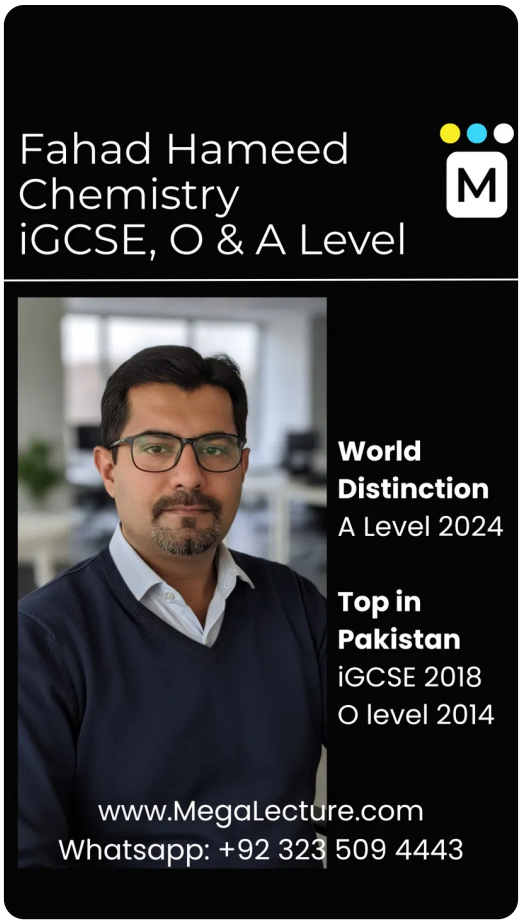
MEGA LECTURE · A LEVEL CHEMISTRY

Chapter 23: Enthalpy, Entropy and Free Energy

OCR A Level Chemistry A (H432) — Structured Practice Worksheet



SPECIFICATION	TOTAL MARKS	SUGGESTED TIME
3.3.4 Lattice enthalpy, Born–Haber cycles, entropy and free energy	96	1 hour 55 minutes

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Instructions to candidates

- Answer **all** questions in the spaces provided. Show all working in calculations.
- Marks are shown in brackets [ ] at the end of each part.

Question 1 — Lattice enthalpy: definitions 3.3.4

a. Define the standard lattice enthalpy of *formation* of an ionic compound. **[2]**

b. State whether this enthalpy change is always exothermic or endothermic, and explain why, in terms of the forces between ions. **[2]**

c. Define lattice *dissociation* enthalpy, and state how its value compares, in magnitude and sign, with the lattice formation enthalpy of the same compound. **[2]**

d. Write an equation, including state symbols, to represent the lattice formation enthalpy of magnesium oxide, MgO. **[2]**

Question 1 total: 8 marks

Question 2 — Constructing a Born–Haber cycle for NaCl 3.3.4

Enthalpy change	Value / kJ mol^{-1}
Enthalpy of formation of NaCl, ΔH_f	−411
Enthalpy of atomisation of Na, ΔH_{at}(Na)	+107
First ionisation energy of Na, IE_1(Na)	+496
Enthalpy of atomisation of Cl, ΔH_{at}(Cl)	+122

First electron affinity of Cl, EA_1(Cl)	−349

a. Sketch the Born–Haber cycle for NaCl as an energy level diagram, labelling each of the five enthalpy changes above and the lattice enthalpy of formation, ΔH_{latt}, in the correct relative positions and directions. **[4]**

Sketch: Born–Haber energy level cycle for NaCl

b. State why the first electron affinity of chlorine is exothermic, and explain why the second electron affinity of oxygen (relevant to a compound such as MgO) is endothermic. **[3]**

c. Using the data given, calculate the lattice enthalpy of formation of NaCl(s). Show all your working. **[6]**

d. Suggest why the experimental (Born–Haber) lattice enthalpy of a compound such as AgCl differs from a lattice enthalpy calculated theoretically assuming a perfect ionic model, and state what this suggests about the bonding in AgCl. **[3]**

Question 2 total: 16 marks

Question 3 — Trends in lattice enthalpy

3.3.4

a. The lattice enthalpy of MgO (−3791 kJ mol^{-1}) is much more exothermic than that of NaCl (−787 kJ mol^{-1}). Explain this difference with reference to ionic charge. **[3]**

b. The lattice enthalpy of NaCl (-787 kJ mol^{-1}) is more exothermic than that of KCl (-711 kJ mol^{-1}). Explain this difference with reference to ionic radius. **[3]**

c. Place the following in order of increasingly exothermic (more negative) lattice enthalpy, and explain your reasoning briefly: NaF, NaCl, NaBr. **[2]**

Question 3 total: 8 marks

Question 4 — Enthalpy of solution and enthalpy of hydration 3.3.4

$\Delta H_{latt}(NaCl) = -787$ kJ mol^{-1} $\Delta H_{hyd}(Na^+) = -406$ kJ mol^{-1} $\Delta H_{hyd}(Cl^-) = -364$ kJ mol^{-1}

a. Define the standard enthalpy of hydration of an ion. **[2]**

b. Define the standard enthalpy of solution of an ionic compound. **[2]**

c. Construct a Hess's law cycle linking $\Delta H_{latt}(NaCl)$, $\Delta H_{hyd}(Na^+)$, $\Delta H_{hyd}(Cl^-)$ and the enthalpy of solution of NaCl, ΔH_{sol}. **[3]**

Hess's law cycle: NaCl(s) → Na⁺(g) + Cl⁻(g) → Na⁺(aq) + Cl⁻(aq)

d. Calculate the standard enthalpy of solution of NaCl using the data given. Show your working. **[5]**

Question 4 total: 12 marks

Question 5 — Entropy: definition and predicting sign 3.3.4

a. Define *entropy*. **[2]**

b. State how the entropy of a substance changes as it changes from solid to liquid to gas, and explain why. **[2]**

c. Predict, with a reason, the sign of the entropy change of the system, ΔS, for each of the following reactions: **[4]**
(i) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(ii) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Question 5 total: 8 marks

Question 6 — Calculating entropy change and using ΔG = ΔH − TΔS 3.3.4

$S°(CaCO_3(s)) = 92.9\ J\ K^{-1}\ mol^{-1}$ $S°(CaO(s)) = 39.7\ J\ K^{-1}\ mol^{-1}$ $S°(CO_2(g)) = 213.6\ J\ K^{-1}\ mol^{-1}$

a. Write the expression used to calculate the standard entropy change of a reaction from the standard entropies of products and reactants. **[1]**

b. Calculate ΔS for the thermal decomposition of $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, using the data given. **[5]**

c. The standard entropy of vaporisation of water, $H_2O(l) \rightarrow H_2O(g)$, is +118.8 J K^{-1} mol^{-1} at 373 K, and ΔH_{vap} = +40.7 kJ mol^{-1}. Use $\Delta G = \Delta H - T\Delta S$ to calculate ΔG for vaporisation at 373 K and show that it is just feasible at this temperature. **[4]**

Question 6 total: 10 marks

Question 7 — Gibbs free energy 3.3.4

a. State the equation linking ΔG, ΔH, T and ΔS, and state the units of each term. **[2]**

b. State the criterion, in terms of ΔG, for a reaction to be thermodynamically feasible. **[2]**

c. For the decomposition $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, ΔH = +178 kJ mol^{-1} and ΔS = +160.4 J K^{-1} mol^{-1}. Calculate ΔG for this reaction at 25 °C (298 K), and state whether the reaction is feasible at this temperature. **[6]**

Question 7 total: 10 marks

Question 8 — Feasibility and temperature 3.3.4

For the decomposition $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$: $\Delta H = +178$ kJ mol^{-1}, $\Delta S = +160.4$ J K^{-1} mol^{-1} (assume both are independent of temperature).

a. Derive an expression for the temperature above which this reaction becomes feasible, starting from $\Delta G = \Delta H - T\Delta S$. **[3]**

b. Calculate the minimum temperature, in K and in °C, at which the decomposition of $CaCO_3$ becomes feasible. **[6]**

c. State and explain the effect of increasing temperature above this value on the feasibility of the reaction, and explain why, in practice, the reaction may not occur instantly even above this temperature. **[3]**

Question 8 total: 12 marks

Question 9 — Limitations of ΔG as a predictor of feasibility 3.3.4

a. The conversion C(diamond) → C(graphite) has a negative ΔG at room temperature, yet diamond does not visibly convert to graphite even over very long periods of time. Explain why. **[3]**

b. State three factors, other than the sign of ΔG, that determine whether a thermodynamically feasible reaction will actually be observed to occur at a measurable rate. **[3]**

Question 9 total: 6 marks

Question 10 — Extended response

Synoptic

The thermal decomposition of calcium carbonate, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, has $\Delta H = +178$ kJ mol^{-1} and $\Delta S = +160.4$ J K^{-1} mol^{-1}. Using ideas about enthalpy, entropy and free energy, explain why this reaction does not occur spontaneously at room temperature but does occur in industrial lime kilns at high temperature, and discuss the limitations of using ΔG alone to predict whether a reaction will actually be observed to happen. **[6]**

This question is marked using a level of response.

Question 10 total: 6 marks

PAPER TOTAL: 96 MARKS

MARK SCHEME — Chapter 23: Enthalpy, Entropy and Free Energy

Award marks independently unless stated. ECF applies to calculations.

Q1 (a) [2]

- The enthalpy change when 1 mole of a solid ionic compound is formed from its constituent gaseous ions (1), under standard conditions (298 K, 100 kPa) (1).

Q1 (b) [2]

- Always exothermic (negative) (1).
- Because attractive electrostatic forces form between oppositely charged gaseous ions as they come together to form the solid lattice, releasing energy (1).

Q1 (c) [2]

- The enthalpy change when 1 mole of a solid ionic lattice is separated (dissociated) into its constituent gaseous ions (the reverse process) (1).
- Equal in magnitude but opposite in sign to the lattice formation enthalpy (always endothermic/positive) (1).

Q1 (d) [2]

- $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$ (2) — (1 for correct species/balancing, 1 for correct state symbols and direction)

Q2 (a) [4]

- Correct overall cycle shape linking Na(s) + ½Cl_2(g) to gaseous atoms to gaseous ions to solid NaCl(s), with arrows in appropriate directions (1).
- ΔH_{at}(Na) and ΔH_{at}(Cl) shown as separate endothermic steps (upward arrows) from elements to gaseous atoms (1).
- IE_1(Na) shown as endothermic (upward arrow); EA_1(Cl) shown as exothermic (downward arrow) (1).
- ΔH_{latt} shown as the exothermic step from gaseous ions $Na^+(g) + Cl^-(g)$ to solid NaCl(s), and ΔH_f shown as the direct (single-step) route from elements to solid (1).

Q2 (b) [3]

- EA_1 of Cl is exothermic because a gaseous Cl atom attracts an added electron into its outer shell due to the attraction of the nuclear charge, releasing energy (1).
- EA_2 of oxygen is endothermic because an electron is being added to an already negatively charged ion (O^-) (1).
- The repulsion between the negative ion and the incoming electron requires energy input to overcome, which outweighs any energy released (1).

Q2 (c) [6]

- $\Delta H_f = \Delta H_{at}(Na) + IE_1(Na) + \Delta H_{at}(Cl) + EA_1(Cl) + \Delta H_{latt}$ (correct cycle equation set up) (1)
- $-411 = 107 + 496 + 122 + (-349) + \Delta H_{latt}$ (correct substitution) (1)
- $-411 = 376 + \Delta H_{latt}$ (sum of known terms = 376) (1)
- $\Delta H_{latt} = -411 - 376$ (1)
- $\Delta H_{latt} = -787$ kJ mol^{-1} (1)
- Negative value confirms an exothermic lattice formation enthalpy, as expected (1)

Q2 (d) [3]

- The experimental (Born–Haber) value is more exothermic (larger negative) than the theoretical value calculated assuming a perfect ionic model (1).
- This suggests there is some covalent character (electron sharing/polarisation of the anion) in the bonding, rather than the bonding being perfectly ionic (1).
- Ag^+ has a high polarising power (small, high charge density), which distorts/polarises the electron cloud of Cl^-, increasing the bond strength (1).

Q3 (a) [3]

- Mg^{2+} and O^{2-} ions have greater ionic charge than Na^+ and Cl^- (2+ and 2− vs 1+ and 1−) (1).
- The electrostatic force of attraction between ions is proportional to the product of their charges (1).
- The greater charges in MgO result in much stronger ionic attraction, so more energy is released forming the lattice (1).

Q3 (b) [3]

- Na^+ has a smaller ionic radius than K^+ (fewer electron shells) (1).
- Smaller ions can pack more closely together, so the distance between the centres of oppositely charged ions is smaller (1).
- Electrostatic attraction increases as the distance between ion centres decreases, so lattice enthalpy is more exothermic for NaCl than KCl (1).

Q3 (c) [2]

- Correct order (least to most exothermic): NaBr < NaCl < NaF, i.e. NaF is most exothermic (1).
- Ionic radius increases down the group, $F^- < Cl^- < Br^-$, so attraction (and lattice enthalpy magnitude) decreases as anion radius increases (1).

Q4 (a) [2]

- The enthalpy change when 1 mole of a specified gaseous ion is dissolved in water (1), to form an infinitely dilute solution, under standard conditions (1).

Q4 (b) [2]

- The enthalpy change when 1 mole of an ionic solid dissolves in water (1), to form an infinitely dilute solution, under standard conditions (1).

Q4 (c) [3]

- Cycle shows $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$, the reverse of the lattice formation enthalpy (i.e. $-\Delta H_{latt}$) (1).
- $Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq)$, the sum of the two hydration enthalpies (1).
- Direct route $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq) = \Delta H_{sol}$, giving (by Hess's law) $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}(Na^+) + \Delta H_{hyd}(Cl^-)$ (1).

Q4 (d) [5]

- $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}(Na^+) + \Delta H_{hyd}(Cl^-)$ (1)
- $= -(-787) + (-406) + (-364)$ (1)
- $= 787 - 406 - 364$ (1)
- $= +17$ kJ mol^{-1} (1)
- The positive value shows that dissolving NaCl is slightly endothermic overall (1)

Q5 (a) [2]

- A measure of the number of ways particles (and their quanta of energy) can be arranged (1); i.e. a measure of the disorder of a system (1).

Q5 (b) [2]

- Entropy increases from solid → liquid → gas (1).
- Because there are more ways to arrange the particles and their energy, as particles have greater freedom of movement and become more disordered (1).

Q5 (c) [4]

- (i) ΔS positive (1); because a gas is produced from a solid — the number of moles of gas increases from 0 to 1, increasing the number of ways of arranging particles/energy (disorder) (1).
- (ii) ΔS negative (1); because the number of moles of gas decreases from 4 to 2, decreasing the number of ways of arranging particles/energy (disorder) (1).

Q6 (a) [1]

- $\Delta S = \Sigma S°(products) - \Sigma S°(reactants)$ (1)

Q6 (b) [5]

- $\Sigma S°(products) = 39.7 + 213.6 = 253.3$ J K^{-1} mol^{-1} (1)
- $\Sigma S°(reactants) = 92.9$ J K^{-1} mol^{-1} (1)
- $\Delta S = 253.3 - 92.9$ (1)
- $\Delta S = +160.4$ J K^{-1} mol^{-1} (1)
- Positive value is consistent with a gas being produced from solid reactants, increasing disorder (1)

Q6 (c) [4]

- $\Delta G = \Delta H - T\Delta S$ (1)
- $= 40700 - (373 \times 118.8)$ (converting ΔH to J mol^{-1}, consistent units) (1)
- $= 40700 - 44312.4$ (1)
- $= -3612$ J mol^{-1} (≈ -3.6 kJ mol^{-1}); negative ΔG confirms vaporisation is (just) feasible at 373 K (1)

Q7 (a) [2]

- $\Delta G = \Delta H - T\Delta S$ (1)
- ΔG and ΔH in J mol^{-1} (or kJ mol^{-1}), T in kelvin, ΔS in J K^{-1} mol^{-1} (1)

Q7 (b) [2]

- A reaction is thermodynamically feasible when $\Delta G \leq 0$ (1); i.e. ΔG is zero or negative (1).

Q7 (c) [6]

- T = 298 K (converting 25 °C to kelvin) (1)
- $\Delta S = 160.4$ J K^{-1} mol^{-1} = 0.1604 kJ K^{-1} mol^{-1} (converting to consistent (kJ) units) (1)
- $\Delta G = \Delta H - T\Delta S = 178 - (298 \times 0.1604)$ (1)
- $= 178 - 47.8$ (1)
- $= +130.2$ kJ mol^{-1} (1)
- ΔG is positive, so the reaction is not feasible at 298 K (1)

Q8 (a) [3]

- At the temperature where the reaction becomes just feasible, $\Delta G = 0$ (1).
- $0 = \Delta H - T\Delta S$ (1).
- Rearranging: $T = \Delta H / \Delta S$ (1).

Q8 (b) [6]

- Convert ΔH to J mol^{-1}: 178 kJ mol^{-1} = 178 000 J mol^{-1} (1)
- $T = \Delta H / \Delta S = 178\,000 \div 160.4$ (1)
- = 1109.7 K (1)
- T ≈ 1110 K (3 s.f.) (1)
- In °C: 1110 − 273 = 837 °C (1)
- This is consistent with the industrial temperatures (approximately 900–1000 °C) used in lime kilns (1)

Q8 (c) [3]

- Above this temperature, ΔG becomes negative (and increasingly negative as T rises further), so the reaction becomes increasingly thermodynamically feasible (1).
- However, ΔG (feasibility) gives no information about the rate of the reaction (1).
- The reaction may still proceed slowly in practice due to a high activation energy/kinetic barrier, even though it is thermodynamically favourable (1).

Q9 (a) [3]

- A negative ΔG shows the reaction is thermodynamically feasible (favourable) (1).
- But ΔG gives no information about the rate of reaction (1).
- The reaction has a very high activation energy (strong C–C covalent bonds must break), so at room temperature the rate is immeasurably slow — the reaction is kinetically controlled (1).

Q9 (b) [3]

- Any three from: activation energy/height of the energy barrier; temperature (affects the proportion of particles with $E \geq E_a$); presence or absence of a catalyst; collision frequency/concentration or pressure of reactants. (3 × 1, max 3)

Q10 [6] — Level of response

- **Level 3 (5–6):** Explains fully and correctly why ΔG is positive at room temperature but negative at high temperature (using $\Delta G = \Delta H - T\Delta S$), and clearly discusses the limitation that ΔG says nothing about reaction rate.
- **Level 2 (3–4):** Explains the temperature dependence of ΔG reasonably well, with only a partial discussion of the rate limitation, or vice versa.
- **Level 1 (1–2):** States that temperature affects feasibility and/or that ΔG has limitations, with limited or generic reasoning.

Indicative content: *Since ΔH (+178 kJ mol^{-1}) and ΔS (+160.4 J K^{-1} mol^{-1}) are both positive, the −TΔS term becomes more negative as T increases, so ΔG = ΔH − TΔS decreases (becomes less positive, then negative) as temperature rises. At 298 K, ΔG is positive (+130.2 kJ mol^{-1}) so the reaction is not feasible; above approximately 1110 K, ΔG becomes negative/zero and the reaction becomes thermodynamically feasible, which is why lime kilns operate at very high temperatures. However, ΔG only indicates whether a reaction is thermodynamically feasible (whether it could happen); it gives no information about the rate at which it will happen. A reaction with negative ΔG can still be extremely slow if it has a high activation energy (kinetically controlled), so ΔG alone cannot be used to predict whether a reaction will actually be observed to occur within a reasonable timescale — this must be assessed separately, e.g. using activation energy or rate data.*

END OF MARK SCHEME · 96 marks