2.3 Energetics and Thermodynamics

AQA 7405 · Calculator allowed · about 215 minutes · Write-in edition

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Methane reacts with chlorine in a substitution reaction: $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$. Mean bond enthalpies (kJ/mol): C-H = +413, Cl-Cl = +242, C-Cl = +346, H-Cl = +431.

(a) State what is meant by the term mean bond enthalpy. **(2)**

(b) Calculate the enthalpy change for this reaction using the mean bond enthalpies given. Show your working. **(3)**

(c) Explain why a value calculated using mean bond enthalpies may differ from the actual (experimentally measured) enthalpy change for this reaction. **(2)**

(d) State one other limitation of using mean bond enthalpies, in terms of the physical states of the reactants and products. **(1)**

(Total for Question 1 is 8 marks)

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2 This question tests key definitions used throughout the energetics and thermodynamics topic.

(a) State what is meant by the standard enthalpy of formation of a compound. **(1)**

(b) State what is meant by the standard enthalpy of combustion of a substance. **(1)**

(c) State what is meant by the standard enthalpy of atomisation of an element. **(1)**

(d) State Hess's law. **(1)**

(Total for Question 2 is 4 marks)

3 Standard enthalpies of combustion (kJ/mol): delta Hc[C(s)] = -393, delta Hc[H_2(g)] = -286, delta Hc[CH_4(g)] = -890.

(a) Write a balanced equation, including state symbols, to represent the standard enthalpy of formation of methane. **(2)**

(b) Using a Hess's law cycle and the enthalpies of combustion given, calculate the standard enthalpy of formation of methane. Show your working. **(3)**

(c) The accepted literature value for the standard enthalpy of formation of methane is -74.8 kJ/mol. Comment on the agreement between your calculated value and this literature value. **(1)**

(d) State Hess's law. **(2)**

(Total for Question 3 is 8 marks)

4 Standard entropies, S degree, at 298 K: $N_2(g)$ = 192 J/(K mol), $H_2(g)$ = 131 J/(K mol), $NH_3(g)$ = 193 J/(K mol). Reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

(a) State what is meant by the term entropy. **(1)**

(b) Predict, with a reason, whether you expect the entropy change for this reaction to be positive or negative, before doing any calculation. **(2)**

(c) Calculate the standard entropy change, delta S, for this reaction. **(3)**

(Total for Question 4 is 6 marks)

5 A student determines the enthalpy of combustion of ethanol using a simple calorimetry method, as in the required practical for measuring an enthalpy change. A spirit burner containing ethanol is weighed, then used to heat 150 g of water in a copper calorimeter; the maximum temperature reached is recorded, and the spirit burner is reweighed.

Data:

mass of water = 150 g

initial temperature of water = 18.5°C

final (maximum) temperature of water = 40.5°C

initial mass of spirit burner + ethanol = 78.23 g

final mass of spirit burner + ethanol = 77.39 g

specific heat capacity of water, c = 4.18 J/(g K)

Mr(ethanol, C_2H_5OH) = 46.0

(a) Calculate the temperature rise of the water. **(1)**

(b) Calculate the mass of ethanol burned during the experiment. **(1)**

(c) Calculate the energy transferred to the water, q = m x c x delta T, giving your answer in kJ. **(2)**

(d) Calculate the amount, in mol, of ethanol burned. **(1)**

(e) Calculate the experimental enthalpy of combustion of ethanol, delta Hc, in kJ/mol. Give your answer to 3 significant figures. **(2)**

(f) The literature value for the standard enthalpy of combustion of ethanol is -1367 kJ/mol. Calculate the percentage difference between the experimental value and the literature value. **(2)**

(g) Suggest two reasons why the experimental value is much less exothermic than the literature value. **(2)**

(Total for Question 5 is 11 marks)

6 Enthalpy of hydration of $Na^+(g)$ ion = -406 kJ/mol. Lattice dissociation enthalpy of NaCl(s) = +771 kJ/mol. Enthalpy of solution of NaCl(s) = +3.9 kJ/mol.

(a) Define enthalpy of hydration. **(2)**

(b) Construct a Hess's law cycle linking the enthalpy of solution, the lattice dissociation enthalpy and the two enthalpies of hydration for NaCl, and use it to calculate the enthalpy of hydration of the chloride ion, $Cl^-(g)$. Show your working. **(4)**

(c) The small positive value for the enthalpy of solution of NaCl shows that dissolving NaCl is only very slightly endothermic overall. Explain what this tells you about the relative magnitudes of the lattice dissociation enthalpy and the total enthalpy of hydration of the ions. **(2)**

(Total for Question 6 is 8 marks)

7 A student reacts 25.0 cm^3 of 1.00 mol/dm3 hydrochloric acid with 25.0 cm^3 of 1.00 mol/dm3 sodium hydroxide solution in an insulated polystyrene cup, as in the required practical for measuring an enthalpy change. Initial temperature of both solutions = 19.2°C. Maximum temperature reached = 26.0°C. Assume the density of the solution is 1.00 g/cm3 and its specific heat capacity is 4.18 J/(g K).

(a) Calculate the total mass of solution in the calorimeter. **(1)**

(b) Calculate the heat energy released in the reaction. **(2)**

(c) Calculate the amount, in mol, of HCl (and of NaOH) that reacted. **(1)**

(d) Calculate the enthalpy change of neutralisation, delta Hneut, in kJ/mol. **(2)**

(Total for Question 7 is 6 marks)

8 This question uses standard enthalpies of formation and Hess's law to calculate the enthalpy of combustion of propane.

(a) Write a balanced symbol equation, including state symbols, for the complete combustion of propane, C_3H_8. **(2)**

(b) Standard enthalpies of formation (kJ/mol): $C_3H_8(g)$ = -104, $CO_2(g)$ = -393, $H_2O(l)$ = -286. Calculate the standard enthalpy of combustion of propane using Hess's law. **(5)**

(c) The literature value for the enthalpy of combustion of propane is -2220 kJ/mol. Comment on the agreement between this value and your calculated value in (b). **(2)**

(Total for Question 8 is 9 marks)

9 This question is about a calorimetry experiment to determine the enthalpy of solution of ammonium nitrate.

(a) A student investigates the enthalpy of solution of ammonium nitrate. 5.00 g of solid NH_4NO_3 (Mr = 80.0) is added to 100 g of water in an insulated cup; the total mass of the resulting solution is 105 g. Calculate the number of moles of NH_4NO_3 used. **(2)**

(b) The temperature of the solution falls from 20.5°C to 15.8°C. Assuming the specific heat capacity of the solution is 4.18 J/(g K), calculate the heat energy, q, absorbed from the solution during dissolving. **(3)**

(c) Hence calculate the molar enthalpy of solution of ammonium nitrate, and state its sign. **(4)**

(Total for Question 9 is 9 marks)

10 The table gives enthalpy data needed to construct a Born-Haber cycle for magnesium chloride, $MgCl_2$.

Enthalpy of formation of $MgCl_2$(s), delta Hf = -641 kJ/mol
Enthalpy of atomisation of Mg(s), delta Hat = +148 kJ/mol
First ionisation energy of Mg, IE1 = +738 kJ/mol
Second ionisation energy of Mg, IE2 = +1451 kJ/mol
Enthalpy of atomisation of chlorine (per mole of Cl atoms), delta Hat = +122 kJ/mol
Electron affinity of Cl, EA = -349 kJ/mol

(a) Define the term first ionisation energy. **(2)**

(b) Explain why the enthalpy of atomisation of chlorine is given as a value per mole of Cl atoms, rather than per mole of Cl_2 molecules. **(1)**

(c) Using the data given, construct a Born-Haber cycle and calculate the lattice enthalpy of formation of magnesium chloride, $MgCl_2$. Show all steps in your working. **(4)**

(d) The theoretical (calculated) lattice enthalpy of $MgCl_2$, based on a perfect ionic model, is -2326 kJ/mol. Compare this with your Born-Haber (experimental) value from part (c), and suggest what this comparison indicates about the bonding in $MgCl_2$. **(2)**

(Total for Question 10 is 9 marks)

11 For the Haber process, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, delta H = -92.0 kJ/mol and delta S = -199 J/(K mol) (as calculated in Question 4(c)). Use delta G = delta H - T x delta S to answer the following.

(a) Calculate delta G for this reaction at 298 K, in kJ/mol. Show your working. **(3)**

(b) State, with a reason, whether this reaction is thermodynamically feasible at 298 K. **(1)**

(c) Calculate the temperature above which this reaction is no longer thermodynamically feasible (i.e. the temperature at which delta G = 0). Give your answer in kelvin. **(3)**

(d) The Haber process is actually carried out industrially at a compromise temperature of around 450°C (723 K), well above the temperature calculated in part (c). Suggest why, in terms of reaction rate and the position of equilibrium, an operating temperature above the calculated feasibility temperature might still be used industrially. **(3)**

(Total for Question 11 is 10 marks)

12 In the ethanol combustion calorimetry experiment described in Question 5, the temperature rise was found to be 22.0°C (using a thermometer that could be read to the nearest 0.5°C) and the mass of ethanol burned was found to be 0.84 g (using a balance that could be read to the nearest 0.01 g). The calculated enthalpy of combustion was delta Hc = -755 kJ/mol. Each quantity (temperature and mass) required two readings (an initial and a final reading) to obtain the value used.

(a) Calculate the total (absolute) uncertainty in the temperature rise, given that each individual thermometer reading has an uncertainty of ± 0.5°C. **(1)**

(b) Calculate the percentage uncertainty in the temperature rise. **(1)**

(c) Calculate the percentage uncertainty in the mass of ethanol burned, given that each individual mass reading has an uncertainty of ± 0.01 g. **(2)**

(d) Hence estimate the total percentage uncertainty in the calculated enthalpy of combustion, and use this to give the value with its absolute uncertainty (in kJ/mol), to an appropriate precision. **(3)**

(Total for Question 12 is 7 marks)

13 Calcium carbonate decomposes on heating: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. For this reaction, delta H = +178 kJ/mol and delta S = +161 J/(K mol).

(a) Explain why delta S is positive for this reaction. **(1)**

(b) Calculate the minimum temperature, in kelvin, at which this decomposition becomes thermodynamically feasible. **(3)**

(Total for Question 13 is 4 marks)

14 Industrially, calcium carbonate (limestone) is decomposed in a lime kiln at temperatures of around 1200 K. Using the data given in Question 13 for this reaction (delta H = +178 kJ/mol, delta S = +161 J/(K mol), and delta G = delta H - T x delta S), explain why this reaction does not occur spontaneously at room temperature (298 K) but does become thermodynamically feasible at the temperature used industrially.

(Total for Question 14 is 6 marks)

15 In the experiment described in Question 7, the student then repeats the experiment using 25.0 cm^3 of 1.00 mol/dm3 ethanoic acid (a weak acid) in place of the hydrochloric acid, keeping the volume and concentration of sodium hydroxide, and all other conditions, the same. The temperature rise recorded is smaller than in the original experiment with hydrochloric acid, giving a less exothermic enthalpy of neutralisation.

Explain, in terms of the energy changes involved, why the enthalpy of neutralisation for ethanoic acid is less exothermic (smaller in magnitude) than for hydrochloric acid.

(Total for Question 15 is 6 marks)

16 This synoptic question links the thermodynamics of the N_2O_4/NO_2 equilibrium to its equilibrium constant and the effect of temperature.

(a) For the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, delta H = +57.2 kJ/mol and delta S = +176 J/(K mol) (assume both are constant with temperature). Calculate delta G for this reaction at 298 K, in kJ/mol. **(3)**

(b) State what the sign of delta G found in (a) indicates about the position of equilibrium at 298 K, and relate this to the fact that N_2O_4 is the predominant species present at room temperature. **(2)**

(c) Use the relationship delta G = -RT ln K, with R = 8.31 J/(K mol), to calculate the equilibrium constant, K, for this reaction at 298 K. **(4)**

(d) Calculate delta G and hence K at 350 K (assume delta H and delta S remain constant), and use your results to explain, in terms of Le Chatelier's principle, why K increases with temperature for this reaction. **(3)**

(Total for Question 16 is 12 marks)

17 This question uses a Born-Haber cycle to determine the lattice enthalpy of formation of calcium oxide.

(a) The bond dissociation enthalpy of $O_2(g)$ is +498 kJ/mol. Calculate the atomisation enthalpy of oxygen, 1/2 $O_2(g)$ -> O(g). **(2)**

(b) Explain why the second ionisation energy of calcium, Ca+(g) -> $Ca^{2+}(g)$ + e-, is greater than the first ionisation energy, Ca(g) -> Ca+(g) + e-. **(2)**

(c) Explain why the second electron affinity of oxygen, O-(g) + e- -> $O^{2-}(g)$, is endothermic even though it brings together a negative ion and an electron. **(2)**

(d) Using delta Hf(CaO) = -635 kJ/mol, atomisation enthalpy of Ca = +178 kJ/mol, first ionisation energy of Ca = +590 kJ/mol, second ionisation energy of Ca = +1145 kJ/mol, atomisation enthalpy of O (from (a), ft) = +249 kJ/mol, first electron affinity of O = -141 kJ/mol, and second electron affinity of O = +798 kJ/mol, use a Born-Haber cycle (Hess's law) to calculate the lattice enthalpy of formation of CaO ($Ca^{2+}(g)$ + $O^{2-}(g)$ -> CaO(s)). **(6)**

(Total for Question 17 is 12 marks)

18 In the experiment described in Question 9, the student's calculated enthalpy of solution for ammonium nitrate (+33.0 kJ/mol) was larger in magnitude than the accepted data book value of +25.7 kJ/mol. Evaluate possible reasons for this difference, and suggest improvements to the experimental method that would improve the accuracy of the result.

(Total for Question 18 is 6 marks)

19 This question analyses the measurement uncertainty in the calorimetry experiment described in Question 9.

(a) The 5.00 g mass of NH_4NO_3 in Question 9 was found by weighing a sample bottle before and after adding the solid to the calorimeter, using a balance that reads to ± 0.005 g per reading. State the absolute uncertainty in the 5.00 g mass value, and calculate its percentage uncertainty. **(3)**

(b) A digital thermometer reading to the nearest 0.1°C (uncertainty ± 0.05°C per reading) was used for both the initial and final temperature readings, giving a temperature change of 4.7°C. Calculate the absolute and percentage uncertainty in this temperature change. **(3)**

(c) Hence estimate the overall percentage uncertainty in the calculated enthalpy of solution, and identify which measurement contributes the larger share of this uncertainty. **(2)**

(d) Using your answer to (c) and the enthalpy of solution calculated in Question 9 (+33.0 kJ/mol), express the result with its absolute uncertainty, to an appropriate number of significant figures. **(2)**

(Total for Question 19 is 10 marks)

Mark scheme · 2.3 Energetics and Thermodynamics

Question 1

(a) the (average) energy required to break one mole of a specified covalent bond **B1**

(a) averaged over that type of bond in a range of different gaseous molecules/compounds oe **B1**

(a) Answer: The average energy needed to break one mole of a given covalent bond, averaged over many different gaseous compounds containing that bond.

(b) bonds broken = C-H + Cl-Cl = 413 + 242 (= 655 kJ/mol) **M1**

(b) bonds formed = C-Cl + H-Cl = 346 + 431 (= 777 kJ/mol) **M1**

(b) delta H = 655 - 777 = -122 (kJ/mol) cao **A1**

(b) Answer: delta H = -122 kJ/mol

(c) mean bond enthalpies are average values, taken across many different compounds containing that bond oe **M1**

(c) the actual bond enthalpy for a specific bond in this particular molecule may differ from the mean value used, so the calculated delta H is only an approximation oe **M1**

(c) Answer: Mean bond enthalpies are averaged over many compounds, so the true bond enthalpy in CH_4, CH_3Cl and HCl may differ slightly from the mean value used, making the calculated delta H only an approximate value.

(d) mean bond enthalpies apply only to gaseous species; they cannot be used directly if any reactant or product is not in the gas phase (e.g. a liquid or solid) oe **B1**

(d) Answer: Mean bond enthalpies are only valid for substances in the gaseous state, so cannot be used directly for reactions involving liquids or solids.

Question 2

(a) the enthalpy change when 1 mole of a compound is formed from its elements in their standard states, under standard conditions, oe **B1**

(a) Answer: Enthalpy change forming 1 mole of compound from its elements in standard states.

(b) the enthalpy change when 1 mole of a substance is completely combusted in excess oxygen, under standard conditions, with all reactants and products in their standard states, oe **B1**

(b) Answer: Enthalpy change when 1 mole of a substance is completely burned in excess oxygen under standard conditions.

(c) the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state, under standard conditions, oe **B1**

(c) Answer: Enthalpy change forming 1 mole of gaseous atoms from the element in its standard state.

(d) the total enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions (states) are the same, oe **B1**

(d) Answer: Total enthalpy change is independent of route, provided initial and final states are the same.

Question 3

(a) $C(s) + 2H_2(g) \rightarrow CH_4(g)$, correctly balanced **M1**

(a) all state symbols correct: (s), (g), (g) cao **A1**

(a) Answer: $C(s) + 2H_2(g) \rightarrow CH_4(g)$

(b) correct Hess's law relationship: delta $Hf(CH_4)$ = delta $Hc(C)$ + 2 x delta $Hc(H_2)$ - delta $Hc(CH_4)$ (oe, allow a correctly drawn or described cycle) **M1**

(b) correct substitution: -393 + 2 x (-286) - (-890) **M1**

(b) delta $Hf(CH_4)$ = -75 (kJ/mol) cao **A1**

(b) Answer: delta $Hf(CH_4)$ = -75 kJ/mol

(c) very good/close agreement (within about 1 kJ/mol, less than 1-2% difference) oe; any sensible comment referencing the closeness of the two values, ecf from (b) **B1**

(c) Answer: Very good agreement - the calculated value (-75 kJ/mol) is within about 1 kJ/mol of the literature value (-74.8 kJ/mol).

(d) the total enthalpy change of a reaction is independent of the route taken **B1**

(d) provided the initial and final conditions/states are the same in each route oe **B1**

(d) Answer: The total enthalpy change of a reaction is independent of the route taken, provided the initial and final conditions are the same.

Question 4

(a) a measure of the number of ways particles (and their energy) can be arranged/distributed (a measure of disorder) oe **B1**

(a) Answer: A measure of the number of ways that particles (and their energy) can be arranged - i.e. a measure of disorder.

(b) negative **B1**

(b) because the number of moles of gas decreases (4 mol of gas reactants forms 2 mol of gas product), so there are fewer ways to arrange the particles (disorder decreases) oe **B1**

(b) Answer: Negative, because 4 mol of gas reactants form only 2 mol of gas product, decreasing the number of ways the particles can be arranged.

(c) delta S = sum S(products) - sum S(reactants), set up correctly **M1**

(c) correct substitution: 2 x 193 - [192 + 3 x 131] **M1**

(c) delta S = -199 (J/(K mol)) cao **A1**

(c) Answer: delta S = -199 J/(K mol)

Question 5

(a) 22.0 (°C) cao **B1**

(a) Answer: 22.0°C

(b) 0.84 (g) cao **B1**

(b) Answer: 0.84 g

(c) correct substitution q = 150 x 4.18 x 22.0 (= 13794 J), ecf from (a) **M1**

(c) 13.8 (kJ) awrt (accept 13794 J), cao **A1**

(c) Answer: q = 13.8 kJ (13794 J)

(d) 0.0183 (mol) cao, ecf from (b) **B1**

(d) Answer: 0.0183 mol

(e) delta Hc = -q / n, ecf from (c) and (d) **M1**

(e) -755 (kJ/mol) awrt, cao, ecf **A1**

(e) Answer: delta Hc = -755 kJ/mol

(f) correct substitution: (1367-755)/1367 x 100, ecf from (e) **M1**

(f) 44.8 (%) awrt (accept 44.7-44.8%), ecf **A1**

(f) Answer: 44.8% (the experimental value is about 44.8% less exothermic than the literature value)

(g) heat loss to the surroundings (not all the energy released is transferred to the water) oe **B1**

(g) incomplete combustion of the ethanol (some carbon forms soot/CO rather than CO_2, releasing less energy) oe; accept heat capacity of the calorimeter/apparatus not accounted for, or evaporation of ethanol before combustion - max 2 sensible reasons **B1**

(g) Answer: Any two of: heat loss to the surroundings; incomplete combustion (soot/CO formed); heat capacity of the calorimeter not included; evaporation of ethanol.

Question 6

(a) the enthalpy change when one mole of gaseous ions is dissolved in (sufficient) water **B1**

(a) to form one mole of aqueous ions, under standard conditions (at infinite dilution) oe **B1**

(a) Answer: The enthalpy change when one mole of gaseous ions dissolves in water to form one mole of aqueous ions, under standard conditions.

(b) correct cycle relationship: delta Hsol = delta H(lattice dissociation) + delta Hhyd(Na^+) + delta Hhyd(Cl^-) (oe, allow cycle described or drawn) **M1**

(b) correct substitution: 3.9 = 771 + (-406) + delta Hhyd(Cl^-) **M1**

(b) correct rearrangement: delta Hhyd(Cl^-) = 3.9 - 365 (= -361.1) **A1**

(b) -361 (kJ/mol) awrt, cao **A1**

(b) Answer: delta Hhyd(Cl^-) = -361 kJ/mol

(c) the lattice dissociation enthalpy and the total (sum of the) hydration enthalpies of the ions are very similar in magnitude (almost equal and opposite) oe **B1**

(c) because the small overall enthalpy of solution is the (small) difference between these two large, opposing enthalpy values oe **B1**

(c) Answer: The lattice dissociation enthalpy (+771 kJ/mol) and the total hydration enthalpy (-406 + -361 = -767 kJ/mol) are almost equal and opposite; the small enthalpy of solution is the small difference between these two large values.

Question 7

(a) 50.0 (g) cao **B1**

(a) Answer: 50.0 g

(b) correct substitution: q = 50.0 x 4.18 x (26.0-19.2), ecf from (a) **M1**

(b) 1.42 (kJ) awrt (accept 1421 J), cao **A1**

(b) Answer: q = 1.42 kJ (1421 J)

(c) 0.0250 (mol) cao **B1**

(c) Answer: 0.0250 mol

(d) correct method: delta Hneut = -q/n, ecf from (b) and (c) **M1**

(d) -56.8 (kJ/mol) awrt, cao, ecf **A1**

(d) Answer: delta Hneut = -56.8 kJ/mol

Question 8

(a) correct formulae and balancing: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ **B1**

(a) correct state symbols: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ **B1**

(a) Answer: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

(b) correct Hess's law expression: delta Hc = sum(delta Hf products) - sum(delta Hf reactants) **M1**

(b) correct substitution for products: (3 x -393) + (4 x -286) **M1**

(b) products sum = -2323 kJ/mol **A1**

(b) correct subtraction using reactants: delta Hc = -2323 - (-104) **M1**

(b) -2219 kJ/mol, cao **A1**

(b) Answer: -2219 kJ/mol

(c) the calculated value (-2219 kJ/mol) agrees very closely with the literature value (-2220 kJ/mol), oe **B1**

(c) this close agreement is expected because the calculation uses accurately known enthalpies of formation and Hess's law, an exact method with no experimental measurement error involved, oe **B1**

(c) Answer: Very close agreement (within about 1 kJ/mol).

Question 9

(a) correct substitution: 5.00/80.0 **M1**

(a) 0.0625 mol, cao **A1**

(a) Answer: 0.0625 mol

(b) correct substitution: q = 105 x 4.18 x 4.7 **M1**

(b) q = 2060 J (accept 2050-2065 J) **A1**

(b) q = 2.06 kJ, correctly converted to kJ **B1**

(b) Answer: 2.06 kJ

(c) correct method: delta H = q / moles, using answers from (a) and (b), ft **M1**

(c) correct substitution: 2.06/0.0625 **M1**

(c) +33.0 kJ/mol (accept +32.9 to +33.1), ft, cao **A1**

(c) positive sign, because the temperature of the solution fell, showing that dissolving absorbed heat energy from the solution (the process is endothermic), oe **B1**

(c) Answer: +33.0 kJ/mol (endothermic)

Question 10

(a) the energy required to remove one electron from each atom in one mole of gaseous atoms **B1**

(a) to form one mole of gaseous 1+ ions oe (gaseous state must be specified for full credit) **B1**

(a) Answer: The energy required to remove one electron from each atom in one mole of gaseous atoms, forming one mole of gaseous 1+ ions.

(b) atomisation is defined as forming one mole of gaseous atoms; $Cl_2(g)$ -> 2Cl(g) produces 2 mol of atoms per mole of Cl_2, so the value must be expressed (halved) per mole of atoms oe **B1**

(b) Answer: Enthalpy of atomisation is defined per mole of gaseous atoms formed; since 1 mol of Cl_2 gives 2 mol of Cl atoms, the value is expressed per mole of atoms.

(c) correct cycle relationship set up: delta Hf = delta Hat(Mg) + IE1 + IE2 + 2 x delta Hat(Cl) + 2 x EA(Cl) + delta H(lattice) (oe, allow cycle drawn or described) **M1**

(c) correct doubling of the chlorine terms: 2 x 122 and 2 x (-349), since 2 mol of Cl are needed per mole of $MgCl_2$ **M1**

(c) correct sum of all non-lattice terms: 148 + 738 + 1451 + 244 - 698 = 1883 (kJ/mol) **A1**

(c) delta H(lattice) = -641 - 1883 = -2524 (kJ/mol) cao **A1**

(c) Answer: Lattice enthalpy of formation of $MgCl_2$ = -2524 kJ/mol

(d) the experimental (Born-Haber) value is more exothermic/larger in magnitude than the theoretical ionic value, ecf from (c) **B1**

(d) this indicates that the bonding in $MgCl_2$ has some covalent character in addition to ionic bonding (the ionic model is not a perfect description) oe **B1**

(d) Answer: The experimental value (-2524 kJ/mol) is more exothermic than the theoretical ionic value (-2326 kJ/mol), suggesting the bonding in $MgCl_2$ has some covalent character (polarisation of the Cl^- ion), so it is not purely ionic.

Question 11

(a) correct conversion so that delta H and T x delta S are in the same units (e.g. delta H = -92000 J) **M1**

(a) correct substitution: delta G = -92000 - (298 x -199) **M1**

(a) -32.7 (kJ/mol) awrt, cao **A1**

(a) Answer: delta G = -32.7 kJ/mol

(b) yes, feasible, because delta G is negative at this temperature, ecf from (a) **B1**

(b) Answer: Yes, feasible - delta G is negative (-32.7 kJ/mol) at 298 K.

(c) delta G = 0, so delta H = T x delta S, giving T = delta H / delta S **M1**

(c) correct substitution using consistent units: T = -92000 / -199 **M1**

(c) 462 (K) awrt, cao **A1**

(c) Answer: T = 462 K

(d) above the temperature found in (c), delta G for the forward reaction becomes positive, so the reverse reaction (decomposition of ammonia) becomes more thermodynamically favourable, and the equilibrium yield of ammonia is lower oe **M1**

(d) however, a higher temperature increases the rate of reaction (more particles have energy greater than or equal to the activation energy, so more frequent successful collisions), so equilibrium is reached faster oe **M1**

(d) 450°C is chosen as a compromise between a reasonable rate of reaction and an acceptable (economically viable) yield, since delta G determines feasibility/position of equilibrium but not the rate at which equilibrium is reached oe **M1**

(d) Answer: Above 462 K, delta G for the forward reaction becomes positive so the equilibrium yield of ammonia falls, but a higher temperature increases the rate of reaction; 450°C is a compromise between reaction rate and equilibrium yield, since delta G governs feasibility/yield, not rate.

Question 12

(a) ± 1.0 (°C) cao **B1**

(a) Answer: ± 1.0°C

(b) 4.5 (%) awrt, ecf from (a) **B1**

(b) Answer: 4.5%

(c) total absolute uncertainty in mass = 0.01 + 0.01 = ± 0.02 (g) **M1**

(c) 2.4 (%) awrt (accept 2.3-2.4%), cao **A1**

(c) Answer: 2.4%

(d) total % uncertainty = sum of individual % uncertainties = 4.5 + 2.4 (= 6.9%), ecf from (b) and (c) **M1**

(d) absolute uncertainty = 6.9% of 755 (= 52.1 kJ/mol), ecf **M1**

(d) delta Hc = -755 (± 52) kJ/mol (accept sensible rounding, e.g. -760 ± 50), ecf **A1**

(d) Answer: delta Hc = -755 ± 52 kJ/mol

Question 13

(a) a gas (CO_2) is produced from a solid reactant only, so the number of moles of gas (and the disorder) increases oe **B1**

(a) Answer: A gas (CO_2) is formed from solids only, increasing the number of gas particles and so increasing entropy/disorder.

(b) delta G = 0, so T = delta H / delta S **M1**

(b) correct substitution using consistent units: T = 178000 / 161 **M1**

(b) 1110 (K) awrt (accept 1100-1110 K; exact value 1105.6 K), cao **A1**

(b) Answer: T = 1110 K (awrt; exact value 1105.6 K)

Question 14

Level 3 A full and coherent explanation that correctly links the positive delta H and positive delta S to delta G = delta H - T x delta S, correctly explains that at low T the T x delta S term is small so delta G is positive (not feasible), and that as T increases the T x delta S term grows, eventually making delta G negative, with reference to the calculated minimum feasibility temperature. **5-6**

Level 2 The answer shows understanding that delta G depends on both delta H and delta S and on temperature, and that increasing temperature makes delta G more negative (or includes a correct comparison of the sign of delta G at different temperatures), but the reasoning is incomplete or lacks full linkage/detail. **3-4**

Level 1 Basic recognition that the reaction is endothermic and/or that entropy increases and/or that a high temperature is needed, without clear linkage to the Gibbs free energy equation or feasibility. **1-2**

Level 0 No relevant content, or the answer does not relate to the question. **0**

Indicative content:

- delta H is positive (endothermic, +178 kJ/mol) and delta S is positive (+161 J/(K mol)) for this reaction.
- Feasibility (spontaneity) is determined by the sign of delta G, where delta G = delta H - T x delta S.
- At 298 K, T x delta S = 298 x 161 = 47978 J = 48.0 kJ (approximately), which is smaller in magnitude than delta H (+178 kJ), so delta G = delta H - T x delta S is positive; the reaction is not feasible at room temperature.
- As temperature increases, the magnitude of the T x delta S term increases, while delta H and delta S are assumed to remain roughly constant with temperature.
- Above the calculated minimum feasibility temperature (approximately 1106 K, i.e. 1110 K to 3 s.f.), T x delta S becomes greater in magnitude than delta H, so delta G becomes negative and the reaction becomes thermodynamically feasible.
- At 1200 K (the temperature used industrially), the temperature is above this minimum feasibility temperature, so delta G is negative and decomposition is thermodynamically favourable/feasible at this temperature.

Question 15

Level 3 A full, coherent explanation that correctly links the partial (incomplete) dissociation of ethanoic acid to an additional endothermic process during the reaction, and explains that this reduces the overall exothermic enthalpy change, using correct chemical terms throughout. **5-6**

Level 2 The answer identifies that ethanoic acid is a weak acid that is only partially dissociated/ionised and links this to a reduced exothermic enthalpy change, but the explanation of the underlying energy changes is incomplete or contains minor inaccuracies. **3-4**

Level 1 A basic statement that ethanoic acid is a weak acid or is only partially dissociated, or that the reaction is still exothermic overall, with little or no linked reasoning about energy changes. **1-2**

Level 0 No relevant content, or the answer does not relate to the question. **0**

Indicative content:

- Hydrochloric acid is a strong acid and is fully (completely) dissociated/ionised in aqueous solution before the reaction takes place.
- Ethanoic acid is a weak acid and is only partially dissociated/ionised in solution; an equilibrium exists between CH_3COOH and CH_3COO^- + H^+.
- The core neutralisation reaction, $H^+(aq)$ + $OH^-(aq)$ -> $H_2O(l)$, releases the same fixed amount of energy in both cases.
- As the reaction with ethanoic acid proceeds, H^+ ions are removed from the equilibrium, so more CH_3COOH molecules must ionise to replace them; this ionisation step requires an input of energy (it is endothermic).
- This additional endothermic ionisation energy partly cancels out the exothermic enthalpy of neutralisation, so the overall (measured) enthalpy change is less exothermic (smaller in magnitude, less negative) than for a strong acid.
- Correct reference to typical values supports the explanation, e.g. HCl with NaOH is about -57 kJ/mol, while ethanoic acid with NaOH is numerically less negative (a smaller magnitude, e.g. around -50 to -55 kJ/mol), consistent with the smaller temperature rise observed.

Question 16

(a) convert units consistently, e.g. delta H = 57200 J/mol **M1**

(a) correct substitution: delta G = 57200 - (298 x 176) **M1**

(a) +4.75 kJ/mol (accept +4.7 to +4.8), cao **A1**

(a) Answer: +4.75 kJ/mol

(b) delta G is positive, so the forward reaction (as written) is not thermodynamically favourable under standard conditions at 298 K, meaning the equilibrium position lies towards the reactant (N_2O_4) side, oe **B1**

(b) this is consistent with N_2O_4 being the predominant species observed at room temperature, oe **B1**

(b) Answer: Positive delta G indicates the equilibrium favours N_2O_4 at 298 K, consistent with observation.

(c) correct rearrangement: ln K = -delta G/(RT) **M1**

(c) correct substitution using delta G in J/mol (4750 J/mol, ft) and T = 298 K **M1**

(c) K = 0.15 (accept 0.14-0.15), ft **A1**

(c) K < 1 is consistent with the equilibrium favouring the reactant (N_2O_4) side, as found in (b), oe **B1**

(c) Answer: K = 0.15 (no units)

(d) delta G(350 K) = 57200 - (350 x 176) = -4400 J/mol (-4.40 kJ/mol) **M1**

(d) correct use of delta G = -RT ln K to find K(350 K) = exp(4400/(8.31 x 350)), giving K = 4.5 (accept 4.3-4.6) **M1**

(d) the forward reaction is endothermic (delta H positive), so by Le Chatelier's principle increasing temperature shifts the equilibrium towards the (endothermic) forward direction/products, increasing K, consistent with the calculated increase from 0.15 to about 4.5, oe **B1**

(d) Answer: delta G(350K) = -4.40 kJ/mol; K = 4.5; K increases with T because the forward reaction is endothermic.

Question 17

(a) correct method: 498/2 **M1**

(a) +249 kJ/mol, cao **A1**

(a) Answer: +249 kJ/mol

(b) the second electron is removed from an ion (Ca+) that already carries a net positive charge, so the remaining electrons are held more strongly by the nucleus than in the neutral atom, oe **B1**

(b) removing an electron from a positive ion therefore requires more energy input than removing one from a neutral atom, since there is a greater effective nuclear attraction per remaining electron, oe **B1**

(b) Answer: More energy is needed to remove an electron from the positively charged Ca+ ion than from the neutral atom.

(c) the O- ion already carries a net negative charge, so bringing another (negatively charged) electron towards it involves overcoming electrostatic repulsion between like charges, oe **B1**

(c) energy must therefore be put in to overcome this repulsion, rather than being released, making the process endothermic, oe **B1**

(c) Answer: Repulsion between the electron and the already negative O- ion must be overcome, requiring energy input.

(d) correct Hess's law cycle: delta Hf(CaO) = atomisation(Ca) + IE1(Ca) + IE2(Ca) + atomisation(O) + EA1(O) + EA2(O) + LE(CaO) **M1**

(d) correct summation of the six known steps: 178 + 590 + 1145 + 249 + (-141) + 798 **M1**

(d) sum = +2819 kJ/mol, ft from (a) **A1**

(d) correct rearrangement: LE(CaO) = delta Hf(CaO) - 2819 **M1**

(d) -3454 kJ/mol, ft, cao **A1**

(d) the large exothermic (negative) value is consistent with the strong electrostatic attraction between the small, highly charged Ca^{2+} and O^{2-} ions in the lattice, oe **B1**

(d) Answer: -3454 kJ/mol

Question 18

Level 3 A detailed evaluation identifying several valid, well-explained sources of error in the calorimetry experiment, each with a clearly linked, practical improvement. The answer is coherent, logically structured and uses appropriate scientific terminology throughout. **5-6**

Level 2 Some valid sources of error are identified, with improvements suggested, but the explanation of one or more points is underdeveloped, or the link between an error and its improvement is not always clear. **3-4**

Level 1 Some relevant, briefly stated points about sources of error and/or improvements are given, but these are isolated and not developed into a coherent evaluation. **1-2**

Indicative content:

- Heat exchanged with the surroundings (through the cup wall, lid gaps, or by evaporation from the solution surface) is not accounted for, so the measured temperature change may not equal the temperature change that would occur under perfectly insulated conditions.
- The specific heat capacity used, 4.18 J/(g K) (the value for pure water), is an approximation; the true specific heat capacity of the ammonium nitrate solution is not identical to that of pure water, introducing an error into the calculated heat energy.
- The heat capacity of the calorimeter itself (cup, lid, thermometer/probe) is ignored in the calculation, even though some of the heat exchanged also changes the temperature of this apparatus, not only the solution.
- The solid may not dissolve completely by the time the minimum (or final) temperature is recorded, or some heat exchange may occur before mixing is complete, so the measured temperature change may not represent the full enthalpy change.
- Improvement: use a well-insulated (lidded, expanded-polystyrene) calorimeter to minimise heat exchange with the surroundings.
- Improvement: use a data logger with a temperature probe to record readings continuously and extrapolate the temperature-time graph back to the moment of mixing, correcting for gradual heat loss or gain.
- Improvement: repeat the experiment and calculate a mean value to reduce the effect of random errors in the temperature and mass measurements.

Question 19

(a) total absolute uncertainty = 0.005 + 0.005 = ± 0.01 g (uncertainties add when two readings are subtracted) **B1**

(a) correct substitution: (0.01/5.00) x 100 **M1**

(a) 0.20%, cao **A1**

(a) Answer: ± 0.01 g; 0.20%

(b) combined absolute uncertainty = 0.05 + 0.05 = ± 0.1°C **M1**

(b) correct substitution: (0.1/4.7) x 100 **M1**

(b) 2.1% (accept 2.1-2.2%) **A1**

(b) Answer: ± 0.1°C; 2.1%

(c) total percentage uncertainty = 0.20% + 2.1% = 2.3% (summing the two dominant contributions) **M1**

(c) the temperature change measurement is the dominant source of uncertainty, since its percentage uncertainty (2.1%) is much larger than that of the mass (0.20%), oe **B1**

(c) Answer: Approximately 2.3%; the temperature change dominates.

(d) absolute uncertainty = (2.3/100) x 33.0 **M1**

(d) (33.0 ± 0.8) kJ/mol, ft, cao **A1**

(d) Answer: (33.0 ± 0.8) kJ/mol