CHAPTER 15

S-BLOCK ELEMENTS

15.1 ALKALI METALS

s-block elements are those in which the differentiating electron enters into n–s orbital. Since n–s orbital can accommodate two electrons so s-block consists of two vertical rows numbered as group I and group II. Group I members are called alkali metals and have ns^1 configuration.

These are called alkali metals because their oxides and hydroxides form strong alkali like NaOH, KOH, etc. Members are Li, Na, K, Rb, Cs and Fr (Francium is radioactive).

15.2 TRENDS IN PROPERTIES

Density: It increases down the group because increase in atomic mass compensates more than the increase in atomic size. K is lighter than Na due to the abnormal increase in atomic size.

Melting and boiling point: For alkali metals, there are low and decrease down the group. Francium is a liquid at room temperature. Alkali metals are soft, malleable, ductile and have metallic luster which is due to the oscillation of electrons.

Ionization enthalpy: For alkali metals, it is minimum in their respective period and decreases down the group. Due to the low ionization enthalpy alkali metals are the most electropositive elements and form unipositive cations.

All alkali metals have body centred cubic structure with coordination number.

Flame colouration: Alkali metals impart characteristic colour to the flame because when heated in Bunsen flame the electrons gets excited to the higher energy level due to tow ionization enthalpy. Excited electron when drops back to the ground state emit radiations in the visible range and impart characteristic colour.

Li	Na	K	Rb	Cs
Crimson red	Golden yellow	Paleviolet	Purple	Sky blue

Photoelectric effect: Due to the low ionization enthalpy alkali metals (except Li and Na) show photoelectric effect. K and Cs are used in photoelectric cells.

Electrical conductivity: Alkali metals are good conductors due to the presence of loosely held valence electrons. Electrical conductivity increases down the group due to the decrease in ionization enthalpy.

Reducing power: Alkali metals are the strongest reducing agents in their respective period due to their lowest ionization enthalpy.

Reducing power is in the order Li > Cs > Rb > K > Na.

During reducing property following changes occur:

$M(s) \rightarrow M(g)$, sublimation energy

$M(g) \rightarrow M^+_{(g)} + e^-$, ionization enthalpy

$M^+_{(g)} + H_2O \rightarrow M^+_{(aq)}$, hydration energy

Hydration energy outweighs ionization enthalpy in lithium. So, lithium is the strongest reducing agent.

Ionic mobility: Smaller the size, greater the extent of hydration and hence lesser the ionic mobility. Lithium ion has the lowest ionic mobility due to its high hydration energy.

Chemical properties: Alkali metals have a tendency to form ionic compounds. Alkali metals do not occur free in nature due to their low ionization enthalpy. When exposed to air these form oxides, hydroxides, carbonates and bicarbonates.

Reaction with water: Alkali metals react with water to give hydrogen: $2M + 2H_2O \rightarrow 2MOH + H_2$

Their reactivity increases down the group.

Alkali metal hydroxides are strong bases.

Thermal stability, solubility and basicity increases down the group.

All alkali metal hydroxides are thermally stable except LiOH.

$$2LiOH \xrightarrow{heat} Li_2O + H_2O$$

Reaction with oxygen: Lithium forms Li_2O; Na forms peroxide (Na_2O_3) and K forms superoxide (KO_2). Superoxides are coloured and paramagnetic due to the presence of unpaired electrons. All oxides, peroxides and superoxides are basic in nature.

Reaction with hydrogen: Stability of hydrides of alkali metals decreases down the group. Hydrides of alkali metals are strong reducing agents.

Reaction with halogen: Alkali metals react with halogens to form ionic halides which are soluble in water. Melting point of alkali metal halides is in the order: MF > MCl > MBr > MI.

Solubility in liquid ammonia: All alkali metals are soluble in liquid ammonia and give deep blue colour. This blue colour is observed due to ammoniated electron, solution is a good conductor of electricity, paramagnetic and a strong reducing agent. Paramagnetism decreases with increasing concentration of metal due to the association of ammoniated electrons. Colour also changes to copper bronze due to the formation of metal ion clusters.

$$2e^-(NH_3)_y \rightarrow [(e^-(NH_3)_y]_2$$

Nature of carbonates and bicarbonate: Except Li_2O_3 all other alkali metal carbonates are stable.

$$Li_2CO_3 \xrightarrow{heat} Li_2O + CO_2$$

$LiHCO_3$ does not exist in the solid state, whereas other bicarbonates exist in solid state.

Bicarbonates of alkali metals decompose easily on heating as follows:

$2\ MHCO_{3(s)} \rightarrow M_2CO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$.

Solubility of carbonates and bicarbonates increases down the group.

Nature of Nitrates: Except $LiNO_3$, alkali metal nitrates decompose to give nitrite and oxygen.

$$2MNO_3 \xrightarrow{heat} 2MNO_2 + O_2\ ; \qquad 4LiNO_3 \xrightarrow{heat} 2Li_2O + O_2 + 4NO_2$$

Nature of sulphate: Except Li_2SO_4, all alkali metal sulphates are soluble in water.

Diagnol relationship between Li and Mg: Due to the same charge-to-size ratio and hence same polarizing power lithium resembles magnesium. These both decompose water only on heating. Both react with oxygen to give monoxide. Hydroxides and carbonates of both decompose on heating. Both react with nitrogen to form nitrides.

Carbonates, oxalates, phosphates and fluorides of lithium and magnesium are sparingly soluble in water. Nitrates of both on heating give NO_2 and O_2.

Anomalous behaviour of lithium: Lithium forms only Li_2O.
Lithium combines with nitrogen to form nitride.
Lithium hydride is stable.
LiOH and Li_2CO_3 are thermally unstable.
$LiNO_3$ decomposes to give NO_2 and O_2.
Li cannot be stored in kerosene oil as it floats in oil due to its low density.
Li_2SO_4 does not form alum because it is too small to have coordination number six.

Key Points

- Fire caused due to alkali metals is extinguished by CCl_4.
- 28 per cent solution of NaCl is known as brine.
- Mixture of Na_2O_2 and dil. HCl is called oxane.
- Sodium sesqui carbonate is Na_2CO_3, $NaHCO_3$, $2H_2O$.
- Common salt fused with little Na_2CO_3, 5 to 10 per cent Na_2SO_4 and a little sugar is called kala namak.
- $Na_2SO_4 . 10H_2O$ – Glauber's salt
- $NaNO_3$ – Chile salt petre
- KNO_3 – Indian salt petre

15.3 PREPARATION OF NaOH

It is prepared by the electrolysis of brine by 1. Nelson cell and 2. Castner-Kellner cell

15.3.1 Nelson Process

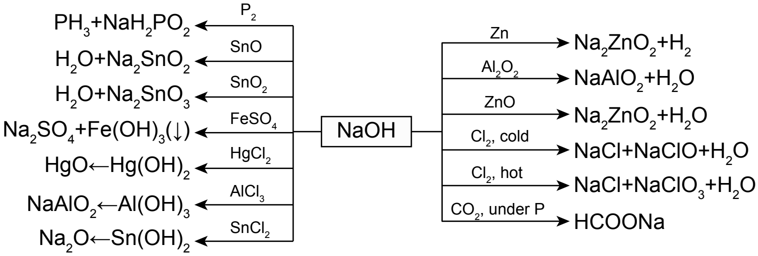
$$NaCl(solution) \rightleftharpoons Na^+ + Cl^-$$

At cathode, $Na^+ + e^- \rightarrow Na$
$Na + 2H_2O \rightarrow NaOH + H_2$
At anode, $2Cl^- \rightarrow Cl_2 + 2e^-$

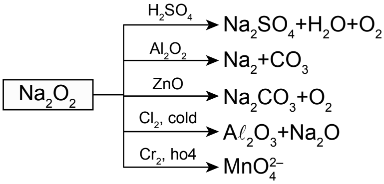
15.3.2 Castener-Kellner Process

In outer compartment, $NaCl \rightleftharpoons Na^+ + Cl^-$

At cathode, $Na^- + e^- \rightarrow Na$; $Na + Hg \rightarrow Na - Hg$
At anode, $2Cl^- \rightarrow Cl_2 + 2e^-$
In middle compartment
At anode, $Na - Hg \rightarrow Na^+ + Hg + e^-$
At cathode, $Na^+ + e^- \rightarrow Na$; $Na + 2H_2O \rightarrow NaOH + H_2$
Properties of NaOH



Properties of sodium peroxide



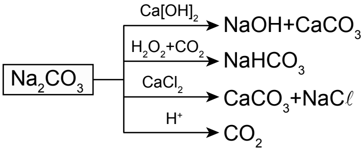
15.3.3 Preparation of Sodium Carbonate

Preparation by Solvay's process:

$NH_3 + H_2O + CO_2 \rightarrow NH_3HCO_3$

$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$

$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_3O + CO_2$



Properties of Na_2CO_3

Na_2CO_3 + K_2CO_3 is a fusion mixture.

$NaHCO_3$ is used as an antacid (Eno), in baking powder, in fire extinguishers and in effervescent drinks.

Preparation of potassium carbonate, K_2CO_3 (potash or pearl ash)

It is not not prepared by Solvay process as $KHCO_3$ is more soluble in water than $NaHCO_3$, therefore it is prepared by Le Blanc process.

K_2CO_3 is a colourless and deliquescent powder used in making soft soap.

15.3.4 Preparation of Alkali Metals

Since alkali metals are the strongest reducing agents, they cannot be prepared by chemical reduction of their oxides.

These cannot be extracted by the electrolysis of their aqueous solution because the metal extrated at once reacts with water. So, alkali metals are prepared by the electrolysis of the fused halides and impurities are added to lower the melting point. During of the manufacture of lithium, electrolyte used is 55 per cent LiCl and 45 per cent KCl. During the manufacture of sodium, electrolyte used is 40 per cent NaCl and 60 per cent $CaCl_2$. Potassium is obtained by the electrolysis of fused KOH.

15.4 ALKALINE EARTH METALS

They are Be, Mg, Ca, Sr, Ba and Ra (Ra is radioactive). Their electronic configuration is ns^2.

Ionization enthalpy: For alkaline earth metals, it is more than group IB and group 1 elements because the electron is being removed from fully filled ns orbital: Second ionization energy of group

II elements is less than group I elements because in alkali metals second electron is being removed from the fully filled inner energy level. They are less electropositive than alkali metals due to higher ionization energy.

Reducing property: These are weaker reducing agents than alkali metals due to higher ionization enthalpy.

Flame colouration: Be and Mg do not impart colour to flame due to higher ionization enthalpy.

Ca	Sr	Ba	Ra
Brick red	Crimson red	Grassy green	Crimson red

15.4.1 Chemical Properties

Reaction with water: They react with water to produce hydrogen gas. Their reactivity with water follows the following trend:

Ba >Sr > Ca > Mg

Reaction with oxygen: Be, Mg and Ca have a tendency to form Ba and Sr forms peroxide.

Reaction with hydrogen: Hydrides of alkaline earth metal: $BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$

BeH_2 and MgH_2 are colvalent and polymeric hydrides are good reducing agents. Stability and solubility of hydrides increase down the group.

Reaction with halogen: $M + X_2 \rightarrow MX_2$

$$BeO + C + Cl_2 \xrightarrow{1070K} BeCl_2 + CO$$

$BeCl_2$ exists as a polymer in solid state. BeF_2 is soluble in water, whereas fluorides of other alkaline earth metals are insoluble, Chlorides, bromides and iodides of Mg, Ca, Sr and Ba are ionic, and have lower melting point than the fluorides.

Solubility decreases in the order of MgX, $CaX_2 > SrX_2 > BaX_2$.

All the halides are hygroscopic in nature.

$$MgCl_2 + 2NaHCO_3 \rightarrow \underset{\text{(Soluble)}}{MgHCO_3} + 2NaCl$$

$$MgHCO_3 \xrightarrow{\text{Heat}} MgCO_3 \downarrow + H_2O + CO_2$$

15.4.2 Nature of Hydroxides

$Be(OH)_2$ is amphoteric. Basic character of hydroxides increases from Be to Ba.

Solubility of alkaline earth metal compounds: For hydroxides of these compounds it increases down the group because the decrease in lattice energy is more than the decrease in hydration energy.

$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

Solubility of sulphates and carbonates decreases down the group.

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

$BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

Thermal stability: Stability of carbonates and sulphates increases down the group.

$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$

$SrSO_4 > CaSO_4 > MgSO_4 > BeSO_4$

15.4.3 Diagonal Relationship Between Be and Al

1. Both become passive on treatment with concentrated nitric acid due to the formation of protective oxide film.
2. Both dissolve in conc. NaOH to form beryllate and aluminate.
   $Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$; $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_3 + 3H_2$
3. Oxides of both are amphoteric.
4. Carbides of both react with water to give methane.
   $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$; $Al_4C_3 + 2H_2O \rightarrow 4Al(OH)_3 + 3CH_4$
5. Anhydrous halide of both are Lewis acids.
6. Both form complexes, e.g., BeF_4^{2-}, AlF_6^{2-}.

15.4.4 Anomalous Behaviour of Be

1. Be is hard but other alkaline earth metals are soft.
2. Be forms covalent compounds; however, others generally form ionic compound.
3. BeO is amphoteric while other oxides are basic in nature.
4. The m.pt., b.pt and ionization energy of Be is maximum amongst alkaline earth metals.
5. Be has bridged polymeric structure.
6. Be does not liberate hydrogen gas from acids while other metals liberate.

Key Points

- $MgSO_47H_2O$ (Epsom salt) is used as purgative.
- $K_2SO_4{\cdot}MgSO{\cdot}6H_2O$ is sold as potash magnesia, a fertilizer.
- $CaSO_4{\cdot}2H_2O$ is called gypsum.
- $CaSO{\cdot}1/2H_2O$ is plaster of paris.
- $CaSO_4{\cdot}H_2O$, called alabaster, is used to make ornaments
- Anhydrous $CaCl_2$ is used as a desiccating agent.
- Fire caused due to alkali and alkaline earth metals is extinguished by asbestos.
- $MgCl_2{\cdot}5MgO, XH_2O$ is called Sorell's cement which is used in dentistry.
- Hardening of plaster of paris is due to the transition of orthorhombic form of gypsum to monoclinic form.
- Mg has the lowest melting point and calcium has the lowest density amongst alkaline earth metals.
- Most of the kidney stones are made up of calcium oxalate, $CaC_2O_4.H_2O$.
- Aqueous solution of $Ba(OH)_2$ is known as baryata water.