Chapter 10

The *s*–Block Elements

Elements of Groups 1 and 2 of the periodic table are called *s*-block elements because the last electron enters the outermost *s*-orbital in the atoms of these elements. Thus, group 1 elements (called alkali metals) have the general outer electronic configuration ns^1 and group 2 elements have ns^2 configuration. s-block elements are the most electropositive elements of the periodic table and they are good reducing agents

ALKALI METALS

The elements lithium, sodium, potassium, rubidium, caesium and francium form group 1 of the periodic table and are called alkali metals. They are called so because they form hydroxides on reaction with water which are strongly alkaline.

1. Occurrence

Among alkali metals, sodium and potassium are abundant and they together make up over 4% by weight of earth's crust. Francium is radioactive and its longest lived isotope has a half life of only 21 minutes.

2. Electronic configuration

The general outer electronic configuration of alkali metals may be represented as ns^1. They readily lose electrons to form M^+ ions. So they are never found in the free state in nature.

3. Atomic and ionic size

The alkali metal atoms have the largest sizes in each period of the periodic table. On moving down the group, the atomic and ionic radii increase because of the increase in the number of shells.

4. Ionisation enthalpy and electropositive character

Alkali metals have the lowest ionisation enthalpies in each period. Within the group, the ionisation enthalpy decreases down the group. They show a stable oxidation state of +1 in their compounds. Due to their low ionisation energies, they are strongly electropositive. The electropositive character increases down the group.

5. Hydration enthalpy

Hydration enthalpy is the enthalpy change involved in the hydration of one mole of ions. The hydration enthalpy of alkali metal ions decrease with increase in size.

i.e., $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Li^+ has the maximum degree of hydration and hence lithium salts are generally hydrated e.g., $LiCl \,.\, 2H_2O$.

6. Reducing property and standard electrode potential (E^o) values

Alkali metals are strong reducing agents due to their greater ease to lose electrons. This is also indicated by the low values of their standard electrode potentials (E^o). The reducing character increases from sodium to caesium. However, lithium is found to be the strongest reducing agent among the alkali metals in aqueous solution in spite of its high ionisation enthalpy. This is because lithium ion, being small in size, is heavily hydrated. The large amount energy released in hydration compensates the high energy required for its ionisation.

The order of decreasing reducing property of alkali metals is $Li > Cs > Rb > K > Na$

7. Flame colouration

Alkali metals and their salts give characteristic colour to the flame. This is because heat from the flame excites the outermost electrons to higher energy levels. As these electrons return to their original level, radiations are emitted which fall in the visible region of electromagnetic spectrum. Thus they appear coloured. *Li* imparts crimson red colour, *Na* gives golden yellow colour, *K* gives violet colour, *Rb* gives red violet and *Cs* gives blue colour to the flame.

Physical Properties

Alkali metals are soft light metals. They have low density and it increases from lithium to caesium. But *K* is lighter than *Na*. Their melting points are low and it decreases from *Li* to *Cs*. The melting point of *Cs* is only 302 K.

Chemical properties

Alkali metals are highly reactive due to (i) lower ionisation enthalpy values and (ii) low heats of atomisation. Chemical reactivity increases down the group.

(i) Reaction with water

Alkali metals react with water to form the corresponding hydroxide and hydrogen. Down the group the reactivity of alkali metal increases.

$$2M + 2H_2O \longrightarrow 2MOH + H_2$$

Alkali metals also liberate hydrogen from alcohols and acetylene. Lithium reacts less vigourously with water because of its small size, high ionisation enthalpy and high hydration energy.

(ii) Reaction with hydrogen

On heating with hydrogen, alkali metals form crystalline ionic hydrides represented by the general formula MH ($M^+ H^-$). Hydrides are strong reducing agents and they give hydrogen with water.

(iii) Reaction with air or oxygen

The alkali metals tarnish in air due to the formation of their oxides which in turn reacts with moisture to form hydroxides. Reactivity of alkali metals with oxygen increases down the group. Lithium when heated in air forms the normal oxide (Li_2O), sodium forms the peroxide (Na_2O_2) while potassium, rubidium and caesium form super oxides (MO_2).

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

$$2Na + O_2 \longrightarrow Na_2O_2$$

$$K + O_2 \longrightarrow KO_2$$

Lithium alone combines with nitrogen of the air when heated to form lithium nitride (Li_3N) also.

(iv) Reactivity towards halogens

Alkali metals react vigorously with halogens to form metal halides of the general formula MX.

$2M + X_2 \longrightarrow 2MX$ X = F, Cl, Br or I and M = alkali metal

Reactivity of alkali metal towards halogen increases from Li to Cs. Halides of alkali metals are ionic compounds readily soluble in water. But lithium halides are somewhat covalent.

(v) Solutions in liquid ammonia

Alkali metals dissolve in liquid ammonia to form blue solutions which are highly conducting in nature. The blue colour of the solution is due to the presence of *solvated electrons*. This solution is paramagnetic.

$$M + (x+y)\,NH_3 \longrightarrow \left[\underset{\text{ammoniated cation}}{M(NH_3)_x}\right]^+ + \left[\underset{\text{ammoniated electron}}{e(NH_3)_y}\right]^-$$

With increase in concentrations colour turns bronze and the solution becomes diamagnetic. These blue solutions lose their colour on keeping and liberate hydrogen and form metal amide.

e.g., $2Na + NH_3 \rightarrow \underset{\text{sodamide}}{2NaNH_2} + H_2$

Uses

1. *Li* is used in making certain alloys. It is also used in thermonuclear reactions and in making electrochemical cells
2. Liquid sodium is used as a coolant in certain nuclear reactors
3. KCl is used as a fertilizer. *KOH* is used to manufacture soft soap.
4. *Cs* is used in photoelectric cells

General characteristics of compounds of alkali metals

1. Oxides and hydroxides

Pure oxides and peroxides of alkali metals are colourless solids, but the superoxides are yellow or orange in colour. *The superoxides are paramagnetic because of the presence of one unpaired electron in* π^* *2p orbital of superoxide ion* (O_2^-). All types of oxides dissolve in water to form the corresponding hydroxide.

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

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

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

The hydroxides of alkali metals are strong bases. The basic character of the hydroxides increases from *LiOH* to *CsOH*.

2. Halides

Alkali metal halides are high melting, colourless solids soluble in water. The melting point follow the order : fluoride > chloride > bromide > iodide.

LiF is only sparingly soluble in water due to its high lattice enthalpy. The solubility of CsI is also low because of lower hydration enthalpy of Cs^+ and I^- ions.

3. Salts of oxo-acids

The carbonates of alkali metals are fairly stable towards heat (except Li_2CO_3). Li_2CO_3 readily decomposes on heating.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

All of them form hydrogen carbonate (or bicarbonate). Li alone does not form solid bicarbonate. The thermal stability of carbonates and bicarbonates increases down the group.

Anomulous behaviour of Lithium

Lithium, the first member of the alkali metal family, differs in many of its properties from the other alkali metals. This anomalous behaviour of *Li* is due to

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

(ii) greater polarising power (i.e., charge/radius ratio) of lithium ion resulting in covalent character in its compounds.

At the same time, lithium shows similarity in properties to magnesium which is diagonally opposite to it in the periodic table. This is known as **diagonal relationship**. The diagonal relationship is due to

(i) similarity in ionic sizes and

(ii) similarity in charge /radius ratio.

Difference between lithium and other alkali metals

1. Li is harder and its melting and boiling points are higher than other alkali metals.
2. Li forms monoxide when heated with oxygen while other alkali metals form peroxides and superoxides.
3. Li combines with nitrogen to form lithium nitride (Li_3N) while other alkali metals do not form nitrides.
4. LiCl is deliquescent and crystallises as a hydrate ($LiCl \cdot 2H_2O$) whereas other alkali metal chlorides do not form hydrates.
5. $LiHCO_3$ is not obtained in the solid state while the bicarbonates of other alkali metals are obtained in the solid state.
6. $LiNO_3$ when heated decompose to form Li_2O, NO_2 and O_2 while other alkali metal nitrates decompose to form the corresponding nitrite and O_2.

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

$$2\,NaNO_3 \xrightarrow{\Delta} 2\,NaNO_2 + O_2$$

7. LiF and Li_2O are comparatively less soluble in water than the fluorides and oxides of other alkali metals.

Similarities between lithium and magnesium

1. Both Li and Mg are harder and lighter than other elements in the respective groups
2. Both Li and Mg combine with nitrogen to form the corresponding nitrides

$$6\,Li + N_2 \xrightarrow{\Delta} 2\,Li_3\,N$$

$$\therefore\ 3\,Mg + N_2 \xrightarrow{\Delta} 2\,Mg_3N_2$$

3. Li and Mg react only slowly with water.
4. Both LiCl and $MgCl_2$ are deliquescent and are soluble in alcohol.
5. The oxides and hydroxides of Li and Mg are much less soluble in water and their hydroxides decompose on heating.
6. The carbonates of Li and Mg decompose easily on heating to form oxides and CO_2.

Biological importance of sodium and potassium

Sodium ions are located in blood plasma and in the interstitial fluid surrounding the cells. These ions take part in (i) transmission of nerve signals (ii) regulation of water flow across cell membranes and (iii) transport of amino acids and sugars into the cells. Potassium ions are the most abundant cations in cell fluids. They take part in (i) oxidation of glucose to form ATP (ii) activation of enzymes and (iii) transmission of nerve signals (with Na^+ ions). The concentrations of Na^+ and K^+ ions vary considerably on the opposite sides of cell membranes. This concentration gradient of ions is due to a mechanism called sodium-potassium pump that operates across cell membranes.

Important Compounds of Sodium

1. Sodium carbonate (soda ash: Na_2CO_3 washing soda: $Na_2CO_3.10H_2O$)

Sodium carbonate is prepared by the **Solvay process** or ammonia–soda process . CO_2 gas is passed through brine solution already saturated with ammonia to form sodium hydrogen carbonate or sodium bicarbonate.

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

$$(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow \underset{\text{ammonium bicarbonate}}{2NH_4HCO_3}$$

$$NH_4HCO_3 + NaCl \longrightarrow \underset{\text{sodium bicarbonate}}{NaHCO_3} + NH_4Cl$$

$NaHCO_3$ so formed precipitates out due to its low solubility. Sodium bicarbonate is filtered and heated to form sodium carbonate.

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

The filterate after the removal of $NaHCO_3$ contains NH_4Cl. It is mixed with calcium hydroxide and heated to recover ammonia.

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

This NH_3 is used again. $CaCl_2$ is a by-product in the process.

It may be noted that Solvay process cannot be used for the manufacture of K_2CO_3 because $KHCO_3$ formed in the intermediate step is highly soluble in water and not precipitaed. So it cannot be separated from solution easily.

Properties

It is a colourless solid soluble in water. The crystals obtained from solution are of the decahydrate called *washing soda* ($Na_2CO_3 \cdot 10H_2O$). On heating washing soda loses the water of crystallisation to form $Na_2CO_3 \cdot H_2O$ (monohydrate). On heating above 373K, it becomes anhydrous sodium carbonate and forms a white powder called **soda ash** (Na_2CO_3). Sodium carbonate hydrolyses in water to form an alkaline solution.

Uses

(i) It is used for washing purposes in laundary.

(ii) It is used for softening of hard water.

(iii) Na_2CO_3 is used in soap, glass and paper industries.

(iv) It is used as a lab reagent.

2. Caustic soda or sodium hydroxide (NaOH)

Sodium hydroxide is manufactured by electrolysing brine solution (NaCl) using a mercury cathode and carbon anode in Castner Kellner Cell. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

$$Na^+ + e^- \xrightarrow{Hg} Na/Hg \text{ (sodium amalgam) (cathode)}; \qquad 2Cl^- \longrightarrow Cl_2 + 2e^- \text{ (anode)}$$

The sodium amalgam formed is brought into contact with water to give sodium hydroxide and hydrogen gas.

$$2Na/Hg + 2H_2O \longrightarrow 2NaOH + H_2 + 2Hg$$

Properties

Sodium hydroxide is a white transluscent solid. It is readily soluble in water and the solution is a strong alkali. Crystals of NaOH are deliquescent.

Uses

(i) Used in the manufacture of soap, paper, artificial silk and a number of chemicals.

(ii) For mercerising cotton and manufacture of rayon.

(iii) For purification of bauxite during extraction of aluminium.

(iv) It is used as a laboratory reagent.

3. Sodium Chloride (NaCl)

Common salt is generally obtained by evaporation of sea water. Crude $NaCl$ obtained by crystallisation of brine contains impurities such as $CaCl_2$ and $MgCl_2$ which make it deliquescent. To get pure $NaCl$, a solution of crude salt is prepared in minimum amount of water. It is filtered and the solution is saturated with HCl gas when $NaCl$ separates out.

It is used as table salt for cooking and also in the manufacture of Na_2O_2, $NaOH$ and Na_2CO_3.

4. Sodium Hydrogen Carbonate (Baking soda $NaHCO_3$)

It can be prepared by saturating a solution of Na_2CO_3 with CO_2 gas. $NaHCO_3$ being less soluble, precipitates out as white solid.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Uses

It is known as *baking soda* because it decomposes on heating to form bubbles of CO_2 which make cakes etc. light and fluffy. It is a mild antiseptic for skin infections.

ALKALINE EARTH METALS

Beryllium, magnesium, calcium, strontium, barium and radium form group 2 of the periodic table. These elements, with the exception of Be, are known as alkaline earth metals because their oxides and hydroxides are alkaline and their oxides are found in the earth's crust.

1. Occurrence

Among alkaline earth metals, Ca and Mg are abundant. Calcium is the fifth most abundant element in earth's crust. Beryllium is not very abundant while the last element radium is radioactive.

2. Electronic configuration

Their general outer electronic configuration may be written as ns^2.

3. Atomic and ionic size

The atomic and ionic radii of alkaline earth metals are smaller than those of the alkali metals in the corresponding periods due to the increased nuclear charge in these elements. The atomic and ionic radii increase with increase in atomic number down the group.

4. Ionisation enthalpies and electropositive character

The alkaline earth metals have low ionisation enthalpies as compared to *p*–block elements and its value decreases down the group. The first ionisation enthalpies of the alkaline earth metals are higher than those of the corresponding alkali metals.

5. Hydration enthalpies

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Hence compounds of alkaline earth metals are more hydrated than those of alkali metals. For example, crystalline calcium chloride and magnesium chloride have the formulae $CaCl_2 . 6H_2O$ and $MgCl_2 . 6H_2O$ respectively while $NaCl$ and KCl do not form such hydrates.

The hydration enthalpies of alkaline earth metal ions decrease with increase in size down the group. It follows the order: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

6. Flame colouration

Calcium imparts brick red colour, strontium gives crimson red colour and barium imparts apple green colour to the bunsen flame. Be and Mg do not give any colour to the flame. This is because the electrons in *Be* and *Mg* are strongly bound to the nucleus and hence are not easily excited by the flame.

7. Melting and boiling point

The melting and boiling points of alkaline earth metals are higher than the corresponding alkali metals due to smaller sizes.

Chemical properties

Generally, reactivity of *s*-block elements increases down the group with increase in electropositive character.

(i) Reactivity towards air and water

Beryllium and magnesium do not react with air and water at ordinary temperature because of the formation of an oxide film on their surface. But powdered *Be* burns in air to form beryllium oxide (BeO) and beryllium nitride (Be_3N_2). Similarly, magnesium burns in air to form MgO and

Mg_3N_2. Ca, Ba and Sr are readily attacked by air to form the corresponding oxide and nitride.

Beryllium is unreactive with water, but Mg reacts with boiling water or steam to form the oxide. Calcium, strontium and barium react with cold water forming their hydroxides.

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

(ii) Reactivity towards hydrogen

Except Be, all the other metals of this group react with hydrogen on heating to form metal hydrides having the general formula MH_2 where M is the group 2 metal. BeH_2 can be prepared by the action of $BeCl_2$ with $LiAlH_4$.

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

(iii) Action of acids

The alkaline earth metals readily react with dilute acids liberating H_2.

(iv) Reactivity towards halogens

Group 2 metals directly combine with halogen to form divalent halides of the formula MX_2 where X is the halogen. $BeCl_2$ is however, prepared by passing Cl_2 over a hot mixture of BeO and coke.

$$BeO + C + Cl_2 \xrightarrow{600-800\,K} BeCl_2 + CO$$

(v) Reaction with liquid ammonia

Like alkali metals, alkaline earth metals dissolve in liquid ammonia to form blue solutions containing ammoniated electrons.

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

(vi) Reducing nature

Alkaline earth metals are good reducing agents. However, their reducing power is less than those of the corresponding alkali metals. Be has less negative reduction potential value compared to other metals of the group. Still it is a good reducing agent due to the large hydration energy of Be^{2+} ion.

Uses

1. Metallic beryllium is used for making windows of X-ray tubes.
2. Magnesium – aluminium alloys are used in air-craft construction.
3. A suspension of magnesium hydroxide in water (milk of magnesia) is used as an antacid in medicine.
4. Ca and Ba are used to remove air from vacuum tubes
5. Radium salts are used in radiotherapy for the treatment of cancer.