GROUP II (A2)

Thermal Decomposition of Group II Carbonates

Generally,

$$\underset{\text{metal carbonate}}{MCO_{3(s)}} \xrightarrow{\text{heat}} \underset{\text{metal oxide}}{MO_{(s)}} + \underset{\text{carbon dioxide}}{CO_{2(g)}}$$

Egs.

$$MgCO_{3(s)} \xrightarrow{\text{heat}} MgO_{(s)} + CO_{2(g)}$$

$$CaCO_{3(s)} \xrightarrow{\text{heat}} CaO_{(s)} + CO_{2(g)}$$

$$SrCO_{3(s)} \xrightarrow{\text{heat}} SrO_{(s)} + CO_{2(g)}$$

$$BaCO_{3(s)} \xrightarrow{\text{heat}} BaO_{(s)} + CO_{2(g)}$$

Decomposition of group II carbonates because of:

a) Group II cations:
- polarizing effect of Group II cations.
- polarizing effect weakens one of the C–O bond (distortion of CO_3^{2-} anion)
- followed by breaking of the bond,

b) carbonate anion:
- large anion CO_3^{2-} (1 carbon atom + 3 oxygen atoms)
- contribute to polarisability of the anion

the readiness to be polarised

Polarizing effect/power is determined by charge density of the cation.

$$\boxed{\text{charge density} = \frac{\text{charge}}{\text{volume}}}$$

size of the cation

size (volume) ↑ ⟶ charge density ↓ ⟶ polarizing power ↓

Thermal Decomposition of Group II Nitrates

generally,

$$\underset{\text{metal nitrate}}{2M(NO_3)_{2(s)}} \xrightarrow{\text{heat}} \underset{\text{metal oxide}}{2MO_{(s)}} + \underset{\text{nitrogen dioxide}}{4NO_{2(g)}} + \underset{\text{oxygen}}{O_{2(g)}}$$

Egs:

$$2Mg(NO_3)_{2(s)} \xrightarrow{\text{heat}} 2MgO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$2Ca(NO_3)_{2(s)} \xrightarrow{\text{heat}} 2CaO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$2Sr(NO_3)_{2(s)} \xrightarrow{\text{heat}} 2SrO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$2Ba(NO_3)_{2(s)} \xrightarrow{\text{heat}} 2BaO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

Decomposition of group II nitrates because of :

a) Group II cations:
- polarizing effect of group II cations.
- N – O bond is polarised. (distortion of NO_3^- anion)
- subsequently the bond is weaken due to polarization
- followed by breaking of the bond.

b) nitrate anion:
- large anion NO_3^- (1 nitrogen atom + 3 oxygen atoms)
- contribute to polarisability of the anion.

↑

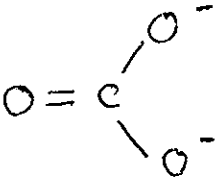
the readiness to be polarised.

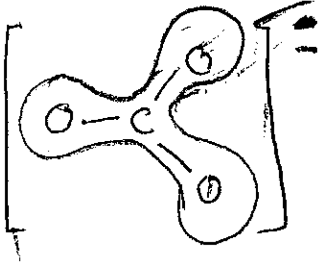
Thermal Stability of Group II Nitrates and Carbonates

Thermal stability increases down the group because:-

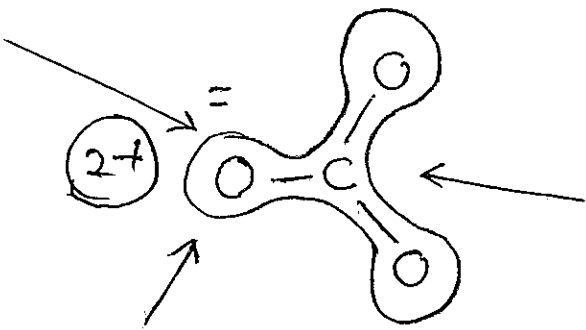
- size of cation ↑ down the group (charge stays the same)
- → charge density ($\frac{\text{charge}}{\text{volume}}$) ↓
- polarising power of the cation ↓
- thus results in less polarization of the NO_3^-/CO_3^{2-} ion by the larger cations.
- therefore, become more difficult to decompose group II carbonates/nitrates when ↓ the group.

Polarisability of a carbonate ion (CO_3^{2-})





the delocalised electrons are pulled towards the positive ion.



this end of the ion is on its way to breaking away and becoming carbon dioxide

this oxygen atom is well on the way to becoming an oxide ion

Solubility of Group II Sulfates

determined by relative magnitudes of :-

① Lattice energy

② Enthalpy change of hydration of cation.

Sulfate	Lattice energy (kJ mol⁻¹)	Enthalpy change of solution (kJ mol⁻¹)
$MgSO_4$	−2959	−91
$CaSO_4$	−2704	−18
$SrSO_4$	−2572	−2
$BaSO_4$	−2459	+26

Ion	Ionic radius (nm)	Enthalpy change of hydration (kJ mol⁻¹)
Mg^{2+}	0.065	−1890
Ca^{2+}	0.099	−1562
Sr^{2+}	0.113	−1414
Ba^{2+}	0.135	−1273
SO_4^{2-}		−1160

Standard Enthalpy Change of Hydration ($\Delta H^{\ominus}_{hyd}$)

Definition: The standard enthalpy change of hydration of an ion is defined as the enthalpy change when one mole of the gaseous ions is dissolved in a large quantity of water under standard conditions.

$$Mg^{2+}_{(g)} + aq \longrightarrow Mg^{2+}_{(aq)} \quad \Delta H^{\ominus}_{hyd} = -1890 kJ mol^{-1}$$

$$SO^{2-}_{4(g)} + aq \longrightarrow SO^{2-}_{4(aq)} \quad \Delta H_{hyd} = -1160 kJ mol^{-1}$$

$$Mg^{2+}_{(g)} + SO^{2-}_{4(g)} + aq \longrightarrow Mg^{2+}_{(aq)} + SO^{2-}_{4(aq)} \quad \Delta H^{\ominus}_{hyd} = -3050 kJ mol^{-1}$$

$\Delta H^{\ominus}_{hyd}$ is always negative.

Lattice Energy

The lattice energy of an ionic crystal is the heat energy evolved when one mole of crystalline solid is formed from its separate gaseous ions under standard conditions.

$$Mg^{2+}_{(g)} + SO^{2-}_{4(g)} \longrightarrow MgSO_{4(s)} \quad \Delta H^{\ominus} = -2959 kJ mol^{-1}$$

$$Ba^{2+}_{(g)} + SO^{2-}_{4(g)} \longrightarrow BaSO_{4(s)} \quad \Delta H^{\ominus} = -2459 kJ mol^{-1}$$

All lattice energy is negative because heat energy is evolved when the ions form electrovalent bonds

The higher the lattice energy (the more exothermic), the stronger the bond.

Standard Enthalpy Change of Solution ($\Delta H^{\ominus}_{sol}$)

Definition: The standard enthalpy change of solution is defined as the enthalpy change when one mole of a substance dissolves in such a large volume of solvent that addition of more solvent produces no further change under standard conditions.

$MgSO_{4(s)} + aq \longrightarrow Mg^{2+}_{(aq)} + SO_{4(aq)}^{2-}$ $\Delta H^{\ominus}_{sol} = -91\ kJ\ mol^{-1}$

$CaSO_{4(s)} + aq \longrightarrow Ca^{2+}_{(aq)} + SO_{4(aq)}^{2-}$ $\Delta H^{\ominus}_{sol} = -18\ kJ\ mol^{-1}$

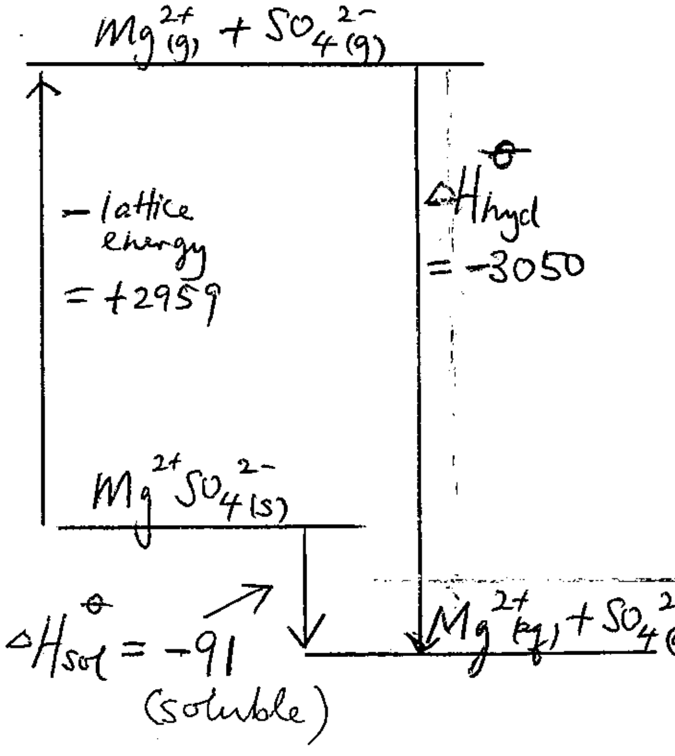
$BaSO_{4(s)} + aq \longrightarrow Ba^{2+}_{(aq)} + SO_{4(aq)}^{2-}$ $\Delta H^{\ominus}_{sol} = +26\ kJ\ mol^{-1}$

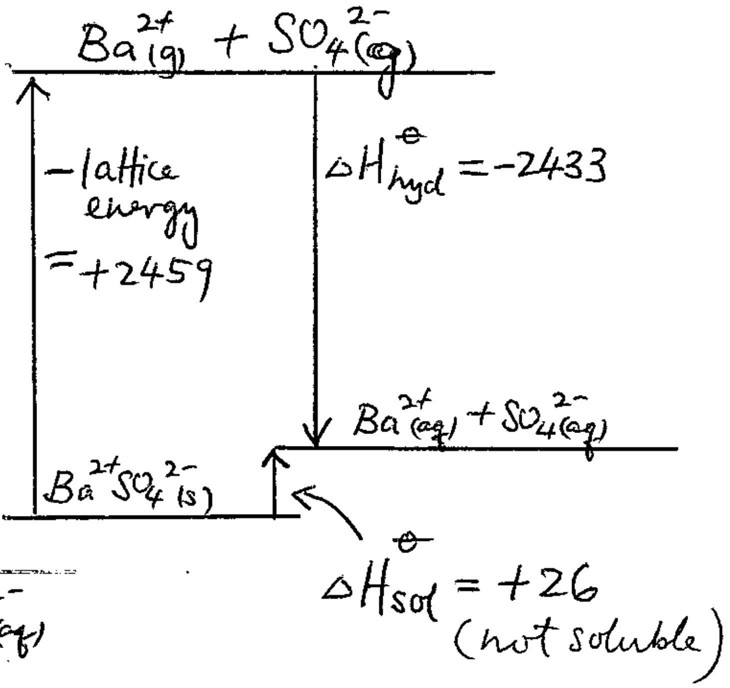
$\Delta H^{\ominus}_{sol}$ can be positive or negative

If $\Delta H^{\ominus}_{sol}$ is very positive – insoluble in water

If $\Delta H^{\ominus}_{sol}$ is very negative – soluble in water

Solubility of sulfates





Variation in solubility of Group II Sulfates

Lattice energy

descending group II,
- size of the M^{2+} ion ↑
- lattice enthalpy ↓ (opposite charged ions packed less closely & charge density M^{2+} ↓)
- (size SO_4^{2-} remains constant)

Enthalpy Change of Hydration

descending group II,
- increasing size of the M^{2+} ion.
- Enthalpy change of hydration ↓ (water molecules can get less closer to M^{2+} ion due to lower charge density)
- (size SO_4^{2-} constant $\rightarrow \Delta H^{\ominus}_{hyd} \equiv$ constant for SO_4^{2-})

Solubility of group II sulfates ↓; down the group

magnitude $\Delta H^{\ominus}_{hyd}$ > magnitude lattice energy $\rightarrow \Delta H^{\ominus}_{sol} = -ve$
salt dissolves readily.

Down group II, $\Delta H^{\ominus}_{hyd}$ decreases in a faster extent compared to decreases in value of lattice energy.

Therefore $\Delta H^{\ominus}_{sol}$ changes from −ve (soluble salt $MgSO_4$) to +ve (not soluble $BaSO_4$)