"INORGANIC CHEMISTRY"

"Points"

s block:

- ns^{1-2}
  - alkaline earth metals – Be, Mg, Ca, Sr, Ba, Ra (rarest) → metal oxides found in Earth's crust + oxides & hydroxides (alkaline)
  - alkali metals – Li, Na, K, Rb, Cs, Fr (abundant: Na, K) — Fr^{223} half life – 21 min
    - ↓ $+H_2O$
    - hydroxides (strongly alkaline in nature)

- Li → Mg, Be → Al (diagonal relationship)
  - ↓ due to ionic size & charge / radius ratio is similar

- Biological fluids – $Na^+, K^+, Mg^{2+}, Ca^{2+}$

- ns^1 : (+1)
  - → most electro + metals
  - → forms M^+ ions (cations)
  - → never found in free state
  - → high reactivity towards air & water ∴ kept in kerosene oil.
  - → Li – most ⊖ E° value – reducing agent – reactⁿ with H_2O is less vigorous
  - → Na – least ⊖ E° value (least powerful reducing agent) ~ due to small size & high H.E
  - → Lithium halides – covalent – due to high polarising ability of Li^+ (LiI – most covalent)
  - → oxides & hydroxides easily hydrolysed.
  - → oxides & peroxides are colorless when pure
  - → superoxides are yellow / orange.
  - → alkali metal hydroxides – strongest base.
  - → all halides are soluble
  - → LiF is less soluble due to high lattice enthalpy
  - → CsI " " " " small H.E.
  - → LiCl is soluble in pyridine also.
  - → salts of all oxo acids – soluble in H_2O + thermally stable
  - → Li_2CO_3 is not stable to heat & $LiHCO_3$ do not exist as solid

- Sodium carbonate (washing soda) – $(Na_2CO_3 \cdot 10H_2O)$
  - ↳ Solvay Process
  - ↳ less solubility of sodium hydrogencarbonate

- NaCl → by crystallisation of brine solⁿ
  - → $MgCl_2$ & $CaCl_2$ – deliquescent
    - ↳ $(MgCl_2 \cdot 8H_2O)$
  - → solubility = 36g in 100g

- Sodium hydroxide (NaOH) → Castner-Kellner cell (electrolysis of NaCl)
  - → Brine soln is electrolysed using Hg cathode & carbon anode
  - → Na at cathode + Hg → Na-Hg amalgam
  - → Cl_2 ↑ (g) at anode

- K^+ → most abundant cation within cell fluid.

[n s2]

- Ca (brick red) | Sr (crimson) | Ba (Apple green) - Color - flame photometry) | Be & Mg do not impart color.
- Oxides & hydroxides of Be - amphoteric
- beryllate ions - $[Be(OH)_4]^{2-}$
- aluminate ions - $[Al(OH)_4]^{2-}$
- Reducing agent. (large ⊖ E° values) • Be - less ⊖ E° value but large HE ∴ reducing nature
- $Mg(OH)_2 + H_2O$ → Milk of magnesia (antacid)
- BeO - amphoteric, covalent & all other MO have rock salt structures. + basic.
- Be halides - covalent + soluble in organic solvents
- $BeCl_2$ → 3c-4e⁻ ; vapour phase if Cl - bridged dimer $\xrightarrow{\Delta}$ monomer
- Be & Mg $\xrightarrow{\Delta}$ hydrolysis
- Carbonates insoluble in H_2O & $BeCO_3$ - unstable & kept in CO_2.
- CaO absorbs CO_2 & H_2O → basic + cheapest
- Addition of H_2O to break lump of lime - slaking of lime
- Quick lime slaked with soda - solid sodalime
- Aq. soln of $Ca(OH)_2$ - slaked lime → lime water
- suspension of slaked lime in H_2O → milk of lime.
- Calcium sulphate ($CaSO_4 \cdot \frac{1}{2}H_2O$) - hemihydrate - Plaster of Paris
- Gypsum - $CaSO_4 \cdot 2H_2O$.
- $CaSO_4$ - dead burnt plaster

13 14 15 16 17 18

"INORGANIC CHEMISTRY"

"Trends:"

s block: [ns^1]

- alkali metals have largest size.
  At radii & ionic radii: Li < Na < K < Rb < Cs < Fr.
- I.E: size $\propto \frac{1}{I.E}$: Li > Na > K > Rb > Cs > Fr
- H.E: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
  max degree of hydration. ($LiCl \cdot 2H_2O$)
- Density: Li < K < Na < Rb < Cs < Fr (silvery white, soft & light metals)
- MP & BP: less due to weak metallic bonding (1 valence e^-)
- color: Li Na K Rb Cs.
  (Crimson red) (yellow) (violet) (Red violet) (Blue)
- Reactivity: Li < Na < K < Rb < Cs < Fr
- stability of peroxides & superoxides: Li ⟶ Cs ↑.
- $\Delta_f H^\circ$ becomes less negative from F to I.
- MP & BP: F > Cl > Br > I (halides) · solubility F < Cl < Br < I.
- stability of carbonates & bicarbonates: Li ⟶ Cs ↑

[ns^2]

- At radii & ionic radii: ($ns^1 > ns^2$) Be < Mg < Ca < Sr < Ba < Ra.
- I.E: $\propto \frac{1}{\text{at radii}}$: Be > Mg > Ca > Sr > Ba > Ra.
  ($ns^2 > ns^1$)
  { $I.E_1$: $ns^1 < ns^2$; $I.E_2$: $ns^1 > ns^2$ } · thermal stability of halides ↓ hydrates ↓
- H.E: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{2+}$
- solubility, thermal stability, basic nature: $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$.
- Tendency to form halide hydrates: $MgCl_2 \cdot 8H_2O > CaCl_2 \cdot 6H_2O > SrCl_2 \cdot 6H_2O > BaCl_2 \cdot 2H_2O$
- Thermal stability of carbonates: (↑ with at size) : $MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$.
- solubility of sulphates: $CaSO_4 > SrSO_4 > BaSO_4$.
- Tendency to form hydrates: Mg > Ca > Sr > Ba

$BI_3 > BBr_3 > BCl_3 > BF_3$

back bonding ↑ lewis acidic ↓

- NaCl (sodium chloride) – impurities Na_2SO_4, $MgCl_2$, $CaCl_2$, $CaSO_4$
- NaOH (Castner Kellner process)
  - Cathode: $Na^+ + e^- \xrightarrow{Hg} Na$ - amalgam $\xrightarrow{H_2O} NaOH + H_2$
  - Anode: $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$
- $Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$ (Baking soda – sodium hydrogencarbonate)

ns^2

→ <u>towards air & water</u>: Be & Mg form oxide film ∴ kinetically inert but:
- powdered Be^{2+} burns → $Be + O_2$ (air) → $BeO + Be_3N_2$

$Mg + air \rightarrow MgO + Mg_3N_2$

→ <u>towards halogens</u>: form halides $M + X_2 \rightarrow MX_2$

$(NH_4)_2BeF_4 \xrightarrow{\Delta} BeF_2$ (heat)

$BeO + Cl_2 + C \longrightarrow BeCl_2 + CO$ (heat)

→ <u>towards hydrogen</u>: hydrides (MH_2)

$2BeCl_2 + LiAlH_4 \xrightarrow[\text{reduction}]{} 2BeH_2 + LiCl + AlCl_3$

→ <u>towards acids</u>:

$M + 2HCl \rightarrow MCl_2 + H_2\uparrow$

→ <u>liquid NH_3</u>:

$M + (x+y)NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^-$

ammoniates $[M(NH_3)_6]^{2+}$ can be recovered.

- $MO + H_2O \rightarrow M(OH)_2$
- $Be(OH)_2 + 2OH^- \rightarrow [Be(OH)_4]^{2-}$ → amphoteric behaviour

  $Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$
- $2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$ (like $LiNO_3$)
- $CaCO_3 \overset{\Delta}{\rightleftharpoons} CaO + CO_2$ (Calcium oxide, Quick lime)

  $CaO \xrightarrow{H_2O} Ca(OH)_2$; $\xrightarrow{CO_2} CaCO_3$
- $CaO + SiO_2 \rightarrow CaSiO_3$ · $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$
- $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
- $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
- $2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + H_2O$ ← bleaching powder
- $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
- $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$
- $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
-

" INORGANIC CHEMISTRY"

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"Reactions"

s block: $[ns^1]$

- highly reactive due to large size & low I.E.
- → towards air: tarnish in dry air → oxides $+ H_2O$ (moisture) → hydroxides

  Li → monoxide (Li_2O) · $4Li + O_2 \rightarrow 2Li_2O$

  Na → peroxide (Na_2O_2) · $2Na + O_2 \rightarrow Na_2O_2$

  K, Rb, Cs → superoxide (KO_2, RbO_2, CsO_2) · $M + O_2 \rightarrow MO_2$

- $Li + N_2 \rightarrow Li_3N$
- alkali metal = +1

→ towards water: $M + H_2O \rightarrow MOH + H_2$

Li - least vigorously

other metals react with water vigorously & with proton donors like gaseous NH_3, alcohols, alkynes etc

→ towards H_2: $2M + H_2 \rightarrow 2M^+H^-$ ← ionic hydrides with high M.P.

H^{-1} with group I & II metals

→ towards halogen:

reacts vigorously to form ionic halides M^+X^-

→ liquid ammonia:

$M + (x+y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$

blue color due to ammoniated e⁻ + paramagnetic → on standing: $H_2\uparrow$ + amide

conc. sol^n → blue ⇝ bronze + diamagnetic.

→ oxide → hydroxides:

$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$

$M_2O_2 + H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$

$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$

- $Li_2CO_3 \rightleftharpoons Li_2O + CO_2$ (not stable)
- $Na_2CO_3 \cdot 10H_2O$ (Sodium carbonate) - (Solvay Process)

$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$

$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

· NH_3 is recovered when the sol^n containing NH_4Cl is treated with $Ca(OH)_2$.

- $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$
- $2NaNO_3 \rightarrow 2NaNO_2 + O_2$

· $Na_2CO_3 \cdot 10H_2O \xrightarrow{375K} Na_2CO_3 \cdot H_2O$

decahydrate $\xrightarrow{>375K} Na_2CO_3$.