THE S-BLOCK ELEMENTS

The elements in which the last electron enters in the outermost s-orbital are called s-block elements. They include elements of group I and II. Group I elements are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs) and Francium (Fr). They are collectively called alkali metals because they dissolve in water to form strong alkalies.

Group II elements are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). They are collectively called alkaline earth metals (except Be) because their oxides and hydroxides are found in earth crust and alkaline in nature.

The general electronic configuration of s-block elements is [noble gas] ns¹ for alkali metals and [noble gas] ns² for alkaline earth metals.

GROUP I ELEMENTS [ALKALI METALS]

General characteristics

- 1. Valence electronic configuration: ns¹
- 2. Atomic and ionic radii: Increases from top to bottom.
- 3. Ionization enthalpy: decrease from Li to Cs.
- 4. Hydration enthalpy: decreases with increase in ionic size. Li⁺ has maximum hydration enthalpy.

5. *Flame colouration*: Alkali metals and their salts give characteristic colour to non-luminous flame. This is because the heat from the flame excites the outer most orbital electron to a higher energy level. When this electron comes back to the ground level, they emit the radiation in the visible region. For example, Li gives crimson red, sodium gives yellow, potassium gives violet, Rubidium gives red violet and Ceasium gives blue colour to the flame. So alkali metals can be detected by flame test.

Chemical Properties

1. *Reaction with air*: They react with air to form oxides, peroxides and super oxides. Li forms only monoxide, sodium forms monoxide and peroxide and other alkali metals form monoxide, peroxide and super oxide.

 $4Li + O_2 \rightarrow 2Li_2O$ $2Na + O_2 \rightarrow Na_2O_2$

 $M + O_2 \rightarrow MO_2$ (where M = K, Rb, Cs)

2. *Reaction with water*: The alkali metals react with water to liberate hydrogen.

 $\rm 2M + H_2O \rightarrow 2MOH + H_2$

But the reactivity of Li with water is less vigorous due to its small size and very high hydration enthalpy.

3. Reaction with Hydrogen:

 $2M + H_2 \rightarrow 2MH$ (metal hydride)

4. Reaction with halogen:

 $2M + X_2 \rightarrow 2MX$

5. *Reducing nature*: They are strong reducing agents. Li being the most powerful reducing agent and sodium the least. Due to the smallest atomic radius, Li has the highest hydration enthalpy. So it has high reducing power.

6. Solution in liquid ammonia:

The alkali metals dissolve in liquid ammonia to give deep blue solutions which are good conductors. $M + (x+y)NH_3 \rightarrow [M(NH_3)_x]^+ + e[(NH_3)_y]^-$

The blue colour of the solution is due to the ammoniated electron, which absorbs energy in the visible region and gives blue colour to the solution. The solution is paramagnetic and on standing slowly liberates hydrogen resulting in the formation of amide (MNH₂).

 $[M(NH_3)_x]^+ \rightarrow MNH_2 + \frac{1}{2}H_2$

In concentrated solution, the blue colour changes to bronze colour and become diamagnetic.

Anomalous Properties of Lithium

Due to its small size and high polarizing power, Lithium shows some properties different from that of other alkali metals. Some of these are:

- 1. Li is much harder and has high melting point and boiling point.
- 2. Li is the least reactive but the strongest reducing agent among all the alkali metals.
- 3. It forms only monoxide with oxygen.
- 4. LiCl is deliquescent and crystallizes as a hydrate (LiCl.2H₂O). But the other alkali metal chlorides do not form hydrates.
- 5. Lithium bicarbonate (LiHCO₃) is stable only in solution.
- 6. Lithium nitrate on heating gives Li_2O , while other alkali metal nitrates decompose to form nitrite.

$$4 \operatorname{LiNO}_3 \rightarrow 2\operatorname{Li}_2 O + 4\operatorname{NO}_2 + O_2$$

 $2NaNO_3 \rightarrow 2NaNO_2 + O_2$

Diagonal relationship

The similarity in properties shown by diagonally placed elements of second and third periods in modern periodic table is called diagonal relationship.

Diagonal relationship between Li and Mg

Li shows the following similarities in properties with Be of the second group.

- 1. Both Li and Be are harder but lighter than other elements of the respective group.
- 2. Both react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating.
- 3. They do not form superoxides.
- 4. Their carbonates decompose easily on heating to form oxides and CO₂.
- 5. Their chlorides are soluble in ethanol and are deliquescent.
- 6. Their bicarbonates are stable only in solution.

Some important compounds of Sodium

1. Sodium Carbonate [Na2CO3.10H2O] (Washing Soda)

Preparation: Solvay Process (Ammonia-Soda Process)

In this process, CO2 is passed through a concentrated solution of NaCl saturated with ammonia. Ammonium carbonate first formed then converted to ammonium bicarbonate and finally reacts with NaCl to form NaHCO₃.

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

 $(\mathsf{NH}_4)_2\mathsf{CO}_3 + \mathsf{H}_2\mathsf{O} + \mathsf{CO}_2 \rightarrow 2\mathsf{NH}_4\mathsf{HCO}_3$

 $NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

Sodium bicarbonate crystals are separated and heated to get sodium carbonate.

 $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

In this process, NH3 is recovered when the solution containing NH₄Cl is treated with Ca(OH)₂.

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

Note: Solvay process cannot be used for the preparation of K_2CO_3 because potassium bicarbonate (KHCO₃) is so much soluble in water that it does not get precipitated by the addition of NH_4HCO_3 to a saturated solution of KCl.

Properties:

Action of Heat: On heating, the decahydrate ($Na_2CO_3.10H_2O$) loses its water of crystallisation to form a monohydrate. Above 373K the monohydrate becomes completely anhydrous and changes to a white powder called "soda ash".

 $\begin{array}{l} \mathsf{Na_2CO_3.10H_2O} \rightarrow \mathsf{Na_2CO_3.H_2O} + \mathsf{9H_2O} \\ \mathsf{Na_2CO_3.H_2O} \rightarrow \mathsf{Na_2CO_3} + \mathsf{H_2O} \end{array}$

Uses

- 1. It is used in water softening, laundering and cleaning.
- 2. it is used in the manufacture of soap, glass, borax and caustic soda.
- 3. It is used in paper, paints and textile industries.
- 4. It is used as a laboratory reagent.

2. Sodium Hydroxide (Caustic Soda) [NaOH]

Preparation: It is prepared commercially by the electrolysis of NaCl in *Castner-Kellner cell*. The Brine solution (NaCl solution) is electrolysed by using a mercury cathode and a carbon anode. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.

Cathode reaction: $Na^+ + e^- \rightarrow Na/Hg$ (Sodium amalgam)

Anode reaction: $Cl^2 \rightarrow \frac{1}{2}Cl_2 + e^{-\frac{1}{2}}$

The amalgam $% \left({{{\rm{B}}}_{2}} \right)$ is treated with water to give NaOH and ${{{\rm{H}}}_{2}}$ gas.

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

Crystals of NaOH are deliquescent. i.e. they absorb moisture from the atmosphere and dissolve in it. **Uses**: It is used:

- 1. in the manufacture of soap, artificial silk, paper and a number of chemicals.
- 2. in petroleum refining.
- 3. in the purification of bauxite.
- 4. in textile industry.
- 5. as a laboratory reagent.

3. Sodium bicarbonate, NaHCO₃ (Baking Soda)

It is prepared by saturating a solution of Sodium carbonate with CO₂.

 $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$

Uses: i) It is a mild antiseptic for skin infection ii) It is used as a fire extinguisher.

Biological Importance of sodium and potassium

Na⁺ ions are found mainly on the outside of cells and in the interstitial fluid which surrounds the cell. These ions participate in the transmission of nerve signals, in regulating the flow of water across the cell membranes and in the transport of sugars and aminoacids.

K⁺ ions are mainly found within cell fluids. They activate many enzymes, participate in the oxidation of glucose to ATP and helps in the transmission of nerve signals along with sodium ions.

GROUP II ELEMENTS [ALKALINE EARTH METALS]

General Characteristics

- 1. General electronic configuration: [Noble gas] ns²
- 2. Ionization enthalpy: have low ionisation enthalpy and decreases down the group. First ionization enthalpies of alkaline earth metals are higher than those of alkali metals.
- 3. Hydration enthalpy: Hydration enthalpy of alkaline earth metal ions decreases with increase in ionic size.

 $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

4. Flame colouration

Alkaline earth metals give characteristic colour to the flame. In flame the electrons are excited to higher energy levels and when they return to the ground state, energy is emitted in the form of visible light. So calcium gives brick red, Strontium gives crimson red and Barium gives apple green colour to the flame.

The electrons in Be and Mg are very strongly bound to the nucleus. So they do not get excited by the flame. Hence these elements do not give flame colouration.

Chemical Properties

1. Reaction with air and water

Be and Mg are inert to O_2 and H_2O because of the formation of oxide film on their surface. However powdered Be burns brilliantly in air to give BeO and Be_3N_2 . Other elements form monoxide with air.

2. Reaction with halogen

 $M + X_2 \rightarrow MX_2$

BeCl2 is prepared by passing chlorine gas to a mixture of BeO and Carbon at 600 – 800K.

$$BeO + C + Cl_2 \rightarrow BeCl_2 + CO$$

It has a chain structure in the solid state.



In the vapour phase, it forms chloro-bridged dimmer.

3. Reaction with hydrogen

 $M + H_2 \rightarrow MH_2$

BeH₂ can be prepared by the reaction of BeCl₂ with lithium aluminium hydride (LiAlH₄).

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

- 4. Reaction with acids: $M + 2HCI \rightarrow MCI_2 + H_2$
- 5. *Reducing nature*: Like alkali metals, group II elements are strong reducing agents. But the reducing power is less than that of alkali metals.
- 6. *Solution in liquid ammonia*: They dissolve in liquid ammonia to form deep blue black solution due to the formation of ammoniated electrons.

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

Anomalous Properties of Beryllium

Beryllium shows some anomalous behaviour as compared to magnesium and other members of the group. Some of the properties are:

- 1. Be has high ionization enthalpy and small size. It forms compounds which are highly covalent and get easily hydrolised.
- 2. It does not show co-ordination number more than 4 as its valence shell contains only 4 orbitals. The remaining members of the group can have a co-ordination number of 6 by making use of vacant d-orbitals.
- 3. The oxide and hydroxide of Be are amphoteric in nature.
- 4. BeCl₂ exists as dimer even in vapour phase and is soluble in organic solvents.

Diagonal relationship between Beryllium and Aluminium

- 1. Like Al, Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
- 2. Be(OH)₂ dissolves in excess of alkali to give beryllate ion, just as $Al(OH)_3$ gives aluminate ion.
- 3. The chlorides of both the elements have bridged structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Crafts catalysts.
- 4. Be²⁺ and Al³⁺ ions have strong tendency to form complexes BeF₄²⁻ and AlF₆³⁻.

<u>Uses of Alkali metals</u>

- 1. *Beryllium* is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes.
- 2. *Magnesium*-aluminium alloys are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, bombs and signals. *A suspension of magnesium hydroxide in water* (called milk of magnesia) is used as antacid in medicine. Magnesium carbonate is used in toothpaste.

3. *Calcium* is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and *barium* metals are used to remove air from vacuum tubes.

Radium salts are used in radiotherapy, for example, in the treatment of cancer

Some Important Compounds of Calcium

1. Calcium Oxide, CaO [Quick lime]

It is prepared commercially by heating lime stone (CaCO₃) in a rotary kiln (furnace) at 1070 – 1270K. CaCO₃ \rightarrow CaO + CO₂

The CO_2 is removed as soon as it is formed to enable the reaction to proceed completion.

Properties:

On exposure to air, it absorbs moisture and CO₂.

 $CaO + CO_2 \rightarrow CaCO_3$

 $CaO + H_2O \rightarrow Ca(OH)_2$

The addition of limited amount of water breaks the big pieces of lime. This process is called *slaking of lime*. The product obtained is called *slaked lime*. Quick lime slaked with soda (NaOH) gives solid *soda lime* (NaOH + CaO).

Because of the basic nature of CaO, it combines with acidic oxides at high temperature to form salts. So it is used as a flux in metallurgy.

 $CaO + SiO_2 \rightarrow CaSiO_3$

 $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$

Uses: 1. It is an important primary material for the manufacture of cement and is the cheapest form of alkali.

2. It is used in the manufacture of Na_2CO_3 from caustic soda.

3. It is used in the purification of sugar and in the manufacture of dye stuffs.

2. Calcium Hydroxide, Ca(OH)₂ [Slaked lime]

Preparation: It is prepared by adding water to quick lime.

 $CaO + H_2O \rightarrow Ca(OH)_2$

An aqueous solution of slaked lime is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

Properties:

When CO_2 is passed through lime water, it turns milky due to the formation of $CaCO_3$. On passing CO_2 continuously, the solution becomes clear due to the formation of soluble calcium bicarbonate [Ca(HCO₃)₂]

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

When dry chlorine gas is passed through dry slaked lime, we get bleaching powder (a mixture of CaCl₂ & calcium hypochlorite)

$$2Ca(OH)_2 + 2CI_2 \rightarrow CaCI_2 + Ca(OCI)_2 + 2H_2O$$

Uses:

- 1. It is used in the preparation of mortar, a building material.
- 2. It is used in white washing due to its disinfectant nature.
- 3. It is used in glass making, in tanning, for the preparation of bleaching powder and for purification of sugar.

3. Calcium Carbonate, CaCO₃ [Lime stone]

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

 $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ $CaCl_2 + Na2CO_3 \rightarrow CaCO_3 + 2NaCl$

Properties

When heated to 1200 K, it decomposes to evolve carbon dioxide.

$$2 \text{ CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$$

It reacts with dilute acid to liberate carbon dioxide.

 $CaCO_3 + 2HCI \rightarrow CaCl_2 + H_2O + CO_2$

 $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

Uses: 1. It is used as a building material in the form of marble and in the manufacture of quick lime.

2. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron.

3. Specially precipitated CaCO₃ is extensively used in the manufacture of high quality paper.

4. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and filler in cosmetics.

4. Calcium Sulphate (Plaster of Paris), CaSO₄.¹/₂ H₂O

It is a hemihydrate of calcium sulphate. It is obtained when gypsum $[CaSO_4 \cdot 2H_2O]$ is heated to 393 K.

 $2 \text{ CaSO}_4.2\text{H}_2\text{O} \rightarrow 2 \text{ CaSO}_4.\text{H}_2\text{O} + 3\text{H}_2\text{O}$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate (CaSO₄) is formed. This is known as '*dead burnt plaster*'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes. During this process its volume increases. So it is used for the preparation of statues.

Uses: 1. The largest use of Plaster of Paris is in the building industry as well as plasters.

2. It is used for immoblising the affected part of organ where there is a bone fracture or sprain.

3. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

<u>Cement</u>

Cement was first introduced by Joseph Aspidine. It is a product obtained by combining lime (CaO) with clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum (CaSO₄·2H₂O) to form cement. The purpose of adding gypsum is to slow down the process of setting of the cement so that it gets sufficiently hardened.

Setting of Cement: When mixed with water, the setting of cement takes place to give a hard mass. During this process the hydration of the silicates and aluminates occurs and a large amount of heat is evolved.

Biological Importance of Magnesium and Calcium

Mg is present in Chlorophyll, the green colouring pigment in plants. All enzymes that use ATP in phosphate transfer require Mg as cofactor.

Ca is present in bones and teeth in the form of calcium phosphate. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation.

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