7. ALKALIMETALS (IA)

SYNOPSIS:

ELECTRONIC CONFIGURATION :

Li, Na, K, Rb, Cs and Fr belongs to IA group.

Oxides of Li, Na, K, Rb and Cs dissolve in water giving strong alkalies. So these elements are known as alkali metals.

General electronic configuration is ns^1, they are members of 's' block

Electronic configuration of Alkali metals:

Element	Atomic Number	Electronic configuration
Li	3	$[He]2S^1$
Na	11	$[Ne]3S^1$
K	19	$[Ar]4S^1$
Rb	37	$[Kr]5S^1$
Cs	55	$[Xe]6S^1$
Fr	87	$[Rn]7S^1$

Occurrence of Alkali metals :

These elements are highly reactive and do not occur in free state.

- All the alkali metals are silvery white, soft and lightmetals

Order of abundence is Na > K >Rb > Li>Cs

Usually They occur as their halides such as common salt - NaCl, sylvine - KCl, Carnalite - $KCl.MgCl_2.6H_2O$.

General properties

Size of the atoms- Atomic Radii .

- The alkali metal atoms have the largest atomic radii in their respective periods.
- These radii go on increasing on going down the group.

Density

Alkali metals are light metals having low densities. Densities of alkali metals increases from lithium to caesium The density of potassium is lesser than that of sodium contrary to the expectations. This is probably because of the abnormal increase in atomic size on moving from Na (186 pm) to K (227 pm) . Hence potassium is lighter than sodium. Lithium is the lightest known metal (density =0.534 g/cc)

Melting and boiling points

Melting and boiling points of alkali metals are quite low and decrease down the group .

Ionisation Energies

The first ionisation energy of alkali metals is the lowest amongst the elements in their respective periods .The alkali metals show great tendencies to lose the only elements in their respective periods. The alkali metals show great tendencies to lose the only s-electron present in their valence shells after which they acquire stable noble gas configuration.

$$M_{(g)} \rightarrow M^{+}_{(g)} + e^{-}$$

$$[Noblegas]ns^1 \quad [Noble\ gas]^{+}$$

The first ionisation energies of elements decrease on moving down the group .

- The second ionisation energies of all the alkali metals are very large because when one electron is lost from these elements the resulting ions acquire noble gas configurations which are very stable and have high effective nuclear charge. thus large amounts of energies are required to remove the second electron.

  On account of their low ionisation energies. Alkali metals have a great tendency to lose electron and form positive ions .

  $M_{(g)} \quad \rightarrow \quad M^{+}{}_{(g)} + e^{-}$

Hydration of Ions

All alkali metals are salts are ionic (except Lithium) and soluble in water .

the amount of energy released when one mole of ionic compound is dissolved in large excess of water is known as hydration energy .

Relative ionic Radii : $Cs^{+} > Rb^{+}K^{+} > Na^{+} > Li^{+}$

Relative ionic radii in water : $Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$

. **Relative degree of hydration :** : $Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$

Ionic moblities in aqueous solutions: $Cs^{+} > Rb^{+}K^{+} > Na^{+} > Li^{+}$

CHEMICAL CHARACTERSTICS OF ALKALI METALS

Action of Air :

Alkali metals are so reactive that they tarnish rapidly when exposed to air because of the formation of oxides, hydroxides and ultimately carbonates at the surface.

$4M_{(s)} + O_{2(g)} \rightarrow 2M_2O_{(s)}$

$M_2O_{(s)} + H_2O_{(l)} \rightarrow 2MOH_{(s)}$

$2MOH_{(s)} \xrightarrow{CO_2} M_2CO_3(s) + H_2O_{(l)}$

When burnt in air Li reacts with O_2 as well as N_2

$4Li_{(s)} + O_{2(g)} \rightarrow 2Li_2O_{(s)}$

$6Li_{(s)} + N_{2(g)} \rightarrow 2Li_3N_{(s)}$

Action of Oxygen

- Alkali metals when heated with oxygen or excess of air form oxides the nature of which depends upon the nature of alkali metals

$4Li + O_2 \rightarrow 2Li_2O$

Lithium monoxide

$2Na + O_2 \rightarrow Na_2O_2$

Sodium peroxide

$K + O_2 \rightarrow KO_2$

Potassium sup *eroxide*

Reaction with water :

- The alkali metals reacts vigorously with water by libration of and large amount of heat

$2M + 2H_2O \rightarrow 2M^{+} + 2OH^{-} + H_2 + HEAT$

Action with Hydrogen

- Alkali metals combine with hydrogen at about 673 K forming ionic hydrides $M^{+} \; H^{-}$.

$2M + H_2 \rightarrow 2MH$ (where $M = Li, Na, K\, etc$)

- These ionic hydrides have high melting points
  Since electropositive character increases from Li to Cs the ease of formation of hydride decreases from Li to Li . reacts with at about 1073 K.
- The Alkali metal hydrides are attacked by water (or any other proton doner like alcohols $NH_{3(g)}$, and alkynes etc) to give back hydrogen.
  $MH + H_2O \rightarrow MOH + H_2$

Action with Halogens :

- Alkali metals combine readily with halogens (X_2) to form ionic halides M^+X^- where M is an Alkali metal $2M + X_2 \rightarrow 2M^+X^-$
  [where M=Li , Na,K,Rb,Cs and X=F,Cl, Br, I]
- Reactively of alkali metals towards a particular halogen $Cs > Rb > K > Na > Li$
  As the electropositive character increases from top to bottom in the group , the ease of formation of alkali metal halides increases from Li to Cs.
- Reactivity of halogens towards a particular alkali metal $F_2 > Cl_2 > Br_2 > I_2$
- All halides of alkali metals (except LiF) are highly soluble in water.

Reducing Nature of Alkali Metals:

All alkali metals are strong reducing agents.

- Among all the alkali metals, Li is the strongest and Na is the weakest reducing agent. Lithium although has the highest ionisation energy (i.e, it holds its valence electrons most tightly) yet it is the strongest reducing agent.

- **Nature of Hydroxides :**
  Alkali metals hydroxides (except Lithium hydroxide) are strongest of all bases.
  $2LiOH \xrightarrow{\Delta} Li_2O + H_2O$
  the basic character of alkali metal hydroxides increases on going down the group
  $CsOH > RbOH > KOH > NaOH > LiOH$

SALT OF OXO-ACIDS :

Nature of carbonates and Bicarbonates:

- Li_2CO_3 is unstable towards heat and decomposes to give CO_2
  $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$
- $LiHCO_3$ does not exist in solid state
- The thermal stability of carbonates and bicarbonates increases on moving down the group.
- The solubility of carbonates and bicarbonates increases when we move down the group.
- The increasing order of solubility is ; $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

Bicarbonates :

- Bicarbonates of alkali metals are crystalline solids ∴Their solubility in water and thermal stability increases in the order
  $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$

Nature of Nitrates

- $LiNO_3$ upon heating decomposed to give NO_2 and O_2 whereas the nitrates of other alkali metals decomposes upon heating to nitrates and evolve only O_2
  $4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$

$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

Nature of sulphates :

- Li_2SO_4 is insoluble in water wheras the other sulphates *i.e* K_2SO_4, Na_2SO_4 are soluble in water
- Lithium does not form alum due to its small size
- All alkali metal form body centred cubic lattices with cor-ordinatoin number 8.
- Alkali metals dissolve in mercury forming amal gams. The dissolution is highly exothermic
- Lithium is the strongest reducing agent due to highest positive oxidation potential (+3.0.5 V)
- Alkali metals cations $(Li^+, Na^+, K^+, Rb^+, Cs^+)$ have no unpaired electrons and are diamagnetic while alkali metals are paramagnetic due to the presence of unpaired electrons.

Anomalous behaviour of Li

- Due to small size absence of vacent d-orbital
  Li behaves abnormally with other alkali metals
- Li shows similarity with N_2 Mg. That means it differs from other alkali metals.
- Li is hard metal. Softness increases down the group. Therefore other elements can cut with knife. Hence M.P. and B.P. of Li is high.
- Li directly combines with N_2 in air on heating to form nitride. No other alkali metals combine directly.
- Li directly form carbide. Remaining elements don't form carbide directly. But all these elements are known to give carbides.

Diagonal relationship of Li(with Mg)

- Li is diagonally related with Mg due to similar polarizing power, electro negativities, size and charge (charge per unit area)
- Li reacts with water slowly but Mg reacts with hot water fastly. Both gives hydroxids and liberate hydrogen.

  $2Li + 2H_2O \rightarrow 2LiOH + H_2$

  $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$
- Li and Mg gives only Mono oxides Li_2O, MgO
- Li Cl and $MgCl_2$ are deliquiscent. Both undergoes hydrolysis with hot water
- Due to covalent nature Li, Mg halides are soluble in organic solvents.
- Li^+ and Mg^{+2} are highly hydrated
- Carbonates, phosphates and Flourides of Li and Mg are sparingly soluble in water.
- Li -R (lithuim alkyl) are similar to RMgx chemically

Compounds of sodium

Sodium Hydroxide (Caustic Soda), $NaOH$ **preparation. :**

Causticizing process (Gossage process). It is an old process and involves heating of a 10 % solutions of Na_2CO_3 with a little excess of milk of lime $Ca(OH)_2$.

$Na_2CO_3 + Ca(OH_2) \rightarrow CaCO_3 \downarrow + 2NaOH$

Electrolytic Method :

Causitc soda is manufactured by the electrolysis of

a concentrated solutions of sodium chloride Cl^- ions are discharges at the anode with Na^+ ion are discharged at the cathode. Since chlorine is one of the by-products, it may react with NaOH forming NaCl and sodium hypochlorite.

Castner - Kellner Cell (Mercury Cathode Process)

This Process is specially used to avoid reaction between $NaOH$ and Cl_2. Here sodium hydroxide is obtained by electrolysis of aq. solution of brine. The cell comprises of rectangular iron tank divided into the compartments, Brine solution is electrolysed in outer compartments. The Central compartment has 2 % solution of NaOH.Na from outer compartments in the form of Na-Hg amalgam is pushed to a central through rocking motion of the cell. Sodium liberated in central compartment reacts with water to produce $NaoH$ and H_2

Properties.

It is deliquescent white crystalline solid .It absorbs moisture and carbon dioxide from the atmosphere forming sodium carbonate.

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

It is highly soluble in water. The resulting solution is bitter in taste, corrosive and soapy to touch. It is only sparingly soluble in alcohol. However KOH dissolves considerably in alcohol.

Reaction with salts :

Sodium hydroxide reacts with meatllic salts to form hydroxides which may be insoluble or soluble in excess of .Some of the hydroxides are unstable and decompose to insoluble oxides,

Forms insoluble hydroxides , $FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 \downarrow + 3NaCl$

Forms unstable hydroxides , *e.g*

$HgCl_2 + 2NaOH \rightarrow 2NaCl + Hg(OH)_2$

$Hg(OH)_2 \rightarrow HgO \downarrow + H_2O$

yellow

$2AgNO_3 + 2NaoH \rightarrow 2NaNO_3 + 2AgOH$

$2AgOH \rightarrow Ag_2O \downarrow + H_2O$

Brown

Forms insoluble hydroxides which dissolve in excess of $NaOH$

e.g Zn, Al, Sb, Pb, Sn and As.

Ammonium salts, when heated with decompose to liberate ammonia.

$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2 \downarrow + Na_2SO_4$

Reaction with non-metals

$3NaOH + P_4 + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

$6NaOH + 4S \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

Reaction with halogens:

$X_2 + 2NaOH(cold) \rightarrow NaX + NaXO + H_2O$

sod.hypohalite

$3X_2 + 6NaOH(hot) \rightarrow 5NaX + NaXO_3 + 3H_2O$

sod.halate

Reaction with metals:

Weakly electropositive metals like Zn,Al and Sn, dissolve in NaOH solution to liberate hydrogen gas $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

Reaction with sand,:

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

$$sod.silicate\,(glass)$$

Reaction with Carbon monoxide

$$NaOH + CO \xrightarrow{150-200^0\,C,5-10\,atm} HCOONa$$

$$sod.formate$$

Uses of NaOH

- In Soap, paper, rayon industries
- In Manufacture of organic colouring matter
- In petroleum refining, mercerizing cotton, preparation of NaOX, $NaXO_3$, Al_2O_3, silicate glass, phosphates etc.
- To absorb SO_2 near electrical generators.
- As reagent, cleaning agent in lab.

$NaNO_3$ (Chile salt petre) :

Na_2CO_3 or NaOH react with HNO_3 to give $NaNO_3$

Properties: White Deliquescent, crystalline solid, soluble to H_2O, decomposes to nitrite on heating.

Uses : As nitrogenous fertilizer, in manufacture of HNO_3, $NaNO_2$, KNO_3

$$NaNO_3 + KCl \rightarrow NaCl + KNO_3$$

- **Sodium nitrite ($NaNO_2$)**

$$2NaNO_3 \xrightleftharpoons{500^0\,C} 2NaNO_2 + O_2$$

$$Na_2CO_3 + NO_2 + NO \rightarrow 2NaNO_2 + CO_2$$

$$NaOH + NO_2 + NO \rightarrow 2NaNO_2 + HNO_2$$

PROPERTIES: Pure $NaNO_2$ = white crystalline solid

impure $NaNO_2$ = yellow colour

$NaNO_2$ acts as oxidising and reducing agent

- $CO(NH_2)_2$ +2$NaNO_2$ + (Acid medium) $2H^+ \rightarrow 2N_2 + 3H_2O + CO_2 + 2Na^+$
  (urea) oxidising agent
- $2NaNO_2 + 2NaI + 4HCl \rightarrow 4NaCl + 2NO + H_2O + I_2$

(oxidising agent) (starch iodide paper turns blue)

- $5NaNO_2 + 3H_2SO_4 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5NaNO_3$
  (Reducing agent)
- $3NaNO_2 + 4H_2SO_4 + K_2Cr_2O_7 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3NaNO_3$
  (Reducing)

Uses : In preparation of azodyes, food preservatives, qualitative and quantitative analysis.

- **Na_2CO_3** :

  $Na_2CO_3.10H_2O$ washing soda

  Na_2CO_3 soda or soda ash

Preparation:

Sodium Carbonate is prepared by:

- Leblanc process.
- Ammonia Soda process or Solvay process.
- Electrolytic process.

LEBLANC PROCESS:

RAW MATERIALS: NaCl, Conc.H_2SO_4, Coke and $CaCO_3$

- In this process a mixture of NaCl and Conc.H_2SO_4 on heating gives salt cake (Na_2SO_4)
- Salt cake, coke and Lime stone mixture on heating gives black ash. Na_2CO_3 + CaS = Black ash
- present in black ash can be separated from CaS by fractional crystallisation.
- The Aqueous solution of black ash is alkaline.
- CaS in Black Ash is called Alkali waste.
- By products in this process are HCl and CaS.

SOLVAY PROCESS:

RAW MATERIALS: NaCl, NH_3 and $CaCO_3$ (for CO_2)

- In this process CO_2 is continuously passed into the brine solution saturated with ammonia gas. $NaHCO_3$ crystallises out from the solution.

the equation for the complete process may be summerized

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$$

Ammonium Bicarbonate.

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

- $NaHCO_3$ on heating gives Na_2CO_3, H_2O and CO_2
- The recycling products in this process are NH_3 and CO_2.
- The by product in this process is $CaCl_2$.

ELECTROLYTIC PROCESS:

- In this process brine solution on electrolysis gives NaOH solution.
- CO_2 and steam are passed simultaneously at high pressure into NaOH to get Na_2CO_3.

PHYSICAL PROPERTIES

- Na_2CO_3 is white crystalline solid efflorescent (looses water to atmosphere)

  $Na_2CO_3.10H_2ONa_2CO_3.\ H_2ONa_2CO_3.H_2O$

  Its melting point is 852.1 ^{0}C
- It dissolves in H_2O to give basic solution

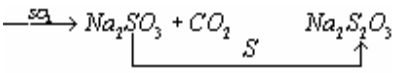
$$Na_2CO_3 + H_2O \rightarrow NaOH + NaHCO_3$$

$$NaHCO_3 + H_2O \rightarrow NaOH + H_2CO_3$$

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

CHEMICAL PROPERTIES: Na_2CO_3

$\xrightarrow{2HCl} 2NaCl + H_2O + CO_2$



$\xrightarrow{CO_2+H_2O} 2NaHCO_3$

$\xrightarrow{SiO_2} Na_2SiO_3 + CO_2$

(water glass)

$\xrightarrow{MgCl_2} MgCO_3 \downarrow +2NaCl$

USES: It is used

- in manufacture of glass and caustic soda**.**
- in softening of hard water.
- in Laundries, paper and dye industries.
- in petroleum industry.
- in Ultramarine industry.
- In qualitative and quantitative analysis

- Na_2CO_3 is used is softening of hard water to ppt of Ca and Mg carbonates.
- Ultramarines are coloured substances used as pigments. They are alumino silicates and do not contain H_2O.

  Ex: Sodalite $Na_3(AlO_2)_6(SiO_2)_6Cl_2$

  When Na_2CO_3 or Na_2SO_4 fused with sodalite - ultramarines are produced.

SODIUM BICARBONATE ($NaHCO_3$):

COMMON NAME - Baking Soda

- It is prepared by passing CO_2 gas into a saturated solution of sodium carbonate.

  $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$

PROPERTIES:

- White crystalline solid
- $NaHCO_3$ Solubility of $NaHCO_3$ in water is less than Na_2CO_3
- Na_2CO_3 solution is less alkaline than because less number of OH^- ions are formed.

  $NaHCO_3 + H_2O \rightarrow NaOH + H_2CO_3$

  $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$
- It undergoes hydrolysis to a lesser extent than Na_2CO_3.
- Aqueous solution of $NaHCO_3$ can not give any colour with phenolphthalein but gives pale yellow colour with methyl orange indicator.
- Aqueous solutions of Na_2CO_3 and $NaHCO_3$ are distinguished by phenolphthalein.
- This is used in quantitative estimation of HCO_3^- and CO_3^{-2} in their mixture.

USES OF $NaHCO_3$: It is used

- in baking powders.
- as antacid for hyper acidity
- in fire extinguishers.
- in effervescent drinks.
- Baking powder contains $NaHCO_3$ and acidic salt like sodium Potassium hydrogen tartarate

  (or)

  $NaHCO_3 + CO(H_2PO_4)_2 + Starch$

Sodium Chloride (NaCl)

Properties : NaCl is hygroscopic in crude form due to impurities of Ca and Mg Chloride.

Uses : as preservative for meat and fish

In preparation of freezing mixture with ice

Essential constituent of diet, starting material for preparation of $Na\ or\ Cl_2$ in downs process

BIOLOGICAL IMPORTANCE OF Na and K

- Na, K, Mg, Ca required in living system
- Metal ions balance the charges, associated with negatively charged organic molecules present in cell. Ions helps in maintaining osmotic pressure in cell.
- Na^+ ion expelled from cell. This ion transport activity is known as sodium pump but K^+ ions are not pumped out
- Energy required for pumping out Na^+ ion or taking in K^+ ion provided by hydrolysis of ATP (adenosine triphosphate) into ADP (adenosine diphosphate)
- Presence of Na^+ and K^+ inside and outside the cell maintain electrical balance.
- K^+ ion essential for metabolism of glucose inside the cell, synthesis of proteins and activation of enzymes.

Uses of Alkali metals

- Na is catalyst in rubber formation (Isoprene as monomer) (2 methyl 1,3 buta diene)
- Na-Hg as reducing agent
- In formation of Na_2O_2, Na , NH_2, NaCN, TEL

  K - Na and k as alloy in high temperature thermo meters.
- In photoelectric cells, KOH in soft soaps, as electrolyte in storage batteries Cs - Cr and Ag as alloy in Television