metals

Alkali metals are useful as metals as well as in the form of their compounds.

3.2 Occurrence

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% lithium, rubidium and calcium in trace amounts 1.8×10^{-3} % , 7.8×10^{-3} % and 0.26×10^{-3} % respectively.

Sodium as sodium chloride is the most abundant metal in sea water (M1.08%). Lithium occurs in alumino silicate rocks, e.g. spodumene, $LiAl(SiO_3)_2$ and Lepidolite $(Li, Na, K)_2$ $(F,OH)_2$ Sodium in rock salt, NaCl, in Chile Saltpetre $NaNO_3$, and in Cryolite, Na_3A1F_6, Potassium in carnallite, KCl, in $MgCl_2$. $6H_20$, in Saltpetre KNO_3 and in Kainite, kCl, $MgSO_4$, $3H_20$.

Rubidium and calcium are rare elements and generally occur in small quantities along with other alkali metals. For example, carmallite contains up to 0.94% rubidium chloride, Lepidolite, and containing about 0.2 to 0.7 per cent of calcium expressed as calcium oxide. Francium being a radioactive element with a very short half-life period (21.8 minutes) occurs in very minute's traces in nature.

3.3 Extraction of Alkali Metals

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 1150K 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 1000K under calcium pressure. Rubidium and caesium salts are obtained during the recrystallisation of other naturally occurring alkali metal salts. Francium is produced as a result of a — emission (1%) during the radioactive decay of actinium (Figure 2.1)

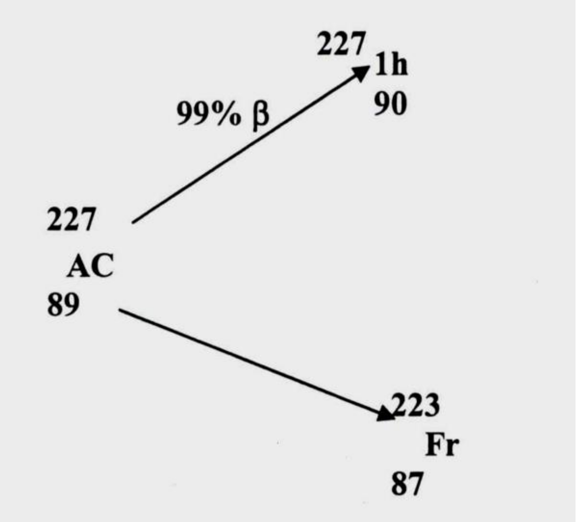


Fig. 2.1: Production of Francium as a Result of Decay

3.4 Uses of Alkali Metals

The alkali metals are very good conductors of heat and electricity. However, 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 a 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 far 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.

Other every day uses of alkali metal compounds include the following:

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.

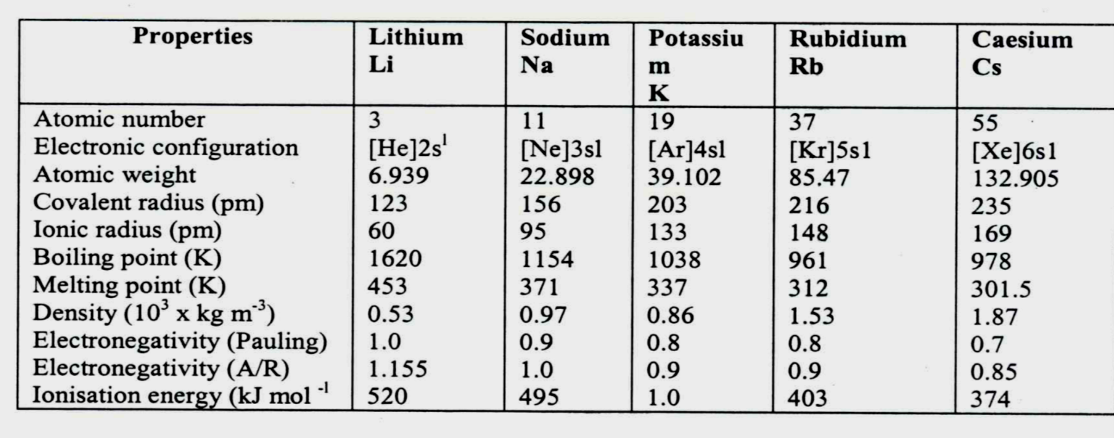
Can you imagine food without common salt! Apart from being an essential constituent of food, sodium chloride has many other important industrial uses like in the manufacture of NaOH, Na_2CO_3, Cl_2 , and H_2 gases. Apart from sodium chloride, other compounds of sodium also have many uses. Caustic soda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

Potassium compounds also have many uses. Potassium hydroxide is used in liquid detergents. Potassium superoxide is used 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 fertilizers, where it is used in form of chloride and nitrate salts.

3.5 Physical Properties

Most of the physical properties of the alkali metals are directly relocated to atomic properties of elements. Variation of physical properties from one element to the other in a group is governed by the trends of the various atomic properties earlier discussed in Module 2. We shall now apply them to understand the group trends in the various physical properties of the Group 1 elements given in Table 2.1

Table 2.1: Properties of Group 1 Elements



Properties	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs
Atomic number	3	11	19	37	55
Electronic configuration	[He]2s^1	[Ne]3sl	[Ar]4sl	[Kr]5s1	[Xe]6s1
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)	1.155	1.0	0.9	0.9	0.85
Ionisation energy (kJ mol^{-1}	520	495	1.0	403	374

Atomic size

From your studies in Unit 4 of Module 1, you will recall that the 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 2.1). 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 out- weighs the effects of increased nuclear charge and thus there is an increase in size from Li to Cs. This trend is shown in Figure 2.2

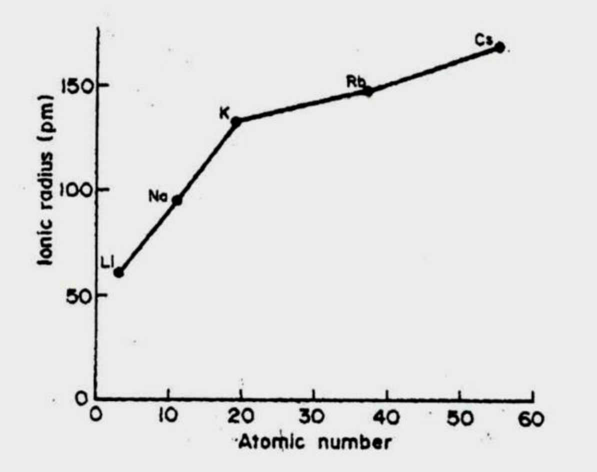


Fig. 2.2: Trend in Ionic Radii of Group 1 Elements

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 (i.e. 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 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 structuring are often the same within any group, the factors which determine the density are atomic mass and volume. As you can see from Table 2.1 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 2.1 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. It's a result of increase in size and repulsion of the non-bonded electrons, their cohesive energy and tendency for metallic bonding decreases 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 decreases as we go down the group (Figure 2.3).

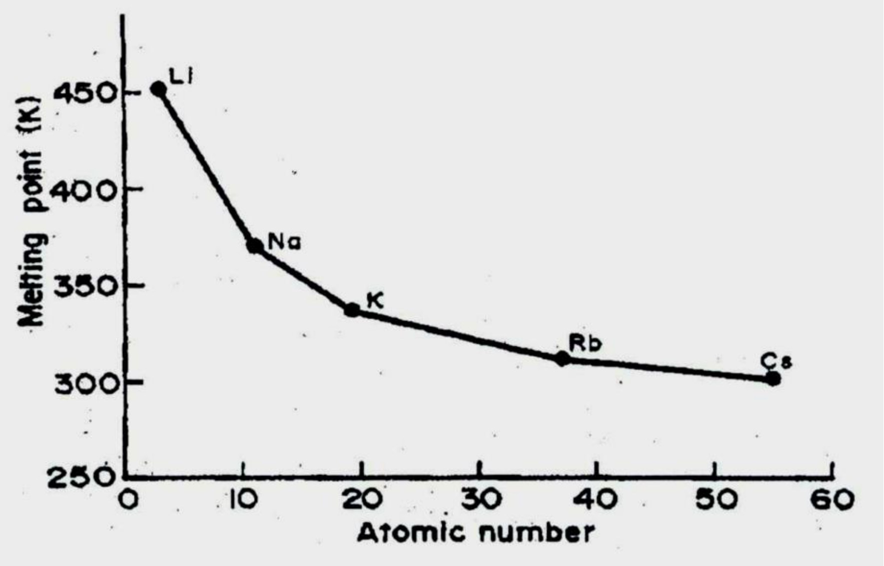


Fig. 2.3: Trend in the Melting Point of Group 1 Elements

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. This makes the alkali metals good conductors of heat and electricity. This loosely bond electron is also responsive for the silvery lustre of the alkali metals when freshly cut.

Ionisation energy

By losing the loosely bond 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 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. It is even more so in the case of the alkali metals, because their charged ions ($Li^{+,}$ Na^+, K^+ etc.) have the stable noble gas configuration of the stable noble gas configuration of the proceeding group. Removal of an electron from a stable noble gas configuration is extremely difficult. These metals, therefore, form univalent cations only. Figure 2.4 shows the trend in the first conisation energies of the alkali metals down the group.

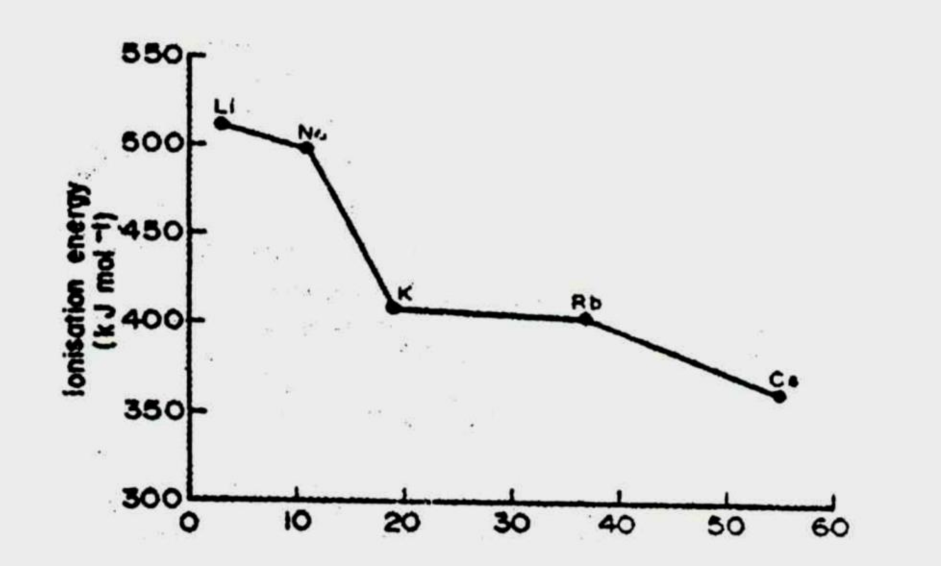


Fig 2.4: Trend in First Ionisation Energies of Alkali Metals

On account of their low ionisation energies these elements have a high tendency to form cations. In other words, they have a 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 photo electric effect.

Electronegativity

Because alkali metals have a tendency to lose electron easily rather than to gain, values of electro negativity 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 the large electro negativity difference.

You can see that the trends in ionic character (Figure 2.5) show that 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. First let us remind ourselves that 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 ions and inversely proportional to the distance between the cation. This distance is taken as the sum of radii of cation and anion (rc + ra).

Let us again remind ourselves that lattice energy is the enthalpy change when one mole of crystal lattice is formed from the isolated gaseous ions and hydration energy is the enthalpy change when one mole of solute is dissolved in water. In a group, the charge on cations remains constant. Thus, lattice energy depends mainly on the size of the cation.

Similarly, hydration energy 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.

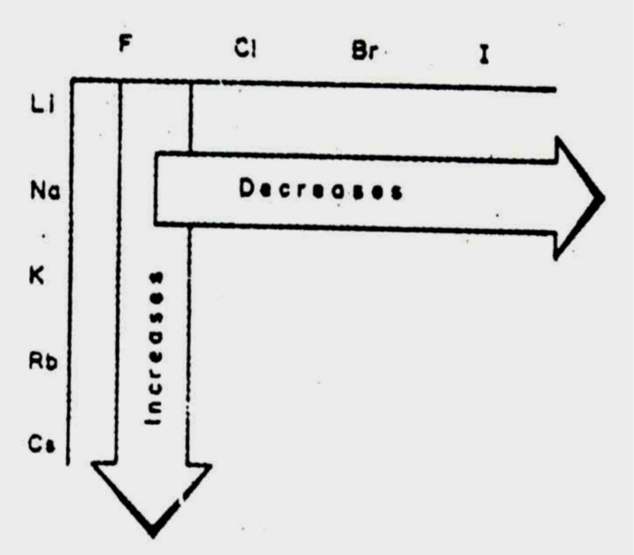


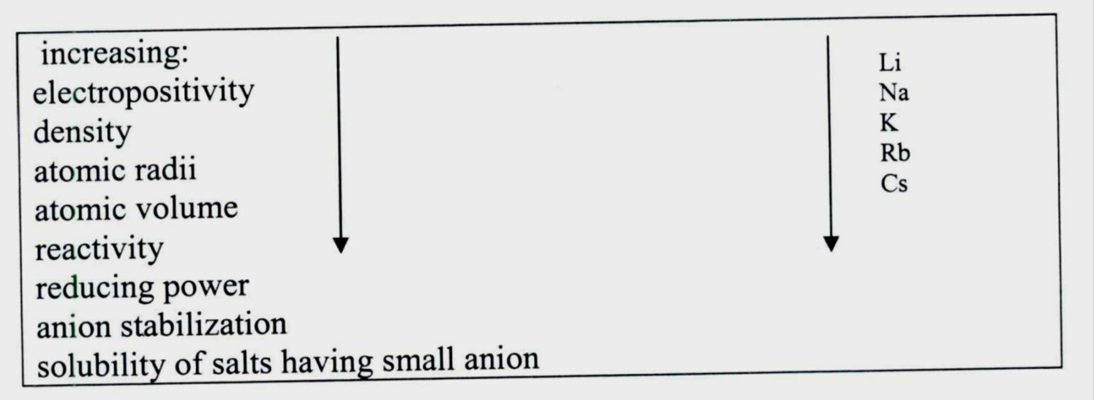
Fig. 2.5: Trend in Ionic Character of Alkali Halides Metals

For the salts of small anions (like F, 0^{2-}, OH^- etc.) the lattice energy which is inversely proportional to rc + ra, 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, + ra) 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< Na F < KF <RbF < CsF.

For the salts having large anions (SO 42-, F, NO3 - HCO3 -, CO3 2-, etc) as ra >>r,, the radii of the cation has little contribution in the total (r + ra) 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 carbonates, lithium carbonate is highly soluble while the solubility of calcium 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 calcium. If we, then change the anion from fluoride to iodide, then the solubility of the compound will vary as CsF > CsCl > CsBr > CsI. Thus, calcium fluoride will be most soluble and calcium iodide will be the least. Similarly, from lithium fluoride to lithium iodide: the solubility will increase in the order: LiF < LiCl <LiBr < LiI.

Table 2.2: The Main Trends in the Properties of Alkali Metals



increasing:
electropositivity
density
atomic radii
atomic volume
reactivity
reducing power
anion stabilization
solubility of salts having small anion

Li
Na
K
Rb
Cs

- The density of K is less than that of Na:

There can be many more examples which can be explained on the basis of above reasoning. Table 2.2 shows a summary of the trends discussed in this section.

4.0 Conclusion

We can conclude this unit by observing that the alkali metals as a group are very reactive, in fact so reactive that they can hardly be found in a free state. They occur in a combined form.

Alkali metal compounds are very useful for everyday life. They are good conductors of heart as well as electricity.

5.0 Summary

In summary, you have studied the following:

- the alkali metals can only be found in a combined state
- tthe alkali metals are very reactive
- the alkali metals are very useful, some of their uses include being used as electrical conductors.

They are also used at homes for example sodium chloride is used as table salt.

Self-Assessment Exercise

1. Given below are some of the statements about the alkali metals. Write `T' if True and "F" if you think it is false.
    - Sodium is the most abundant alkali metal in the earth
    - Sodium is the most abundant metallic element in sea water
    - Alkali metals occur in the free state in nature
    - Lepidolite is an ore of lithium
    - Atomic radii of the alkali metals decrease down the group
    - Ionisation energy increases from lithium to francium
    - Melting and boiling points of alkali metals decrease down the slope.
    - Lithium is the highest of all the metallic elements
    - Solubility of alkali metal fluorides in water increases down the group
    - Ionic character of alkali metal halides decreases down the group.
2. Explain in brief why the hydride bridge in $(BeH_2)n$ considered to be electron deficient, but not the halide bridge in $(BeCl_2)n$

6.0 Self-Assessment Exercise

1. Why are the elements of Group I called alkali metals?
2. Why do alkali metals not occur as free elements in nature?
3. Explain why:
    - alkali metals are good conductors of electricity

- lithium has the highest ionisation energy in the group
- sodium forms +1 ion and not +2 ion
- group 1 elements form ionic compounds

4. Explain why hydroxides become stronger alkalis on descending the group.
5. Why do peroxides and super oxides oxidize in aqueous solution?

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry.* Cambridge: Cambridge University Press.

Unit 3 Compounds Alkali Metals

1.0 Introduction

In the last unit, you studied the elements of group 1 otherwise known as, Alkali metals. You studied the occurrences, extraction, uses and physical properties of the alkali metals.

In this unit, you will be studying the chemical properties of the alkali metals. You will also study the oxides, hydroxides sulphides, hydrides carbides and thermal stability of salts of the alkali metals.

2.0 Objectives

At the end of this unit, you should be able to:

- list the types of oxides formed by alkali metals
- explain using equations, the reactions involved in the formation of the oxides
- explain using equations the formation of sulphides, carbides and hydrides by alkali metals
- explain using examples the stability of salts formed by alkali metals.

3.0 Main Content

3.1 Compounds of Alkali Metal

In Unit 2 you 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 solution. Now we shall discuss some of the important classes of these salts.

3.2 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: normal oxides having 0^{2} ion and the peroxides having 0^{2-} [0 — 0] ion, both of which are dia-magnetic and colourless. The third one which is coloured and **paramagnetic** is super oxide containing 0^{2} $^{-}$ ion. Controlled oxidations of these metals are as follows:

$$2\,Li \xrightarrow{\frac{1}{2}O_2} \mathbf{Li_2O} \xrightarrow{\frac{1}{2}O_2} Li\ {}_2O_2$$

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

$$2K \xrightarrow{\frac{1}{2}O_2} K_2o \xrightarrow{\frac{1}{2}O_2} K_2O_2 \xrightarrow{O_2} \mathbf{2KO_2}$$

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

$$2\,Cs \xrightarrow{\frac{1}{2}O_2} CS_2O \xrightarrow{\frac{1}{2}O_2} CS_2O_2 \xrightarrow{O_2} \mathbf{2CSO0_2}$$

In the scheme shown above the products underlined 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 I metal oxides are strongly basic and react vigorously to give hydroxide.

$$Li\,O + H_2O \longrightarrow 2\,Li0H \text{ (less violent)}$$
$$Na_2O_2 + 2H_2O2 \longrightarrow Na\,0H + H_20_2$$
$$2KO_2 + 2H_2O \longrightarrow 2K0H + H_20_2 + 0_2$$

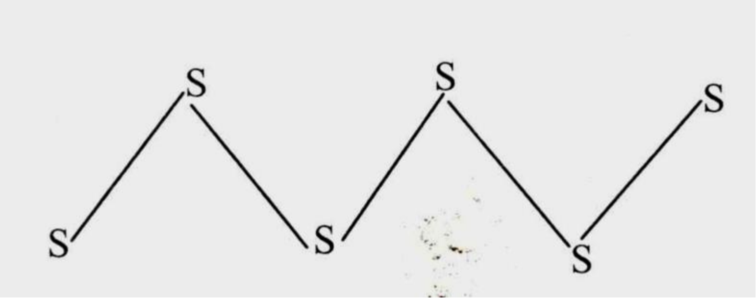
As shown, the peroxides and the super oxides on reaction with water give H_20_2 which in turn is a powerful oxidising agent. Thus the peroxides and the super oxides are also oxidising in nature.

The basic strength of the hydroxides increase down the group. As the charge density (charge/size ratio) of the cation decreases between M^+ and $0H^-$ also decreases. So,OH^- can be liberated readily into the solution and O as we go down the group.

3.3 Sulphides

Alkali metals reacts with sulphur to form two types of sulphides; simple sulphides of Na_2S and polysulphides like Na_2S, where n — 2, 3, 4, or 6.

These polysulphides have a zig-zag chain structure as shown below.



3.4 Hydrides

Alkali metals react with hydrogen and form ionic hydrides, MH. 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 $A1C1_3$ in other 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.

3.5 Carbides

Lithium reacts with carbon to form ionic carbides, whereas similar carbides of other metals are not formed on reacting 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:

$$Na + C_2 H_2 \xrightarrow{LiQ\ .NH_3} Na\ HC_2 \longrightarrow Na_2\ C_2^-$$

These carbides contain the carbide ion (C = C) 2- on hydrolysis they give acetylene. Hence, are termed as acetylides;

$$Na_2\ C_2 + 2\ H_2O \longrightarrow 2\ Na\ OH + C_2\ H_2.$$

Alkali metals also form covalent compounds such as methylithium, LiCH3 and ethylsodium $NaC_2\ H_5$. These come under the separate class of organometallic compounds. The main reactions of group I elements are summarised in Table 3.1

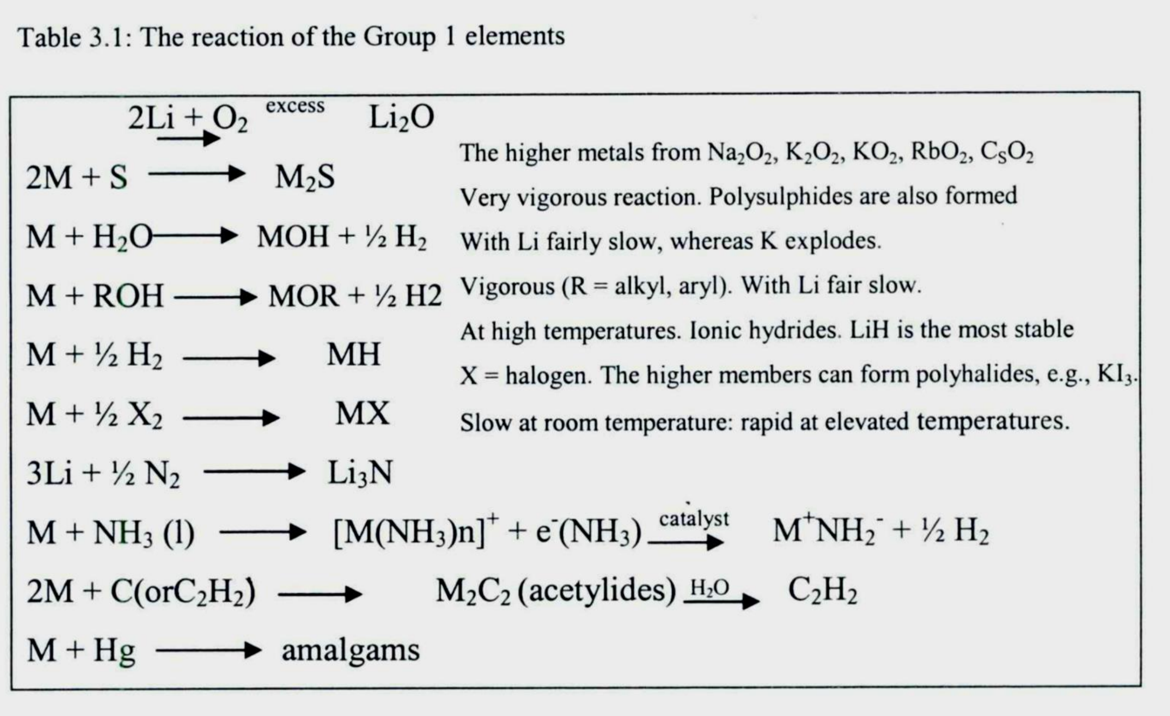


Table 3.1: The reaction of the Group 1 elements

$2Li + O_2 \xrightarrow{excess} Li_2O$	The higher metals from Na_2O_2, K_2O_2, KO_2, RbO_2, C_SO_2
$2M + S \longrightarrow M_2S$	Very vigorous reaction. Polysulphides are also formed
$M + H_2O \longrightarrow MOH + ½ H_2$	With Li fairly slow, whereas K explodes.
$M + ROH \longrightarrow MOR + ½ H2$	Vigorous (R = alkyl, aryl). With Li fair slow.
$M + ½ H_2 \longrightarrow MH$	At high temperatures. Ionic hydrides. LiH is the most stable
$M + ½ X_2 \longrightarrow MX$	X = halogen. The higher members can form polyhalides, e.g., KI_3.
$3Li + ½ N_2 \longrightarrow Li_3N$	Slow at room temperature: rapid at elevated temperatures.
$M + NH_3\ (l) \longrightarrow [M(NH_3)n]^+ + e^-(NH_3) \xrightarrow{catalyst} M^+NH_2^- + ½ H_2$	
$2M + C(orC_2H_2) \longrightarrow M_2C_2\ (acetylides) \xrightarrow{H_2O} C_2H_2$	
$M + Hg \longrightarrow amalgams$	

3.6 Thermal Stability of Salts

The case with which a salt decomposes is related to the enthalpy of formation of the salt. (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). The enthalpy of formation **Hf** of a salt MA (M is the metal, A the anion) is given by

$$H_f = (\ H + I) \quad + \quad (\ H - E_A) \quad - \quad H_{latt}$$

Where H is the enthalpy of atomisation, **I** is the ionisation energy and EA is the electron affinity. Since for any salt in a particular group the terms involving the anion alone remain constant the value of .H °F for such compounds is dependent upon the sum of the enthalpy terms of the particular metal (.H atom + I metal) and the lattice energy .H latt . The larger the lattice energy, the more negative the enthalpy of formation and so, the 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 decide by the parameter which decreases more rapidly — the lattice energy or the sum of the metal enthalpies.

In the salts having small anions of high charge density, eg F -, N3-, OW, 0_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 sun 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 > Na F> KF > RbF > CsF.

The opposite trend is observed in the stability of the salts containing large anions of low charge density, eg Br $^-$, I$^-$, NO$^-$ 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 the 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 polarising anions, relative to some decomposition product decreases. In general, the least polarising metal ion 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 with large anions.

Let us take for example carbonate of Group I metals. The carbonates of sodium potassium and caesium are resistant to the heat of a burner flame. However, lithium carbonate decomposes to its oxide and carbon dioxide under the same conditions.

$$Li_2\,CO_3 \longrightarrow Li_2O + CO_2$$

The tendency of Li 2CO3 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 (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 solution 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.

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

The thermal stability of group I hydroxides also follows a similar trend as that of carbonates. Thus with the exception of LiOH which on heating d decomposes to Li_20, all other group I hydroxides are stable. Similarly, lithium nitrate also decomposes on heating to give Li_20 NO_2 and O_2 but all other alkali metal nitrates decompose on strong heating to nitrates liberating oxygen.

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

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

4.0 Conclusion

We can conclude this unit by observing that alkali metals being very reactive form oxides hydroxides and peroxides. Also that the stability of alkali salts depends on the enthalpy of formation of the salt.

5.0 Summary

In summary, you have studied the following:

- alkali metals form oxides, hydroxides and peroxides
- three types of oxides are formed viz normal oxides, peroxides and super oxides
- three normal oxides, peroxides and super oxides
- the alkali salt's stability is dependent upon the enthalpy of formation.

Self-Assessment Exercise

1. Explain briefly why alkali metals act as strong reducing agents.
2. The thermally least stable alkali metal fluoride is;
    - LiF
    - NaF
    - KF
    - RbF
    - CsF
3. Why is it that Be forms mostly complexes with tetrahedral structure?

6.0 Self-Assessment Exercise

1. Why do peroxides and superoxide oxidise in aqueous solution?
2. Explain why lithium forms more complexes?

7.0 References/Further Reading

Cotton &Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry.* Cambridge: Cambridge University Press.

Unit 4 Solvation of Alkali Metal Ions

1.0 Introduction

In Unit 2, you studied the formation of oxides, hydroxides, carbides and sulphides by the alkali metals. In this unit you will be studying the behaviour of the alkali metals in solutions. You will also study the complexation behaviour of the alkali metals. In your study of the chemical properties of the alkali metals, you must have noticed that lithium behaved differently from the rest of the alkali metals. In this unit, you will be studying the anomalous behaviour of lithium.

2.0 Objectives

At the end of this unit, you should be able to:

- discuss the solvation of alkali metals describing the behaviour of each member of the alkali metals when in solution of water
- describe using equations the behaviour of the alkali metals when dissolved in liquid ammonia
- explain what is meant by complexation (complex formation) by describing the role of the alkali metal in relation to the surrounding molecules
- list at least four anomalous behaviour of lithium.

3.0 Main Content

3.1 Solvation of the Alkali Metal

When a metal is surrounded by solvent molecules, the phenomenon is called **Solvation** of the metal ion. When the solvent is water the phenomenon is now called **Hydration**.

Hydration is therefore solvation with water as the solvent. The alkali metal ions are highly hydrated. The smaller the size of the ion, the greater 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 (Unit 1). Thus Li^+ ion, which is the smallest gets more hydrated than Na^+ 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. Lithium 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 of the alkali metals, but it is not so. This is because the hydrated Li+ is the largest of all the alkali metal ions. In solution its mobility is less and so Li+ ion is the least conducting in solution. The ionic conductance in solution actually decreases in the order C s+ > Rb+ + > Na+ > Lit > K.

3.2 Solutions of Alkali Metals in Liquid Ammonia

All the alkali metals are highly soluble in liquid ammonia giving a deep blue colour. The solubilities of the metals for 100g of ammonia 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 value 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 Para magnetizing suggesting that the electron can get associated to form diamagnetic electron pairs. Although there may be other equilibria also.

$$Na_{(s)}\ \text{(dispersed)} \rightleftharpoons Na\ \text{(in solution)} \rightleftharpoons Na^{+}e^{-}$$
$$2e \rightleftharpoons e_2$$

On increasing the concentration above 3M, the colour of the solution changes to copper bronze having metallic luster, because the metal ions form clusters. Apart from lithium other alkali metals can be recovered unchanged from solution. Lithium, in ammonia solution form 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. The reaction that results in the formation of an amide.

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

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.

3.3 Complex\a\tion Behaviour of Alkali Metals

A complex compound can be defined as a compound with a central atom or ion surrounded by a group of ions of molecules called "ligands". These ligands are usually bond to the metal by a "coordinate bond" i.e a bond formed by the donation of a lone pair of electrons from one atom (of the liquid) to the other (metal/ion). Although both metal and the legend 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. It does not dissociate into Fe+ and CN - , as a result it will not give any positive result when tested in Fe + and CN- . It is thus complex specie. The most stable complexes would be formed by the lightly polarising cations. This is because they have a strong tendency of interacting with electron clouds of other anionic or neutral electron rich species (ligands).

According to the model above, a very weak coordinating ability is expected in the group I 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.

Alkali metals form few complexes mostly **chelates** with the ligands like B- ducetones, nitrophenils, nitroso naphthols etc. as shown in Figure 4.1. They have low stability.

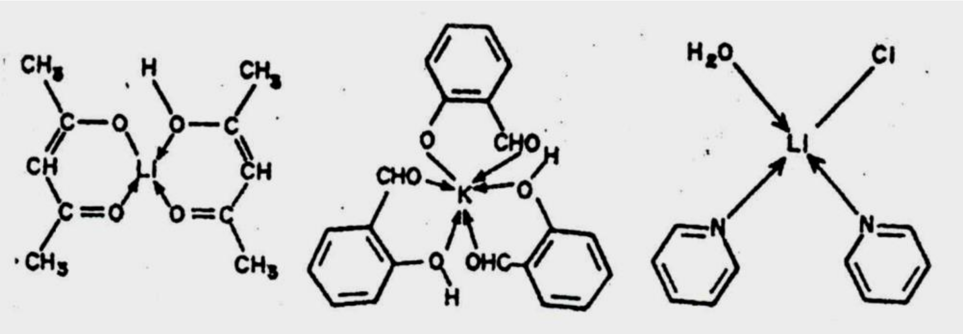


Fig. 4.1: Source Complex of Alkali Metal Ions

Lithium, being the most polarizing cation of all the alkali metals forms tetrahedral complexes with ligands like NH_3, L_5H_5N etc. With ammonia it forms the complex of the type [Li $(NH_5)_4$]I, whereas with pyridine a complex of the type [LiCl(C_5 $H_5N)_2$ (H_20)] formed .

3.4 Anomalous Natures of Lithium

On descending any group of S or P block elements of the periodic table, one notices that, there is a general decrease in electro negativity or increase in electro negativity. The difference in electro negativity between the first and 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 element more electronegative than the other elements of the group, but it is much more electronegative than expected by simple extrapolations.

This trend of bigger than expected differences in properties between the first member of a group and the rest of the elements is shown in group I where Li elements markedly different from the rest of the members of the group.

Let us take a look at these summaries again as they apply in Group 1. 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 point, and boiling point, hardness and homonuclear bond energy.

The relatively higher attraction of lithium for its outer electron results in its relatively higher centre 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 different appear greater as we shall see in the following accounts.

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

(ii) Lithium does not form solid bicarbonate trioxide or superoxides, because these are unstable at room temperature. On the other hand 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 soluble in organic solvents.

(iv) Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For examples, 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 as earlier seen in section 3.3 of this unit. For example, lithium cannot be recovered unchanged from its liquid ammonia solution. Owing to the formation of $[Li(NH_3)_4]_4$.

4.0 Conclusion

We can conclude this unit by stating that the alkali metal ions are very soluble in both water and liquid behaviour. Also that lithium shows the anomalous ammonia observed for first members of any group of the elements in the periodic table.

5.0 Summary

In summary, you have learned the following from the foregoing unit:

- the alkali metals are highly soluble in water and in liquid ammonia
- Li+ ion is the least conducting in solution, when compared to the ions of the other members of the alkali metal ions in solution.
- the stability of alkali metal complexes is low
- the stability of the complexes decrease as you go down the group. ie Li >Na>K>Rb>Cs

- lithium shows anomalous behaviour in relation to the other members of group 1. That is that in each of the properties shared by members of the group, Li shows wide differences between it and the next member of the group immediately below it.

Self-Assessment Exercise

i. Briefly explain the variation of conductivity in alkali metal salts giving reasons for the trend.

ii. Why are alkali metals poor complexing agents?

iii. Why does ammonia acts as a lewis base

iv. Why is hydrazine unstable?

6.0 Self-Assessment Exercise

i. Explain why lithium forms more complexes than the other elements of group I.

ii. Give the trend in the solubility of alkali metal iodides

7.0 References/Further Reading

Cotton and Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.

Unit 5 Alkaline Earth Metals

1.0 Introduction

In Units 2 — 4, you studied the general characteristics of group 1 elements, i.e the Alkali metals, and their compounds. Groups 1 and 2 elements belong to the s-block of the periodic table. Their electronic configurations show an outer shell of ns^1 and ns^2 for alkali and alkaline earth metals respectively. s-block elements are known to be very reactive metals and generally form ionic compounds. In this unit you will be studying 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. (Remember that the alkali metals are so called because they form hydroxides which are strong alkalis).

Beryllium is not counted as an alkaline earth metal since its oxides is not alkaline. We shall start our study of the alkaline earth metals by studying their occurrence, extraction uses and physical properties.

2.0 Objectives

At the end of this unit, you should be able to:

- list at least four places where the alkaline earth metals can be found
- describe at least two methods used in the extraction of the alkaline earth metals
- list at least three uses of members of the group
- compare the physical properties of members of the group with each other.

3.0 Main Content

3.1 Alkaline Earth Metals

The alkaline earth metals, like alkali metal are very reactive; therefore, do not occur free in nature. All of them are found in form of their salts. Let us now study their occurrences, extraction and uses. We shall also go on to study their physical properties.

3.2 Occurrence

Beryllium, the first member of the group is found in small quantities in the silicate mineral, phenacite, Be_2SiO_4, and beryll, $3BeO.Al_20_3$.$6Si0_2$.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 sodium (chloride) in sea water. It occurs as magnesite, $MgCO_3$; dolomite $MgCa(CO_3)_2$; kieserite, $MgSO_4.H_20$ and carmallite, $KMgC1_3$ .6H20 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 (chlorophyll) 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.

3.3 Extraction of Alkaline Earth Metals

These metals are extracted by electrolysis of their fused chlorides, though magnesium has been manufactured by the carbon reduction of its oxide.

Beryllium is obtained by the electrolysis of molten beryllium chloride. Sodium chloride must be added to the melt as an electrolyte because $BeC1_2$ is covalent and, therefore is a very poor electrical conductor. During the electrolysis, the less active metal Be is produced at the cathode and C12 is evolved at the anode. Calcium is extracted from fused calcium chloride using a graphite anode and iron cathode.

Strontium chloride and Barium chloride are fused for the extraction of strontium and barium respectively.

3.4 Uses of Alkaline Earth Metals

Beryllium is used for making atomic fuel containers because it absorbs very few neutrons and does not become radioactive. Being transparent to X-rays it is used as a window material in X — ray apparatus.

It has a number of uses as alloys, eg when mixed with Cu, Berylium increases the strength of Cu. Six fold. Beryllium alloys are non sparking, therefore, they are used in making hand tools for use in the petroleum industry. Magnesium, because of its lightness, is used as a construction alloy material, e.g. in aircrafts. For this purpose it is alloyed with aluminium.

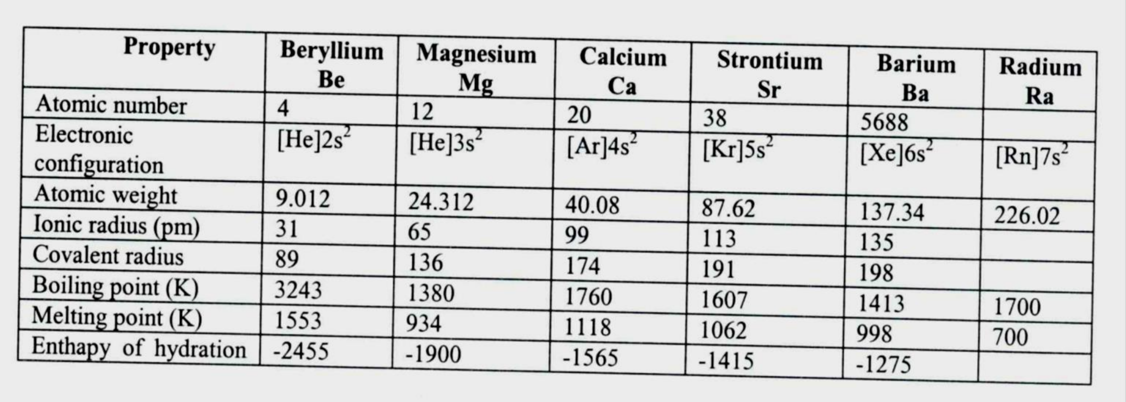
Magnesium is also used as a reducing agent in the extraction of some metals like titanium and uranium. It forms Gringard reagents RMgX, which are important organic reagents.

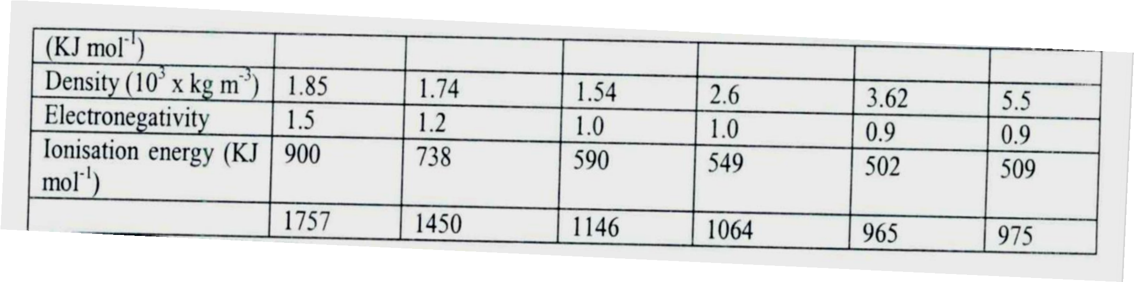
Calcium, strontium and barium as free metals do not find extensive uses because they are very reactive. Calcium oxide (quicklime) is a constituent of glass, mortar and port land cement.

3.5 Physical Properties

The alkaline earth metals are quick soft metals, but are harder than the corresponding Group 1 elements. This is because of their two valence electrons which participate in metallic bonding. They are good conductors of electricity. In pure form they are silver coloured, but on exposure to the atmosphere, the silvery lustre is lost, because of the formation of an oxide layer on the surface of the metal. Their physical properties are given in Table 5.1

Table 5.1: Properties of the Group 2 Metals





Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	5688	
Electronic configuration	$[He]2s^2$	$[He]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$	$[Rn]7s^2$
Atomic weight	9.012	24.312	40.08	87.62	137.34	226.02
Ionic radius (pm)	31	65	99	113	135	
Covalent radius	89	136	174	191	198	
Boiling point (K)	3243	1380	1760	1607	1413	1700
Melting point (K)	1553	934	1118	1062	998	700
Enthapy of hydration (KJ mol^{-1})	-2455	-1900	-1565	-1415	-1275	
Density (10^3 x kg m^{-3})	1.85	1.74	1.54	2.6	3.62	5.5
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9
Ionisation energy (KJ mol^{-1})	900	738	590	549	502	509
	1757	1450	1146	1064	965	975

The atoms of the alkaline earth metals are smaller than those of the corresponding Group I elements. This is because of the increase atomic number. Because of the resulting increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the nucleus, thereby reducing the size of the atom.

Similarly, their ionic radii are also smaller than those of Group I elements, because the removal of two orbital electrons increases the effective nuclear charge even further.

The elements are denser than Group I metals because they have two valence electrons per atom for bonding the atoms into a metallic lattice and as a result more mass can be packed into a smaller volume.

The density decreases slightly on moving down the group from Be to Ca but increases considerably thereafter up to Ra.

The atomic/ionic radii increase from Be to Ra due to the effect of extra shells of electrons added. This outweighs the effect of increased nuclear charge. Group 2 metals have higher melting points when compared to group I metals. The reason being the +2 charge on the cations in the metallic lattice causing them to be more strongly attracted to the 'Sea of electrons and making it difficult to pull them apart.

The first ionisation energy (Table 5.1) of alkaline earth metals is more than that of corresponding alkali metals. This is because the alkaline earth metals have higher nuclear charge and are smaller in size. The electrons are therefore more tightly held to the nucleus. The second ionization energy of these elements is almost twice their first ionization energy. This is because once one electron has been removed, the effective nuclear charge felt by the orbital electrons is increased, so that the remaining electrons are more lightly held and hence much more energy is needed to remove the second electron.

However, their second ionisation energy is less than that of the corresponding alkali metals because of stability of a closed shell configuration of the univalent cations that are formed in the cases of the alkali earth metals.

The ionization energy of alkaline earth metals decreases on moving down the group.

The metals of this group (beryllium is an exception) form ionic compounds. This is because the assembly of positive and negative ions into a symmetrical crystal lattice results in the liberation of large amounts of energy.

Electropositive character and the reducing property (tendency to lose elections) increase on moving down the group.

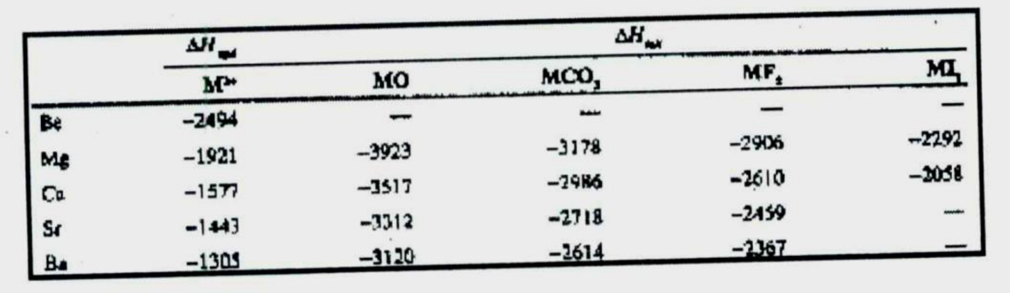
Since alkaline earth metals loose electrons easily, they form divalent anions which have noble gas structure with no unpaired electrons. Their compounds are diamagnetic and colourless, unless the anion is coloured. Ca, Sr and Ba compounds give characteristics flame colourations which are used to identify them - Ca(brick red flame), Sr (crimson red flame) and Ba (apple green flame).

3.6 Solubility, Lattice Energy and Hydration Energy

The solubility of alkaline earth metal compounds shows some interesting trends. The metal ions are easily hydrated, e.g. $MgC1_2$.$6H_20$, $CaC1_2$.$6H_20$, $BaC1_2$.$2H_20$. The hydrogen energies of these metals ions are much greater than those of alkali metal ions (Table 5.2) because of their smaller size and increased cationic charge. The lattice energies of alkaline earth metal salts (Table 5.2) are also much higher than those of alkali metal salts.

Hydration and lattice energies decrease with increase in size of metal ions. Decreasing lattice energy favours increased solubility, whilst decreasing hydration energy favours decreased solubility. If on moving down the group the hydration energy decreases more rapidly than the lattice energy, the compound becomes less soluble. This occurs with most of the compounds except for fluorides and hydroxides for example, solubility of sulphates decreases from $BeSO_4$ to $BaS0_4$. Due to their small ionic radii, Be^{2+} and Mg^{2+}have high hydration energies. Because of that BeSO 4 and MgSO4 only slightly soluble in water, where as SrSO4 and $BaSO_4$ are almost insoluble in water. In the case of fluorides and hydroxides the lattice energy decreases more rapidly than the hydration energy. This causes a reverse trend i.e., the fluorides and hydroxides increases in solubility on moving down the group.

Table 5.2: The Lattice Energies of Alkaline Earth Metal Salts



	ΔH_{hyd}	ΔH_{latt}			
	M^{2+}	MO	MCO_3	MF_2	MI_2
Be	−2494	—	—	—	—
Mg	−1921	−3923	−3178	−2906	−2292
Ca	−1577	−3517	−2986	−2610	−2058
Sr	−1443	−3312	−2718	−2459	—
Ba	−1305	−3120	−2614	−2367	—

Enthalpies of hydration, OH,, alkaline of alkali earth metal ions M^{2+} and lattice energies ΔH_{latt} of their oxides, carbonates fluorides and iodides in kg mol-1

4.0 Conclusion

In conclusion we can say alkaline earth metals, like metals are only found combined inform of their salts, because of their reactiveness. Alkaline earth metals are usually extracted by electrolysis. They are used as alloys and some e.g. Beryllium are used as fuel containers.

5.0 Summary

In this unit, you have learned the following:

- alkali earth metals are very reactive
- because of this reactiveness alkaline earth metals exist mainly in combined forms, as salts
- alkaline earth metals are extracted by electrolysis
- that beryllium is used as an alloys with other metals
- the atoms of the alkaline earth metals are smaller than those of the corresponding Group I elements.

Self-Assessment Exercise

i. Explain briefly why of all nitrogen halides, only NF 3 is Stable

ii. The mechanism of the hydrolysis of phosphorous trichloride, involves the formation of an intermediate four coordinate species. Why is it impossible for $NC1_3$ to hydrolyse using the same mechanism?

iii. Why are Group 2 elements smaller in size than their counter parts in Group 1?

6.0 Self-Assessment Exercise

i. Explain why the first ionisation energy of beryllium is greater than that of lithium, but the position is reversed in the case of the second ionisation energy.

ii. Explain why beryllium forms covalent compounds

7.0 References/Further Reading

Cotton & Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.