

10.3 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 polarising 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.

10.3.1 Points of Difference between Lithium and other Alkali Metals

- Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.
- 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 unlike other alkali metals.
- LiCl is deliquescent and crystallises as a hydrate, $\text{LiCl}\cdot 2\text{H}_2\text{O}$ whereas other alkali metal chlorides do not form hydrates.
- Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
- Lithium nitrate when heated gives lithium oxide, Li_2O , whereas other alkali metal nitrates decompose to give the corresponding nitrite.

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

$$2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$$
- LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

10.3.2 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, $\text{Li} = 152 \text{ pm}$, $\text{Mg} = 160 \text{ pm}$; ionic radii : $\text{Li}^+ = 76 \text{ pm}$, $\text{Mg}^{2+} = 72 \text{ pm}$. The main points of similarity are:

- Both lithium and magnesium are harder

and lighter than other elements in the respective groups.

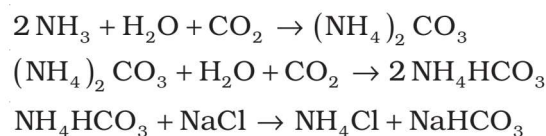
- Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride, Li_3N and Mg_3N_2 , by direct combination with nitrogen.
- The oxides, Li_2O and MgO do not combine with excess oxygen to give any superoxide.
- 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.
- Both LiCl and MgCl_2 are soluble in ethanol.
- Both LiCl and MgCl_2 are deliquescent and crystallise from aqueous solution as hydrates, $\text{LiCl}\cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2\cdot 8\text{H}_2\text{O}$.

10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below:

Sodium Carbonate (Washing Soda), $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$

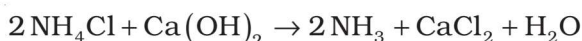
Sodium carbonate is generally prepared by Solvay Process. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing CO_2 to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed. The equations for the complete process may be written as :



Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.

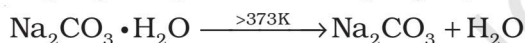
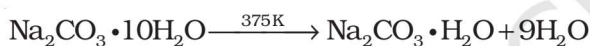


In this process NH_3 is recovered when the solution containing NH_4Cl is treated with $\text{Ca}(\text{OH})_2$. Calcium chloride is obtained as a by-product.

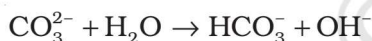


It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

Properties : Sodium carbonate is a white crystalline solid which exists as a decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. This is also called washing soda. It is readily soluble in water. On heating, the decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.



Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.



Uses:

- (i) It is used in water softening, laundering and cleaning.
- (ii) It is used in the manufacture of glass, soap, borax and caustic soda.
- (iii) It is used in paper, paints and textile industries.
- (iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride, generally obtained by crystallisation

of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride, CaCl_2 , and magnesium chloride, MgCl_2 are impurities because they are deliquescent (absorb moisture easily from the atmosphere). To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

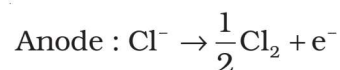
Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

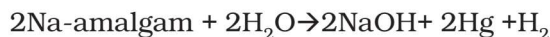
- (i) It is used as a common salt or table salt for domestic purpose.
- (ii) It is used for the preparation of Na_2O_2 , NaOH and Na_2CO_3 .

Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed 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.



The amalgam is treated with water to give sodium hydroxide and hydrogen gas.



Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3 .

Uses: It is used in (i) the manufacture of soap, paper, artificial silk and a number of chemicals, (ii) in petroleum refining, (iii) in the purification of bauxite, (iv) in the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and (vi) as a laboratory reagent.

Sodium Hydrogencarbonate (Baking Soda), NaHCO_3

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.



Sodium hydrogencarbonate is a mild antiseptic for skin infections. It is used in fire extinguishers.

10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions

found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of 143 mmolL^{-1} , whereas the potassium level is only 5 mmolL^{-1} within the red blood cells. These concentrations change to 10 mmolL^{-1} (Na^+) and 105 mmolL^{-1} (K^+). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table 10.2.

10.6.1 Electronic Configuration

These elements have two electrons in the s-orbital of the valence shell (Table 10.2). Their general electronic configuration may be represented as [noble gas] ns^2 . Like alkali metals, the compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe] $6s^2$
Radium	Ra	[Rn] $7s^2$

10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the