

- Assumptions  
(need confirmation)
- Raj bhaiya imp notes
- Stuff I added  
(confirmed)

## Chemical Energetics

(priorly mentioned  
during class)

- Define Lattice Energy ( $\Delta H_{\text{latt}}$ )
- ↳ It is the amount of energy released when 1 mol of an ionic compound is formed from its gaseous ions under standard conditions  
 e.g.  $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s) \quad \Delta H_{\text{latt}}[\text{NaCl}]$   
 $\text{Ca}^{2+}(g) + 2\text{Cl}^-(g) \rightarrow \text{CaCl}_2(s) \quad \Delta H_{\text{latt}}[\text{CaCl}_2]$
- #  $\Delta H_{\text{latt}}$  is always negative (-ve)

### Factors affecting Lattice Energy

- The greater the charge of the ion, the more exothermic the  $\Delta H_{\text{latt}}$
- The smaller the ionic radius of the ion, the more exothermic the  $\Delta H_{\text{latt}}$

$$\Delta H_{\text{latt}} \propto \frac{q_1 \cdot q_2}{r_1 + r_2}$$

- i+ii) Ions with greater charge density have more exothermic  $\Delta H_{\text{latt}}$

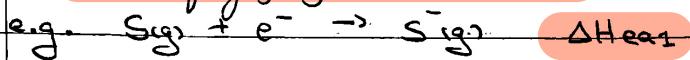
### A Predict and explain the difference in the value of $\Delta H_{\text{latt}}$ of $\text{CaCl}_2$ and $\text{CaBr}_2$

- ↳  $\Delta H_{\text{latt}}[\text{CaCl}_2]$  more exothermic than  $\Delta H_{\text{latt}}[\text{CaBr}_2]$  as both compounds form the same no. of bonds per mol and have the same cation. However  $\text{Cl}^-$  ions and  $\text{Br}^-$  ions have the same charge but  $\text{Cl}^-$  has a smaller ionic radius thus greater -ve charge density thus greater,  $\Delta H_{\text{latt}}$  of  $\text{CaCl}_2$  than  $\text{CaBr}_2$ . more exothermic

→ Define electron affinity

↪ It is the amount of energy change when 1 mol of  $e^-$  is added.

↪ 1 mol of gaseous atom or ion



→ Define  $\Delta H_{\text{ea2}}$

↪ It is the amount of energy change when 1 mol of  $e^-$  is added to 1 mol of gaseous ion with a charge of -1 to form 1 mol of gaseous ion with a charge of -2.

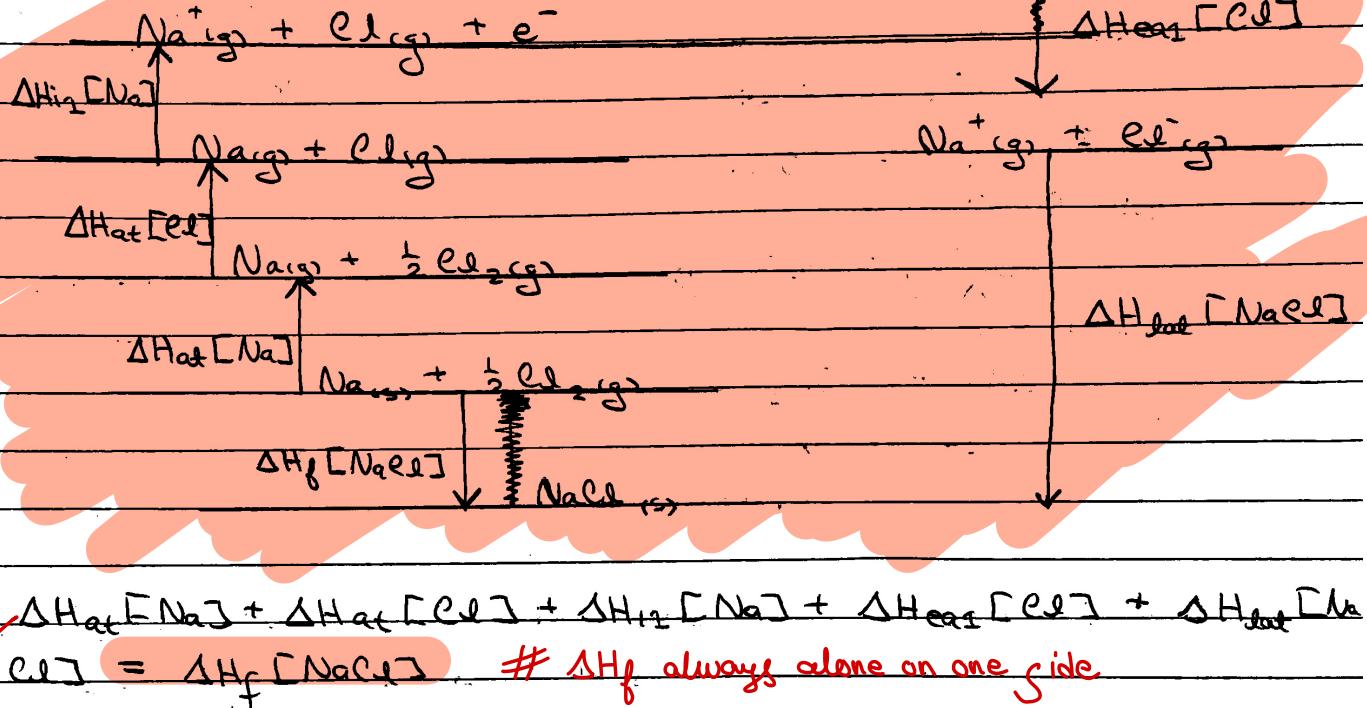
→ Only  $\Delta H_{\text{ea1}}$  is exothermic, rest are endothermic

→  $\Delta H_{\text{ea2}} < \Delta H_{\text{ea3}} < \Delta H_{\text{ea4}} \dots$

L,  
Consecutive  $\Delta H_{\text{ea}}$  become more and more endothermic as the -ve charge on the ion keeps increasing each  $e^-$  added. Thus the repulsion acting on any "incoming"  $e^-$  increases thus more energy is required to overcome the repulsion and add the next  $e^-$ .

→  $e^-$  is added, attraction between  $e^-$  and nucleus, bond forming, energy released > energy required to add  $e^-$ , exothermic

## Born Haber Cycle

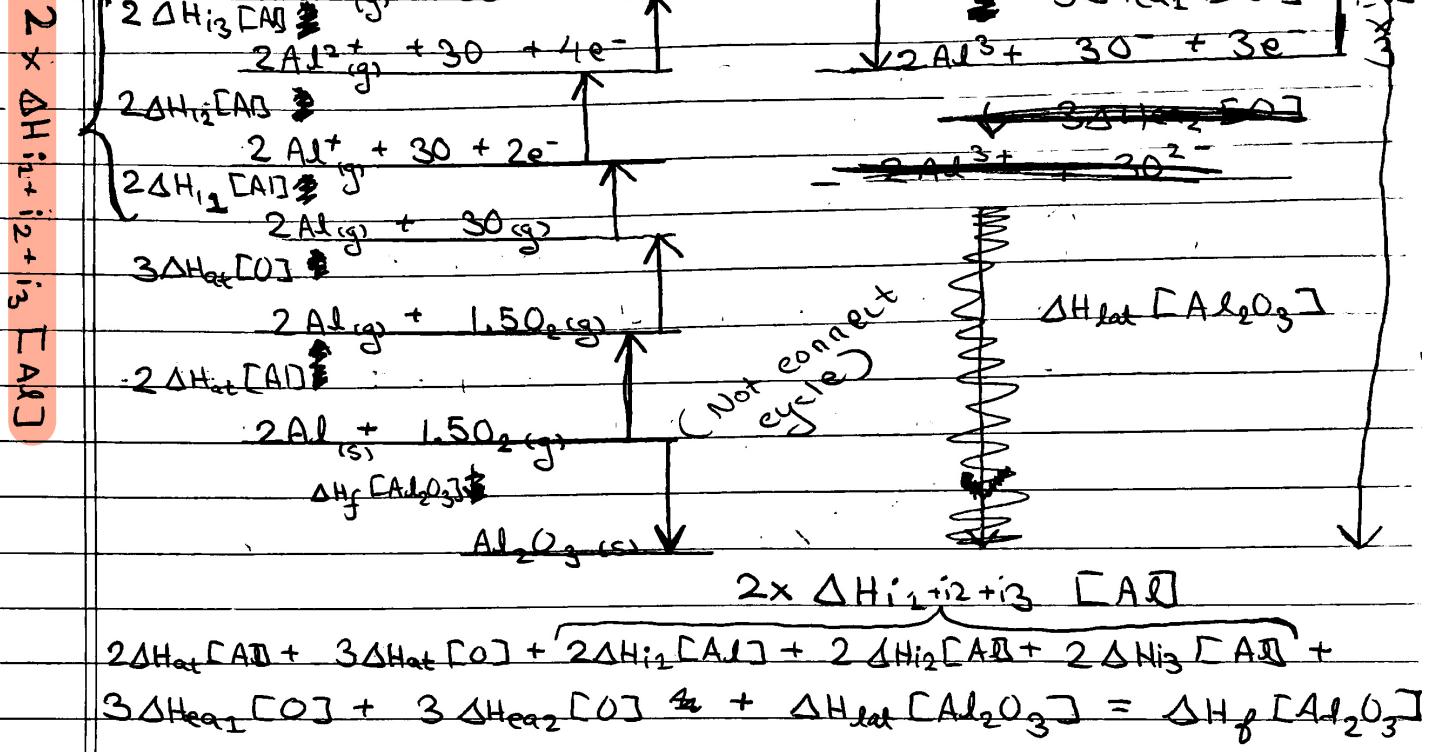


# upward for endothermic and downward for exothermic

# For non-metallic elements in gaseous state that exist as diatomic molecules,  $\frac{1}{2} \times$  bond energy is equal to  $\Delta H_{\text{lat}}$

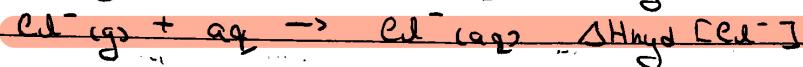
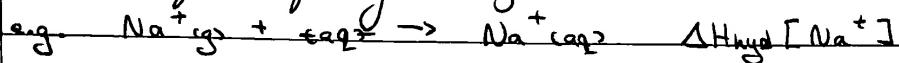
$$\Delta H_f = \Delta H_{\text{lat}} + \Delta H_{+1} + \Delta H_{+2} + \Delta H_{\text{lat}}$$

Construct a 3-term Haber cycle for  $\text{Al}_2\text{O}_3$



→ Define enthalpy change of hydration (for gaseous ion) ( $\Delta H_{\text{hyd}}$ )

↳ It is the amount of energy change when 1 mol of gaseous ion is dissolved in water to form infinitely dilute soln.



↳  $\Delta H_{\text{hyd}}$  is always exothermic: Energy released due to the attraction (bond) forming between the ion and the dipole of  $\text{H}_2\text{O}$  molecule  
This is called ion-dipole interaction

↳ Factors affecting  $\Delta H_{\text{hyd}}$

↳ Ions with greater charge have greater  $\Delta H_{\text{hyd}}$

↳ Ions with smaller radii have greater  $\Delta H_{\text{hyd}}$

#  $\Delta H_{\text{hyd}}$  works individually,  $\Delta H_{\text{hyd}}$  of the cation and anion are independent of each other, whereas  $\Delta H_{\text{lat}}$  depends on both the ions;  $\Delta H_{\text{lat}} \propto \frac{Z_1 Z_2}{r_1 + r_2}$

→ No such thing as "Insoluble".  
All salts are at least sparingly soluble, NEVER Insoluble.

→ Define enthalpy change of solution. ( $\Delta H_{\text{sol}}$ )

↳ It is the amount of energy when 1 mol of an ionic compound is dissolved in water to form an infinitely dilute soln.

↳  $\Delta H_{\text{sol}}$  can be both exothermic or endothermic.

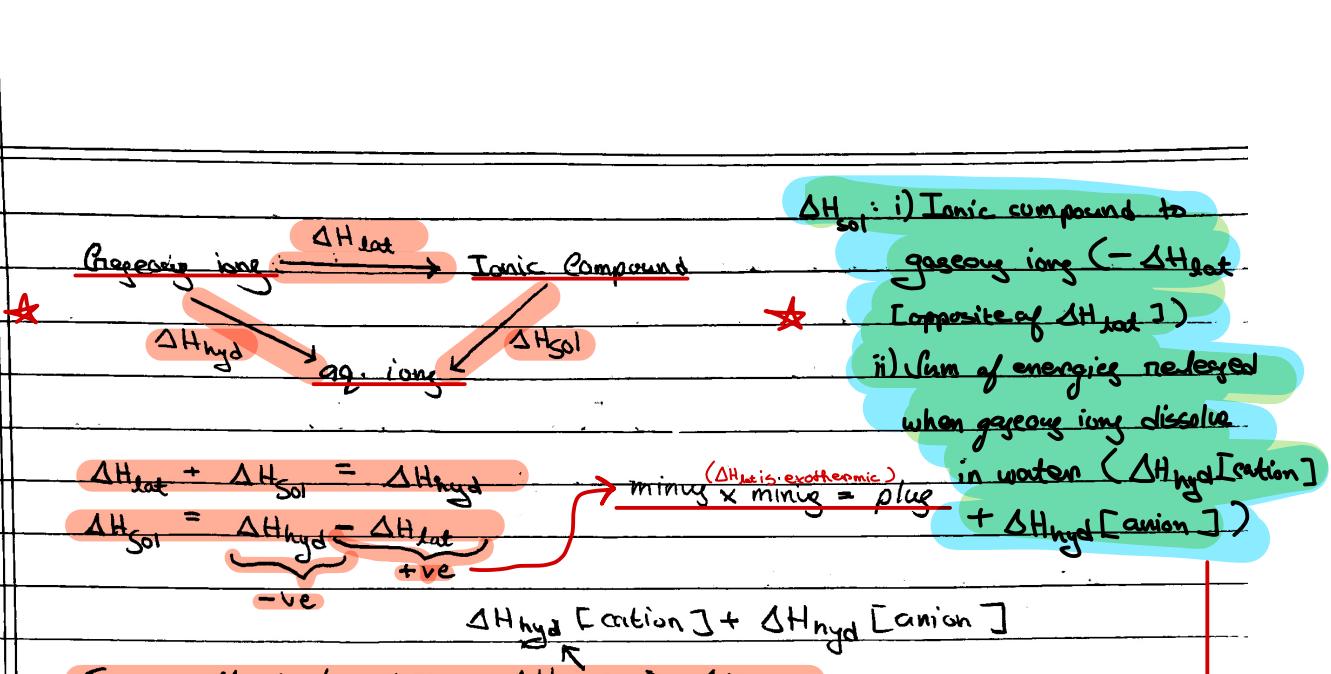
↳ For a salt to be soluble, its  $\Delta H_{\text{sol}}$  is exothermic or slightly endothermic  $\approx +30 \text{ kJ/mol}$

↳ For sparingly soluble salts, its  $\Delta H_{\text{sol}}$  is highly endothermic

# Simply put, when a salt is "insoluble", it requires a LOT of energy to dissolve that salt in water. Thus the  $\Delta H_{\text{sol}}$  of an insoluble salt is always highly endothermic. Energy released by the ion-dipole interaction is negligible compared to the energy required to dissolve the insoluble salt

# When a salt is "soluble", it requires little to no energy to dissolve it in water thus it is exothermic (due to energy released from ion-dipole interaction) or very slightly endothermic

# Salts whose  $\Delta H_{sol}$  are slightly endothermic can still be soluble because this small amount of energy can be easily provided by the surroundings



# For a salt to be soluble,  $\Delta H_{hyd} > \Delta H_{lat}$

# The energy that is released by  $\Delta H_{hyd}$  if used to break the ionic bond ( $-\Delta H_{lat}$ )

# For a partially soluble salt,  $\Delta H_{hyd} < \Delta H_{lat}$ . Thus the energy from multiple ion-dipole interactions is used to break a few than proportionate numbers of ionic bonds

#  $\Delta H_{lat}$  is the energy released when an ionic bond is formed, thus.

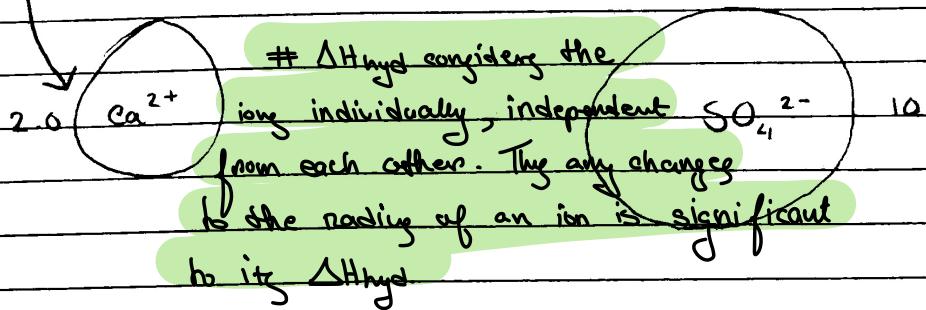
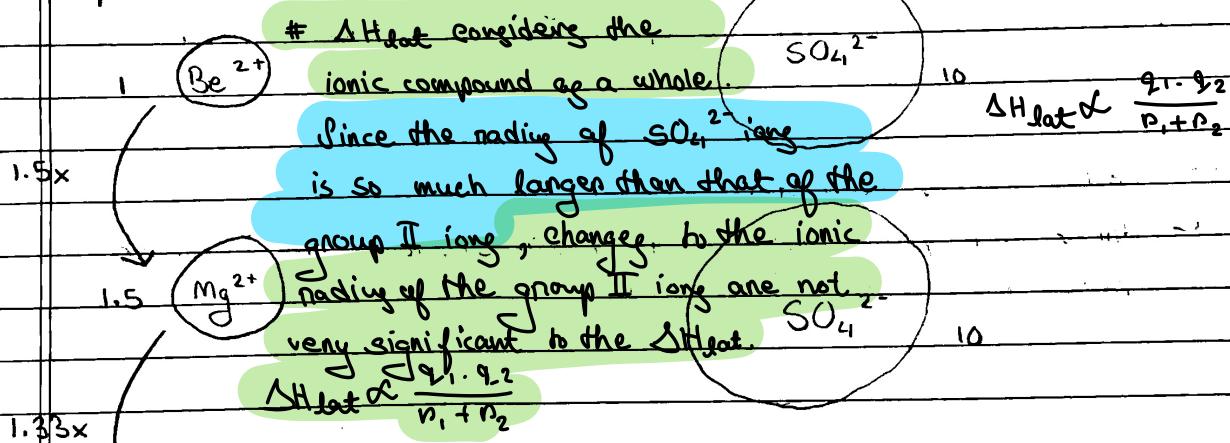
-  $\Delta H_{lat}$  is the energy required to break the ionic bond (into gaseous ion). Thus  $\Delta H_{hyd}$  must be greater than  $\Delta H_{lat}$  for a salt to readily be soluble; so that the  $\Delta H_{hyd}$  from dissolving the gaseous ion ( $-\Delta H_{lat}$ ) can provide enough energy to break <sup>\* an equal or greater no. of</sup> the ionic bonds, creating further gaseous ions and go on until all the salt is dissolved.

\* In the above explanations,  $\Delta H_{hyd}$  refers to  $\Delta H_{hyd}$  [formula unit] where  $\Delta H_{hyd}$  [formula unit] =  $\Delta H_{hyd}$  [Cation] +  $\Delta H_{hyd}$  [Anion] when compared to the  $\Delta H_{lat}$  of a formula unit  $\star$  ONLY applicable for the above explanations and NOT in practice. No such thing as  $\Delta H_{hyd}$  [formula unit] in practice

→ Explain the trend in the solubility of Group-II Sulfates (4) \*

↳ Down the group solubility decreases. Down the group ionic radius of the cation increases which causes both  $\Delta H_{\text{lat}}$  and  $\Delta H_{\text{hyd}}$  to decrease. However  $\Delta H_{\text{hyd}}$  decreases more significantly, causing  $\Delta H_{\text{sol}}$  to be less exothermic exothermic and more endothermic - me

#### # Explanation



→ Thermal stability of Group-II Carbonate or Nitrate

→ Define Polarization

↳ It is the distortion of the charge cloud of an anion by the cation.

→ Factors affecting polarization ability of cations

↳ Cations with smaller size and greater charge have greater polarizing ability

→ Factors affecting polarization of anions

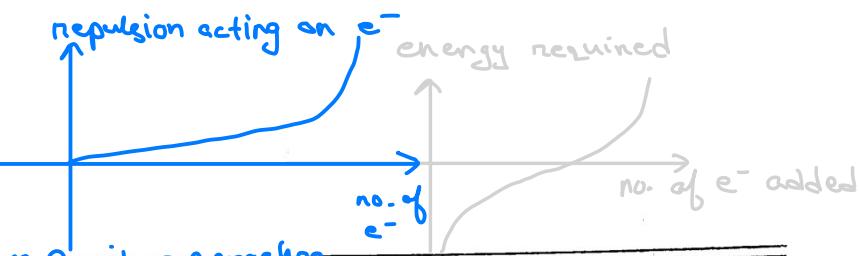
↳ Anions with greater charge and greater ionic radius → experience greater polarization

→ Going down the group, thermal stability increases. Size of cation down the group increases causing polarization ability of cation decreases. Thus polarization of anion ↑ to decreases which causes increase in ionic character

# Greater radius means greater distance from nucleus, they feel attraction towards the nucleus, thus the cation can more easily pull the charge cloud towards itself, thus more distortion

# Greater charge means greater attraction between the cation and anion, thus more distortion. Greater charge can mean nuclear attraction divided among greater than proportionate no. of  $e^-$  thus weaken attraction acting on each  $e^-$  individually

★ Graph is not linear



# The smaller the size of the atom, the steeper the gradient

# Gradient gets steeper as it approaches the max no. of  $e^-$  the shell can store

→ Trend in  $\Delta H_{\text{heat}}$  for group - VII elements (new sub-topic; no pp question)

↳ Down the group, due to increase in atomic size and shielding effect, effective nuclear attractive force decreases despite the increase in nuclear charge. Thus less work is done by this attractive force to pull the  $e^-$  inside the atom, causing  $\Delta H_{\text{heat}}$  to be less exothermic (do not write "decrease", instead use "less exo/endo thermic")\*

Group - VII Elements	$\Delta H_{\text{heat}} / \text{kJ mol}^{-1}$
Fluorine	- 328 * (does not follow trend)
Chlorine	- 349
Bromine	- 324.6
Iodine	- 295.4

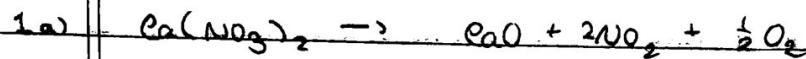
↳ Fluorine  $\Delta H_{\text{heat}}$  should be more exothermic than  $\Delta H_{\text{heat}}$  [F<sub>2</sub>] however in reality it is less exothermic

↳ This is due to very small size of F atom. The  $e^-$  of the F atom are very close to each other, resulting in the production of strong repulsion forces thus the effective nuclear attractive force that is used to pull the  $e^-$  inside the atom is minimized

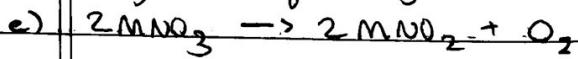
$\Delta H_{\text{heat}} \uparrow$   
Repulsion acting on 7<sup>th</sup>  $e^- < 8^{\text{th}} e^-$  significantly

★ This does not apply to  $\Delta H_{\text{int}}$  [F<sub>2</sub>] and  $\Delta H_{\text{int}}$  [e<sup>-</sup>] because the effect of the nuclear attraction on an  $e^-$  outside the atom is already very much less, thus the increased repulsion due to the small size of the F atom decreases the nuclear attraction on the outer  $e^-$  more significantly than on the  $e^-$  in the atom

★ Group I Nitrates are more stable than their corresponding Group II, Nitrates due to smaller charge and larger radius, thus...



b) Down the group, thermal stability increases due to increase in cationic radius, same cationic charge, overall less cationic charge density, less polarising ability of cation, thus greater polarization distortion of  $\text{NO}_3^-$  ion thus more ionic character.



$$\frac{16}{\text{Ar} + 14 + 16 \times 3} = 0.1085$$

$$\text{Ar} = \frac{16}{0.1085} - 14 - (16 \times 3)$$

$$\therefore \text{Ar} = 85.5$$

thus the metal is Rb (Rubidium)

2i)  $\Delta H_{\text{sol}} \quad \Delta H = -467 + 2 \times -167 - (-641)$   
 $= -160 \text{ kJ mol}^{-1}$

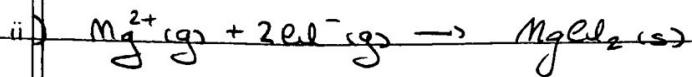
ii)  $\Delta H_{\text{sol}}$  is HIGHLY exothermic

$\hookrightarrow$  (because question says VERY soluble)

iii) Down the group, due to increase in cationic radius  $\Delta H_{\text{sol}}$  and  $\Delta H_{\text{hyd}}$  decrease however  $\Delta H$  by  $\Delta H_{\text{hyd}}$  decreases more significantly

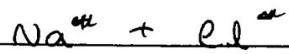
Amount of energy change when 1

3) i)



ii) Compared to  $\text{Mg}^{2+}$  ion,  $\text{Na}^{+}$  ion has smaller charge and greater ionic radius. Thus less cationic charge density. Thus  $\text{Na}(\text{el})_2$  has lower less exothermic  $\Delta H_{\text{lat}}$  than  $\text{Mg}(\text{el})_2$ .

ii)  $\text{Ca}(\text{el})_2$  has less less lower  $\Delta H_{\text{lat}}$  than  $\text{Mg}(\text{el})_2$  because ..



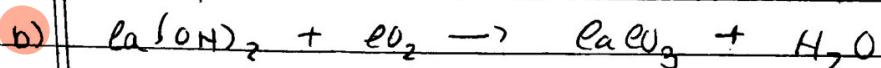
$$\Delta H_f = \Delta H_{\text{at}} + \Delta H_{\text{iz}} + \Delta H_{\text{ear}} + \Delta H_{\text{lat}}$$

$$\begin{aligned}\Delta H_{\text{lat}} &= -411 - (107 + 122 + 494 - 349) \\ &= -785 \text{ kJ mol}^{-1}\end{aligned}$$

i) Reaction is endothermic  
Reaction has high  $E_a$

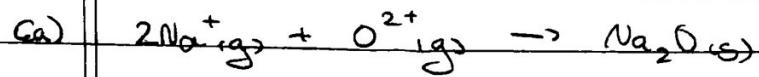
~~2 reasons for  
heating a reaction~~

ii)  $\text{MgCO}_3$  will require lower temperature than  $\text{CaCO}_3$  because ionic radius of  $\text{Mg}^{2+}$  is smaller than  $\text{Ca}^{2+}$  ion, same charge, greater +ve charge density, stronger polarizing ability, more distortion of  $\text{CO}_3^{2-}$  ion, less ionic character, less thermal stability.



$$-96 \text{ kJ mol}^{-1}$$

Q8



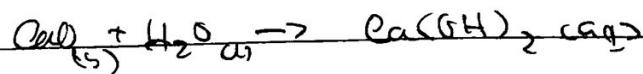
b)  $A = 2\text{Na}_{(\text{aq})} \quad 1 = \Delta H_{\text{f}}^{\circ} [\text{Na}] \times 2$   
 $B = \text{O}_{(\text{g})} \quad 2 = \Delta H_{\text{ea},1}^{\circ} + \Delta H_{\text{ea},2}^{\circ} [\text{O}]$   
 $\cdot \quad 3 = \Delta H_{\text{lat}}^{\circ} [\text{Na}_2\text{O}]$   
 $\cdot \quad 4 = \Delta H_f^{\circ} [\text{Na}_2\text{O}] \quad \Delta H_i^{\circ}[\text{Na}] = 494$   
 $\cdot \quad O = O = 496$

$$\Delta H_f^{\circ} = \Delta H_{\text{at}} + 2\Delta H_i^{\circ} + \Delta H_{\text{ea},1}^{\circ} + \Delta H_{\text{ea},2}^{\circ}$$

$$\Delta H_{\text{ea},1}^{\circ} = -414 \left( \frac{496}{2} + 107 \times 2 + 2 \times 494 - 141 + 798 \right)$$

$$\Delta H_{\text{ea},2}^{\circ} = -2414 \text{ kJ mol}^{-1} - 2521 \text{ kJ mol}^{-1}$$

MgO is used as furnace lining due to high m.p.  
due to strong ionic bond as seen from highly  
exothermic  $\Delta H_{\text{lat}}$ .



3d) More energy required for Al<sup>3+</sup> as it has ~~higher~~ smaller  
radius

O combines with haemoglobin to form a very  
stable complex

This was also fairly well answered, although a significant number of candidates argued that  $\text{Sr}(\text{OH})_2$  would be more soluble in hot water for kinetic reasons, forgetting that *solubility* is an equilibrium process.

**Why does more salt dissolve in a solution with an increase of temperature? Could you explain it in terms of Le Chatelier's principle?**

S

Sudhagar Sudhanthiranathan

Former Employee in Waste Management Firm · Author has 832 answers and 529.6K answer views · 2y

Let me put it simply...

First, What do you mean by the solution- a normal one or saturated or super saturated ones????

SATURATED SOLUTION ONLY maintains an EQUILIBRIUM. SO, LE CHATLIER'S principle holds only for that...

Normal solution ISN'T a system of EQUILIBRIUM. You CAN'T APPLY le chatlier's principle to this one!!!

So, in the normal solution, solubility increases with temperature due to rise in kinetic energy of ions! it means that rate of dissolution increases

In a saturated solution, when temperature rises, it seems that more NaCl should dissolve ,since NaCl dissolution is slightly endothermic

It becomes only possible if your saturated solution is in contact with good number of NaCl crystals!

339 views · Answer requested by Jeff Johnson

# Bond Energy : The amount of energy change when 1 mol of bond is broken in the gas phase

# It is not possible to find  $\Delta H_{\text{hyd}} [\text{O}^{2-}]$  because  $\text{O}^{2-}$  reacts with water to give  $\text{OH}^-$  or  $\text{O}^{2-} + \text{H}_2\text{O} \xrightarrow{\text{any}} 2\text{OH}^-$

# insulated calorimeter used in enthalpy change experiment

(d) Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate.

(d)

- solubility:  $\text{MgSO}_4 > \text{BaSO}_4$  or decreases down the group
- because  $\Delta H_{\text{sol}}$  is more endothermic for  $\text{BaSO}_4$  or more exothermic for  $\text{MgSO}_4$
- due to larger  $r_{\text{ion}}$  or smaller charge density of  $\text{Ba}^{2+}$  (ion has to be mentioned)
- leading to smaller LE and HE or LE and HE decrease
- but difference in HE (between  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$ ) is larger than the difference in LE (between  $\text{MgSO}_4$  and  $\text{BaSO}_4$ )  
or HE is dominant or HE decreases more than LE

any 4 points [4]

[4]