Solvation, hydration, ligation

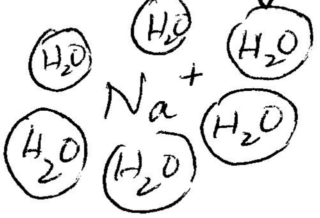
When a gaseous cation or a gaseous anion reacts with a solvent in liq. state, Solvated cation or Solvated anion is obtained and in this process, energy is liberated ie solvation energy

$M^+_{(g)} + Sol \longrightarrow M^+_{(sol)} + \underset{exo}{\text{Solvation energy}}$

If the solvent is water, we call that process hydration and energy released is called hydration energy

$M^+_{(g)} + H_2O\,(l) \longrightarrow M^+_{(aq)} + \text{hydration energy}$

Higher the hydration energy higher the solubility



Hydration Number

Hydration sphere.

If H_2O/Solvent can act as a ligand the process is called ligation.

eg NH_3 is ligand $M \leftarrow :NH_3$

$H^+ = 1091$ kJ/mol hydration energy

$Cs^+ = 280$ "

$F^- = 515$ "

Higher the ionic potential, ϕ higher the hydration energy

$\Delta H_{hyd} = H_{latt} + H_{solv}$

Q The lattice energy of NaCl calculated is −788 kJ/mol. Enthalpy of hydration of Na^+ & Cl^- ions are 406 & 363 kJ/mol. Estimate $H_{solvation}$ for NaCl

$H_{hyd} = H_{latt} + H_{sol}$

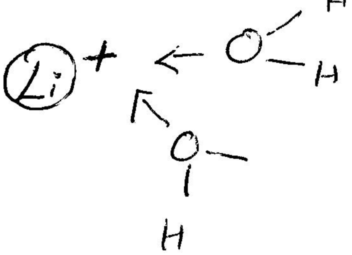
$406 + 363 = -788 + \_\_\_$

$H_{sol} = -769 - (-788)$ kJ $= \underline{19 \text{ kJ/mol}}$

<u>Ionic mobility</u>

	radius	hydration No:	hydrated radius	ionic mobility
Li^+	0.76 Å	25.3	3.4 Å	33.5
K^+	1.38 Å	10.5	2.32 Å	64.5

Li is the smallest atom in gp 1 and size goes on increasing as we move towards K. Ionic potential, ϕ is much higher for Li, $\phi = \frac{charge}{radius}$



Li^+ will be hydrated to a greater extend than K^+. Consequently hydration No: would be higher and hydrated radius would be higher.

Li ion experiences a drag, its mobility is compromised because of large hydration sphere. Consequently its electrical condution would be much lower than K^+ or Cs

$$Li^+ < Na^+ < \underrightarrow{K^+ < Rb^+ < Cs^+}$$ mobility increases

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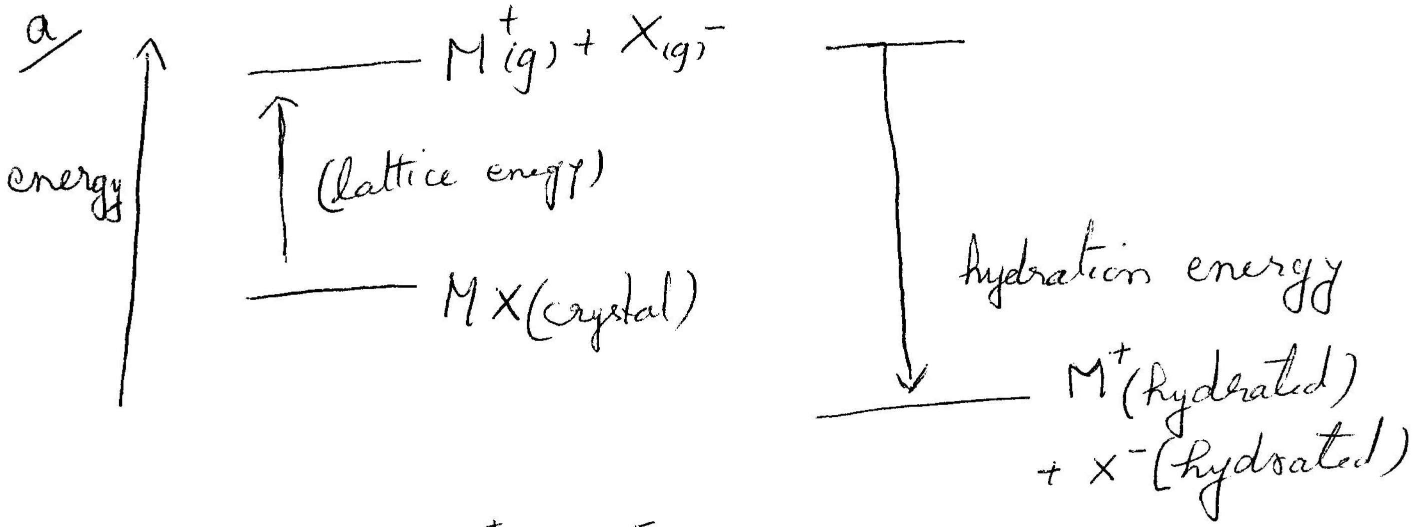
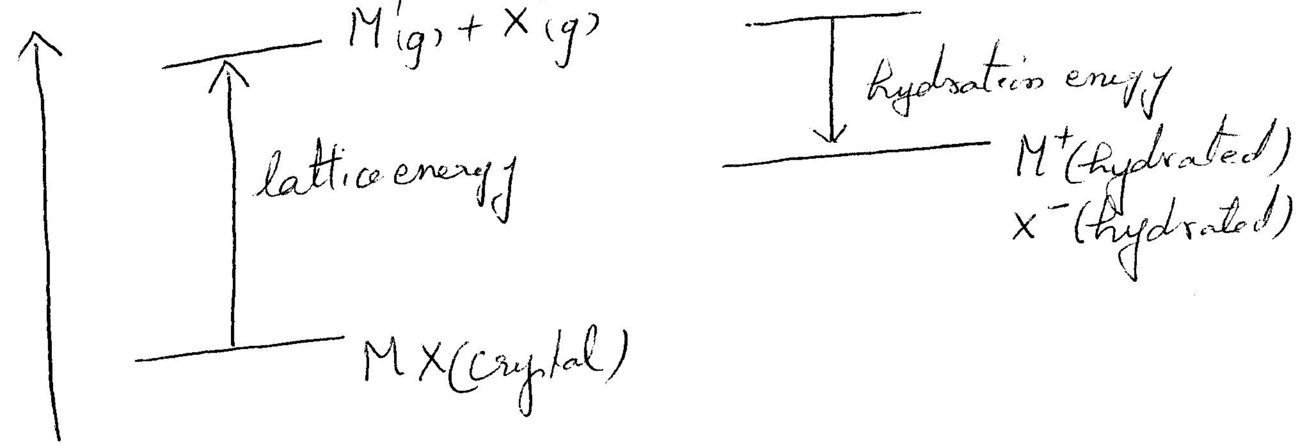
Solubility & lattice energy

a/



b/



(a) solid dissolves

If $\Delta H_{hyd} > \Delta H_{latt}$

b) Solid is insoluble

If $\Delta H_{latt} > \Delta H_{hyd}$

Results of polarization

M.P and B.P can be affected by the Covalency arising out of polarization

M.P of $BeCl_2$ is 405°C & $CaCl_2$ is 772°C
Be is smaller in size than Ca, $BeCl_2$ is more covalent than $CaCl_2$.
Covalent bonding is weaker than ionic bonding and M.P would be lower than ionically bonded compounds.

NaBr – 755°C $MgBr_2$ – 700°C $AlBr_3$ – 97.5°C

Al^{3+} is having highest charge, ϕ is high, bonding is highly covalent. Covalent bonds are weaker and MP would be low

LiCl – 613°C LiI – 446°C

I^- is bigger than Cl^-, I^- would be easily polarised and bonding will be covalent
So melts at lower temperature.
Higher the covalency lower the solubility in water.
AgI is more covalent than AgF
AgI is less soluble in water

Thermal stabilities

Decomposition of alkaline earth carbonates

$MCO_3 \longrightarrow MO + CO_2$

The ease with which this reaction proceeds decreases with increasing cation size.

$BeCO_3$ - 100°C ; $MgCO_3$ - 400° : $CaCO_3$ 900°C

The smallest cation Be polarises the Carbonate ion, splitting it into O^{2-} & CO_2

This take place at 100°C.

$BaCO_3$ decomposes at 1390°C only.

Ba is big, it dosent deform the e cloud on CO_3 ion that easily. Bonding is strong, less covalent. CO_3^{2-} is a large anion, is better stabilised by a large cation like Ba^{2+}. They are compatible size wise and decomposes at very high T only.

$MgSO_4 < CaSO_4 < BaSO_4$

$\longrightarrow$ Decomposition T increas

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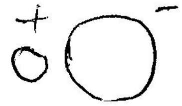
There is size mismatch in $MgSO_4$



this leads to its instability

Compounds that contain ions with widely different radii are generally soluble in water. Conversly the least water soluble salts are those of ions with similar radii, they are thermodynamically stable.

$Mg(OH)_2$ is sparingly soluble

$Ba(OH)_2$ is highly soluble.

OH^- ion is small in size. This would be better stabilised by Mg^{2+} (small) than Ba^{2+} which is very large

Ion size asymmetry can result in exothermic dissolution.

If both ions are small, then H_{latt} and H_{hyd} will be large, dissolution is not easily promoted. It forms a crystalline ppt eg $BaSO_4$, $Mg(OH)_2$