NARAYANA
IIT ACADEMY
INDIA

SRAMAYEVA JAYATHE

40 YEARS OF EXCELLENCE

BASARA SARASWATHI BHAVAN_MDP N-120

SECTION : SENIORS	GROUP – IA &IIA	PREPARED BY: Dr. A.P.R

| Group – IA	Group – IIA
• **Elements :** Li, Na, K, Rb, Cs& Fr Fr is Radio active C_s (golden yellow coloured) & other metals are silvery white. Other two metals which are intense coloured like Cu, and Au. • **G.E.C :** ns^1 • **Oxidation States :** +1 forms only mono positive cation, can't form dipositive due to high IE_2. • **Atomic & ionic radii :** Down the group regularly increases • **Polarising power :** Tendency to cause distortion in the electronic cloud of neighbouring anion polarising power $\propto \dfrac{\text{(+ve) charge}}{\text{size of cation}}$ $\therefore Li^+ > Ni^+ > K^+ > Rb^+ > Cs^+$ 2nd group cations are more Polarising than IA – group cations due to their smaller ionic radii and higher +ve charge. • **Hydration Energy :** $\propto \dfrac{charge}{ionic\ radii}$ Down the group extent of Hydration decreasing due to increasing in ionic radii; $\therefore Li^+ > Ni^+ > K^+ > Rb^+ > Cs^+$ • **Hydrated ionic radii:** Depends on extent of hydration of cation. Higher the hydration energy greater the hydrated ionic radii $Li^+_{(aq)} \ldots \ldots Cs^+_{(aq)}$ decreasing order of hydrated ionic radii • **Conductivity of Salt Solutions:** Higher the Hydration, larger the size of hydrated cation lesser the conductivity or ionic mobility. $\therefore Li^+ < Ni^+ < K^+ < Rb^+ < Cs^+$ increasing order of conductivity or ionic mobility.des^s	• **Elements :** Be, Mg, Ca , Sr, Ba & Ra Ra is Radio active Be silvery white, Ca, Sr, Ba are Pale yellow coloured. • **G.E.C :** ns^2 • **Oxidation States :** +2 forms only dipositive cations • **Atomic & ionic radii :** Down the group regularly increases. • **Polarising power :** Tendency to cause distortion in the electronic cloud of neighbouring anion polarising power $\propto \dfrac{\text{(+ve) charge}}{\text{size of cation}}$ $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$ • Higher the polarising power greater the covalent character (lesser the ionic character) • **Hydration Energy:** Down the group extent of Hydration decreases $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$ Hydration Energy of 2nd group cations is larger than first group cation due to their smaller size and higher positive charge • **Hydrated ionic radii:** Depends on extent of hydration of cation. Higher the hydration energy greater the hydrated ionic radii $Be^{+2}{}_{(eq)} \ldots \ldots Ba^{+2}{}_{(eq)}$ decreasing order • **Conductivity of Salt Solution:** Higher the Hydration, larger the size of hydrated cation lesser the conductivity or ionic mobility: $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$ increasing order of conductivity or ionic mobility in aq.solution.

- **Flame test :** metal of lower I.E can impart colour to the flame.
  All alkali metal impart colour due to low I.E. Li→(C.R) Na (G.yellow) , K (Lilac),
  Rb (Ruby red), Cs (violet)
- **Density:** Regular ($\uparrow$) down the group observed except 'K' 'Li' lowest density at R.T (0.534g/cc). Density of 'K' slightly less than Na.

- **M.P and B.P :** Regular ($\downarrow$) in M.P is observed Regular ($\downarrow$) is observed in B.P

- **Cohesive Energy**: Indicates force of attraction between atoms of a metal
  Cohesive energy $\propto \dfrac{\text{no.of valance } \bar{e}s}{\text{radius of metal}}$.
  Down the group cohesive E($\downarrow$) due to ($\uparrow$)in radius of metal. Li, Na, K, Rb & Cs($\downarrow$) order of cohesive 'E'.
- **Hardness and heat of atomization** :
  Both these properties depends on force of attraction between metal atoms. Which is indicated by cohesive 'E'
  Hardness and Heat of atomization $\propto$ cohesive energy.
  Li, Na, K, Rb & Cs ($\downarrow$) order of hardness and heat of atomization
  Cohesive 'E' of 2nd group metals is greater than Ist group due to more no.of valancy electrons and smaller size.
- **Amalgams:** all form amalgams
- **Reducing property:** (SRP value) The tendency of an element to lose an electron in solution is measured by the standard reduction potential of the elements.
  Li (-3.04); Na(-2.71); K(-2.95) Rb(-2.93) Cs(-2.927)

  1) Low values indicates that alkali metal have strong tendency to act as reducing agents and'Li' strongest of

- **Flame test :** Be, Mg cant impart colour due to their high I.E, others can impart colour,
  Ca(BR); Sr(C.R), Ba(A.G)

- **Density:** Slightly ($\downarrow$)on moving down the group upto 'Ca' but it ($\uparrow$) considerably up Ra
  $Be(1.84)Mg(1.74)Ca(1.55)$
  $Sr(2.54)Ba(3.75)Ra(6.00)$
- **M.P and B.P :** expected to ($\downarrow$) down the group but no regular trend is observed.

Be, Ca → Sr → Ba
Mg → Lowest m.p & B.p
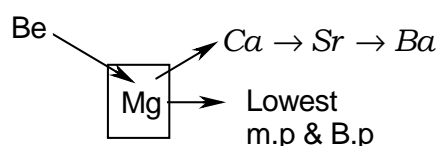
- **Cohesive Energy:** Cohesive energy decreases regularly.

- **Hardness and heat of atomization**:
Both these properties Depends on force of attraction between metal atoms. Which is indicated by cohensive 'E'
Be Mg Ca Sr Ba decreasing order of hardness and heat of atomization.

- **Amalgams:** all form amalgams
- **Reducing property: (**SRP value) The tendency of an element to lose an electrons in solution is measured by the standard reduction potential of the elements.

$Be(-1.85); Mg(-2.37); Ca(-2.87)$
$Sr(-2089)Ba(-2.90)$

Reducing character and electropositive character $\propto \dfrac{1}{SRP}$ values.

them all.

2) However if we look at I.E, 'Li' has highest indicating, it is not ready to lose electron. This at First sight, seems contrary to lower value of SRP (-3.04) of 'Li' Which indicates 'Li' gives off it electron most readily. The anomaly can be explained as....

- Ionization energy involves only the following change: $M_{(g)} \rightarrow M^+_{(g)} + 1e$

- SRP on the other hand involves........

Step – I: $M_{(s)} \rightarrow M(g) : \Delta H_{(sub)}$

'E' required in step-I is Heat of sublimation. Which is similar for all alkali metals

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

The 'E' required for this change is I.E which is highest for 'Li'

Step-III: $M^+_{(g)} + H_2O \rightarrow M^+_{(aq)}$

'E' liberated in this step is called hydration energy. Highest for 'Li'
SRP values depends on net effect of all the three steps For 'Li' hydration energy is very large
(Step III) Compensates energy required to take off the electron (step-II) this explain lower SRP value of 'Li'.

- **Alkali metals in liquid NH₃**
  1. All alkali metals dissolves in liquid NH₃ without impurity like iron and form blue coloured solution
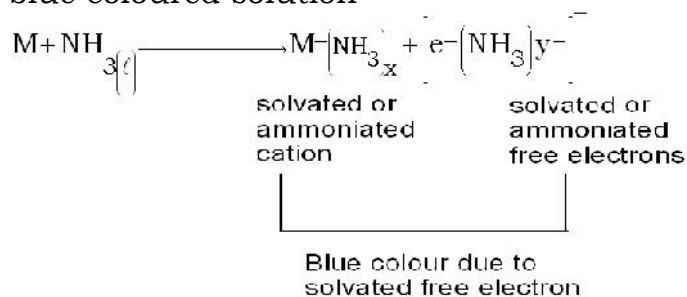
2. On long standing blue colour Fades and alkali metal amide (MNH₂) is formed
3. On evapouration alkali metal is recovered.

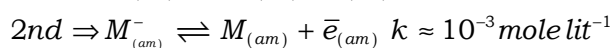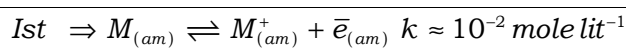**Properties of Blue solution**
  1. Conductivity: conductive due to solvated cation and solvated free electron, conductivity higher than that of completely ionised metal salt in water.

1. Electro positive and reducing character increase regularly down the group
2. 2nd group element are less electro positive and less reducing than Ist group (based on SRP)

- **Alkali earth metals in liquid NH₃**
Except 'Be' and Mg all dissolves in liquid NH₃ and forms blue coloured solution

$$Ist \Rightarrow M_{(am)} \rightleftharpoons M^+_{(am)} + \bar{e}_{(am)} \quad k \approx 10^{-2}\, mole\, lit^{-1}$$
$$2nd \Rightarrow M^-_{(am)} \rightleftharpoons M_{(am)} + \bar{e}_{(am)} \quad k \approx 10^{-3}\, mole\, lit^{-1}$$
$$3rd \Rightarrow M_{2(am)} \rightleftharpoons 2M_{(am)} \quad\quad k \approx 10^{-4}\, mole\, lit^{-1}$$
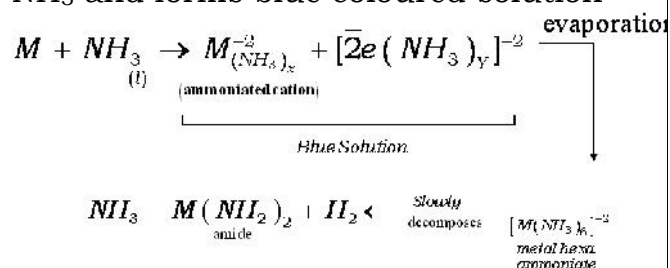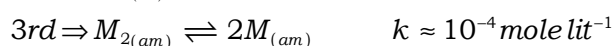
- As concentration of solu. increases (0.04M) Conductivity decreases and reaches to minimum value then increases dramatically reaches value of liquid metal

Reason : a) at low concentration first equation predominates higher mobility results in higher conductivity

b) as conc. $(\uparrow)$ 2nd equilibrium removes free electron $M^-_{(am)}$ and reaches to minimum value

Magnetic propertiesof Blue solution :

a) Dilute sol. are paramagnetic one unpaired electron per metal atom

b) Susceptibility $(\downarrow)$ with $(\uparrow)$ in conc . of solution and becomes diamagnetic at conc. of minimum conductivity which is due to 3rd eq. state

$\left[M_{2(am)} \rightleftharpoons 2M_{(am)} K = 10^{-4} \right]$ weakly para magnetic at still higher Concentration.

Reducing Character of Blue Solution

More reducing than alkali metal in dry state due to free electrons

eg:

$$O_2 + \left[\bar{e}(NH_3)_n \right]^- \to O_2^- \xrightarrow{[\bar{e}(NH_3)_n]^-} O_2^{-2}$$

$$K_2 \left[\overset{"}{Ni}(CN)_4 \right] \xrightarrow[{[\bar{e}(NH_3)_n]^-}]{} K_3 \left[\overset{I}{Ni}(CN)_4 \right]$$
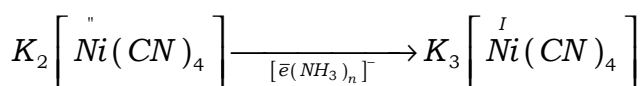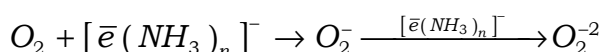
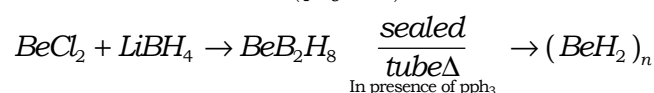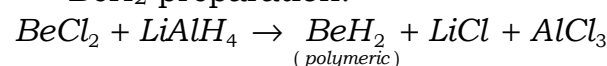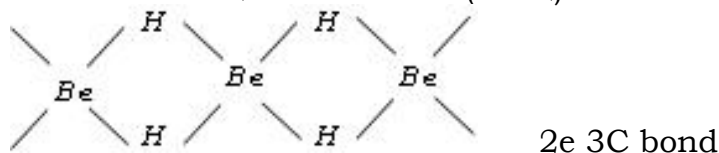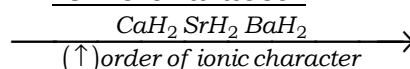| Group – IA	Group – IIA
Hydrides: MH All alkali metals directly combines with H_2 and form 'MH' type of hydrides(2 M+$H_2 \to$ 2MH) Nature of Hydrides: $\Rightarrow$ all are ionic Larger cation greater ionic character $\xrightarrow{\underset{(\uparrow)order\,of\,ionic\,character}{LiH\,NaH\,KH\,RbH\,CsH}}$ On Hydrolysis liberates H_2. LiH used for military purpose to produce H_2 gas to fill the balloons.	**Hydrides:** MH_2 except 'Be' all elements directly combines with hydrogen to form hydride. M+$H_2 \to MH_2$(M= Mg, Ca, Sr, Ba) - BeH$_2$ preparation: $BeCl_2 + LiAlH_4 \to \underset{(polymeric)}{BeH_2} + LiCl + AlCl_3$ $BeCl_2 + LiBH_4 \to BeB_2H_8 \xrightarrow[\underset{\text{In presence of pph}_3}{tube\Delta}]{sealed} (BeH_2)_n$ - BeH$_2$, MgH$_2$ are covalent and polymeric with non classical bonding other are ionic on hydrolysis liberates H_2. Structure of $(BeH_2)_n$ 2e 3C bond - **Ionic character** $\xrightarrow{\underset{(\uparrow)order\,of\,ionic\,character}{CaH_2\,SrH_2\,BaH_2}}$
Thermal decomposition : All decompose below their m.p **Stability:** H^- smaller anion is stabilized by smaller cation. Order: LiH ....CsH Stability $(\downarrow)$ $\Rightarrow$ Reducing character: H^- is electron donr and all ionic hydrides contains H^-.	**Thermal decomposition :** All decompose below their m.p **Stability:** CaH$_2$........ BaH$_2$ stability $(\downarrow)$ CaH$_2$....BaH$_2$ reducing character$(\uparrow)$
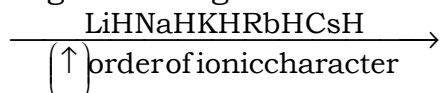
∴ acts as reducing agents.

Reducing characters $\propto \dfrac{1}{stability}$.

LiH...CsH $(\uparrow)$ order of reducing character

Bicarbonates
IA : MHCO₃

Physical state: All are solids except LiHCO₃ only Na, K, Rb, Cs and NH_4^+ form solid bicarbonates, No other metal form
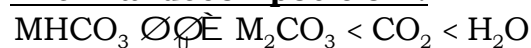
Solubility: Soluble. Solubility $(\uparrow)$ down the group (Reason : change in L.E is more than change in H.E)

Sodium Bicarbonate:
In crystal state contains infinite no.of HCO₃⁻ units with H bonding. Where as KHCO₃ contains 2HCO₃⁻ units with H bonding
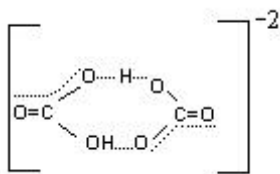
Thermal decomposition :
$MHCO_3 \xrightarrow{\;\;} M_2CO_3 < CO_2 < H_2O$

Thermal stability:
HCO_3^- larger anion stabilized by larger cation
Li HCO₃ ...... CsHCO₃ stability increases

M₂CO₃ Carbonates:
Thermal decomposition: Only Li₂CO₃ decomposes on heating other carbonates no decomposition (stable to heat)
$Li_2CO_3 \xrightarrow{\;\Delta\;} Li_2O + CO_2$
Lattice 'E' of Li₂O is more than Li₂CO₃
∴ decomposes
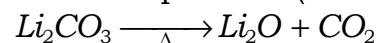
Thermal stability ⇒ same as bicarbonates
$[CO_3^{-2}$ larger anion
stabilized by larger cation]
Li₂CO₃ covalent due to high polarising power of Li⁺ others are
$Na_2CO_3..........Cs_2CO_3$ ionic character $(\uparrow)$

Solubility:
All are soluble except Li₂CO₃. Solubility increases down the group.

Group – II hydrides are more stable than group – I and are less reducing than group – I hydrides
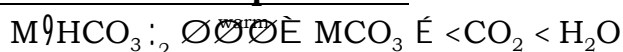
Bicarbonates
IIA M(HCO₃)₂

Physical state:
No bicarbonate exist in solid state all exist in aqueous solution.

Solubility : All are soluble

Thermal decomposition :
$M(HCO_3)_2 \xrightarrow{\;warm\;} MCO_3 \downarrow < CO_2 < H_2O$
$\qquad$ solution $\qquad$ ppt(carbonates are insoluble)

Thermal stability:
$Be(HCO_3)_2 ....Ba(HCO_3)_2$ Stability increases

Carbonates: IIA: MCO₃
Thermal decomposition :
All decomposes to oxides
$MCO_3 \xrightarrow{\;\Delta\;} MO + CO_2$
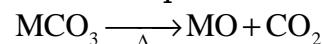
Thermal stability:
Same as bicarbonates.
BeCO₃ covalent due to high polarising power of Be⁺². Others ionic down the group ionic character $(\uparrow)$

Solubility:
Insoluble in water but dissolves in presence of CO₂, due to formation of soluble bicarbonates.
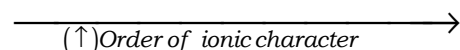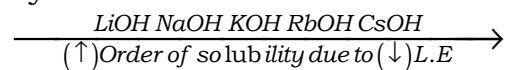$MCO_3 + H_2O + CO_2 \rightarrow M(HCO_3)_2$

Oxides and Hydroxides

Group – I	Group – II
Mono oxides: (M₂O)	**Mono oxides: (MO)**

Mono oxides: (M$_2$O)

$\text{Li} + \text{air} \xrightarrow{\Delta} \text{Li}_2\text{O}(\text{Li}_2\text{O}_2 \text{ little})$

$\text{Na} + \text{air} \xrightarrow{\Delta} \text{Na}_2\text{O}_2(\text{Na}_2\text{O little})$

$\text{M} + \text{air} \xrightarrow{\Delta} \text{MO}_2 [\text{M} = \text{K}, \text{Rb}, \text{Cs}]$
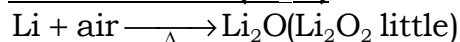
Solubility : all are soluble in water forms hydroxides

$$\xrightarrow[\text{($\uparrow$)Order of solubility due to ($\downarrow$)L.E}]{LiOH\ NaOH\ KOH\ RbOH\ CsOH}$$

$$\xrightarrow{\text{($\uparrow$)Order of ionic character}}$$

Crystal structure: Li$_2$O to Rb$_2$O have anti fluorite crystal structure. CS$_2$O have CdCl$_2$ Crystal structure.

   All metals are induced to form normal, peroxides and super oxides by passing cal. quantity O$_2$ through alkali metal liquid NH$_3$ Solution.

Stability of oxides of group –I and group – II elements:

Down the group stability of oxides decreases

$\text{Li}_2\text{O}\ \text{Na}_2\text{O}\ \ \text{K}_2\text{O}\ \text{Rb}_2\text{O}\ \text{Cs}_2\text{O}$

$\text{BeO}\ \text{MgO}\ \text{CaO}\ \text{SrO}\ \text{BaO} \longrightarrow$
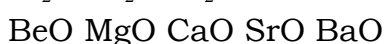
(Decreasing order of stability
Based on heat of formation values)

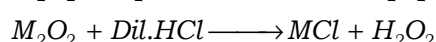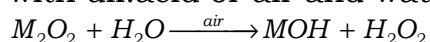**Stability of hydroxides of group –I and group – II elements:**

LiOH NaOH KOH RbOH CsOH

$\text{Be(OH)}_2\ldots\ldots\ldots\ldots\ldots\ldots\text{Ba(OH)}_2 \longrightarrow$

increasing order of stability
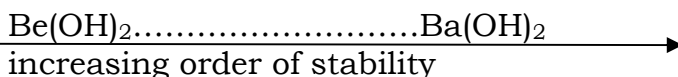
Peroxides: IA(Salt of dibasic acid H$_2$O$_2$)

G.F: M$_2$O$_2$(diamagnetic)

Ionic character

All are ionic. Ionic character ($\uparrow$) due to ($\uparrow$) size of cation.

Oxidising power: oxidising as forms H$_2$O$_2$ with dil.acid or air and water

$M_2O_2 + H_2O \xrightarrow{air} MOH + H_2O_2$

$M_2O_2 + Dil.HCl \longrightarrow MCl + H_2O_2$

Stability : O_2^{-2} larger anion is stabilized by larger cation
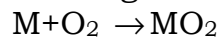
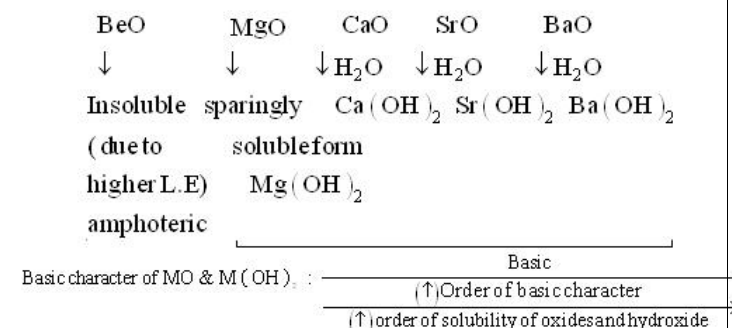Li$_2$O$_2$............Cs$_2$O$_2$($\uparrow$) order of stability higher the stability lesser the oxidizing capacity.
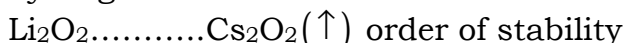
Mono oxides: (MO)

Metal burn in O$_2$ to form MO type of oxide, Ba, Ra being more electro positive forms peroxides

$\text{M} + \text{O}_2 \rightarrow \text{MO}_2$

[M=Ba, Ra]

Nature of oxides: BeO covalent other are ionic. Ionic character($\uparrow$) down the group

Solubility:

BeO	MgO	CaO	SrO	BaO
$\downarrow$	$\downarrow$	$\downarrow$ H$_2$O	$\downarrow$ H$_2$O	$\downarrow$ H$_2$O
Insoluble	sparingly	Ca(OH)$_2$	Sr(OH)$_2$	Ba(OH)$_2$
(due to	soluble form			
higher L.E)	Mg(OH)$_2$			
amphoteric				

Basic character of MO & M(OH)$_2$:
$$\xrightarrow[\text{($\uparrow$)order of solubility of oxides and hydroxide}]{\text{($\uparrow$)Order of basic character}} \overset{\text{Basic}}{}$$

Solubility depend on L.E . L.E ($\acute{E}$) down the group solubility increases.

$\Rightarrow$ Crystal structure: BeO – wurtzite (C.NO:4) Other oxides are basic have NaCl type (F.C.C) structure.
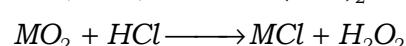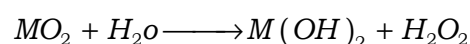
Peroxides: IIA

O_2^{-2} diamagnetic anion : salts of dibasic acid H_2O_2

G.F: MO$_2$(diamagnetic)

MO_2 all are ionic. Be cannot form peroxide.

Ionic character ($\uparrow$) down the group due to ($\uparrow$) in size of cation

Oxidising power: oxidizing as forms H$_2$O$_2$ with dil.acid or air and water

$MO_2 + H_2o \longrightarrow M(OH)_2 + H_2O_2$

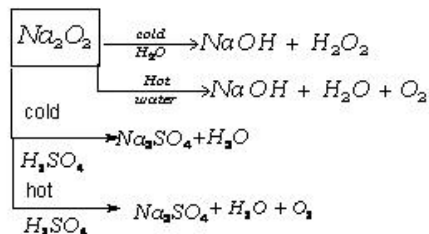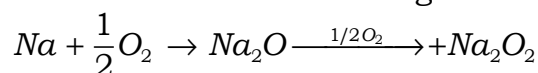$MO_2 + HCl \longrightarrow MCl + H_2O_2$

BeO$_2$..........BaO$_2$($\uparrow$) order of stability higher the stability lesser the oxidizing capacity.

IA group peroxides are more stable than IIA as O_2^{-2} is more stabilized by larger cation of alkali metals.
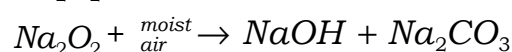
Na_2O_2 sodium peroxide
Preparation :
Industrial method two stage reaction

$$Na + \frac{1}{2}O_2 \rightarrow Na_2O \xrightarrow{1/2O_2} +Na_2O_2$$

$$Na_2O_2 \xrightarrow[H_2O]{cold} NaOH + H_2O_2$$
$$\xrightarrow[water]{Hot} NaOH + H_2O + O_2$$
cold
$$\xrightarrow{} Na_2SO_4 + H_2O$$
H_2SO_4
hot
$$\xrightarrow{} Na_2SO_4 + H_2O + O_2$$
H_2SO_4

Properties : Yellow solid;
Na_2O_2 exposed to moist air

$$Na_2O_2 + \underset{air}{moist} \rightarrow NaOH + Na_2CO_3$$
(yellow)   (white)

Strong Oxidising:
1) oxidizes $Cr^{+3} \rightarrow Cr^{+6}\left(CrO_4^{-2}\right)$
2) oxidizes $Mn^{+2} \rightarrow Mn^{+7}\left(manganate\right)$
3) oxidizes $SO_2 \rightarrow SO_3$
4) oxidizes $S^{-2} \rightarrow SO_3^{-2} \rightarrow SO_4^{-2}$

in presence of strong oxidizing agent like KMnO₄ it acts as reducing agent

Crystal structure of Na_2O_2: (3 different structures)
1. Marcasite at Liquid air temp
2. Fe S₂ pyrite structure (55 – 77⁰C) similar to NaCl but unit cell tetragonal
3. CS₂ structure at R.T similar to NaCl cubic.

- absorbs CO₂ releases O₂

∴used in submarines and crowded places. $Na_2O_2 + CO_2 \rightarrow Na_2CO_3 + O_2$

Super Oxides (IA) :
MO₂ contains O_2^- para and coloured LiO₂ NaO₂ yellow; KO₂, CsO₂ orange RbO₂ brown

Stability : larger cation have more tendency to form

Super oxides ∴ stability $(\uparrow)$ down the group

Oxidising cap: $MO_2 + H_2O \rightarrow MOH + H_2O_2 + O_2$

Stronger oxidizing than corresponding peroxides due to liberation of O₂ and formation of H₂O₂

$Na_2O_2 + O_2 \xrightarrow[T\&P]{high} NaO_2$ (commercial method)
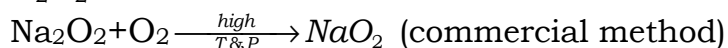
KO₂ Potassium Super Oxide:
Properties:

1) $\underset{(excess)}{K} + O_2 \xrightarrow{Red'p'} K_2O$

2) $K + \underset{(excess)}{O_2} \xrightarrow{burn} K_1O_2$

3) dry $KOH + O_3 \rightarrow KO_3 + H_2$

4) 'K' Liq $NH_3 + 3O_2 \rightarrow K_2O_3$(sesquioxide)

Properties of KO₂:
KO₂ Potassium Super Oxide:
Preparation:

$$KO_2 \xrightarrow{CO_2} K_2CO_3 + O_2$$
$$\xrightarrow{CO} K_2CO_3 + O_2$$
$$CO_2 + H_2O$$
$$\xrightarrow{} K_2CO_3 + H_2O + O_2 \xrightarrow{CO} KHCO_3 + O_2$$

Nitrates: IA: MNO₃	**Nitrates IIA: M(NO₃)₂**
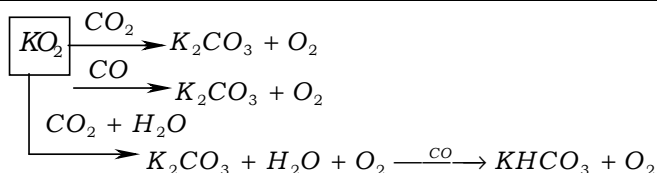
Nitrates: IA: MNO$_3$

Solubility: All are soluble. Solubility $(\downarrow)$ down the group

Preparation:

M OH or M$_2$CO$_3$+HNO$_3$ $\longrightarrow$ MNO$_3$
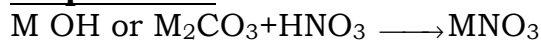
Thermal decomposition: most stable nitrates known. On strong heating decomposes as

$$MNO_3 \xrightarrow{500^0C} MNO_2 + O_2$$

$[M = Na, K, Rb, Cs]$ $\qquad \downarrow^{800^0C}$

$$M_2O + O_2 + N_2$$

$$LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$$
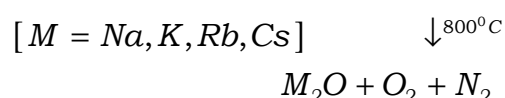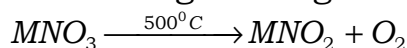
Thermal Stability : Larger anion NO_3^- stabilized by large cation:

LiNO$_3$.........$CsNO_3 (\uparrow)$ order of stability

LiNO$_3$ used in fire works gives red coloured distress flares.

$(KNO_3 + S + charcoal) \Rightarrow Gun\ powder$

$LiNO_3$, $NaNO_3$ are not used in gun powder as they are deliquisent.

Nitrates IIA: M(NO$_3$)$_2$

Solubility: All are soluble. Solubility $(\downarrow)$ down the group

Preparation:

$M(OH)_2 + MCO_3 + HNO_3 \rightarrow M(NO_3)_2$ hydrated.
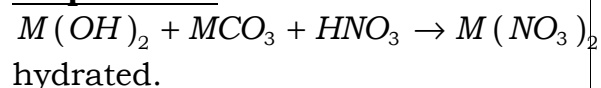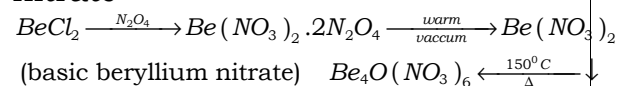
- Hydrated nitrate cant be converted to any hydrous by heating, because nitrate on heating decomposes to oxide $[M(NO_3)_2 \rightarrow MO + NO_2 + O_2]$

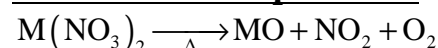Anhydrous can be prepared using N$_2$O$_4$ or ethyl acetate

$\Rightarrow$ Be forms normal nitrate and basic nitrate

$BeCl_2 \xrightarrow{N_2O_4} Be(NO_3)_2.2N_2O_4 \xrightarrow[vaccum]{warm} Be(NO_3)_2$

(basic beryllium nitrate) $Be_4O(NO_3)_6 \xleftarrow{150^0C}{\Delta} \downarrow$

Around 'O' atoms four 'Be' atoms. Nitrate acts as bidenate ligand.

Thermal decomposition:

$M(NO_3)_2 \xrightarrow{\Delta} MO + NO_2 + O_2$
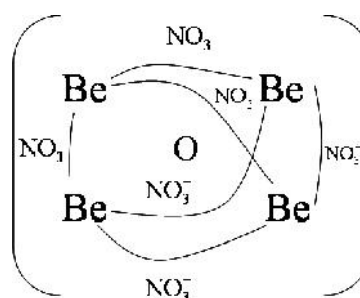
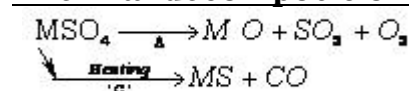**Stability:**

Larger anion is stabilized by larger cation. $\therefore$ Down the group stability $(\uparrow)$.

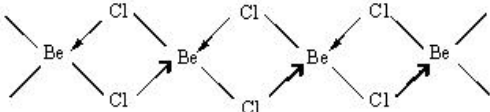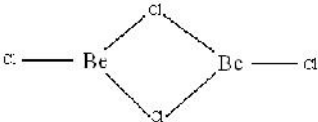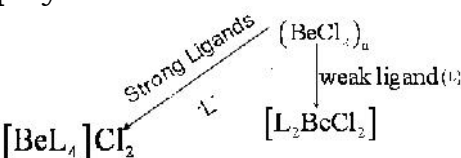| Group – I H₂SO₄(Solids)	Group – II MSO₄(Solids)	
Solubility : Li$_2$SO$_4$ insoluble others are soluble **Thermal decomposition:** $M_2SO_4 \xrightarrow{C}{\Delta} M_2S + CO$ **Thermal stability :** down the group $(\uparrow)$	BeSO$_4$ soluble, and greater ability to form complexes makes the Be salts more toxic MgSO$_4$ soluble; other sulphates insoluble **Thermal decomposition:** $MSO_4 \xrightarrow{\Delta} MO + SO_3 + O_3$ $\searrow \xrightarrow[\text{'C'}]{Heating} MS + CO$ **Stability :** $(\uparrow)$ down the group same as carbonates.	

Group – I (all are ionic) carbides	Group – II(all are ionic) carbides
• Only 'Li' combines directly with 'C' and forms ionic carbide of type Li_2C_2, other elements form ionic carbides when heated with C_2H_2 or passing C_2H_2, gas through alkali metal in liquid NH_3 solution.	• Mg, Ca, Sr & Ba form hydrides by direct combination with 'C' and M or MO with 'C' • 'Be' cant directly combine with carbon to form Be_2C[carbide] It is prepared as by the following methods. $Be + C_2H_2 \longrightarrow Be_2C$ ⎱ *unusually carbride* $BeO + C \xrightarrow[1900-2000^0C]{} Be_2C$ ⎰ *have anti fluorite structure* $Mg + C \longrightarrow MgC_2 \xrightarrow{\Delta} Mg_2C_3(acetylide)$ $\downarrow H_2O$ $Mg(OH)_2 + CH_3 - C \equiv CH$

CHEMICAL REACTIVITY

IA	II A
• Highly reactive due to low ionization potential $\therefore$ stored in kerosene • Reactivity increases down the group due to $(\downarrow)$ in I.E • Li Na K Rb Cs $(\uparrow)$ order of reactivity • Reactivity with water $2M + 2H_2O \rightarrow 2MOH + H_2 + heat$ Li<Na<K<Rb<Cs When metal is reacted with water, the heat evolved converts the metals in to fused state by which surface area increases and reactivity increases **With hydrogen :** Li>Na>K>Rb>Cs$(\downarrow)$ order of reactivity **Reactivity with air :** When fresh ly cut metal exposed to air looses its luster due to primarily formation of its oxide layer $M + O_2 \rightarrow M_2O(oxide) \xrightarrow{air} MOH \xrightarrow{CO_2(air)} M_2CO_3$ When li metal heated in air Li_2O and Li_3N are formed other alkali metals cannot form Nitride	**Chemical reactivity :** • Less reactive than group – I • In group from top to bottom, reactivity $(\uparrow)$ Be Mg Ca Sr Ba$(\uparrow)$increasing order **Reactivity with water:** $Be + cold\ H_2O \rightarrow$ no reaction $Be + steam \rightarrow BeO + H_2 (probably)$ $Mg + steam \rightarrow Mg(OH)_2 + H_2$ or $MgO + H_2$ Ca, Sr, Ba can react with cold water, and liberate $H_2 \uparrow$ $M + H_2O \rightarrow M(OH)_2 + H_2 \uparrow$ • All alkali metals, Ca, Sr, Ba – active metals (can react with cold H_2O • Massive Be (bulk solid) cannot be oxidized even when heated to 600^0C in air. • 'Be' becomes passive(un reactive) by conc. HNO_3 due to the Formation of its own oxide which acts as a protective layer. However it liberates H_2 from dil. HNO_3 and HCl All these elements on heating form oxides and Nitride (MO, M_3N_2) Be_3N_2 - volatile nature due to its covalent character

HALIDES

| IA	II A
Nature of halides: All are ionic except LiI ionic character increases down the group. LiI is covalent due to high polarising power of Li^+ and higher polarisability of I^-	**Nature of halides:** BeF_2 and $BeCl_2$ are covalent $MgBr_2$, MgI_2 are also covalent rest of the halides are ionic. Ionic character increases down the group. $BeCl_2$ solid polymer chain.

Ionic character:

LiCl………… CsCl $(\Uparrow)$ order of ionic character

(lager the size of cation greater the ionic character)

Melting point : For a given metal order of melting point is $F^- > Cl^- > Br^- > I^-$

Ex: NaF > NaCl> NaBr> NaI

(higher the L.E greater the m.p)

Melting point of Chloride and bromides

$NaX > KX > RbX > CsX > LiX(\downarrow)$ order of m.p

X = Cl and Br

Melting points of iodides:

$KI > NaI > RbI > CsI > LiI(\downarrow)$ order of m.p

Solubility: 1) Flurodies: depends on L.E LiF spairing soluble. Others soluble, soubility increases down the group due to decreases L.E.

Bromides solubility depends on H.E as H.E decreases down the group solubility of bromides decreases

Solubility of chlorides is irregular

AgF is soluble AgCl, AgBr, AgI are insoluble.

II A column:

Vapour state at > 1210K monomer,

Cl – Be – Cl ($\mu = 0$)

at < 1210K dimmer.

BeF_2 have little tendency to dimerise. Chain structure of polymer can be cleaved by weak ligands like Et_2O.

polymeric chain.

Solubility: BeF_2 soluble rest of them are sp.soluble

$$\begin{bmatrix} & BaF_2 & SrF_2 & CaF_2 & MgF_2 \\ solubility & 0.12 & 0.011 & 0.0016 & 0.008 \end{bmatrix}$$

Solubility of others halides: MX_2 .

X = Cl, Br, I all are soluble regular trend is not observed.

STABILITY OF HALIDES

Stability of Halides:

1) For given metal F > Cl > Br > I

2) Fluorides stability:

  LiF>NaF > KF > RbF > CsF
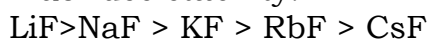
Explained based on L.E effect.

3) Stability of iodides:

LiI < NaI < KI < RbI < CsI ; Explained based on (stabilisation of larger anion by larger cation)

4) Stability of Chlorides and Bromides

KCl > CsCl > RbCl > NaCl > LiCl

CsBr > KBr > RBr > NaBr > LiBr

The above stability order is based on the ΔH_f (Heat of formation) values.

Hydrated halides: LiF and NaF as anhydrous other fluorides may be hydrated M.F.nH_2O. [M = K Rb Cs]; n = 2 or 4. • only 'Li' forms hydrated halides (x = Cl, Br, I) max no. of water molecules is : 3 other metal Halides (MX) have no tendency to form hydrated halides. • LiCl and LiBr have great affinity to water are hygroscopic used in dehumidifying air conditioners. • **Hydrolysis of Halides :** LiX only in hot water undergoes hydrolysis to some extent.	**Hydrated halides:** Hygroscopic and all can form hydrated halides tendency to form hydrated halides decreases down the group. 'Be' max no. of water molecules – 4. (only S & P orbitals) Other can have more than 4 by providing vaccant 'd' orbitals. $BaCl_2 \cdot 2H_2O$. the H_2O is present in voids of $BaCl_2$, but not attached to metal with → (dative bond) **Hydrolysis:** Be, Mg halides under goes hydrolysis and forms acidic solution. tendency to undergo hydrolysis decreases down the group.

Differences between Li and other alkali metals

1) lithium directly combines with nitrogen. Other alkali metals do not combine

$$Li + N_2 \rightarrow Li_3N \xrightarrow{H_2O} LiOH + NH_3 \uparrow$$

2) Only lithium directly combines with carbon to form Li_2C_2 type of carbides

3) $\left.\begin{array}{l} Li_2CO_3 \\ LiF \\ Li_3PO_4 \end{array}\right\}$ insoluble other alkali metal compounds are soluble

4) $LiHCO_3$ exists in solution while the other metal bicarbonates are solids

5) Only Li_2CO_3 on heating decomposes. Other carbonates of group I are thermally stable.

6) LiI is covalent, other alkali metal halides are ionic.

7) $LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$

$MNO_3 \xrightarrow{\Delta} MNO_2 + O_2$

8) LiH is more stable than the other hydrides.

Differences between Be and other Alkaline earth metals

1) BeX_2 is covalent rest of the halides are ionic.

2) Be dissolves in both acid and base liberates H_2.

$Be + 2HCl \rightarrow BeCl_2 + H_2 \uparrow$, $Be + 2NaOH_2 \rightarrow Na_2BeO_2 + H_2 \uparrow$

Other alkaline earth metals liberates H_2 only from dilute acid

$M + dil.HCl \rightarrow MCl_2 + H_2$

3) Berillyium oxide and hydroxide are amphoteric. Rest of the metal oxides and hydroxides are basic

4) All alkaline earth metals directly combines with N_2 and forms corresponding nitride

$M + N_2 \rightarrow M_3N_2 \xrightarrow{H_2O} M(OH)_2 + NH_3 \xrightarrow{HCl} NH_4Cl$ (white fumes). Only Be_3N_2 is volatile

5) "Be" cannot directly combine with C (carbon). But Be_2C can be indirectly prepared by following method

$BeO + C \xrightarrow{\Delta} Be_2C + CO \xrightarrow{H_2O} Be(OH)_2 + CH_4$. Other alkaline earth metals directly combines with carbons forms carbides

$$M + C \rightarrow MC_2 \left(\overset{+2}{M} \overset{C^{-1}}{\underset{C^{-1}}{|||}} \right) \xrightarrow{H_2O} M(OH)_2 + C_2H_2$$

Be is diagonally related to Al due to same electronegativity Be(l.5), Al(1.5) and same charge per unit area.

Solubility of compounds:

Solubility depends on

$$\underbrace{\qquad\qquad\qquad\qquad\qquad}$$

1).   Lattice energy   2) Hydration energy

      If depends on L.E   if depends on H.E

      Solubility $\propto \dfrac{1}{L.E}$ Solubility $\propto$ H.E

If solubility of a compound depends on lattic energy, down the group, L.E decreases, solubility of the salt increases

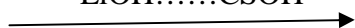If solubility of a salt depends on hydration energy, down the group , H.E decreasws, solubility of the salt decreases

Solubility of alkali metal salts :-

The solubility of fluorides oxides and hydroxides depend on the lattic energy. Down the group, L.E decreases , solubility increases.

      LiF Naf……CSF

      Li_2O........CS_2O

      LiOH……CSOH

      $\xrightarrow{\qquad\qquad\qquad\qquad}$

      $(\uparrow)$ order of solubility

Solubility of bicarbonates and carbonates:

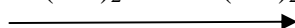In case of bicarbonates and carbonates, down the group the group, change in L.E is more than change in hydration energy

Down the group L.E of HCO_3^-, CO_3^{2-} decreases. Therefore solubility increase

Solubility of 2nd group salts:-

Solubility of O^{-2} and OH^- depends on lattice energy. Down the group, L.E $\downarrow$. Therefore solubility increases.

      BeO MgO CaO SrO BaO

      Be(OH)$_2$……Ba(OH)$_2$

      $\xrightarrow{\qquad\qquad\qquad\qquad}$

      $(\uparrow)$ order of solubility

Fluorides :-

Only BeF_2 is soluble. Rest of the group2 fluorides are sparingly soluble

Solubility: $BeF_2 > BaF_2 > SrF_2 > MgF_2 > CaF_2$

- ## Extraction of sodium:

  1. Can't be extracted by reduction of their oxides and other compounds as they are strong reducing agents.

  2. Displacement method can't be applied as they are most electro positive metals, No other metal can displace them from aq: solution of their salts, as H_2 liberated at cathode.

  3. Can't be extracted by electrolysis of aq. Solu. of their salt.

     m extracted by electrolysis of fused salt (chloride)

(I)   **Down's process:** Electrolyte – fused NaCl cathode – Iron; anode: graphite

- Cathode and anode are separated by steel gauze, only molten NaCl can pass through

  but not sodium.

- 60% $CaCl_2$ added to lower the m.p of NaCl (40%) (1081 K to 850K)

  NaCl $\grave{E}$ Na$^<$ < Cl$^>$

Cathode: $2Na^+ + 2e^- \rightarrow 2Na$ [both Na, Ca are liberated at cathode rise through

cooling pipe, 'Ca' solidifies and falls back to mother electrolyte]

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

- **Reasons for lowering temperature:**

  1) Lowering of temperature reduces the consumption of electricity.

  2) molten Na at high temperature vapourises

  3) Na and Cl_2 exert corrosive action on vessel used for electrolysis at high temperature.

  4) At higher temperature molten NaCl forms metallic fog which short circuit the electrodes.

(II) **Castner Process:**   Electrolyte – fused NaOH (330^0C)
                                         Cathode – Iron
                                         Anode – Ni

Reactions during electrolysis: $NaOH \rightleftharpoons Na^+ + OH^-$

Cathode : $Na^+ + e^- \rightarrow Na$

Anode : $4OH^- \rightarrow 2H_2O + O_2 + 4\bar{e}$

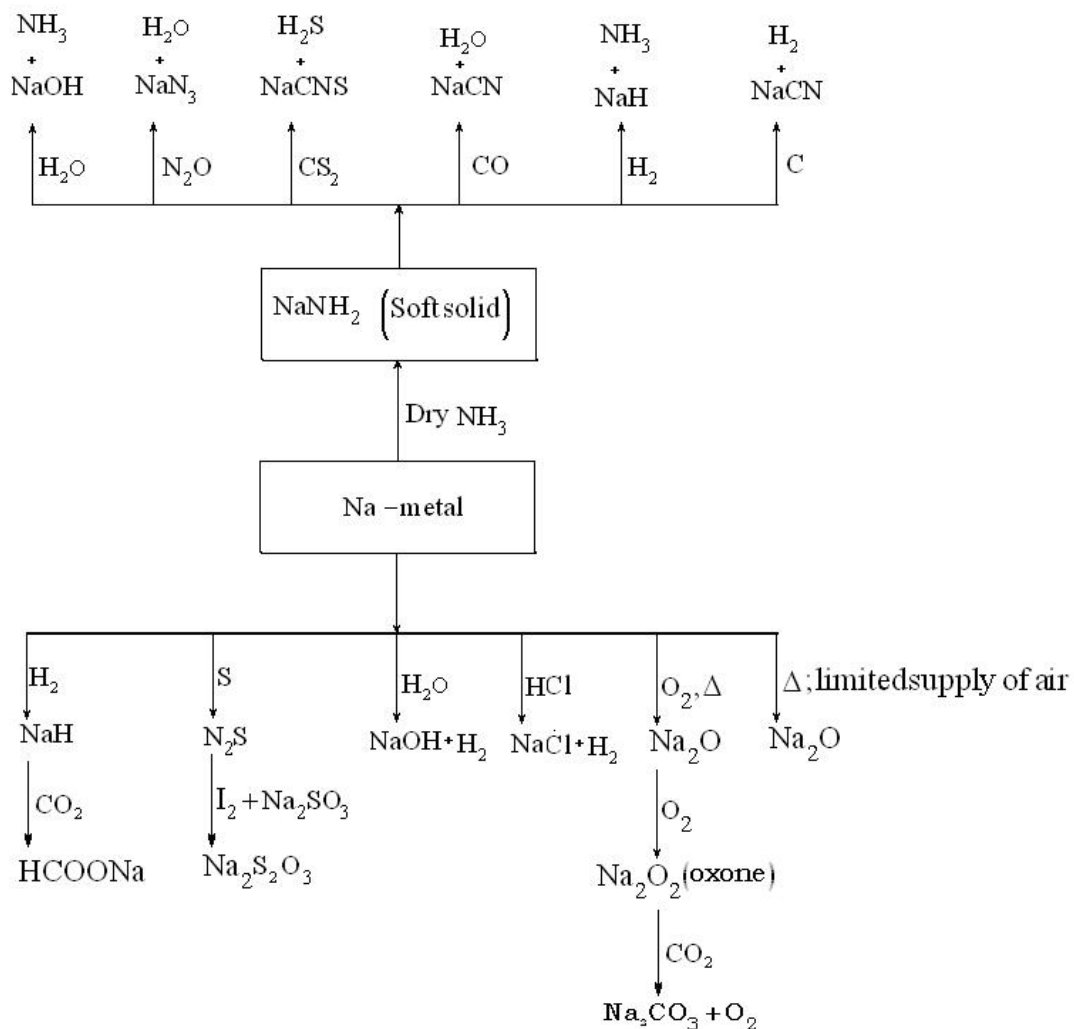Water formed at anode partially gets evaporated and partially broken and H_2 formed at cathode.

- **Properties of Na – metal :** M.P low 97.8^0C

  Exposed to moist air loses it's lusture due to formation of 1,2&3

$$Na + O_2 \rightarrow \underset{1:}{Na_2O} \xrightarrow{H_2O} \underset{2:}{NaOH} \xrightarrow{CO_2} \underset{3:}{Na_2CO_3}$$
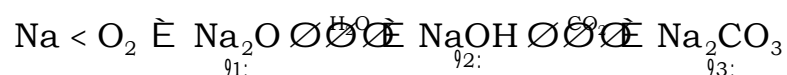
- Stable isotope Na^{23} ; Na^{24} is radio active (lowest t ½ 0.02 sec).

The reactions of NaNH₂ (Soft solid):

$$H_2O \rightarrow NH_3 + NaOH$$
$$N_2O \rightarrow H_2O + NaN_3$$
$$CS_2 \rightarrow H_2S + NaCNS$$
$$CO \rightarrow H_2O + NaCN$$
$$H_2 \rightarrow NH_3 + NaH$$
$$C \rightarrow H_2 + NaCN$$

$$NaNH_2 \ (Soft\,solid) \xleftarrow{Dry\ NH_3} Na-metal$$

From Na – metal:

$$H_2 \rightarrow NaH \xrightarrow{CO_2} HCOONa$$
$$S \rightarrow N_2S \xrightarrow{I_2 + Na_2SO_3} Na_2S_2O_3$$
$$H_2O \rightarrow NaOH + H_2$$
$$HCl \rightarrow NaCl + H_2$$
$$O_2, \Delta \rightarrow Na_2O \xrightarrow{O_2} Na_2O_2 \ (oxone) \xrightarrow{CO_2} Na_2CO_3 + O_2$$
$$\Delta;\ limited\ supply\ of\ air \rightarrow Na_2O$$

- **Extraction of 'K':**

  $$[density\ of\ 'Na' \approx 0.968\,g/cc;\quad density\ of\ 'K' \approx 0.868\,g/cc]$$

  'K' cant be extracted by similar method

  Reasons : 1) 'K' soluble in molten KCl

             2) Does not float on the surface of molten KCl

             3) evaporates at temperature of electrolysis

  Extracted from molten KCl by reduction with 'Na' metal at 1120 – 1150K

  $$\underset{(molten)}{K} + \underset{(s)}{Na} \rightleftharpoons \underset{(l)}{Na} + \underset{(g)}{K}$$
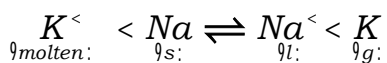
  By distillation 'K' can be eliminated and eq. shifted to RT side

  Purified by fractional distillation (99.5 purity)

- **Reduction of Oxides by 'Na & K':**
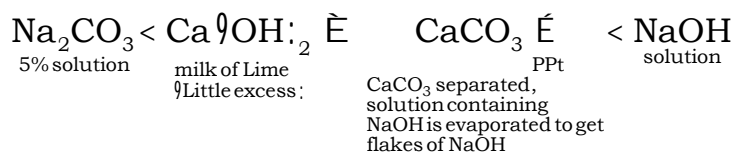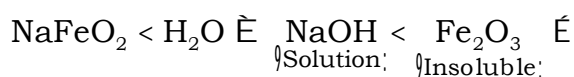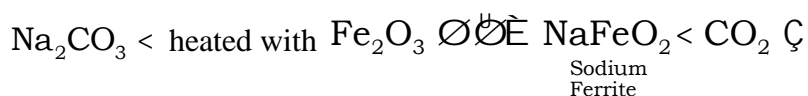

$$M\ (Na\ or\ K)$$

$$SiO_2 \rightarrow Si + H_2O$$
$$CO_2 \rightarrow C + M_2CO_3$$
$$Al_2O_3 \rightarrow Al + M_2O$$
$$BeCl_2 \rightarrow Be + MCl$$
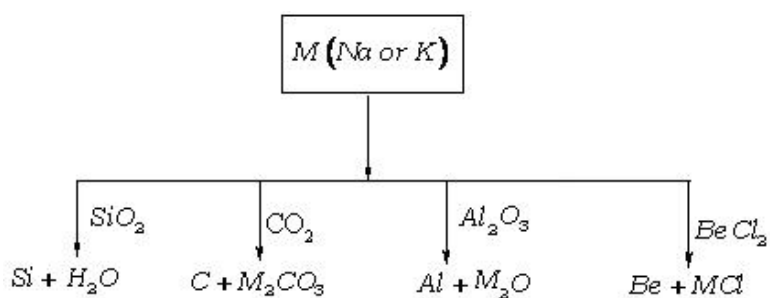
NaOH – Caustic Soda

Using Na_2CO_3 as starting material.

(I) **(Gossage process) Causticisation:**

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + NaOH$$

(5% solution) (milk of Lime Little excess) (CaCO₃ separated, solution containing NaOH is evaporated to get flakes of NaOH) (PPt) (solution)

(II) **Lowig's process:**

$$Na_2CO_3 + \text{heated with } Fe_2O_3 \xrightarrow{\Delta} NaFeO_2 + CO_2 \uparrow$$

Sodium Ferrite

$$NaFeO_2 + H_2O \rightarrow NaOH + Fe_2O_3 \downarrow$$

(Solution) (Insoluble)

Methods involving aq.solution of NaCl:

(I) Nelson Cell:

Anode : graphite

Cathode : perforated steel

Electrolyte : aq. solu. of NaCl

Reactions during electrolysis:

$$NaCl \rightarrow Na^+ + Cl^-$$

$$H_2O \rightarrow H^+ + OH^-$$

Cathode : $2H^+ + 2e \rightarrow H_2$

Anode : $2Cl^- \rightarrow Cl_2 + 2\bar{e}$
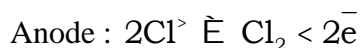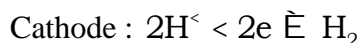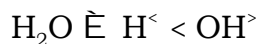
$Na^+ + OH^- \rightarrow NaOH$ solution (containing 10-15 % of NaOH)

• Anode is covered by asbestos diaphragm to prevent mixing of NaOH with Cl_2

Otherwise $NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$

(II) Castner – kellner Cell:

Outer Compartment :

Anode : graphite

Cathode : Hg

Electrolyte : aq.NaCl.

Cathode : $Na^+ + e \rightarrow Na$

$Na + Hg \rightarrow NaHg (moves\ in\ to\ middle\ Compartment)$

Anode : $2Cl^- \rightarrow Cl_2 + 2e$
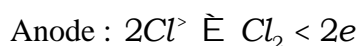
Changes in middle compartment :

Cathode : iron

Anode : Hg

Electrolyte : dil.NaOH

Anode : $Na_2Hg_x < H_2O$ È $NaOH < Hg < H_2$ Ç $cathode$:

- **Properties of NaOH:**

Exposed to moist air : $NaOH < H_2O < CO_2$ È Na_2CO_3

1. Reaction with Non-metals:

$$NaOH$$

P_4	S	B	Si
$NaH_2PO_2 + PH_3$	$Na_2S_2O_3$ $+Na_2S + H_2O$	Na_3BO_3 $+H_2$	$Na_2SiO_3 + H_2$
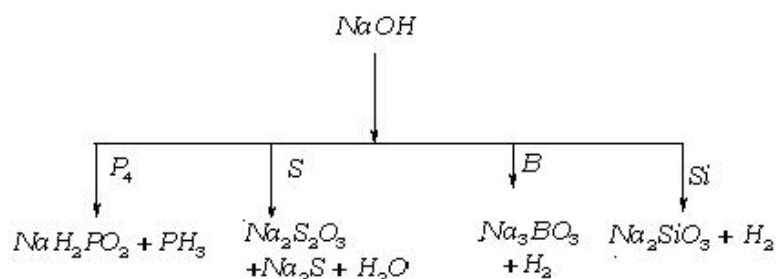
2. Action of metals : metals like Al, Zn, Sn and Pb dissolves and liberated H_2:

$$NaOH$$

Pb	Zn	Al	Sn
$Na_2[PbO_3]$ $+H_2$	$Na_2[ZnO_2]$ $+H_2$	Na_3AlO_3 $Na[Al(OH)_4]+H_2$	$Na_2SnO_2 +H_2$
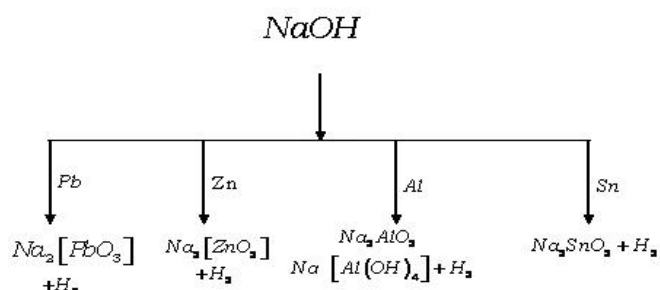
3. Reaction with Salts : Mn, Fe, Cu, Ni salts from insoluble Hydroxides

$$NaOH$$

$MnCl_2$	Fe^{+2}	Cu^{+2}	Ni^{+2}	Fe^{+3}
$Mn(OH)_2$	$Fe(OH)_2$	$Cu(OH)_2$	$Ni(OH)_2$	$Fe(OH)_3$
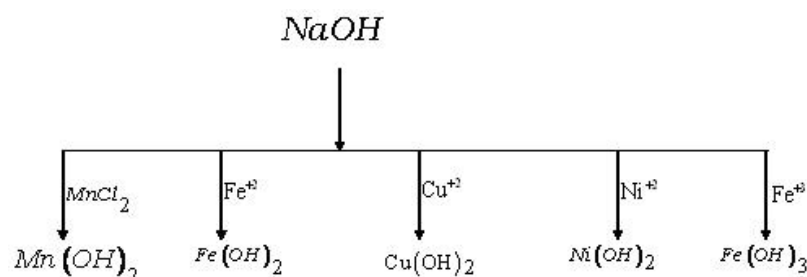
$Al^{<3}$, $Sn^{<2}$, $Zn^{<2}$ and $Cr^{<3}$ (salts) forms insoluble hydroxide which dissolves in excess of NaOH

$$NaOH$$

Al^{+3}	Zn^{+2}	Sn^{+2}	Cr^{+3}
$Al(OH)_3$	$Zn(OH)_2$	$Sn(OH)_2$	$Cr(OH)_3$
excess NaOH	excess NaOH	excess	excess NaOH
$NaAlO_2$ solution	Na_2ZnO_2 (or) $Na_2[Zn(OH)_4]$ solution	Na_2SnO_2 solution	$[Cr(OH)_4]^-$ solution
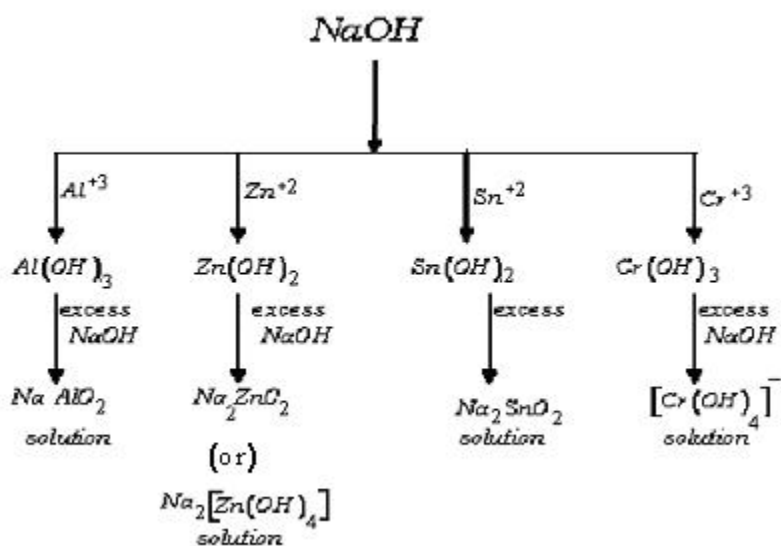
- **Na_2CO_3 (Sodium carbonate) :**

- $Na_2CO_3 \cdot 10H_2O$ washing soda

- 50% of its production is used in glass industry

- Sodium phosphate and poly phosphates (water softners) are used in cleaning powder.

  $Na_2CO_3 \cdot H_2O$ heavy ash used in glass industry

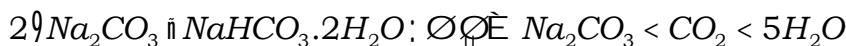 Na_2CO_3 anhydrous (from solvay process)

  ↓ Recrystallization from hot water

  $Na_2CO_3 \cdot H_2O$ (heavy ash)

  Used in pet and textile industry

  In Prehistoric times Na_2CO_3 prepared from <u>Trona</u>

  Which is obtained from dried lake beds of Egypt

  $2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \xrightarrow{\Delta} Na_2CO_3 + CO_2 + 5H_2O$

       Trona

  (Sodium sesqui carbonate)

- **Manufacture of Na₂CO₃:**
  - (I)   Leblanc process
  - (II)   Solvay Ammonia process
  - (III)   Electrolytic process

(I)   **Leblanc process :**

Step –I: Raw material : $NaCl, H_2SO_4, coke, CaCO_3$

$$\left[NaCl + H_2SO_4 \xrightarrow[\text{cal.quantity}]{\text{heating with}} NaHSO_4 + HCl \right]$$

$$NaHSO_4 + NaCl \xrightarrow[\Delta]{\text{High temperature}} \underset{\text{(Salt cake)}}{Na_2SO_4} + HCl$$
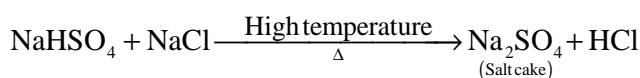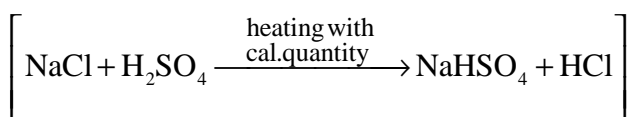
Step –II: Salt cake to Black ash

Na₂SO₄ mixed with CaCO₃ & Coke and strongly heated $\left(Na_2SO_4 + C \rightarrow Na_2S + CO_2 \right)$

$Na_2S + CaCO_3 \rightarrow \underset{\text{Black ash}}{\underline{Na_2CO_3 + CaS}}$
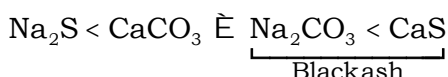
Solution : $\underset{\text{(solution)}}{Na_2CO_3} \rightarrow \underset{\text{(Solid)}}{Na_2CO_3}$ soluble Na_2CO_3 extracted with water : CaS (ppt) is

     removed

(II)   **Modern method :** (Solvay ammonia process)

step – I: Saturation of Brine with NH₃ (carried out in ammonia absorber)

[purification of brine if it contains $Mg^{+2}, Ca^{+2}, Fe^{+3}$]

Brine saturated with NH₃, allowed to stand for some time for precipitate to settle down

Reactions : $NH_3 + H_2O \rightarrow NH_4OH$

$Mg^{+2} + NH_4OH \rightarrow \underset{ppt}{Mg(OH)_2} \downarrow$

$Ca^{+2} + NH_4OH \rightarrow \underset{ppt}{Ca(OH)_2} \downarrow$

If little CO_2 is used Mg^{+2} and Ca^{+2} are precipitated as their carbonates:

$Ca^{+2} + NH_4OH + CO_2 \rightarrow \underset{ppt}{CaCO_3} \downarrow + NH_4Cl$

$Mg^{+2} + NH_4OH + CO_2 \rightarrow \underset{ppt}{MgCO_3} \downarrow + NH_4Cl$

- Step – II : purified ammonical brine is saturated with CO_2 in carbonating tower

$NH_4OH + \underset{(excess)}{CO_2} + NaCl \rightarrow NaHCO_3 + NH_4Cl.$

NaHCO$_3$ (sparingly soluble but completely insoluble in brine due to common ion effect)

- Step – III : NaHCO$_3$ (Solid) separated from solution ($\underset{Filtrate}{NH_4Cl, NH_4HCO_3}$] by filtration

- Step – IV: $NaHCO_3 \xrightarrow[250^0C]{calcinated} Na_2CO_2 + H_2O + CO_2$

- Step – V: recovery of NH_3:

$\underset{(NH_4Cl, NH_4HCO_3)}{Solution\ filtrate} \xrightarrow[2)pass\ steam]{1)Ca(OH)_2} NH_3 + CaCl_2$

Reactions :

$NH_4HCO_3 \xrightarrow{\Delta} NH_3 + H_2O$

$NH_4Cl + Ca(OH)_2 \rightarrow NH_3 + \underset{\downarrow}{CaCl_2} + H_2O$
$(waste\ product\ left)$
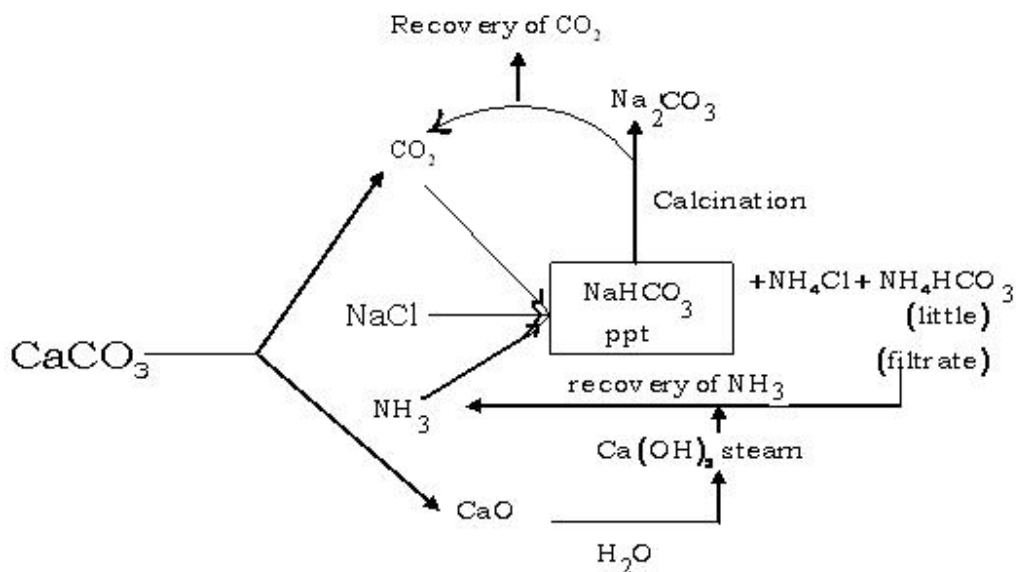
(III) **Electrolytic process :**

- NaCl solution is converted to NaOH by Nelson cell

- NaOH + CO_2 + steam $\dot{E}$ Na_2CO_3 solution

$$\downarrow \text{evapouration}$$

$$Na_2CO_3 \text{(solid)}$$
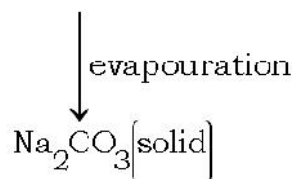
- properties of $Na_2CO_3 \cdot 10\,H_2O$

$$Na_2CO_3 \cdot 10H_2O \xrightarrow[\text{to air}]{\text{exposed}} \underset{\substack{\text{Heavy ash} \\ \text{powder}}}{Na_2CO_3 \cdot H_2O} \xrightarrow{} \underset{\substack{\text{soda ash} \\ \text{or} \\ \text{light ash}}}{Na_2CO_3}$$
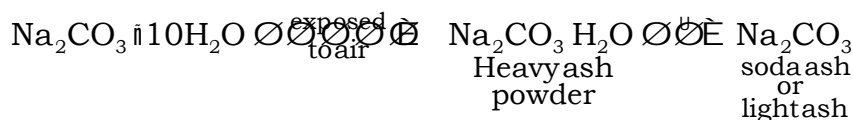
- **Action of acidic oxides and acids:**

$$Na_2CO_3$$

SiO_2	SO_2	CO_2	HCl
$Na_2SiO_3 + CO_2$	$NaHSO_3$	$NaHCO_3$	$NaHCO_3$

$NaHSO_3 \xrightarrow{Na_2CO_3} Na_2SO_3 \xrightarrow{S} Na_2S_2O_3$

$NaHCO_3 \xrightarrow{HCl} NaCl + CO_2 + H_2O$
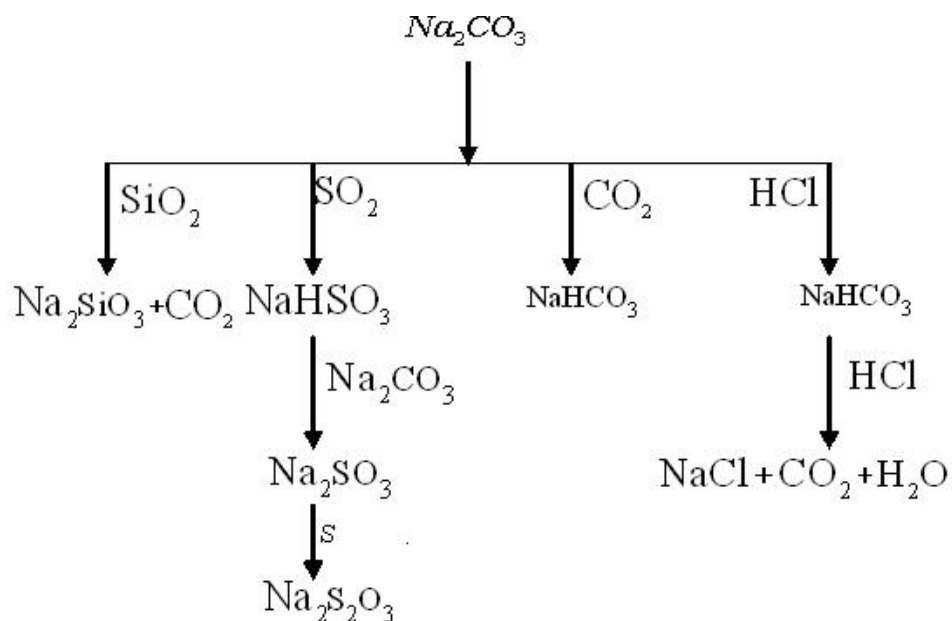
- **Reaction with Non-alkali metal salts to form normal carbonates and basic carbonates:**

$$Na_2CO_3$$

$CuSO_4$	$CaCl_2$	$BaCl_2$	$MgCl_2$	$ZnSO_4$
$CuCO_3$ $Cu(OH)_2$ (basic copper carbonate) green colour on copper vessel and statues	$CaCO_3 + NaCl$	$BaCO_3 + NaCl$	$MgCO_3 + Mg(OH)_2$ (basic magnesium carbonate)	$ZnCO_3 \cdot 3Zn(OH)_2$ Basic zinc carbonte

$Pb(CH_3COO)_2$

$2PbCO_3 \cdot Pb(OH)_2$ basic lead carbonate
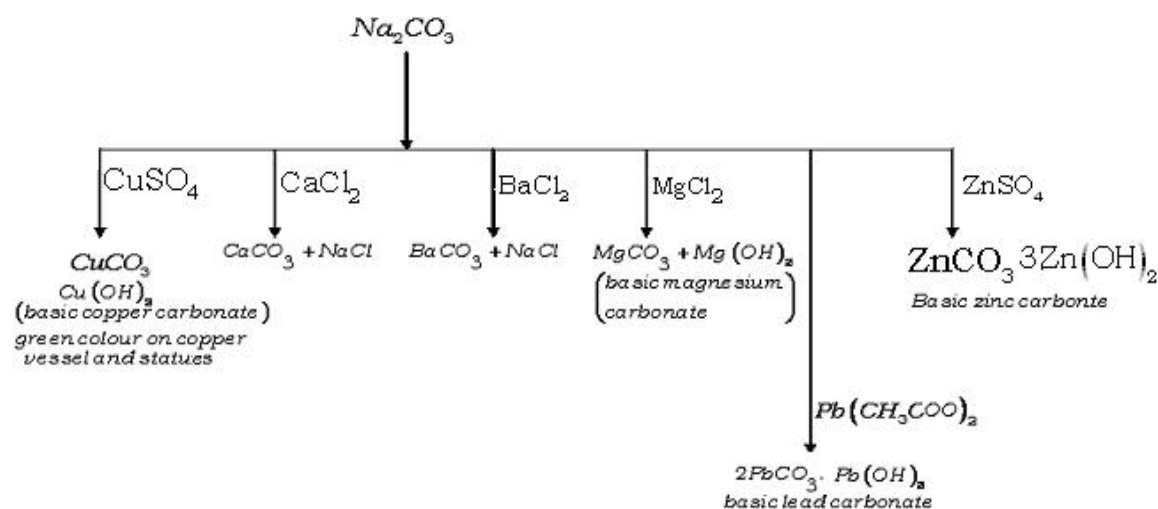
- Fe, Al, Sn carbonates formed undergoes hydrolysis

  eg:

$$Fe(SO_4)_3 + Na_2CO_3 \longrightarrow Fe(CO_3)_3 + Na_2SO_4$$
$$\downarrow 3H_2O$$
$$Fe(OH)_3$$
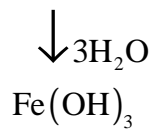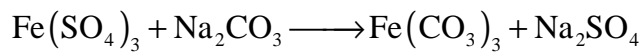
- **<u>Baking soda ($NaHCO_3$):</u>**

  Baking powder (improved) composition

  1) $30\% NaHCO_3$

  2) $20\% NaAlSiO_4$

  3) $10\% Ca(H_2PO_4)_2$

  4) $40\% starch$

- role of $Ca(H_2PO_4)_2$ is to liberate CO_2 from $NaHCO_3$ [

  $Ca(H_2PO_4)_2 < H_2O \; È \; H_3PO_4 < Ca(OH)_2$]
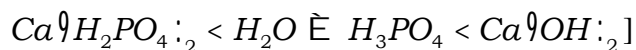
  H_3PO_4 liberates CO_2 from $NaHCO_3$

- role of $NaAlSiO_4$ is to slow down the above reaction so that CO_2 is given out slowly

- Starch acts as filler.

Compounds of group – 2 elements:

1) Cement

   Cement is a binding material

Compounds is a binding material

Composition of element:

CaO : 62% Al_2O_3 : 7.5%

SiO_2 : 22% Na_2O. K_2O: 1.5%

Fe_2O_2 : 2% SO_3 : 1%

Cement containing excess of SiO_2 results in late setting   (even other mixing with water it takes long time to harden)

element containing excess of Al_2O_3 results in quick setting (hardens of cement is cement is due to Fe_2O_3 is called white cement

Important compounds present in cement:

1) C_3S: tricalciumsillcate (3 $CaOSiO_2$) (Ca_3SiO_5)

2) C_3S: dicalciumsillicate (2 $CaO \, SiO_2$ or $Ca_2 \, SiO_4$)

3) C_3A: tricalciumaluminate (3 $CaO \, Al_2O_3$ or $Ca_3 \, Al_2 \, O_6$)

4) $CuAl$: tetral alciumaluminoferrate (4 $Cao \, Al_2O_3 \, Fe_2 \, O_3$)

Good quality of cement contains:

1) C_3S: 51% $\rightarrow$ responsible for early strength of the cement

2) C_2S: 26% $\rightarrow$ responsible later strength, (15-20yrs) of the cement.

3) C_3A: 11%

Setting of cement:

Reaction involved:

$C_3S + 6H_2O \rightarrow C_3S.\ 6H_2O$ colloidal gel $\left.\begin{array}{l}\\\\\\\end{array}\right\}$ exothermic reactions.

$C_2S + x\ H_2O \rightarrow C_2S\ x\ H_2O$

$Cu\ AF + 6H_2O \rightarrow C_3A.6H_2O + Fe_2O_3 + CaO$
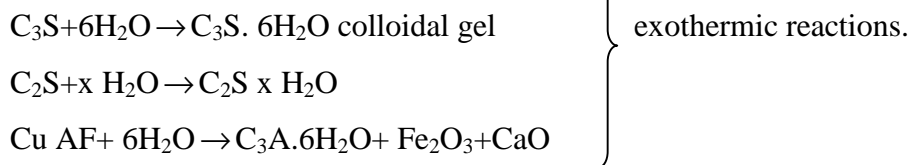
Manufacture :

Raw ,materials:

1) high grade limestone (80% $CaCO_3$)

2) SiO_3

3) Fe_2O_3

4) Al_2O_3 (bauxite ore)

All the raw meterials are grinded to fine powder and burned at $1200 - 1400^0C$ in rotator kiln.

The final product formed is called "clinker"

Clinker is quick setting. To increase the setting time or retard the quick

Octting, calculated quantity of gypsum is added to clinker.

Good quality of cement contains $\dfrac{SiO_2}{Al_2O_3} = 2.5$ to 4

$$\dfrac{CaO}{SiO_2 + Fe_2O_3 + Al_2O_3} \simeq 2$$

CaO (Quick lime)

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$
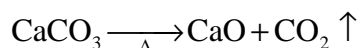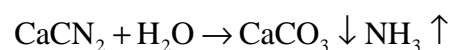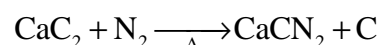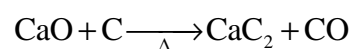
When dissolved in water, forms $Ca(OH)_2$ which is highly exothermic $CaO + H_2O \rightarrow Ca(OH)_2$

Clear solution of $Ca(OH)_2$ is called lime water.

Reaction with acid and acidic oxide:
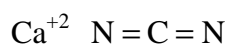
$CaO + 2HCl_2 \rightarrow CaCl_2 + H_2O$

$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$

$CaO + CO_2 \rightarrow CaCO_3$

$CaO + SO_2 \rightarrow CaSO_3$

$CaO + P_4O_{10} \rightarrow Ca_3(PO_4)_2$

Reaction with carbon:

$CaO + C \xrightarrow{\Delta} CaC_2 + CO$

$CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$

$CaCN_2 + H_2O \rightarrow CaCO_3 \downarrow NH_3 \uparrow$
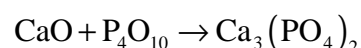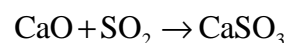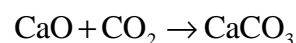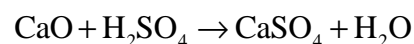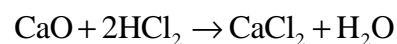
Structure of CaCN$_2$

$$Ca^{+2} \quad N=C=N$$
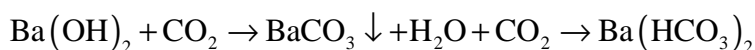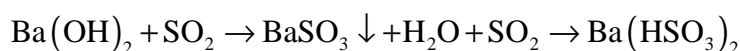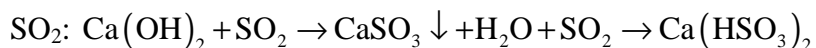
Carbonates on reaction with dil. acids liberates CO$_2$ Color less ⌐

Sulphites on reaction with dil. Acids liberates SO$_2$ pungent smell

Sulphides on reaction with dil. Acids liberates H$_2$S   rotten egg smell

   SO$_2$ - turns K$_2$Cr$_2$O$_7$

   CO$_2$ – turns lime water milky or barita water $\left(Ba(OH)_2 \right)$ milky

The milkyness disappears by passing excess of CO$_2$/SO$_2$

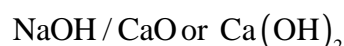SO$_2$: $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \downarrow + H_2O + SO_2 \rightarrow Ca(HSO_3)_2$

       $Ba(OH)_2 + SO_2 \rightarrow BaSO_3 \downarrow + H_2O + SO_2 \rightarrow Ba(HSO_3)_2$

   CO$_2$: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

   $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow + H_2O + CO_2 \rightarrow Ba(HCO_3)_2$

   CO$_2$ and SO$_2$ can be disingushed using acidified $K_2Cr_2O_7$ or $KMnO_4 / H^+$

   Only SO$_2$ turns K_2MnO_4 / H^+ colorless and $K_2Cr_2O_7 / H^+$ green

   Reaction of $Ca(OH)_2$ **with Cl$_2$:**

1) $Ca(OH)_2 + Cl_2 \rightarrow CaCl_2 + H_2O$

   2) $Ca(OH)_2 + Cl_2 \xrightarrow{\text{cold}} CaCl_2 + H_2O + Ca(OCl)_2$

   3) $Ca(OH)_2 + Cl_2 \xrightarrow{\text{hot}} CaCl_2 + H_2O + Ca(ClO_3)_2$
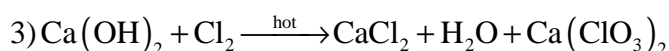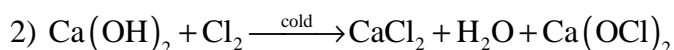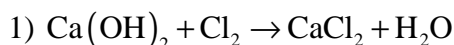
   Composition of soda lime :

$$NaOH / CaO \text{ or } Ca(OH)_2$$

   Used in de carboxylation

   $MgCl_2 6H_2O$

   Preparation:

   1) $MgO + 2HCl \rightarrow MgOHCl + HCl + H_2O$

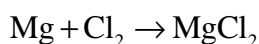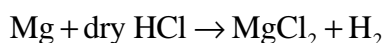   2) $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + H_2O$

   3) $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + H_2O + O_2$
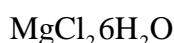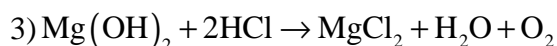
   None of the methods are used for preparation of anhydrous MgCl$_2$ Hydrated MgCl$_2$ cannot be converted into anhydrous MgCl$_2$ by heating.

   $MgCl_2 6H_2O \xrightarrow{\Delta} MgOHCl + HCl + H_2O$

   But can be converted into anhydrous by heating in presence of diyttel.

   $Mg + dry\ HCl \rightarrow MgCl_2 + H_2$

   $Mg + Cl_2 \rightarrow MgCl_2$

By above methods, anhydrous $MgCl_2$ is prepared

$CaSO_4\ 2H_2O$ (gypsum)

1. sparingly soluble in water

2. completely soluble in presence of $(NH_4)_2\ SO_4$ due to formation of double salt or soluble complex

$$CaSO_4 + (NH_4)_2 \rightarrow SO_4 CaSO_4 + (NH_4)_2 \left[Ca(SO_4) \right]$$

Effect of heat :

$$CaSO_4\ 2H_2O \xrightarrow{120^\circ C} + CaSO_4\ \frac{1}{2}H_2O \xrightarrow[200^0 C]{} CaSO_4$$

Reaction involved in setting of POP:

$$CaSO_4\ \frac{1}{2}H_2O + H_2O \xrightarrow{setting} CaSO_4.2H_2O \xrightarrow{harding} CaSO_4\ 2H_2O$$