Topic 13: Energetics II

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

13.1 Be able to define lattice energy as the energy change when one mole of an ionic solid is formed from its gaseous ions.

Lattice energy (ΔLE): the enthalpy change when one mole of an ionic solid is formed from its gaseous ions under standard conditions.

E.g. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

Lattice energy is always exothermic (negative) because energy is released when the ionic lattice forms due to the strong electrostatic attraction between oppositely charged ions.

Note: Edexcel uses the formation definition (exothermic). Some textbooks define it as the energy to break apart the lattice (endothermic).

13.2 Be able to define the terms: (i) enthalpy change of atomisation, ΔatH, (ii) electron affinity.

(i) Enthalpy change of atomisation ($\Delta atH^{\ominus}$): the enthalpy change when one mole of gaseous atoms is formed from the element in its standard state. Always endothermic (positive).

E.g. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

(ii) First electron affinity (ΔEA1): the enthalpy change when one mole of gaseous atoms gains one mole of electrons to form one mole of gaseous 1– ions. Exothermic (negative) for most elements.

E.g. $Cl(g) + e^- \rightarrow Cl^-(g)$

Second electron affinity (ΔEA2): adding a second electron to an already negative ion is endothermic (positive) due to repulsion. E.g. $O^-(g) + e^- \rightarrow O^{2-}(g)$.

13.3 Be able to construct Born-Haber cycles and carry out related calculations.

A Born-Haber cycle is an application of Hess's Law to calculate lattice energy (or any other unknown step). The cycle links:

$\Delta fH^{\ominus}$ (enthalpy of formation of the ionic compound)

= ΔatH (metal) + ΔatH (non-metal) + IE (ionisation energies of metal) + EA (electron affinities of non-metal) + ΔLE (lattice energy)

Rearrange to find the unknown. Always be careful with signs – some steps are endothermic (+) and some exothermic (–). Draw the cycle as an energy level diagram with gaseous atoms/ions at the top and the ionic solid at the bottom.

13.4 Know that lattice energy provides a measure of ionic bond strength.

A more exothermic (more negative) lattice energy indicates stronger ionic bonding. This means more energy is released when the lattice forms, and more energy would be required to break it apart. Lattice energy depends on ionic charge and ionic radius.

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13.5 Understand that a comparison of experimental lattice energy (from Born-Haber cycle) with theoretical value (from electrostatic theory) indicates the degree of covalent bonding.

Theoretical lattice energy assumes the compound is perfectly ionic (spherical ions with no distortion).

Experimental lattice energy (from a Born-Haber cycle) reflects the actual bonding.

If the experimental value is more exothermic than the theoretical value, the compound has some covalent character – the cation has polarised the anion, increasing electron density between the ions.

E.g. AgI has significant covalent character (large discrepancy); NaCl has very little (values are close).

13.6 Understand the meaning of polarisation as applied to ions.

Polarisation is the distortion of the electron cloud of an anion by a nearby cation. The cation attracts the electron density of the anion towards itself, pulling the electron cloud out of shape. This introduces covalent character into an ionic bond.

13.7 Know that the polarising power of a cation depends on its radius and charge.

A cation has high polarising power if it has:

- A small ionic radius (charge is concentrated in a small volume)
- A high charge (greater attraction for the anion's electrons)

This gives a high charge density. E.g. Al^{3+} is highly polarising (small, 3+ charge); Na^{+} is weakly polarising (larger, 1+ charge).

13.8 Know that the polarisability of an anion depends on its radius and charge.

An anion is easily polarised if it has:

- A large ionic radius (outer electrons are far from the nucleus, loosely held)
- A high negative charge (more electrons to be distorted)

E.g. I^{-} is much more polarisable than F^{-} (larger radius). This is why AgI has more covalent character than AgF.

13.9 Be able to define the terms 'enthalpy change of solution, ΔsolH', and 'enthalpy change of hydration, ΔhydH'.

Enthalpy of solution ($\Delta solH^{\ominus}$): the enthalpy change when one mole of a solute dissolves in sufficient water to form an infinitely dilute solution. Can be exothermic or endothermic.

Enthalpy of hydration ($\Delta hydH^{\ominus}$): the enthalpy change when one mole of gaseous ions is surrounded by water molecules to form aqueous ions. Always exothermic (negative) because ion-dipole bonds form between the ion and water molecules.

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13.10 Be able to use energy cycles and energy level diagrams to carry out calculations involving enthalpy change of solution, enthalpy change of hydration and lattice energy.

The key relationship:

$\Delta sol H = -\Delta LE + \Delta hyd H(cation) + \Delta hyd H(anion)$

Draw a Hess's Law cycle:

- Top route: ionic solid → gaseous ions (reverse of lattice energy, so $+\Delta LE$) → aqueous ions ($\Delta hyd H$ for each ion)
- Bottom route: ionic solid → aqueous ions ($\Delta sol H$, directly)

If $\Sigma \Delta hyd H > |\Delta LE|$, dissolving is exothermic. If $\Sigma \Delta hyd H < |\Delta LE|$, dissolving is endothermic.

13.11 Understand the effect of ionic charge and ionic radius on the values of: (i) lattice energy, (ii) enthalpy change of hydration.

(i) Lattice energy becomes more exothermic with smaller ions (ions are closer, stronger attraction) and higher ionic charges (greater electrostatic attraction). E.g. MgO has a much more exothermic lattice energy than NaCl.

(ii) Enthalpy of hydration becomes more exothermic with smaller ions (higher charge density attracts water molecules more strongly) and higher charges. E.g. $\Delta hyd H$ of Mg^{2+} is more exothermic than Na^{+}.

13.12 Understand that, since some endothermic reactions can occur at room temperature, enthalpy changes alone do not control whether reactions occur.

Some endothermic reactions occur spontaneously at room temperature (e.g. dissolving NH_4NO_3 in water – the solution gets cold but it still dissolves). This shows that ΔH alone does not determine feasibility. There must be another factor – entropy – that also drives reactions.

13.13 Know that entropy is a measure of the disorder of a system and that the natural direction of change is increasing total entropy.

Entropy (S) is a measure of the disorder (number of possible arrangements) of a system. Units: $J\ K^{-1}\ mol^{-1}$.

The Second Law of Thermodynamics: the total entropy of the universe always increases for a spontaneous process. A reaction is feasible if $\Delta S total > 0$ (positive).

13.14 Understand why entropy changes occur during: (i) changes of state, (ii) dissolving of a solid ionic lattice, (iii) reactions with a change in moles of gas.

(i) Changes of state: solid → liquid → gas involves increasing disorder, so ΔS is positive. Reverse: ΔS is negative.

(ii) Dissolving: when an ionic solid dissolves, the ordered lattice breaks apart and ions become dispersed in solution → ΔS is usually positive.

(iii) Change in moles of gas: if moles of gas increase, ΔS is positive. If they decrease, ΔS is negative. Gases have much higher entropy than solids or liquids.

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13.15 Understand that the total entropy change is: ΔStotal = ΔSsystem + ΔSsurroundings.

For a reaction to be feasible (spontaneous): ΔStotal must be positive.

ΔStotal = ΔSsystem + ΔSsurroundings

ΔSsystem comes from the change in disorder of the reactants/products.

ΔSsurroundings comes from the heat transferred to/from the surroundings.

13.16 Be able to calculate the entropy change for the system, ΔSsystem, given the entropies of reactants and products.

ΔSsystem = ΣS(products) – ΣS(reactants)

Multiply each entropy value by its stoichiometric coefficient. Units: J K^{-1} mol^{-1}.

A positive value means the products are more disordered than the reactants.

13.17 Be able to calculate ΔSsurroundings, and hence ΔStotal, using: ΔSsurroundings = –ΔH / T.

ΔSsurroundings = –ΔH / T

Where ΔH is in J mol^{-1} (not kJ!) and T is in K.

For an exothermic reaction (ΔH negative): ΔSsurroundings is positive (heat released increases disorder of surroundings).

For an endothermic reaction (ΔH positive): ΔSsurroundings is negative.

Then: ΔStotal = ΔSsystem + ΔSsurroundings. If positive, the reaction is feasible.

13.18 Know that the balance between entropy and enthalpy determines feasibility, represented by ΔG = ΔH – TΔSsystem.

Gibbs free energy: ΔG = ΔH – TΔSsystem

A reaction is thermodynamically feasible when ΔG < 0 (negative).

ΔG < 0 can occur when:

- ΔH is negative and TΔS is positive (always feasible)
- ΔH is negative and |ΔS| is small (feasible at all temperatures)
- ΔH is positive but TΔS is large enough to overcome it (feasible at high temperatures)
- ΔH is negative but ΔS is negative (feasible at low temperatures)

Note: ΔH must be in kJ and ΔS in kJ K^{-1} (or convert consistently).

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13.19 Be able to use ΔG = ΔH – TΔSsystem to: (i) predict feasibility, (ii) determine the temperature at which a reaction becomes feasible.

(i) Feasibility: calculate ΔG. If ΔG < 0, the reaction is feasible. If ΔG > 0, it is not feasible under those conditions.

(ii) Temperature for feasibility: set ΔG = 0 and rearrange:

T = ΔH / ΔSsystem

Above this temperature (if ΔH > 0 and ΔS > 0) the reaction becomes feasible. Below it (if ΔH < 0 and ΔS < 0) the reaction is feasible. Ensure ΔH and ΔS have consistent units (both in kJ or both in J).

13.20 Be able to use ΔG = –RT ln K to show that feasible reactions have large K values and vice versa.

ΔG = –RT ln K where R = 8.314 J K^{-1} mol^{-1}, T in K.

Rearranging: ln K = –ΔG / RT

If ΔG is negative (feasible): ln K is positive, so K > 1 (products favoured).

If ΔG is positive (not feasible): ln K is negative, so K < 1 (reactants favoured).

If ΔG = 0: K = 1. This links thermodynamics to equilibrium quantitatively.

13.21 Understand why a reaction for which ΔG is negative may not occur in practice.

ΔG < 0 means a reaction is thermodynamically feasible but it may still not occur because:

- The activation energy may be too high (kinetic barrier) – the reaction is too slow to observe.
- The reaction may need a catalyst or an energy input to overcome the activation energy.

Thermodynamic feasibility ≠ kinetic feasibility. E.g. diamond → graphite is thermodynamically feasible but kinetically inert at room temperature.

13.22 Know that reactions that are thermodynamically feasible may be inhibited by kinetic factors.

Kinetic stability means a reaction does not proceed at a measurable rate despite being thermodynamically favourable. The rate of reaction depends on the activation energy, temperature, and presence of catalysts. A high activation energy acts as a kinetic barrier, preventing an otherwise feasible reaction from occurring.

ABOUT THESE NOTES

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