ALUMS

The general representation of alums is $[(M^{I})_2SO_4][(M^{III})_2(SO_4)_3].24H_2O$ where M^{I} represents the metal with +1 oxidation state and M^{III} represents the metal with +3 oxidation state. These alums are double salts, which dissolve in water to give $[M^{I}(H_2O)_6]^{+}$, $[M^{III}(H_2O)_6]^{3+}$ and SO_4^{2-} ions and therefore., the alums are also represented as $[M^{I}(H_2O)_6][M^{III}(H_2O)_6](SO_4)_2$. They form octahedral crystals.

If M^{I} is K^{+} and M^{III} is Al^{3+}, then the alum is potash alum $(K_2SO_4.Al_2(SO_4)_3.24H_2O$ or $[K(H_2O)_6][Al(H_2O)_6](SO_4)_2)$

M^{I} can be K^{+}, NH_4^{+}, Rb^{+}, Cs^{+}, Tl^{+} and M^{III} can be Fe^{3+}, Al^{3+}, Co^{3+}, Ga^{3+}, Mn^{3+}. $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ is called ferric ammonium alum while $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ is chrome alum. Potash alum on heating dissolves in its own water of crystallisation and on further heating forms $K_2SO_4.Al_2(SO_4)_3$ called *burnt alum*.

Micro Cosmic Salt $[Na(NH_4)HPO_4]$

Microcosmic salt is a white crystalline solid and is prepared from NH_4Cl and Na_2HPO_4 as follows :

$$NH_4Cl + Na_2HPO_4 \longrightarrow Na(NH_4)HPO_4 \downarrow + NaCl$$

On decomposition the following is obtained :

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} NH_3 \uparrow + NaH_2PO_4$$

$$NaH_2PO_4 \xrightarrow{\Delta} NaPO_3(\text{Calgon}) + H_2O$$

Microcosmic salt can be used as a substitute for borax in the Bead Test

Similar salt are also formed by Magnesium :

$$MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow Mg(NH_4)PO_4$$

$$Mg(NH_4)PO_4 \xrightarrow{\Delta} NH_3 \uparrow + MgHPO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + H_2O$$

IMPORTANT THINGS TO REMEMBER — Section - 4

Anomalous properties of Lithium :

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarizing power (i.e., charge/radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

Points of Difference between Lithium and other Alkali Metals :

(i) Lithium is much harder. Its M.P. and B.P. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li_2O and the nitride, Li_3N while other metals form only oxide.

(iii) LiCl is deliquescent and crystallizes as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

(iv) Lithium hydrogencarbonate being unstable is not obtained in the solid form while all other elements form solid hydrogencarbonates.

(v) Li_2CO_3, $LiNO_3$, LiOH all form oxide on gentle heating, though the analogous compounds of the rest of the group are stable.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

(vi) Li_2CO_3, LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

(vii) Lithium is much heavily hydrated than those of the rest of the group.

Points of Similarities between Lithium and Magnesium :

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li^+ = 76 pm, Mg^{2+} = 72 pm. The main points of similarity are:

(i) Both lithium and magnesium are harder and lighter than other element in the respective group.

(ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen.

(iii) The oxides Li_2O and MgO do not combine with excess oxygen to give any superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO_2. Solid hydrogencarbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol.

(vi) Both LiCl and $MgCl_2$ are deliquescent and crystallize from aqueous solution as hydrates, $LiCl.2H_2O$ and $MgCl_2.8H_2O$.

Anomalous Behaviour of Beryll ium :

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

(i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionization enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.

(ii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

Diagonal Relationship between Beryllium and Aluminum :

The ionic radius of Be^{2+} is estimated to be 31 pm; the charge / radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are :

(i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide gives aluminate ion, $[Al(OH)_4]^-$.

(iii) $BeCl_2$ and $AlCl_3$ exist in form of chain. $BeCl_2$ forms polymeric chain (chain with a large no. of $BeCl_2$ molecules) and $AlCl_3$ forms dimeric chain (chain with two $AlCl_3$ molecules).

(iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-} , AlF_6^{3-} .

IN-CHAPTER EXERCISE - D

1. *$NaHCO_3$ and NaOH can not exist together in solution. Why ?*

2. *The hydroxide and carbonates of Na and K are easily soluble in water while the corresponding salts of Mg and Ca are sparingly soluble in water. Explain.*

3. *Solvay Process is used to manufacture sodium carbonate but it is not extended to the manufacture of potassium carbonate. Why ?*

4. *Why are MgO and BeO used for the lining of steel making furnace.*

5. *On the treatment with cold water, an element (A) reacted quietly, liberating a colourless, odourless gas (B) and a compound (C). Gas (B) further reacts with element (A) to yield a solid product (D) which reacted with water to give a basic solution (E). (E) is found to be same as (C). When carbon dioxide was bubbled through solution (C) initially a white precipitate (F) is formed, but this redissolved forming solution (G) when more CO_2 was added. Precipitate (F) effervesced when moistened with conc. HCl acid and gave deep red colouration to the burner flame. When (F) was heated at 1000°C, a white compound (H) was formed which when heated with carbon at 1000°C gave a solid (I) of some commercial importance. Name the substances (A) to (I).*

Choose the correct alternative. Only One choice is correct. However, question marked with '*' may have more than one correct option.

6. *Molecular formula of Glauber's salt is :*

(A) $Na_2SO_4.10H_2O$ **(B)** $MgSO_4.7H_2O$ **(C)** $FeSO_4.7H_2O$ **(D)** $Na_2CO_3.10H_2O$

7. *A solution of Na_2SO_4 in water is electrolysed using inert electrodes. The product at the cathode and anode are respectively.*

(A) H_2, O_2 **(B)** O_2, H_2 **(C)** O_2, Na **(D)** O_2, SO_2

8. *Asbestos diaphragm is used in :*

(A) *Nelson cell* **(B)** *Castner - Kellner cell*

(C) *Both of these* **(D)** *None of these*

***9.** *Which of the following cations form solid stable bicarbonates?*

(A) Li^+ **(B)** K^+ **(C)** NH_4^+ **(D)** Ca^{2+}

***10.** *Which of the following are manufactured in the solvay's process ?*

(A) $Ca(OH)_2$ **(B)** Na_2CO_3 **(C)** $NaHCO_3$ **(D)** $CaCl_2$

***11.** *The correct properties of the pure form of common salt are :*

(A) *It is hygroscopic* **(B)** *It is colourless* **(C)** *It is sublimable* **(D)** *It increases m.p. of ice*

***12.** *$CaCl_2$ is known to be an excellent drying agent. However it is unable to dry all substances. The compounds which can be dried by using $CaCl_2$ are :*

(A) HCl **(B)** CH_3OH **(C)** H_2O **(D)** NH_3

13. *Mark the correct statement about oxosalts of s-block :*

(A) *$NaOH$, Cl_2 and Na_2CO_3 are classified as heavy inorganic chemical due to high tonnages involved*

(B) *$BeCO_3$ is ionic*

(C) *$BeCl_2$ forms a covalent dimer*

(D) *$MgCl_2.6H_2O$ looses water of crystallisation on heating*