B.Sc Part-I (Sub.), Paper-I, Group-B (Inorganic Chemistry)

Unit: 2 Chemistry of elements: Lithium (By Dr. Birendra Kumar, Maharaja College)

⟹ **Anomalous behaviour of Lithium:** Lithium has electronic configuration: $1s^2 2s^1$. It has position in Group-1 of modern periodic table along with other alkali metals (Na, K, Rb, Cs & Fr) due to some similarity properties. However, lithium (Li) differs from other alkali metals, called anomalous behaviour of Li due to smaller size, high electronegativity, low polarisability and absence of d-orbital. Li differs from other alkali metals in following: (i) Li burns in oxygen (air) to give normal oxide (Li_2O) only, others give peroxides (M_2O_2) & super oxides (MO_2) also. $2M + O_2 \longrightarrow M_2O_2$; $M + O_2 \longrightarrow MO_2$ (M = Na, K, Rb.)

(ii) Li burns in nitrogen to form nitride, others do not. $6Li + N_2 \longrightarrow 2Li_3N$.

(iii) Li^+ ion gets heavily hydrated, others do not.

(iv) Li_2CO_3 decomposes on heating, carbonates of others are stable. $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$

(v) $LiNO_3$, on heating decomposes to give Li_2O, NO_2 & O_2 while nitrates of others give nitrites. $4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$; $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$

(vi) LiOH decomposes at red hot temp. to give Li_2O, hydroxides of others do not decompose. $2LiOH \longrightarrow Li_2O + H_2O$.

(vii) Its sulphate does not form alum, others can form alum.

(viii) Li_2O is much less basic than oxides of other alkali metals.

(ix) It is least reactive in group-1. Li decomposes water only slowly at room temp., whereas Na decomposes water vigorously. In the case of K, evolved H_2 catches fire.

(x) Oxide, fluoride, phosphate, carbonate of Li are insoluble in water, others are soluble in water.

⟹ **Diagonal relationship of Li with Mg:** The first member of a group of PT often behaves in a peculiar manner but resembles the second member of the next group diagonally related to it. This is called diagonal relationship. Li resembles Mg, i.e; Li show diagonal relationship with Mg in following respects due to similar polarising power.

(i) Both Li & Mg have identical size/radius, electronegativity & polarising power.

(ii) Both form nitrides with N_2. $6Li + N_2 \longrightarrow 2Li_3N$; $3Mg + N_2 \longrightarrow Mg_3N_2$

(iii) LiCl & $MgCl_2$ are deliquescent.

(iv) $LiNO_3$ & $Mg(NO_3)_2$ decompose on heating giving oxide, NO_2 & O_2.

$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$; $2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$

(v) Li^+ & Mg^{2+} ions are easily hydrated.

(vi) They decompose readily water (H_2O) giving H_2 gas. $2Li + 2H_2O \longrightarrow 2LiOH + H_2$; $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$

⟹ **Important sources/ores of Lithium:** Lithium is distributed throughout the biological system in traces. It is found in nature/earth crust as combined form. Its important ores are:

1. Lepidolite, $Li(Na,K)Al_2(Si_2O_3)_3F_2(OH)_2$ (Li content: 2-6%)
2. Spodumene, $LiAl(SiO_3)_2$ (Li content: 4-6%)
3. Petelite, $LiAl(Si_2O_5)_2$ (Li content: 2-3%)
4. Amblygonite, $Li(AlF)PO_4$ 5. Triphylite, $Li(Na)_3PO_4 \cdot Fe(Mn)_3(PO_4)_3$ (Li content: 2-4%)

⟹ **Extraction of Lithium:** Lithium is extracted from silicate and phosphate minerals in two ways. In both the cases, the unwanted materials are removed and LiCl is obtained, which on electrolysis gives Lithium. The method involves two main steps:

Step-I: Separation of Li as LiCl: It is done by two methods:
(i) Separation from silicate ores (ii) separation from phosphate ores

(i) **Separation of Li from silicate ore:** It is done by fusing the powdered ore with $BaCO_3$, $BaSO_4$ and K_2SO_4. The fused mass separates in two layers. Li, Na, K are converted into sulphate and forms upper layer. SiO_2 & Al_2O_3 dissolve in $BaSO_4$ and form lower layer. The upper layer is separated. It contains Na_2SO_4, K_2SO_4 & Li_2SO_4. It is extracted with water and then $BaCl_2$ solution is added.

$$Li_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2LiCl$$

Li, Na & K are thus converted into Chlorides which remain in solution. $BaSO_4$ precipitates is filtered out. The clear solution is now evaporated to dryness, when LiCl, NaCl & KCl are obtained. From this mixture LiCl is separated by dissolving in pyridine, in which NaCl & KCl are insoluble. Pyridine solution on distillation gives LiCl as solid residue, which is fused and electrolysed.

(ii) **Separation of Li from phosphate ore:** Amblygenite or Triphylite ore contains phosphates of Li, Na, K, Al, Fe & Mn. The phosphate ore is first digested with conc HCl to remove insoluble impurities. The clear solution is now treated with HNO_3 to oxidise Fe^{2+} into Fe^{3+}. The solution is now diluted, made neutral with NH_4OH. A part of the phosphate is precipitated. The clear solution is then acidified by adding CH_3COOH & CH_3COONa, and $FeCl_3$ is added. Rest of phosphate separates as $FePO_4$. It is removed. The solution now contains Mn which is precipitated as MnS by BaS. $MnCl_2 + BaS \longrightarrow MnS\downarrow + BaCl_2$

Barium is then precipitated as $BaSO_4$ by adding H_2SO_4 to the solution.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl.$$

After separation of phosphate as $AlPO_4$, $FePO_4$ and MnS & $BaSO_4$, the clear solution now contained Li, Na & K as sulphates. It is now evaporated with oxalic acid. Lithium oxalate is obtained and separated from sodium & potassium oxalates, which are more soluble.

$$Li_2SO_4 + H_2C_2O_4 \longrightarrow Li_2C_2O_4 + H_2SO_4.$$

Lithium oxalate ($Li_2C_2O_4$) on heating gives Lithium carbonate, which is then converted into LiCl. $Li_2C_2O_4 \longrightarrow Li_2CO_3 + CO\uparrow$, $Li_2CO_3 + 2HCl \longrightarrow 2LiCl + H_2O + CO_2\uparrow$.

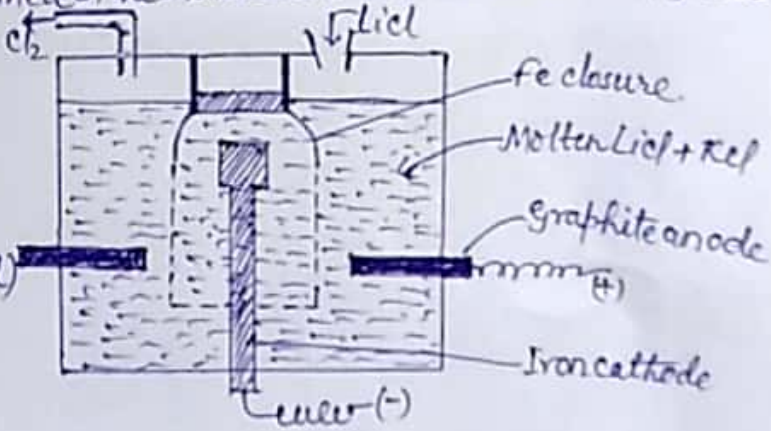
Step-II Electrolysis of LiCl: Lithium metal is now obtained by the electrolysis of fused LiCl between iron cathode and graphite anode. Some KCl is added to the molten LiCl, which increases conductivity. Electrolysis is carried out at 400°C with electric current of 8-9 volts. Lithium is obtained in the molten state at the cathode and floats above the molten electrolyte.

Cell reactions:

$$LiCl \rightleftharpoons Li^+ + Cl^-$$

At anode: $2Cl^- \longrightarrow Cl_2\uparrow + 2e$

At cathode: $Li^+ + e \longrightarrow Li$ (Lithium metal)



⟹ Important properties: 1. Lithium is a white, hard metal having high melting point, boiling point and electronegativity. It shows a crimson red colour in bunsen flame.

2. Reaction with air (O_2): Li burns in air/O_2 to give normal oxide (Li_2O) only.

$$4Li + O_2 \xrightarrow{\Delta} 2Li_2O \text{ (Lithium oxide)}$$

3. Reaction with nitrogen: It burns in nitrogen to form Lithium nitride (Li_3N).

$$6Li + N_2 \longrightarrow 2Li_3N \text{ (Lithium nitride)}$$

4. Reaction with water: It readily reacts with water to form LiOH & H_2.

$$2Li + 2H_2O \longrightarrow \underset{\text{(Lithium hydroxide)}}{2LiOH} + H_2$$

5. Reaction with acids: It reacts vigorously with dilute acids to liberate H_2 gas.

$$2Li + 2HCl \longrightarrow \underset{\text{(Lithium chloride)}}{2LiCl} + H_2\uparrow \; ; \; 2Li + H_2SO_4 \longrightarrow \underset{\text{(Lithium sulphate)}}{Li_2SO_4} + H_2\uparrow$$

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