

Introduction

The elements in the long form of the periodic table have been divided into four blocks — s, p, d and f- block elements. This classification is based on the type of the atomic orbital in which the outermost electron is located. The s orbital can accommodate two electrons, while the three p orbitals can accommodate a maximum of six electrons. Thus there are two groups of s - block elements — Groups 1 and 2 whose electronic configurations are represented as [Noble gas] ns^1 and [Noble gas] ns^2 respectively. There are six groups of p - block elements — Groups 13 to 18. The s and p block elements are collectively called the main – group elements or representative elements. The d and f - block elements are located between the s and p - block elements.

The s - block elements are located on the left of the periodic table and comprise of highly reactive metals. The p -block elements comprise of both metals and non-metals. On moving from left to right in the periodic table the metallic character decreases, while on moving downwards, in a particular group, it increases. Hence it is apparent that we come across both non-metals and metals in p- block elements with metallic character being more apparent in the heavier members of a group. It is more convenient for us to discuss the s and p - block elements separately since the elements in these two blocks differ significantly in their physical and chemical properties. Our main focus will be on general group trends alongwith comparative study of important compounds.

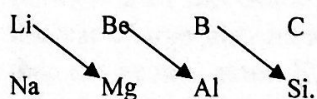
I. s - block elements

The elements of groups 1 and 2 are called the s- block elements because the outermost electron(s) occupy the s -orbital. They are highly electropositive metals and form ionic compounds. They are referred to as alkali and alkaline- earth metals respectively. Due to their high reactivity the metals do not occur in the free state in nature but are present in form of halides, silicates, nitrates (Group1) and silicates, carbonates, sulphates and phosphates (Group 2).

The elements show similarities in physical and chemical properties within a group — however the first elements exhibit considerable differences from the rest of the elements of the same group. This anomalous behaviour is mainly due to the following factors — (i) comparatively higher value of the first ionization energy and electronegativity (ii) small size (iii) high polarizing power of the cation, consequently a greater tendency to form covalent compounds (Fajan's rules) and complexes, (iii) inability to display a coordination number exceeding 4 due to non-availability of d - orbitals in the valence shell.

Diagonal Relationship

A close similarity is observed in certain cases between the first element of a group with the second element of the following group. This is referred to as the diagonal relationship and is observed in the following pairs.



On descending a group, the size increases and the charge on the ion remains the same, thus the polarizing power decreases. On moving across a period, the charge on the ion increases while the size decreases, causing the polarizing power to increase. On moving diagonally the effects of size and charge partly cancel each other, so the polarizing powers are comparable and there is no significant change in properties, particularly for the lighter elements. The

elements along the diagonal also have comparable electronegativities — Li (1.0) & Mg (1.2); Be (1.5) & Al (1.5). However, diagonal similarity is much weaker than the general group similarity.

Group 1 — the Alkali Metals

The elements in this group are lithium, sodium, potassium, rubidium, caesium and the radioactive, francium. They have one electron in their valence shell (ns^1 configuration). Due to similarity in electronic configuration, they exhibit similarities in chemical properties. They are soft, highly reactive, univalent metals, excellent conductors of heat and electricity and form colourless ionic compounds. Lithium shows considerable differences from the lower members and exhibits diagonal relationship with magnesium.

The physical properties of alkali metals are summarized in Table 1.

Table 1: Physical Properties of Group 1 Elements

| Property | Li | Na | K | Rb | 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 |
| Covalent radius (pm) | 123 | 156 | 203 | 216 | 235 |
| Ionic radius (M ⁺) (pm) | 60 | 95 | 133 | 148 | 169 |
| Ionization Energy (KJmol ⁻¹) | 520 | 496 | 419 | 403 | 376 |
| Electron Affinity (KJmol ⁻¹) | 60 | 53 | 48 | 47 | 46 |
| Electronegativity | 0.912 | 0.869 | 0.734 | 0.706 | 0.659 |
| Melting Point (°C) | 180.5 | 97.8 | 63.2 | 39.0 | 28.5 |
| Boiling Point (°C) | 1347 | 881 | 766 | 688 | 705 |
| E ⁰ (M ⁺ → M) (V) against S.H.E, | -3.04 | -2.71 | -2.92 | -2.92 | -2.92 |

General Group Trends

Size & Density

The atoms are the largest in the corresponding horizontal periods of the periodic table. On moving down the group the size of the atom increases as additional shells are introduced to accommodate the electrons. This out-weighs the effect of increased nuclear charge. Formation of the cation involves removal of the outermost shell of electrons; the effective nuclear charge also increases and the electrons are held tightly. Thus the cation is smaller than the neutral atom. Even so, the cations are quite large and an increase in size is observed on descending the group. The atoms are large and the atomic mass is low; thus the Group 1 elements have low densities.

Ionization Energy

The first ionization energies of the atoms are the lowest in the corresponding period. The atoms are large and the outermost electron is loosely held. Moreover; loss of this electron gives a stable noble gas configuration. On moving down the group, the ionization energy

decreases as the size increases. The second ionization energy is extremely high as it is difficult to remove an electron from a cation having noble gas configuration. The elements form unipositive cations, they are highly electropositive and the metallic character increases down the group.

Melting and Boiling Points

These metals are soft and can be cut with a knife. At room temperature they adopt a body-centred cubic lattice. They have one electron that can participate in metallic bond formation and thus they have low cohesive energy, which is reflected in low melting and boiling points. On moving down the group, the metallic bonding becomes weaker and the melting and boiling points decrease.

Electronegativity and Type of Bond

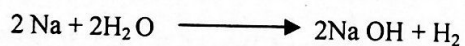
These elements have low electronegativity; consequently when they react with other elements a large electronegativity difference is possible and ionic bonds are formed.

Flame Colours

The alkali metal atoms have low ionization energy and may emit electrons when irradiated with light, hence they find use in photocells. Electrons may also be excited to higher energy levels, for example in the flame test. When an alkali metal salt is introduced to a Bunsen burner flame, a characteristic colour is observed. (Li – red, Na – golden- yellow, K – lilac). The colour arises from electronic transitions, which occur due to excitation of electrons from valence shell to higher excited state energy levels. When the excited electrons return to the original level, the extra energy is emitted and lies in the visible range of the electromagnetic spectrum.

Chemical Properties

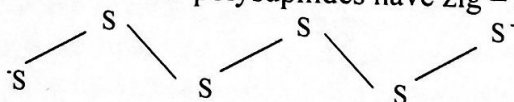
The alkali metals are very similar in their chemical properties, which are governed by the ease with which they can lose their valence electron. They are excellent reducing agents and react with water forming hydrogen.



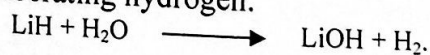
The reaction is highly exothermic.

They react with oxygen to form oxides, peroxides or superoxides depending on the metal. Lithium forms the oxide (Li_2O), sodium, the peroxide (Na_2O_2) while others form the superoxide (M O_2 , $\text{M} = \text{K, Rb, Cs}$). Lithium is the only element that forms a nitride by direct combination with nitrogen.

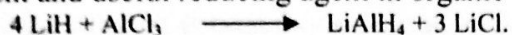
Alkali metals react with sulphur forming sulphides e.g. Na_2S and polysulphides Na_2S_n where $n = 2$ to 6 . The polysulphides have zig – zag chain of sulphur atoms.



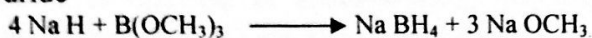
The metals react with hydrogen forming ionic hydrides, M^+H^- . The stability of the hydrides decreases down the group. The hydrides are ionic solids and are the only example of species containing H^- ion. During electrolysis hydrogen is liberated at the anode. They react with water liberating hydrogen.



Lithium hydride reacts with aluminum hydride to form lithium aluminium hydride, an excellent and useful reducing agent in organic chemistry



Sodium hydride reacts with trimethyl borate to form another useful compound, sodium borohydride



The alkali metals react violently with halogens to form halides. The reactivity of an alkali metal towards a particular halogen increases down the group. The reactivity of halogen towards an alkali metal follows the order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. The general reactions of alkali metals are summarized in Table 2.

Table 2: Reaction of Group 1 Metals

| Reagent | Reaction | Remarks |
|------------------------|--|--|
| O_2 | $\text{M} + \text{O}_2 \longrightarrow \text{M}_x\text{O}_y$ | $x = 2, y = 1$ for Li (monoxide); $x = 2, y = 2$ for Na (peroxide) $x = 1, y = 2$ for others (superoxide) |
| S | $2\text{M} + \text{S} \longrightarrow \text{M}_2\text{S}$ | Polysulphides also formed |
| H_2O | $\text{M} + 2\text{H}_2\text{O} \longrightarrow \text{MOH} + \text{H}_2$ | Slow for Li, explosive for K |
| H_2 | $2\text{M} + \text{H}_2 \longrightarrow 2\text{MH}$ | Ionic hydrides formed |
| X_2 (halogen) | $2\text{M} + \text{X}_2 \longrightarrow 2\text{MX}$ | All halogens react |
| N_2 | $6\text{Li} + \text{N}_2 \longrightarrow 2\text{Li}_3\text{N}$ | Only Li reacts |
| ROH | $2\text{M} + 2\text{ROH} \longrightarrow 2\text{MOR} + \text{H}_2$ | Slow for Li, Vigorous for others |
| NH_3 | $\text{M} + \text{NH}_3(\text{e}) \longrightarrow [\text{M}(\text{NH}_3)_x]^+ + \text{e}^-(\text{NH}_3)$ | Excellent reducing agents |

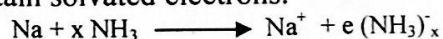
Solvation of Alkali Metal Ions

Solvent molecules always surround a metal ion in solution. This is referred to as solvation. If the solvent is water, then it is called hydration. The alkali metal ions are extensively hydrated. A small ion has high charge density and attracts the solvent molecules strongly, resulting in extensive hydration. The energy evolved during hydration is called hydration energy. Li^+ being smallest is most heavily hydrated and has highest hydration energy. The extent of hydration decreases down the group. Hydration directly affects ionic mobility. Li^+ , the smallest ion is expected to be highly mobile, but in fact the reverse is true. This is because the hydrated radius of Li^+ is the largest and is least mobile and least conducting in solution.

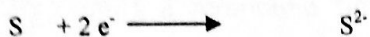
The decrease in hydration from Li^+ to Cs^+ is revealed by the fact that most crystalline salts of lithium are hydrated. Most salts of alkali metals are soluble in water. For any substance to dissolve the hydration energy must exceed lattice energy.

Solution of Metals in Liquid Ammonia

The alkali metals dissolve in liquid ammonia and other amines to give blue solution believed to contain solvated electrons.



Due to the presence of these solvated electrons, dilute solution of alkali metals conduct electricity far better than completely dissociated electrolytes. As the concentration of the metal increases the conductivity decreases initially and then increases. At sufficiently high concentrations the solution develops a bronze metallic luster and the conductivity approaches the value of a molten metal. The dilute solutions are paramagnetic but the paramagnetism decreases with increase in concentration. The blue colour is attributed to the solvated electrons. These solutions are excellent reducing agents.



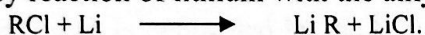
The solutions undergo slow decomposition to give amides.



The Group 2 metals and some lanthanides also dissolve in liquid ammonia.

Alkyls and Aryls

Lithium shows a stronger tendency to covalency than the other alkali metals. It forms covalent alkyls and aryls. These compounds are frequently tetrameric or hexameric and are made by reaction of lithium with the alkyl / aryl halide.



The methyl derivative is tetrameric $[(LiCH_3)_4]$, covalent and soluble in organic solvents. The four Li atoms occupy the corners of a tetrahedron with the methyl groups above the face of the tetrahedron. The classical theories of bonding cannot explain the formation of these compounds, which involve multi-centred bonds. These compounds are starting materials for synthesis of organometallic and organic compounds. The alkyls of Na, K, Rb and Cs are ionic.

Complexation Behaviour of Alkali Metals

The alkali metals generally have weak complexing ability. This is because the factors that favour complexation viz, small size, high nuclear charge and availability of empty orbitals of low energy are lacking in alkali metals.

Aqua complexes like $[Li(H_2O)_4]^+$, $[Cs(H_2O)_6]^+$ are known. A number of chelates are known e.g. those with salicylaldehyde and acetyl acetone.

An important development in the field of alkali metal chemistry is the discovery of complexes with cyclic ethers and cryptands (cryptates) i.e. with macro cyclic molecules containing nitrogen and oxygen. The cyclic ethers are called crown ethers; they have varying sizes of rings and form complexes with alkali metal ions by donating electron density through the oxygen atoms. Examples of such molecules are shown in Fig. 1.

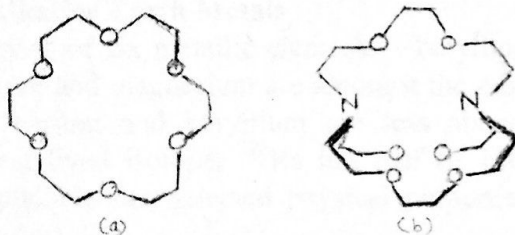


Fig. 1: a. A crown ether b. A cryptand

The cryptates are more selective and stronger complexing agents than the crown ethers, with eight donor atoms (nitrogen and oxygen) surrounding the metal ion completely. The ability of crown ether or a cryptands to trap a metal ion depends on the size of both the cavity and the metal ion.

The chemistry of alkali metals is almost exclusively of the M^+ ion, but examples of anions of the type M^- (alkalide) have been reported. The first such ion to be reported was Na^- formed by cooling a solution of Na in ethylamine with 2, 2, 2 - crypt. A crystalline compound, $[Na(2,2,2 - crypt)]^+ Na^-$ was obtained. The K^- ion was made in a similar way but is less stable. Very recently (2002), a compound "inverse sodium hydride" has been reported containing Na^- and H^+ .

Biological Importance ✓

Living organisms need about 15 metals for different biological processes. Some of the alkali metals are biologically active. Sodium and potassium ions act as charge carriers and are involved with balancing the electrical charges associated with negatively charged macromolecules in the cell. Na^+ is the major cation in the extra cellular fluid and its concentration is about 0.15 M, it is actively expelled from the cell where its concentration is about 0.01 M. K^+ is the major cation inside the cell (0.15 M) whereas its concentration in the extra cellular fluid is about 0.03 M. This uneven concentration of Na^+ and K^+ on either side of the cell wall is controlled by the sodium-potassium pump and a large amount of energy is needed to maintain this disequilibrium. The energy is provided by hydrolysis of ATP. Na^+ and K^+ are also involved in maintaining the osmotic pressure inside the cell, thereby keeping it turgid. The different ratio of Na^+ to K^+ inside and outside the cell produces a characteristic electrical potential across the cell membrane and muscle cells. They also activate specific enzymes. Lithium salts are used as anti-depressants. The exact mode of action is however not clear.

Anomalous Behaviour of Lithium

Lithium in many ways differs from the other members of the group. Lithium also shows diagonal relationship with magnesium in Group 2. Due to the very small size of lithium, the metallic bonding between the atoms in the lattice is strong giving rise to strong cohesive forces. This is reflected in comparatively high melting and boiling points and hardness. The electronegativity of lithium is comparatively high, it also has a high polarizing power and its compounds show appreciable covalent character. The halides of lithium are soluble in organic solvents and it forms covalent alkyls and aryls.

Lithium is the only element to form a nitride and normal oxide. Lithium hydroxide is less basic than other hydroxides and many salts of lithium like the carbonate and nitrate are thermally less stable than the analogous compounds of the heavier members. The lithium ion and its compounds are more heavily hydrated than those of the rest of the group. ✎