(iii) ***Salts of oxoacids (Sulphates and carbonates):*** The solubility of sulphates and carbonates of alkaline earth metals decreases down the group with increase in atomic number. This is in contrast to the behaviour of their hydroxides. The difference in solubilities can be understood from the energy of hydration and lattice energy values. As the energy of hydration decreases down the group, the solubilities of sulphates and carbonates of group 2 elements decrease in the order

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

Carbonate of alkaline earth metals are insoluble in water.

While the sulphates are stable towards heat, the carbonates decompose on heating to form the oxide. The thermal stability of carbonates increases down the group.

(iv) Nitrates: The nitrates are prepared by treating the carbonate with dilute HNO_3.

All nitrates of alkaline earth metals decompose on heating to form the oxide, nitrogen dioxide and oxygen.

$$2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2 \qquad (M = Be, Mg, Ca, Sr, Ba)$$

Anomalous behaviour of beryllium

Beryllium differs from the rest of the elements in some of its properties. This is due to (i) the small size of *Be* atom (ii) relatively high ionisation enthalpy and (iii) the absence of vacant *d*-orbitals.

Difference between beryllium and other members of group - 2

1. Be does not react with water even at high temperature while other members of the group react with water.
2. Compounds of Be are largely covalent whereas other members form ionic compounds.
3. Be shows maximum coordination number of 4 whereas the other members of the group can have a coordination of 6 by making use of d-orbitals
4. The oxide and hydroxides of Be are amphoteric whereas those of other members are basic.

Diagonal relationship between Be and Al

1. The hydroxides of Be and Al are amphoteric. $Be(OH)_2$ dissolves in excess alkali to give beryllate ion $[Be(OH)_4]^{2-}$ just like $Al(OH)_3$ which gives aluminate ion $[Al(OH)_4]^-$
2. Like Al, Be is not readily attacked by acids because of the presence of an oxide film on its surface.
3. Both $BeCl_2$ and $AlCl_3$ are soluble in organic solvents and are strong Lewis acids.

4. Both beryllium chloride and aluminium chloride have bridged chloride structures in the vapour phase.

5. Beryllium and aluminium ions have strong tendency to form complexes.

Compounds of Calcium

Calcium oxide (CaO)

Calcium oxide, known as *quick lime* is prepared on a large scale by heating limestone in a rotary kiln at 1070-1270K.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

It is a white amorphous solid which melts at 2870K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.

$$CaO + H_2O \longrightarrow Ca\,(OH)_2 \;;\; CaO + CO_2 \longrightarrow CaCO_3$$

Since CaO is a basic oxide, it combines with acidic oxides on heating

$$CaO + SiO_2 \longrightarrow \underset{\text{calicium silicate}}{CaSiO_3}$$

Uses

(i) Quick lime is used in building industry. (ii) In the purification of sugar and in the manufacture of dye stuffs. (iii) It is used as a flux in metallurgy. (iv) Used in the manufacture of Na_2CO_3.

Calcium hydroxide ($Ca\,(OH)_2$)

Calcium hydroxide, known as *slaked lime* is obtained by adding limited amount of water to quick lime. Addition of small amount of water to quick lime produces large amount of heat and the process is called *slaking of lime*. $CaO + H_2O \longrightarrow Ca(OH)_2$

Slaked lime is a white amorphous solid sparingly soluble in water. A suspension of slaked lime in water is called *milk of lime*. Chlorine reacts with slaked lime to form bleaching powder.

$$2\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow CaCl_2 + Ca\,(OCl)_2 + 2\,H_2O$$

An aqueous solution of slaked lime is known as lime water. When carbon dioxide gas is passed through lime water, it turns milky due to the formation of insoluble $CaCO_3$.

$$Ca\,(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

When excess CO_2 is passed, the milkiness disappears due to the formation of soluble calcium bicarbonate.

$$Ca\,CO_3 + CO_2 + H_2O \longrightarrow Ca\,(HCO_3)_2$$

Uses

(i) Used in white wash due to its disinfectant nature. (ii) Slaked lime is used for softening hard water. (iii) It is used as a building material and for absorbing acidic gases.

Calcium carbonate ($CaCO_3$)

Calcium carbonate occurs in nature as *lime stone*, chalk and *marble*. It is prepared by passing CO_2 gas through lime water or by adding sodium carbonate soution to calcium chloride.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

Calcium carbonate is a white fluffy powder almost insoluble in water.

It decomposes to form its oxide on heating to 1200K. $CaCO_3$ produces CO_2 gas on treatment with dilute acids.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Uses

(i) To make quick lime, cement etc. (ii) Marble is used as a building material. (iii) It is also used as antacid and as a constituent of chewing gum.

Plaster of Paris ($CaSO_4 \cdot \frac{1}{2} H_2O$ or $2\,(CaSO_4) \cdot H_2O$)

It is prepared by heating gypsum at 393K. It is a hemihydrate of calcium sulphate.

$$2\,(CaSO_4 \cdot 2H_2O) \xrightarrow{393K} 2\,(CaSO_4) \cdot H_2O + 3H_2O$$

It is a white powder. On mixing with sufficient quantity of water, it forms a plastic mass which sets into a hard solid. This is called *setting of Plaster of Paris*. This is due to hydration of Plaster of Paris.

When heated above 393K, Plaster of Paris loses water of crystallisation and becomes *dead burnt plaster* ($CaSO_4$) which does not set in presence of water.

Uses

Plaster of Paris is used (i) for making moulds for pottery, ceramics etc. (ii) for making models, statues and decorative materials. (iii) as plasters for setting broken and fractured bones in the body.

Cement

Cement is an important building material. It was first introduced in England by Joseph Aspdin in 1824. Cement is a product obtained by heating a mixture of limestone with aluminosilicates such as clay. The approximate composition of Portland cement is: CaO : 50–60%, SiO_2 : 20–25%, Al_2O_3 : 5–10%, Fe_2O_3 : 1–2%, MgO : 2–3% and SO_3 : 1–2%.

For a good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) should be close to 2.

Manufacture of cement

The main raw materials for the manufacture of cement are lime stone and clay. When a mixture of powdered limestone and clay is heated strongly, they react to form *cement clinker*. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4 \cdot 2H_2O$) and is well powdered. This is called portland cement. The function of gypsum is to slow down the setting of cement.

The important constituents of cement are dicalcium silicate (Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5) and tricalcium aluminate ($Ca_3Al_2O_6$).

Setting of cement

When mixed with water, cement slowly sets into a hard mass. This is called setting of cement and it is an exothermic process. Setting is due to the hydration of the molecules of the constituents of cemnt and their rearrangement.

Biological importance of Mg and Ca

Human body contains about 25g of Mg and 1200 g of Ca. Mg is a cofactor in enzymes which use ATP in phosphate transfer process in our body. Photosynthesis in plants takes place in presence of chlorophyll which contains Mg. About 99% of body calcium is found in teeth and bones. Calcium concentration in plasma is regulated at 100 mg/litre by of hormones such as calcitonin and parathyroid hormone.

Keep in Memory

- Group I metals are called alkali metals because they from hydroxids on reaction with water which are strongly alkaline.
- The hydration enthalpy of alkali metal ions is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
- Order of reducing power: $Na < K < Rb < Cs < Li$
- Colour observed in flame test: Li: Crimson red, Na: golden yellow, K: Violet, Rb: red violet, Cs: blue colour
- All alkali metals react with water to form hydroxide and H_2.

NCERT Exercise Questions and Answers

1. Why are alkali metals not found in nature?

Ans: They are highly reactive and hence do not occur free.

2. Find the oxidation state of sodium in Na_2O_2

Ans: In peroxide links, oxygen is –1. So oxidation state of Na is +1

3. Explain why Na is less reactive than K?

Ans: Ionisation enthalpy of K is less than that of Na and hence K is more electropositive and reactive.

4. Compare alkali metals and alkaline earth metals with respect to ionisation enthalpy, basicity of oxides and solubility of hydroxides.

Ans: Ionisation enthalpy of alkaline earth metals are higher than that of corresponding alkali metals. Alkali metal oxides are more basic than oxides of group 2 elements because alkali metals are more electropositive than alkaline earth metals. The hydroxides of alkali metals are more soluble in water than those of alkaline earth metals.

5. Explain why can alkali metals and alkaline earth metals not be obtained by chemical reduction methods?

Ans: Metals of group 1 and 2 are reducing agents by themselves. So they cannot be formed by reduction.

6. Why are K and Cs, rather than Li used in photoelectric cells?

Ans: Compared to Li, K and Cs have lower ionisation energy which makes the release of valence electrons easier in K and Cs.

7. When alkali metal dissolves in liquid NH_3, the solution can acquire different colours. Explain the reason.

Ans: A dilute solution of alkali metal in NH_3 has deep blue colour due to the formation of ammoniated electrons which absorb in the red region of visible light. At higher concentrations the colour changes to bronze due to the formation of metal ion clusters.

8. Be and Mg do not give colour to flame whereas other alkaline earth metals do so. Why?

Ans: Due to smaller size Be and Mg have relatively higher ionisation energies. Thus a large amount of energy is required to excite their valence electrons to higher levels and this much energy cannot be supplied by a Bunsen flame.

9. Potassium carbonate cannot be prepared by Solvay process. Why?

Ans: In Solvay's process; initially $KHCO_3$ will be formed which is more soluble and cannot be precipitated.

10. Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

Ans: Li_2CO_3 is the salt of $LiOH$ (weak base) and CO_2 (weak acid). The weak base is not capable of reacting strongly with weak acid and hence the product Li_2CO_3 will decompose readily. Na_2CO_3 is the salt of strong base ($NaOH$) and CO_2. $NaOH$ can interact strongly with CO_2 to form relatively more stable Na_2CO_3.

11. Starting with $NaCl$ how would you proceed to prepare (i) Na metal (ii) $NaOH$ (iii) Na_2O_2 and (iv) Na_2CO_3?

Ans: (i) By the electrolysis of molten $NaCl$ (containing $CaCl_2$) at 873 K using iron cathode and graphite anode (Down's method). Na is deposited at the cathode and Cl_2 at anode.

(ii) By the electrolysis of $aq.NaCl$ (Castner-Kellener Cell) using carbon anode and mercury cathod. Sodium formed at cathode becomes sodium amalgam which reacts with water to form $NaOH$ and H_2.

(iii) At first Na is prepared from fused $NaCl$ as in (i). Sodium metal is heated with excess oxygen (air) to form Na_2O_2.

$4Na + O_2 \rightarrow 2Na_2O$; $2Na_2O + O_2 \rightarrow 2Na_2O_2$

(iv) By Solvay process. CO_2 is passed through $aq.NaCl$ containing NH_3 to form $NaHCO_3$. This on heating yields Na_2CO_3

12. What happens when (i) Mg is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacted with slaked lime (iv) calcium nitrate is heated?

Ans: (i) $2Mg + O_2 \rightarrow 2MgO$ (ii) $CaO + SiO_2 \rightarrow CaSiO_3$

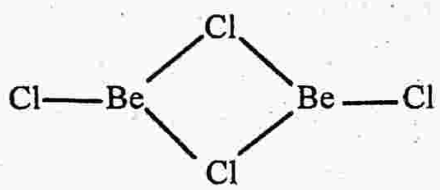
(iii) $2\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + H_2O$ (bleaching powder)

(iv) $2Ca\,(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$

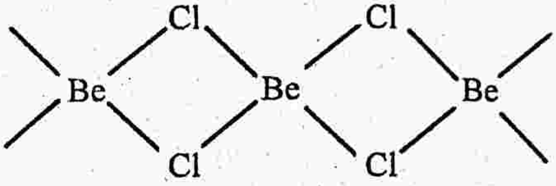
13. Draw the structures of (i) $BeCl_2$ (vapour) (ii) $BeCl_2$ (solid)

Ans:

(i)



(ii)



14. The hydroxides and carbonates of *Na* and *K* are soluble in water while those of *Mg* and *Ca* are spairingly soluble. Explain.

Ans: Lattice energies of the hydroxides and carbonates of *Na* and *K* are much smaller than those compounds of *Ca* and *Mg*. (This is due to the larger size of *Na* and *K* compared to *Mg* and *Ca*). Hence hydroxides and carbonates of *Na* and *K* readily dissolve while those of *Mg* and *Ca* are only partially soluble.

15. Why are lithium salts commonly hydrated and those of other alkali metal ions usually anhydrous?

Ans: Li^+ ion being very small in size readily polarises water molecules. Thus H_2O molecules are easily attached to lithium salts (hydration).

16. Why is *LiF* almost insoluble in water while *LiCl* is soluble not only in water but also in acetone?

Ans: *LiF* is only slightly soluble in water due to its high lattice energy. The hydration enthalpy is greater than the lattice enthalpy for *LiCl* and it dissolves in water. *LiCl* dissolves in organic solvents (acetone) due to its more covalent nature compared to *LiF*.

17. What happens when (i) *Na* is dropped in water (ii) *Na* is heated in free supply of air (iii) sodium peroxide dissolves in water?

Ans: (i) $2Na + 2H_2O \rightarrow 2NaOH + H_2$ (ii) $2Na + O_2 \longrightarrow Na_2O_2$

(iii) $Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$

18. Comment on the following observations

(i) The mobility of alkali metal ions in aqueous solution is $Li^+ < Na^+ < K^+ < Rb^+$

(ii) Lithium is the only alkali metal which forms nitride directly

(iii) $E°$ of $M^{2+}(aq) + 2e^- \rightarrow M(s)$ (M = Ca, Sr or Ba) is nearly constant.

Ans:(i) A smaller ion is heavily hydrated which makes it slow moving. Hydration varies in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ and hence mobility is in the reverse order.

(ii) Li forms nitride as Mg does (diagonal relationship). Other alkali metals do not have such diagonal relationship.

$$6Li + N_2 \rightarrow 2Li_3N$$

(iii) $E°$ of an electrode M^{2+}/M depends on ionisation energy, hydration energy and enthalpy of vapourisation. For Ca, Sr and Ba the gross effect of these properties is almost the same and hence $E°$ is almost a constant.

19. State as to why (a) a solution of Na_2CO_3 is alkaline (b) alkali metals are prepared by electrolysis of their fused halides (c) sodium is more useful than potassium.

Ans:(a) An aqueous solution of Na_2CO_3 is alkaline due to hydrolysis.

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$$

(b) When aqueous solution of alkali metal halide is electrolysed, H_2 gas is formed at cathode (not the metal). So fused halides are used for electrolysis so as to deposit the metal at cathode. (Further, alkali metals being reactive and good reducing agents, common methods of reduction cannot be used to prepare them).

(c) K^+ ions are present within cell fluids while Na^+ ions are present in blood plasma and in the fluids surrounding the cell. Na^+ ions control flow of water across cell membranes and in the transport of carbohydrates and amino acids into the cells. So Na^+ is more useful than K^+ in our body.

20. (i) Which alkali metal has least melting point?

(ii) Which of the following gives hydrated salts. Li, Na, K or Cs?

(iii) Which is the most thermally stable carbonate among $MgCO_3$, $CaCO_3$, $SrCO_3$ and $BaCO_3$?

Ans: (i) Cs (ii) Li (iii) $BaCO_3$ (due to greater electropositivity of Ba)