23. CHEMICAL ENERGETICS

23.1 Lattice Energy & Born-Haber Cycles

Define lattice energy

- Energy change when 1 mole of an ionic solid/ compound
- Is formed from its gaseous ions.

Ionic radius of Pb2+ = 0.120nm.
Ionic radius of K+ = 0.133nm.
Suggest how the $\Delta H_{latt}^{\ominus}$ of PbI2(s) differs from $\Delta H_{latt}^{\ominus}$ of KI(s). Explain your answer.

- Pb2+ has a greater charge
- Pb2+ is smaller (than K+) OR (Pb2+) smaller ionic radius
- Thus there is greater attraction between Pb2+ and I– OR ionic bond between Pb2+ and I– is stronger OR lattice energy is more exothermic / more negative

State and explain the main factors that affect the magnitude of lattice energies.

- As ionic radii increases, ΔH_{latt} less exothermic
- As ionic charge increases, ΔH_{latt} increases/more exothermic

Suggest the trend in the magnitude of the lattice energies of the metal nitrates, NaNO3(s), Mg(NO3)2(s) and RbNO3(s).

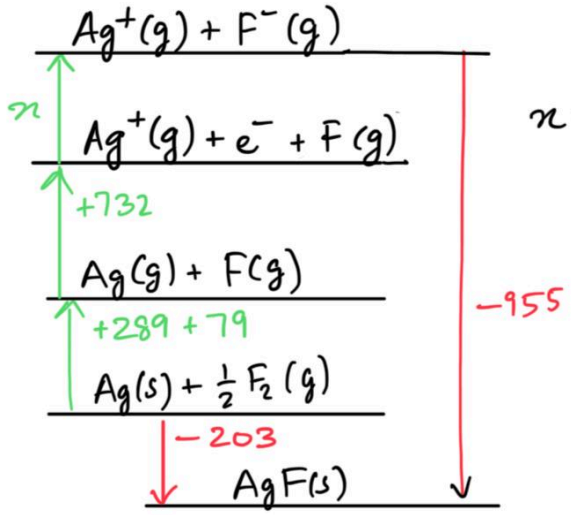
- Mg(NO3)2(s) (most exothermic) > NaNO3(s) > RbNO3(s) (least exothermic)
- Mg2+ has higher charge than Na+ and Rb+ AND
  Na+ has smaller ionic radius than Rb+.
- Higher charge and smaller ionic radius means stronger attraction between ions/ ionic bond, so more energy released when forming it.

Write the equation for the standard enthalpy change of atomisation of silver.

$$Ag(s) \rightarrow Ag(g)$$

standard energy change	value / kJ mol^{-1}
first ionisation energy of silver	+732
enthalpy change of atomisation of silver	+289
enthalpy change of atomisation of fluorine	+79
enthalpy change of formation of silver(I) fluoride	–203
lattice energy of silver(I) fluoride	–955

Use the data to calculate the first electron affinity, EA1, of fluorine.



$x = -203 - (-955 + 289 + 79 + 732)$
$= -348$

NOTE: although F2 is already in gaseous state, atomisation is needed to convert it from ½F2(g) to F(g)!!

silver(I) halide	first electron affinity of halogen / kJ mol^{-1}	lattice energy / kJ mol^{-1}
AgCl	–349	–905
AgBr	–325	–890
AgI	–295	–876

Explain the trend in the first electron affinities of the halogens, Cl to I.

- greater the distance between the nucleus and (the shells of the) electrons OR atomic radii increases / atomic size increases / more shells OR more shielding by inner shells
- the less attraction between nucleus / protons AND incoming electron / added electron

Explain the trend in the lattice energies of the silver(I) halides, AgCl to AgI.

- halide/X– /ions get larger (down the group), so decreasing attraction between ions / weaker ionic bond.

Define enthalpy change of atomisation, ΔHat.

- Energy required when one mole of gaseous atoms is formed from its element.

Define first electron affinity.

- Energy released when one mole of gaseous atoms gains one mole of electrons and becomes one mole of gaseous 1– ions.

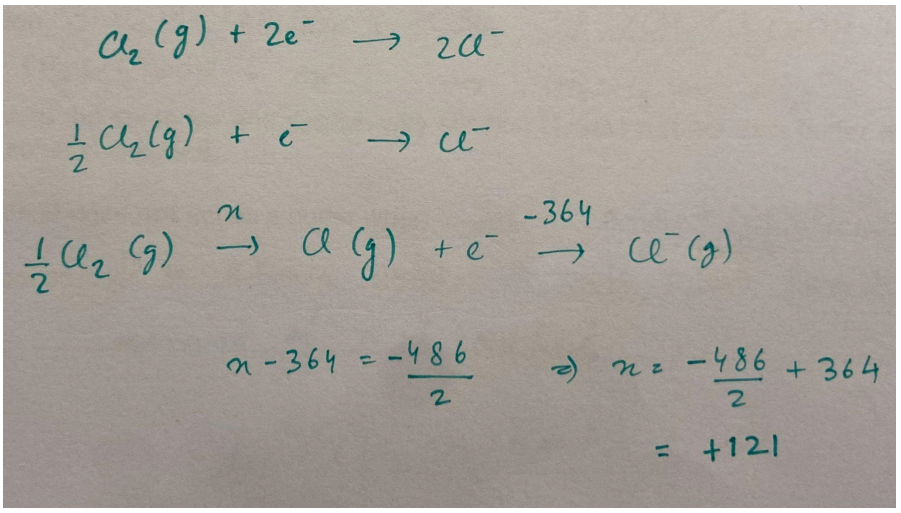
Explain why the value for the second electron affinity is positive.

- due to repulsion between negative ion and incoming / gained electron.

The enthalpy change for the reaction $Cl_2(g) + 2e^- \rightarrow 2Cl^-(g)$ is $-486\,kJ\,mol^{-1}$.

The first electron affinity of chlorine is $-364\,kJ\,mol^{-1}$.

Calculate the enthalpy change of atomisation of chlorine.



23.2 Enthalpies of Solution & Hydration

Define enthalpy of solution

- Change in enthalpy when one mole of a substance / solute dissolves in water to form aqueous solution of infinite dilution.

Enthalpy change of hydration

- enthalpy change when one mole of gaseous ions forms an aqueous solution / dissolves in water.

KI(s) has a high solubility in water although its enthalpy change of solution is endothermic. Explain how this is possible.

- There is a large increase in entropy OR ΔS is positive OR TΔS is positive.
- TΔS outweighs ΔH, so ΔG is negative.

Explain the trend in the enthalpy change of hydration of the halide ions.

- Anionic charge density decreases down the group.
- So hydration enthalpies become less negative / less exothermic down group because ion-dipole force/attraction between halide ions and water molecules weaken.

halide ion	enthalpy change of hydration, ΔH_{hyd} / kJ mol^{-1}	lattice energy of potassium halide, ΔH_{latt} / kJ mol^{-1}
Cl^-	–364	–701
Br^-	–335	–670
I^-	–293	–629

The ΔHsol values of these potassium halides are almost constant. Use the ΔH_{hyd} and ΔH_{latt} data to explain why.

- Difference between ΔH_{hyd} and ΔH_{latt} remains roughly constant OR ΔH_{hyd} and ΔH_{latt} become less exothermic by a similar amount

Enthalpy change of solution, ΔHsol, of AgF(s) = –15 kJ mol^{-1}. Suggest whether AgF is soluble in water at 198K. Explain your answer.

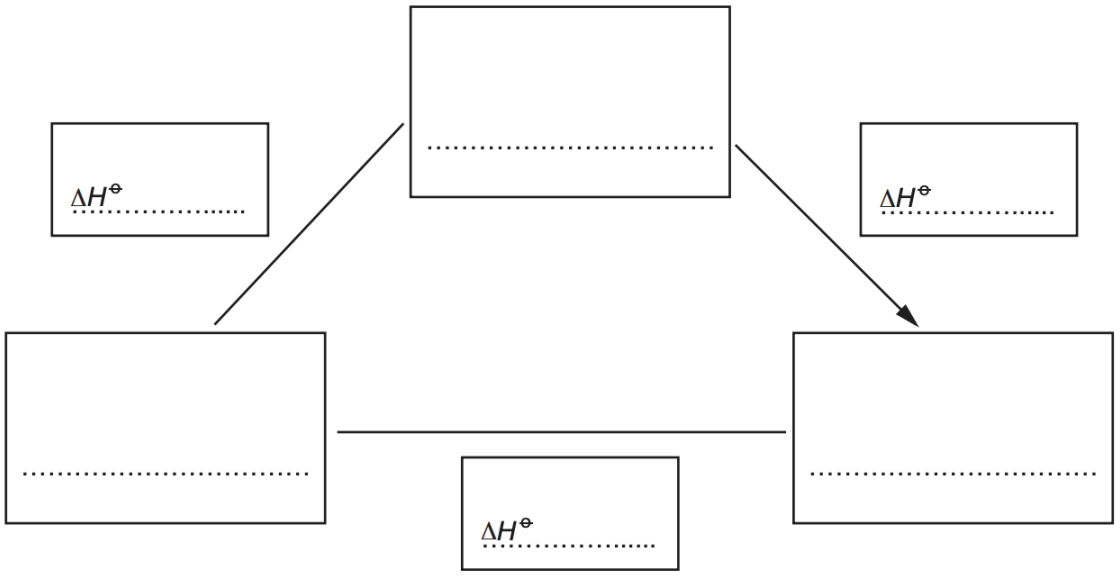
- Yes, it is slightly soluble as enthalpy change of solution is slightly exothermic/ negative.

(ii) Aluminium fluoride, AlF_3, is an ionic solid.

Complete and label the energy cycle to show the relationship between:

- the enthalpy change of solution of AlF_3, $\Delta H^{\ominus}_{sol}$
- the lattice energy of AlF_3, $\Delta H^{\ominus}_{latt}$
- the enthalpy changes of hydration of Al^{3+} and F^-, $\Delta H^{\ominus}_{hyd}$.

Include state symbols for all substances and ions.



[2]

(iii) Relevant data for this question are given.

$$\Delta H^{\ominus}_{sol} AlF_3 = -209\,kJ\,mol^{-1}$$

$$\Delta H^{\ominus}_{hyd} Al^{3+} = -4690\,kJ\,mol^{-1}$$

$$\Delta H^{\ominus}_{hyd} F^- = -506\,kJ\,mol^{-1}$$

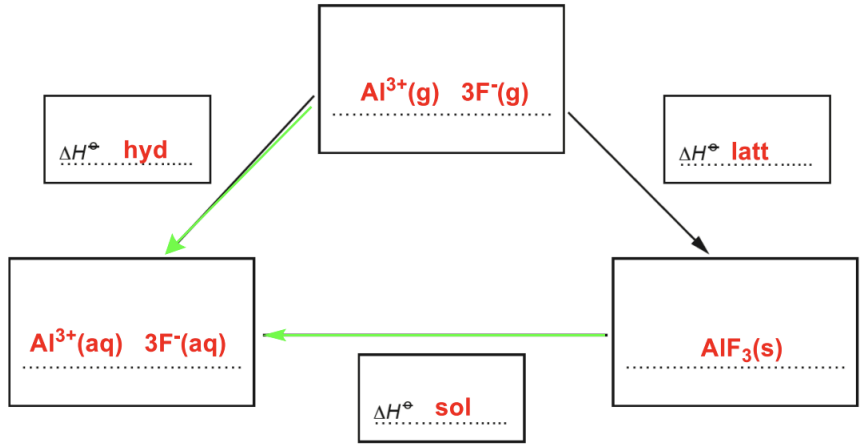
Use these data and your energy cycle in **(g)(ii)** to calculate the $\Delta H^{\ominus}_{latt}$ of AlF_3.

Substances with state symbols:

- Al F3(s)
- Al F3(aq) OR Al3+(aq) + (3)F⁻(aq)
- Al3+(g) (3)F⁻(g)

[1]

changes identified and three correct arrow directions (one given) [1]



ΔH_{latt} = –4690 + (3 × – 506) – (–209) = –5999 (kJ mol–1)

NOTE: remember to use the correct stoichiometric ratios!! 3F–

23.3 Entropy Change, ΔS

state of H_2O	standard entropy, $S^{\ominus}$ / J K^{-1} mol^{-1}
solid	+48.0
liquid	+70.1
gas	+188.7

Explain the difference in S° values of H2O(s) and H2O(l)

- H2O(l) particles / molecules have more randomness / disorder OR H2O(l) has more ways to arrange particles / energy (than in solid).

Explain why the increase in S° is much greater when H2O boils than when it melts.

- H2O(g) particles / molecules has much more randomness / disorder OR
- H2O(g) has many more ways to arrange particles / energy (than in liquid).

Define entropy

- number of possible arrangements of particles and energy in a system.

Predict the sign of the standard entropy change of the following reaction. Explain your answer.

$2H_2O_2(l) \rightarrow 2H_2O\ (l) + O_2\ (g)$

- positive / +
- more gas molecules / particles in products OR more moles / molecules in products / RHS

23.4 Gibbs Free Energy Change, ΔG

Carbon disulfide reacts with chlorine to form tetrachloromethane, as shown in reaction 2.

reaction 2 $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ $\Delta H^{\ominus} = -261.6\,kJ\,mol^{-1}$

$\Delta S^{\ominus} = -365.5\,J\,K^{-1}\,mol^{-1}$

Calculate the maximum temperature, in K, for reaction 2 to be feasible.

M1 $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ **AND** $\Delta G^{\ominus} = 0$
OR $T = \Delta H^{\ominus} / \Delta S^{\ominus}$ [1]

M2 $T = 261.6 \div 0.3655 = 715.7 / 716 / 715$ K min 3sf

A reaction is highly endothermic. Suggest the effect of an increase in temperature on the feasibility of this reaction. Explain your answer.

- As T increases, TΔS becomes greater than ΔH)
  OR as T increases, TΔS becomes more positive.
- As T increases, feasibility will increase as ΔG becomes more negative.