AC3D Energetics and Thermodynamics: Depth and Exam Drill

Total Marks

AQA 7405 · Calculator allowed · about 160 minutes

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 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 1 is 4 marks)

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2 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 2 is 9 marks)

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3 This question uses mean bond enthalpies to calculate the enthalpy change for the catalytic cracking of butane.

(a) Butane can be cracked to give ethane and ethene: $C_4H_{10}(g) \rightarrow C_2H_6(g) + C_2H_4(g)$. Explain why, in a mean bond enthalpy calculation for this reaction, the C-H bonds broken and formed do not need to be included. **(2)**

(b) Mean bond enthalpies (kJ/mol): C-C = 347, C=C = 612. Using these values, calculate the enthalpy change for the cracking reaction, showing the bonds broken and bonds formed, and state what the sign of your answer shows about the reaction. **(5)**

(Total for Question 3 is 7 marks)

4 This question is about the entropy change and thermodynamic feasibility of the thermal decomposition of sodium hydrogencarbonate.

(a) Sodium hydrogencarbonate decomposes on heating: 2NaHCO3(s) -> Na2CO3(s) + H2O(g) + CO2(g). Standard entropies, S, at 298 K (J/(K mol)): NaHCO3(s) = 102, Na2CO3(s) = 136, H2O(g) = 189, CO2(g) = 214. Calculate the standard entropy change, delta S, for this reaction. **(3)**

(b) State, with a reason based on the chemical equation, whether you would expect delta S for this reaction to be positive or negative before doing the calculation. **(2)**

(c) The reaction is endothermic, with delta H = +129 kJ/mol. Using your answer to (a), calculate T delta S at 450 K and hence explain, in terms of delta G, why this reaction is thermodynamically feasible at this temperature even though it is endothermic. **(3)**

(Total for Question 4 is 8 marks)

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5 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 NH4NO3 (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 NH4NO3 used. **(2)**

(b) The temperature of the solution falls from 20.5 degrees C to 15.8 degrees 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 5 is 9 marks)

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

(a) The bond dissociation enthalpy of O2(g) is +498 kJ/mol. Calculate the atomisation enthalpy of oxygen, 1/2 O2(g) -> O(g). **(2)**

(b) Explain why the second ionisation energy of calcium, Ca+(g) -> Ca2+(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- -> O2-(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 (Ca2+(g) + O2-(g) -> CaO(s)). **(6)**

(Total for Question 6 is 12 marks)

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7 This question is about the thermodynamic feasibility of extracting zinc by reducing zinc oxide with carbon.

(a) State the condition, in terms of delta G, for a reaction to be thermodynamically feasible (spontaneous), and give the equation linking delta G to delta H and delta S. **(2)**

(b) Zinc oxide can be reduced by carbon: ZnO(s) + C(s) -> Zn(l) + CO(g). Explain, in terms of the signs and relative sizes of delta H and delta S, why this reaction becomes more feasible at higher temperatures. **(2)**

(c) For this reaction, delta H = +237 kJ/mol and delta S = +197 J/(K mol). Calculate the minimum temperature at which the reaction becomes thermodynamically feasible. **(4)**

(d) Suggest one reason why, in industrial practice, this reaction might be carried out at a temperature somewhat higher than the minimum feasibility temperature found in (c). **(2)**

(Total for Question 7 is 10 marks)

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8 In the experiment described in Question 5, 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 8 is 6 marks)

9 This question analyses the measurement uncertainty in the calorimetry experiment described in Question 5.

(a) The 5.00 g mass of NH4NO3 in Question 5 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 degrees C (uncertainty ± 0.05 degrees C per reading) was used for both the initial and final temperature readings, giving a temperature change of 4.7 degrees 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 5 (+33.0 kJ/mol), express the result with its absolute uncertainty, to an appropriate number of significant figures. **(2)**

(Total for Question 9 is 10 marks)

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10 This synoptic question links the thermodynamics of the N2O4/NO2 equilibrium to its equilibrium constant and the effect of temperature.

(a) For the equilibrium N2O4(g) ⇌ 2NO2(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 N2O4 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 10 is 12 marks)

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Question 1

- (a) **B1** the enthalpy change when 1 mole of a compound is formed from its elements in their standard states, under standard conditions, oe
- **(a) Answer: Enthalpy change forming 1 mole of compound from its elements in standard states.**
- (b) **B1** 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
- **(b) Answer: Enthalpy change when 1 mole of a substance is completely burned in excess oxygen under standard conditions.**
- (c) **B1** the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state, under standard conditions, oe
- **(c) Answer: Enthalpy change forming 1 mole of gaseous atoms from the element in its standard state.**
- (d) **B1** the total enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions (states) are the same, oe
- **(d) Answer: Total enthalpy change is independent of route, provided initial and final states are the same.**

Question 2

- (a) **B1** correct formulae and balancing: C3H8 + 5O2 -> 3CO2 + 4H2O
- (a) **B1** correct state symbols: C3H8(g) + 5O2(g) -> 3CO2(g) + 4H2O(l)
- **(a) Answer: C3H8(g) + 5O2(g) -> 3CO2(g) + 4H2O(l)**
- (b) **M1** correct Hess's law expression: delta Hc = sum(delta Hf products) - sum(delta Hf reactants)
- (b) **M1** correct substitution for products: (3 x -393) + (4 x -286)
- (b) **A1** products sum = -2323 kJ/mol
- (b) **M1** correct subtraction using reactants: delta Hc = -2323 - (-104)
- (b) **A1** -2219 kJ/mol, cao
- **(b) Answer: -2219 kJ/mol**
- (c) **B1** the calculated value (-2219 kJ/mol) agrees very closely with the literature value (-2220 kJ/mol), oe
- (c) **B1** 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
- **(c) Answer: Very close agreement (within about 1 kJ/mol).**

Question 3

- (a) **B1** butane (C4H10) contains 10 C-H bonds
- (a) **B1** ethane (C2H6) and ethene (C2H4) together also contain 10 C-H bonds (6 + 4), so exactly the same number of C-H bonds is broken as is reformed, giving no net contribution to delta H, oe
- **(a) Answer: The same number of C-H bonds (10) appear on both sides, so they cancel.**
- (b) **M1** bonds broken: 3 mol C-C bonds in butane
- (b) **M1** energy to break bonds: 3 x 347 = 1041 kJ/mol
- (b) **M1** bonds formed: 1 mol C-C (in ethane) + 1 mol C=C (in ethene); energy released forming bonds: 347 + 612 = 959 kJ/mol
- (b) **A1** delta H = bonds broken - bonds formed = 1041 - 959 = +82 kJ/mol, cao
- (b) **B1** the positive value shows the reaction is endothermic, consistent with cracking needing heat (and a catalyst) to proceed, oe
- **(b) Answer: +82 kJ/mol (endothermic)**

Question 4

- (a) **M1** sum of products' entropies: 136 + 189 + 214 = 539 J/(K mol)
- (a) **M1** sum of reactants' entropies: 2 x 102 = 204 J/(K mol)
- (a) **A1** delta S = 539 - 204 = +335 J/(K mol), cao
- **(a) Answer: +335 J/(K mol)**
- (b) **B1** positive
- (b) **B1** because gases (H2O(g) and CO2(g)) are produced from a solid reactant, and gases have much greater entropy (more disordered, more ways of arranging particles and energy) than solids, oe
- **(b) Answer: Positive, because gaseous products are formed from a solid reactant.**
- (c) **M1** correct substitution: T delta S = 450 x 0.335
- (c) **A1** T delta S = 150.75 kJ/mol (accept 150-151), which exceeds delta H (129 kJ/mol)
- (c) **B1** since delta G = delta H - T delta S, and T delta S is now larger than delta H, delta G is negative at 450 K, so the reaction is thermodynamically feasible at this temperature, oe
- **(c) Answer: T delta S = 150.75 kJ/mol > delta H, so delta G is negative and the reaction is feasible at 450 K.**

Question 5

- (a) **M1** correct substitution: 5.00/80.0
- (a) **A1** 0.0625 mol, cao
- **(a) Answer: 0.0625 mol**
- (b) **M1** correct substitution: q = 105 x 4.18 x 4.7
- (b) **A1** q = 2060 J (accept 2050-2065 J)
- (b) **B1** q = 2.06 kJ, correctly converted to kJ
- **(b) Answer: 2.06 kJ**
- (c) **M1** correct method: delta H = q / moles, using answers from (a) and (b), ft
- (c) **M1** correct substitution: 2.06/0.0625
- (c) **A1** +33.0 kJ/mol (accept +32.9 to +33.1), ft, cao
- (c) **B1** positive sign, because the temperature of the solution fell, showing that dissolving absorbed heat energy from the solution (the process is endothermic), oe
- **(c) Answer: +33.0 kJ/mol (endothermic)**

Question 6

- (a) **M1** correct method: 498/2
- (a) **A1** +249 kJ/mol, cao
- **(a) Answer: +249 kJ/mol**
- (b) **B1** 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
- (b) **B1** 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
- **(b) Answer: More energy is needed to remove an electron from the positively charged Ca+ ion than from the neutral atom.**
- (c) **B1** 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
- (c) **B1** energy must therefore be put in to overcome this repulsion, rather than being released, making the process endothermic, oe
- **(c) Answer: Repulsion between the electron and the already negative O- ion must be overcome, requiring energy input.**
- (d) **M1** correct Hess's law cycle: delta Hf(CaO) = atomisation(Ca) + IE1(Ca) + IE2(Ca) + atomisation(O) + EA1(O) + EA2(O) + LE(CaO)
- (d) **M1** correct summation of the six known steps: 178 + 590 + 1145 + 249 + (-141) + 798
- (d) **A1** sum = +2819 kJ/mol, ft from (a)
- (d) **M1** correct rearrangement: LE(CaO) = delta Hf(CaO) - 2819
- (d) **A1** -3454 kJ/mol, ft, cao
- (d) **B1** the large exothermic (negative) value is consistent with the strong electrostatic attraction between the small, highly charged Ca2+ and O2- ions in the lattice, oe
- **(d) Answer: -3454 kJ/mol**

Question 7

- (a) **B1** delta G is zero or negative (delta G ≤ 0), oe
- (a) **B1** delta G = delta H - T delta S
- **(a) Answer: delta G ≤ 0; delta G = delta H - T delta S.**
- (b) **B1** the reaction has a positive delta H (endothermic) and a positive delta S (entropy increases, since a gas, CO, is produced from solids), oe
- (b) **B1** as T increases, the (positive) T delta S term becomes larger and eventually outweighs the positive delta H, making delta G negative, oe
- **(b) Answer: As T rises, T delta S grows and eventually exceeds delta H, making delta G negative.**
- (c) **M1** set delta G = 0, so delta H = T delta S
- (c) **M1** convert units consistently: delta H = 237000 J/mol
- (c) **M1** correct substitution: T = 237000/197
- (c) **A1** 1200 K (accept 1200-1210 K), cao
- **(c) Answer: Approximately 1200 K**
- (d) **B1** identify a valid practical reason, e.g. to increase the rate of reaction to an economically useful rate (thermodynamic feasibility does not guarantee a fast rate), oe
- (d) **B1** elaborate/justify, e.g. operating well above the minimum feasibility temperature also allows for heat losses from the furnace, ensuring the mixture does not fall below the temperature needed to remain feasible, oe
- **(d) Answer: A higher temperature ensures a useful reaction rate and allows a margin for heat losses.**

Question 8

- **Level 3** (5-6): 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.
- **Level 2** (3-4): 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.
- **Level 1** (1-2): 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.
- **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 9

- (a) **B1** total absolute uncertainty = 0.005 + 0.005 = ± 0.01 g (uncertainties add when two readings are subtracted)
- (a) **M1** correct substitution: (0.01/5.00) x 100
- (a) **A1** 0.20%, cao
- **(a) Answer: ± 0.01 g; 0.20%**
- (b) **M1** combined absolute uncertainty = 0.05 + 0.05 = ± 0.1 degrees C
- (b) **M1** correct substitution: (0.1/4.7) x 100
- (b) **A1** 2.1% (accept 2.1-2.2%)
- **(b) Answer: ± 0.1 degrees C; 2.1%**
- (c) **M1** total percentage uncertainty = 0.20% + 2.1% = 2.3% (summing the two dominant contributions)
- (c) **B1** 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
- **(c) Answer: Approximately 2.3%; the temperature change dominates.**
- (d) **M1** absolute uncertainty = (2.3/100) x 33.0
- (d) **A1** (33.0 ± 0.8) kJ/mol, ft, cao
- **(d) Answer: (33.0 ± 0.8) kJ/mol**

Question 10

- (a) **M1** convert units consistently, e.g. delta H = 57200 J/mol
- (a) **M1** correct substitution: delta G = 57200 - (298 x 176)
- (a) **A1** +4.75 kJ/mol (accept +4.7 to +4.8), cao
- **(a) Answer: +4.75 kJ/mol**
- (b) **B1** 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
- (b) **B1** this is consistent with N_2O_4 being the predominant species observed at room temperature, oe
- **(b) Answer: Positive delta G indicates the equilibrium favours N_2O_4 at 298 K, consistent with observation.**
- (c) **M1** correct rearrangement: ln K = -delta G/(RT)
- (c) **M1** correct substitution using delta G in J/mol (4750 J/mol, ft) and T = 298 K
- (c) **A1** K = 0.15 (accept 0.14-0.15), ft
- (c) **B1** K < 1 is consistent with the equilibrium favouring the reactant (N_2O_4) side, as found in (b), oe
- **(c) Answer: K = 0.15 (no units)**
- (d) **M1** delta G(350 K) = 57200 - (350 x 176) = -4400 J/mol (-4.40 kJ/mol)
- (d) **M1** 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)
- (d) **B1** 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
- **(d) Answer: delta G(350K) = -4.40 kJ/mol; K = 4.5; K increases with T because the forward reaction is endothermic.**