2.4 Kinetics and Equilibria

AQA 7405 · Calculator allowed · about 240 minutes · Write-in edition

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question tests your understanding of reaction orders and how they can be identified from graphs.

(a) Define what is meant by the order of reaction with respect to a particular reactant. **(1)**

(b) State the units of the rate of a chemical reaction. **(1)**

(c) In an experiment monitoring the concentration of reactant X over time, a graph of [X] against time is a straight line with a constant negative gradient for as long as X remains present in the mixture. State the order of reaction with respect to X, and explain how the graph shows this. **(2)**

(d) In a separate experiment, a graph of initial rate against the initial concentration of reactant Y is a straight line passing through the origin. State the order of reaction with respect to Y, and explain how the graph shows this. **(2)**

(e) In a third experiment, a graph of initial rate against the initial concentration of reactant Z is a curve passing through the origin, such that doubling [Z] causes the initial rate to increase by a factor of four. State the order of reaction with respect to Z, and explain how this observation shows this. **(2)**

(Total for Question 1 is 8 marks)

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2 This question tests key definitions used throughout the kinetics and equilibria topic.

(a) State the two conditions necessary, according to collision theory, for a reaction to occur when two particles collide. **(2)**

(b) Define activation energy. **(1)**

(c) State what is meant by the order of reaction with respect to a reactant. **(1)**

(d) State the Arrhenius equation. **(1)**

(Total for Question 2 is 5 marks)

3 A reaction between reactants A and B was investigated using the initial rates method. The table shows the results of three experiments carried out at the same constant temperature.

Experiment	[A] (mol dm-3)	[B] (mol dm-3)	Initial rate (mol dm-3 s-1)
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	4.0×10^{-3}
3	0.20	0.20	1.6×10^{-2}

(a) Using experiments 1 and 2, determine the order of reaction with respect to A. Show your reasoning. **(2)**

(b) Using experiments 2 and 3, determine the order of reaction with respect to B. Show your reasoning. **(2)**

(c) Deduce the overall order of reaction and write the rate equation for this reaction. **(2)**

(d) Using the data from Experiment 1, calculate the rate constant, k, for this reaction, including its units. **(3)**

(Total for Question 3 is 9 marks)

4 The concentration of reactant A was monitored during its decomposition at a constant temperature. The results are shown in the table.

Time (min)	0	10	20	30	40
[A] (mol dm-3)	0.800	0.400	0.200	0.100	0.0500

You may use: for a first order reaction, $k = \ln 2 / t(1/2)$; $[A]t = [A]0 \times e^{-kt}$, where [A]t is the concentration remaining after time t.

(a) Show that these data are consistent with the reaction being first order with respect to A. **(3)**

(b) Calculate the rate constant, k, for this reaction in s-1, giving your answer to 3 significant figures. **(3)**

(c) Using your value of k (or $k = 1.16 \times 10^{-3}$ s-1 if you did not obtain an answer to (b)), calculate the concentration of A remaining after 25.0 minutes have elapsed, giving your answer to 3 significant figures. **(2)**

(Total for Question 4 is 8 marks)

5 The reaction between nitrogen dioxide and carbon monoxide has the overall equation:
$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$
The experimentally determined rate equation is rate = $k[NO_2]^2$. This is consistent with the following two-step mechanism:
Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$
Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

(a) Identify the reaction intermediate in this mechanism, and explain how you can recognise it as an intermediate. **(2)**

(b) Deduce which step, 1 or 2, is the rate-determining step, using the given rate equation to support your answer. **(3)**

(c) Explain why the rate equation for a multi-step reaction cannot be predicted directly from the stoichiometric coefficients of the overall balanced equation, and must instead be found by experiment. **(2)**

(d) A student suggests an alternative single-step mechanism in which one molecule of NO_2 and one molecule of CO collide directly and simultaneously with a second molecule of NO_2, in a single three-body (termolecular) collision. Suggest why this proposed mechanism is very unlikely. **(1)**

(Total for Question 5 is 8 marks)

6 This question is about the equilibrium constant, Kc, for homogeneous equilibria.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(a) Write the expression for Kc for this equilibrium. **(1)**

(b) State the units of Kc for this equilibrium. **(1)**

(c) At a particular temperature, the equilibrium concentrations in a sealed 2.00 dm3 container are $[H_2] = 0.100$ mol dm-3, $[I_2] = 0.0500$ mol dm-3 and [HI] = 0.400 mol dm-3. Calculate Kc at this temperature. **(3)**

(d) Explain why changing the concentration of H_2 at constant temperature does not change the value of Kc, even though it does change the position of equilibrium. **(2)**

(e) State what is meant by a dynamic equilibrium. **(1)**

(f) Which expression correctly gives Kc for the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$? **(1)**

- ☐ A) $Kc = [N_2][H_2]^3 / [NH_3]^2$
- ☐ B) $Kc = [NH_3]^2 / ([N_2][H_2]^3)$
- ☐ C) $Kc = [NH_3] / ([N_2][H_2])$
- ☐ D) $Kc = 2[NH_3] / ([N_2] \times 3[H_2])$

(Total for Question 6 is 9 marks)

7 A sealed container holds an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium, the total pressure is 2.00 atm, and the mole fractions are 0.400 for N_2O_4 and 0.600 for NO_2.

(a) State what is meant by the mole fraction of a gas in a mixture. **(1)**

(b) Calculate the partial pressure of N_2O_4 and of NO_2 in this equilibrium mixture. **(2)**

(c) Write the expression for Kp for this equilibrium, and use your answers to (b) to calculate its value, stating units. **(4)**

(d) State and explain the effect of increasing the total pressure of this equilibrium mixture, at constant temperature, on the position of equilibrium. **(2)**

(Total for Question 7 is 9 marks)

8 2.00 mol of PCl_5 gas is placed in a sealed 5.00 dm3 container and allowed to reach equilibrium at a constant temperature:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

At equilibrium, 1.20 mol of PCl_5 remains.

(a) Calculate the number of moles of PCl_3 and of Cl_2 present at equilibrium. **(2)**

(b) Calculate the equilibrium concentration, in mol dm-3, of each of the three species. **(3)**

(c) Write the expression for Kc for this equilibrium, and calculate its value, stating units. **(4)**

(Total for Question 8 is 9 marks)

9 In an experiment to determine the equilibrium constant for esterification, 0.100 mol of ethanoic acid, CH_3COOH, and 0.100 mol of ethanol, C_2H_5OH, together with a small (catalytic) amount of concentrated sulfuric acid, are sealed in a flask and left at a constant temperature until equilibrium is reached:

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

The whole of the equilibrium mixture is then titrated with 1.00 mol dm-3 sodium hydroxide solution, using phenolphthalein indicator, to find the amount of unreacted ethanoic acid. The titration requires 40.0 cm^3 of the sodium hydroxide solution. This question is based on practical techniques for determining an equilibrium constant.

(a) Suggest why the flask is sealed (stoppered) throughout the time the mixture is left to reach equilibrium. **(1)**

(b) Suggest why the titration should be carried out quickly (without delay). **(1)**

(c) Calculate the number of moles of ethanoic acid present in the flask at equilibrium. **(2)**

(d) Hence deduce the number of moles of ethanol, ethyl ethanoate and water present at equilibrium. **(3)**

(e) Write the expression for Kc for this equilibrium, and use your answers to calculate its value. Explain why Kc has no units for this equilibrium. **(4)**

(Total for Question 9 is 11 marks)

10 Ammonia is manufactured industrially by the Haber process:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ deltaH = -92 kJ/mol

Industrially, a compromise temperature of about 450°C and a pressure of about 200 atm are used, together with an iron catalyst.

(a) State and explain the effect of increasing the pressure on the position of this equilibrium, and on the equilibrium yield of ammonia. **(2)**

(b) Explain, in terms of the frequency of collisions, why increasing the pressure also increases the rate at which this equilibrium is reached. **(2)**

(c) The iron catalyst is essential for making this process economically viable. Explain why the catalyst has no effect on the position of equilibrium or on the equilibrium yield of ammonia. **(2)**

(d) Explain why a compromise temperature of about 450°C, rather than a much lower temperature, is used industrially in the Haber process, given that the forward reaction is exothermic. Your answer should refer to the effect of temperature on both the position of equilibrium and the rate of reaction. **(6)**

(Total for Question 10 is 12 marks)

11 The rate constant for a first order reaction is 2.00×10^{-5} s-1 at 300 K and 3.51×10^{-4} s-1 at 350 K.

You may use: $\ln(k2/k1) = (Ea/R)(1/T1 - 1/T2)$; $k = A \times e^{-Ea/(RT)}$; R = 8.31 J K-1 mol-1.

(a) Calculate the activation energy, Ea, of this reaction in kJ/mol. Give your answer to 3 significant figures. **(5)**

(b) Using your value of Ea (or Ea = 50.0 kJ/mol if you did not obtain an answer to (a)), calculate the Arrhenius constant, A, for this reaction, stating its units. **(3)**

(Total for Question 11 is 8 marks)

12 The Arrhenius equation can be written in the linear form:

$\ln k = -(Ea/R)(1/T) + \ln A$

so a graph of ln k (y-axis) against 1/T (x-axis) gives a straight line. For a particular first order reaction, this graph has a gradient of -9640 K and a y-intercept of 28.5. (R = 8.31 J K-1 mol-1.)

(a) State the units of the quantity plotted on each axis of this graph. **(2)**

(b) Use the gradient of the graph to calculate the activation energy, Ea, of the reaction in kJ/mol. Give your answer to 3 significant figures. **(3)**

(c) Use the y-intercept of the graph to calculate the Arrhenius constant, A, for this reaction, stating its units. **(3)**

(Total for Question 12 is 8 marks)

13 This synoptic question links the activation energies of the forward and reverse reactions, the reaction enthalpy profile, and the effect of a catalyst.

(a) For a reversible, exothermic reaction, the activation energy of the forward reaction is Ea(forward) = 75 kJ/mol, and the overall enthalpy change is delta H = -58 kJ/mol. Describe the shape of the reaction (enthalpy) profile for this reaction, and how Ea(forward) and delta H are represented on it. **(2)**

(b) Calculate the activation energy of the reverse reaction, Ea(reverse), explaining your method. **(3)**

(c) Explain, in terms of the reaction profile, why Ea(reverse) is greater than Ea(forward) for this exothermic reaction. **(2)**

(d) A catalyst is added, lowering Ea(forward) to 52 kJ/mol without changing delta H. Calculate the new activation energy of the reverse reaction, and explain why a catalyst affects the rate of the forward and reverse reactions equally. **(3)**

(Total for Question 13 is 10 marks)

14 This question is about the first-order decomposition kinetics of a compound X, determined from concentration-time data.

(a) A compound X decomposes; its concentration is monitored over time: t = 0 min, [X] = 0.800 mol/dm3; t = 10 min, [X] = 0.400 mol/dm3; t = 20 min, [X] = 0.200 mol/dm3; t = 30 min, [X] = 0.100 mol/dm3. Using this data, show that the reaction is first order with respect to X. **(2)**

(b) Calculate the rate constant, k, for this reaction using k = ln2 / t(1/2), stating its units. **(3)**

(c) Convert your answer to (b) into units of s^{-1}. **(2)**

(d) Using your rate constant from (b), calculate the concentration of X remaining after 45 minutes, using $[X] = [X]0\ e^{-kt}$. **(2)**

(Total for Question 14 is 9 marks)

15 This question uses rate constants at two temperatures to calculate an activation energy using the Arrhenius equation.

(a) State the form of the Arrhenius equation used to calculate an activation energy from rate constants measured at two different temperatures. **(1)**

(b) For a reaction, k1 = 4.00×10^{-4} s^{-1} at T1 = 298 K and k2 = 5.30×10^{-3} s^{-1} at T2 = 328 K. Calculate the activation energy, Ea, in kJ/mol. **(5)**

(c) Use your value of Ea from (b) to calculate the Arrhenius constant, A, given k1 = 4.00×10^{-4} s^{-1} at 298 K. **(3)**

(Total for Question 15 is 9 marks)

16 This question is about determining the order of reaction with respect to peroxodisulfate ions using an iodine clock reaction.

(a) In the peroxodisulfate-iodide clock reaction, $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$, a small, fixed volume of sodium thiosulfate solution and starch indicator is added to the reaction mixture, and the time, t, taken for a blue-black colour to appear is measured. Explain why the initial rate of reaction can be taken as proportional to 1/t. **(2)**

(b) Three experiments give: Experiment 1, $[S_2O_8^{2-}] = 0.020$ mol/dm3, t = 40.0 s; Experiment 2, $[S_2O_8^{2-}] = 0.040$ mol/dm3, t = 20.0 s; Experiment 3, $[S_2O_8^{2-}] = 0.060$ mol/dm3, t = 13.3 s. Deduce the order of reaction with respect to $S_2O_8^{2-}$. **(4)**

(c) Describe how a graph of 1/t (y-axis) against $[S_2O_8^{2-}]$ (x-axis) for this data would appear, and explain how this confirms the order found in (b). **(2)**

(d) State two variables, other than temperature, that should be kept constant across the three experiments to ensure a valid comparison. **(2)**

(Total for Question 16 is 10 marks)

17 This question is about the equilibrium constant, Kp, for the contact process equilibrium used in industrial sulfuric acid manufacture.

(a) Write the expression for Kp for the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, and state its units. **(2)**

(b) At equilibrium in a sealed container at a total pressure of 2.00 atm, the partial pressures are $p(SO_2) = 0.40$ atm, $p(O_2) = 0.60$ atm, $p(SO_3) = 1.00$ atm. Calculate Kp, including units. **(3)**

(c) State and explain, using Le Chatelier's principle, the effect of increasing the total pressure on the position of equilibrium, and on the value of Kp. **(3)**

(d) The forward reaction is exothermic. State and explain the effect of increasing temperature on the value of Kp. **(2)**

(Total for Question 17 is 10 marks)

18 A small increase in temperature (for example, a rise of just 10°C) can approximately double the rate of many reactions, even though the average kinetic energy of the particles increases by a relatively small amount. Using the Boltzmann distribution and the Arrhenius equation, explain why a small increase in temperature causes such a large increase in reaction rate, and explain how a catalyst increases reaction rate without any increase in temperature.

(Total for Question 18 is 6 marks)

19 This question analyses the measurement uncertainty in the clock-reaction timings from Question 16.

(a) In the experiment described in Question 16, times were measured using a hand-held stopwatch, with a combined uncertainty of ± 0.3 s in each measured time. Calculate the percentage uncertainty in the time recorded in Experiment 1 (t = 40.0 s). **(2)**

(b) Calculate the percentage uncertainty in the time recorded in Experiment 3 (t = 13.3 s). **(2)**

(c) Explain why the percentage uncertainty is larger for Experiment 3 than for Experiment 1, even though the absolute uncertainty in the stopwatch timing is the same in both cases. **(2)**

(d) Suggest one change to the experimental method that would reduce the percentage uncertainty in the faster experiments, such as Experiment 3, and explain why it would help. **(2)**

(Total for Question 19 is 8 marks)

Mark scheme · 2.4 Kinetics and Equilibria

Question 1

(a) the power to to which the concentration of that reactant is raised in the (experimentally determined) rate equation oe **B1**

(a) Answer: The power to which that reactant's concentration is raised in the rate equation.

(b) mol dm^{-3} s^{-1} (or another valid concentration/time combination, e.g. mol dm^{-3} min^{-1}) oe **B1**

(b) Answer: mol dm-3 s-1

(c) zero order **B1**

(c) the gradient (rate) is constant and does not change as [X] falls, so the rate is independent of [X] oe **B1**

(c) Answer: Zero order; a constant gradient shows the rate does not depend on [X].

(d) first order **B1**

(d) rate is directly proportional to [Y] (shown by the straight line through the origin) oe **B1**

(d) Answer: First order; rate is directly proportional to [Y].

(e) second order **B1**

(e) rate is proportional to $[Z]^2$, so doubling [Z] increases the rate by a factor of $2^2 = 4$, consistent with the observation oe **B1**

(e) Answer: Second order; rate is proportional to $[Z]^2$, so doubling [Z] quadruples the rate.

Question 2

(a) the particles must collide with energy equal to or greater than the activation energy **B1**

(a) the particles must collide with the correct orientation (geometry), oe **B1**

(a) Answer: Sufficient energy (≥ activation energy) and correct collision orientation.

(b) the minimum energy that colliding particles must have in order to react, oe **B1**

(b) Answer: The minimum energy needed for colliding particles to react.

(c) the power to which the concentration of that reactant is raised in the (experimentally determined) rate equation, oe **B1**

(c) Answer: The power to which that reactant's concentration is raised in the rate equation.

(d) $k = A\,e^{-Ea/RT}$, with terms defined (k = rate constant, A = Arrhenius constant/pre-exponential factor, Ea = activation energy, R = gas constant, T = temperature in K) **B1**

(d) Answer: $k = A\,e^{-Ea/RT}$

Question 3

(a) [A] doubles (0.10 to 0.20) with [B] constant, and the initial rate doubles ($2.0x10^{-3}$ to $4.0x10^{-3}$) oe **M1**

(a) order with respect to A = 1 cao **A1**

(a) Answer: Order with respect to A = 1

(b) [B] doubles (0.10 to 0.20) with [A] constant, and the initial rate increases by a factor of 4 ($4.0x10^{-3}$ to $1.6x10^{-2}$) oe **M1**

(b) order with respect to B = 2 cao **A1**

(b) Answer: Order with respect to B = 2

(c) overall order = 1 + 2 = 3 **M1**

(c) rate = $k[A][B]^2$ **A1**

(c) Answer: Overall order = 3; rate = $k[A][B]^2$

(d) $k = rate / ([A][B]^2) = 2.0x10^{-3} / (0.10 \times 0.10^2)$, ft from (c) **M1**

(d) k = 2.0 cao **A1**

(d) units: mol^{-2} dm^6 s^{-1} **A1**

(d) Answer: $k = 2.0$ mol^{-2} dm^6 s^{-1}

Question 4

(a) identifies successive half-lives: 0.800 to 0.400 takes 10 min; 0.400 to 0.200 takes a further 10 min; 0.200 to 0.100 takes a further 10 min; 0.100 to 0.0500 takes a further 10 min **M1**

(a) the half-life is constant at 10 min throughout the reaction **A1**

(a) a constant half-life (independent of concentration) is characteristic of first order kinetics, so the data are consistent with the reaction being first order with respect to A cso **A1**

(a) Answer: Half-life is constant at 10 min throughout, confirming first order kinetics with respect to A.

(b) t(1/2) = 10 min = 600 s **M1**

(b) k = ln2 / 600 **M1**

(b) k = 1.16 x 10^{-3} s-1 awrt **A1**

(b) Answer: k = 1.16 x 10^{-3} s-1

(c) converts t = 25.0 min to 1500 s and substitutes into $[A]t = [A]0 \times e^{-kt}$, ft from (b) **M1**

(c) [A]t = 0.141 mol dm-3 awrt (accept 0.140 if k = 1.16 x 10^{-3} s-1 is used) **A1**

(c) Answer: 0.141 mol dm-3 (0.140 mol dm-3 if k = 1.16 x 10^{-3} s-1 is used)

Question 5

(a) NO_3 **B1**

(a) it is formed in step 1 and used up (reacts) in step 2, so it does not appear in the overall equation oe **B1**

(a) Answer: NO_3 is the intermediate; it is produced in step 1 and consumed in step 2, so it cancels out of the overall equation.

(b) the rate equation, rate = $k[NO_2]^2$, involves only NO_2, to the power 2 oe **M1**

(b) step 1 involves two molecules of NO_2 colliding, matching the species and the order (2) shown in the rate equation oe **M1**

(b) step 1 is the rate-determining (slow) step; step 2 (involving CO) must be fast, since CO does not appear in the rate equation oe **A1**

(b) Answer: Step 1 is the rate-determining step, because the rate equation (rate = $k[NO_2]^2$) matches the two NO_2 molecules reacting in step 1; CO's absence from the rate equation shows step 2 (fast) occurs after the RDS.

(c) the rate equation depends only on the species (and their powers) involved in the rate-determining (slowest) step of the mechanism, not on the overall equation oe **B1**

(c) the overall balanced equation gives no information about the individual steps of the mechanism, so the rate equation cannot be deduced from it and must be found experimentally oe **B1**

(c) Answer: The rate equation reflects only the rate-determining step, which cannot be identified from the overall equation alone, so it must be found experimentally.

(d) a simultaneous, correctly orientated collision between three separate particles at once, each also possessing sufficient energy, is statistically far less probable than a two-body collision oe **B1**

(d) Answer: Simultaneous three-particle collisions with correct orientation and sufficient energy are far less probable than two-particle collisions.

Question 6

(a) $Kc = [HI]^2 / ([H_2][I_2])$ **B1**

(a) Answer: $Kc = [HI]^2 / ([H_2][I_2])$

(b) no units (Kc is dimensionless for this equilibrium) **B1**

(b) Answer: No units.

(c) $Kc = (0.400)^2 / (0.100 \times 0.0500)$, ft from (a) **M1**

(c) = 0.160 / 0.00500 **M1**

(c) Kc = 32.0 cao **A1**

(c) Answer: Kc = 32.0

(d) Kc is a constant that depends only on temperature (for a given equilibrium) oe **B1**

(d) although adding more H_2 shifts the position of equilibrium (more HI forms, by Le Chatelier's principle), the equilibrium concentrations adjust so that the value given by the Kc expression returns to the same value at that temperature oe **B1**

(d) Answer: Kc depends only on temperature; concentrations re-adjust as the equilibrium shifts so that the value of the Kc expression is unchanged.

(e) in a closed system, the forward and reverse reactions occur at the same (equal) rate, so the concentrations of reactants and products remain constant over time oe **B1**

(e) Answer: Forward and reverse reaction rates are equal, so concentrations remain constant, in a closed system.

(f) B **B1**

(f) Answer: B

Question 7

(a) the number of moles of that gas divided by the total number of moles of gas present in the mixture oe **B1**

(a) Answer: Moles of that gas / total moles of gas in the mixture.

(b) partial pressure = mole fraction x total pressure, for each gas **M1**

(b) $P(N_2O_4) = 0.800$ atm; $P(NO_2) = 1.20$ atm **A1**

(b) Answer: $P(N_2O_4) = 0.800$ atm; $P(NO_2) = 1.20$ atm

(c) $Kp = (P(NO_2))^2 / P(N_2O_4)$ **B1**

(c) $Kp = (1.20)^2 / 0.800$, ft from (b) **M1**

(c) Kp = 1.80 awrt **A1**

(c) units: atm **B1**

(c) Answer: Kp = 1.80 atm

(d) position of equilibrium shifts towards N_2O_4 (to the left, towards fewer moles of gas) **B1**

(d) the system opposes the increase in pressure (Le Chatelier's principle) by favouring the side with fewer gas molecules (1 mol N_2O_4 compared with 2 mol NO_2), reducing the total moles of gas and so the pressure oe **B1**

(d) Answer: Equilibrium shifts left, towards N_2O_4, since this side has fewer gas moles, partially opposing the pressure increase.

Question 8

(a) moles of PCl_5 reacted = 2.00 - 1.20 = 0.80 mol **M1**

(a) moles PCl_3 = moles Cl_2 = 0.80 mol (1:1:1 stoichiometry) **A1**

(a) Answer: PCl_3 = Cl_2 = 0.80 mol

(b) divides each number of moles by the volume, 5.00 dm3, ft from (a) **M1**

(b) $[PCl_5]$ = 1.20/5.00 = 0.240 mol dm-3 **A1**

(b) $[PCl_3]$ = $[Cl_2]$ = 0.80/5.00 = 0.160 mol dm-3 (each) **A1**

(b) Answer: $[PCl_5]$ = 0.240 mol dm-3; $[PCl_3]$ = $[Cl_2]$ = 0.160 mol dm-3

(c) Kc = $[PCl_3][Cl_2] / [PCl_5]$ **B1**

(c) Kc = (0.160 x 0.160) / 0.240, ft from (b) **M1**

(c) Kc = 0.107 awrt **A1**

(c) units: mol dm-3 **B1**

(c) Answer: Kc = 0.107 mol dm-3

Question 9

(a) to prevent the loss (by evaporation) of any of the volatile reactants or products (e.g. ethanol or ethyl ethanoate), which would introduce error into the amounts present oe **B1**

(a) Answer: Sealing prevents evaporation of volatile reactants/products, which would introduce error.

(b) adding sodium hydroxide removes the free ethanoic acid from the system, which could disturb/shift this reversible equilibrium; titrating quickly minimises the extent to which the equilibrium shifts during titration, so the result better reflects the true equilibrium composition oe **B1**

(b) Answer: Quick titration minimises the extent to which removing the acid disturbs the equilibrium, keeping the result close to the true equilibrium composition.

(c) moles NaOH = (40.0/1000) x 1.00 **M1**

(c) = 0.0400 mol, so moles CH_3COOH at equilibrium = 0.0400 mol (1:1 neutralisation) cao **A1**

(c) Answer: 0.0400 mol CH_3COOH

(d) moles of CH_3COOH reacted = 0.100 - 0.0400 = 0.0600 mol, ft from (c) **M1**

(d) moles ethanol remaining = 0.100 - 0.0600 = 0.0400 mol **A1**

(d) moles ethyl ethanoate = moles water = 0.0600 mol each (1:1:1:1 stoichiometry) **A1**

(d) Answer: Ethanol = 0.0400 mol; ethyl ethanoate = water = 0.0600 mol each

(e) Kc = $[CH_3COOC_2H_5][H_2O] / ([CH_3COOH][C_2H_5OH])$ **B1**

(e) since all species share the same fixed volume, the volume terms cancel, so Kc = (0.0600 x 0.0600) / (0.0400 x 0.0400), ft from (d) **M1**

(e) Kc = 2.25 cao **A1**

(e) no units, because there are two concentration terms on the top and two on the bottom of the expression, so the units cancel exactly oe **B1**

(e) Answer: Kc = 2.25 (no units)

Question 10

(a) the position of equilibrium shifts towards NH_3 (to the right), because this side has fewer moles of gas (4 mol of gaseous reactants forming 2 mol of gaseous product) oe **B1**

(a) so increasing the pressure increases the equilibrium yield of ammonia oe **B1**

(a) Answer: Equilibrium shifts right (towards NH_3, the side with fewer gas moles), increasing the yield of ammonia.

(b) increasing the pressure increases the concentration of the gas particles (they are pushed closer together in the same volume) oe **B1**

(b) this increases the frequency of collisions between particles, increasing the rate of both the forward and reverse reactions oe **B1**

(b) Answer: Higher pressure increases gas particle concentration, so collisions happen more often, increasing both forward and reverse reaction rates.

(c) the catalyst provides an alternative reaction pathway of lower activation energy, increasing the rate of both the forward and reverse reactions by the same factor oe **B1**

(c) equilibrium is reached more quickly, but the equilibrium position (and therefore the equilibrium yield) is unchanged oe **B1**

(c) Answer: The catalyst speeds up the forward and reverse reactions equally, so equilibrium is reached faster but its position (and yield) is unaffected.

(d) **L3** A detailed, coherent and logically structured explanation that correctly links the effect of temperature on the position of equilibrium (via Le Chatelier's principle, since the forward reaction is exothermic) with its effect on the rate of reaction (via collision theory/the Maxwell-Boltzmann distribution), and clearly explains why a compromise is needed for economic reasons. Accurate scientific terminology is used throughout. **5-6**

(d) **L2** Some relevant scientific points relating to either the equilibrium yield or the rate of reaction are made, with some correct reasoning, but the discussion is not fully developed, may focus mainly on one aspect (yield or rate) with limited linkage between them, or contains minor inaccuracies. **3-4**

(d) **L1** Basic, isolated relevant statements are made (e.g. only that the reaction is exothermic, or only that a lower temperature gives a slower rate), with little structure, linkage or use of scientific reasoning. **1-2**

(d) **L0** No relevant content, or the answer does not relate to the question. **0**

(d) Indicative content:

- The forward reaction is exothermic (deltaH = -92 kJ/mol); by Le Chatelier's principle, decreasing the temperature shifts the position of equilibrium to the right (towards NH_3), increasing the equilibrium yield of ammonia.
- However, decreasing the temperature also decreases the rate of both the forward and reverse reactions, because fewer particles have energy greater than or equal to the activation energy (from the Maxwell-Boltzmann distribution), so fewer collisions are successful.
- At a very low temperature, although the equilibrium yield would be high, the rate of reaction would be far too slow for the process to be economically viable, since it would take too long to reach equilibrium.
- At a very high temperature, the rate of reaction would be fast (equilibrium reached quickly), but the equilibrium would shift to the left (towards N_2 and H_2), lowering the equilibrium yield of ammonia.
- A compromise temperature (around 450°C) is therefore chosen to give a reasonably fast rate of reaction while still achieving an acceptable equilibrium yield of ammonia, balancing rate and yield to maximise overall economic efficiency.
- Any unreacted N_2 and H_2 can be recycled through the reactor, so a lower yield per single pass is an acceptable trade-off if the overall rate of production is high enough, reinforcing why rate is weighed against yield rather than yield alone being maximised.

(d) Answer: Levels-of-response answer; see indicative content.

Question 11

(a) calculates the ratio k2/k1 = $3.51 \times 10^{-4} / 2.00 \times 10^{-5} = 17.6$ awrt **M1**

(a) ln(17.6) = 2.87 awrt **M1**

(a) calculates 1/T1 - 1/T2 = 1/300 - 1/350 = 4.76×10^{-4} K-1 awrt **M1**

(a) rearranges to Ea = R x ln(k2/k1) / (1/T1 - 1/T2) and substitutes values **M1**

(a) Ea = 50.0 kJ/mol awrt **A1**

(a) Answer: Ea = 50.0 kJ/mol

(b) rearranges $k = A e^{-Ea/RT}$ to $A = k \times e^{Ea/RT}$, using the data at T = 300 K, ft from (a) **M1**

(b) Ea/(RT) = 50000/(8.31x300) = 20.1 awrt; $A = 2.00 \times 10^{-5} \times e^{20.1}$ **M1**

(b) $A = 1.03 \times 10^4$ s-1 awrt (units s-1, same as k, since the reaction is first order) **A1**

(b) Answer: $A = 1.03 \times 10^4$ s-1

Question 12

(a) y-axis (ln k): no units (dimensionless) **B1**

(a) x-axis (1/T): K-1 **B1**

(a) Answer: ln k has no units; 1/T has units K-1.

(b) Ea = -gradient x R = 9640 x 8.31 **M1**

(b) Ea = 80100 J/mol awrt **A1**

(b) Ea = 80.1 kJ/mol cao **A1**

(b) Answer: Ea = 80.1 kJ/mol

(c) $A = e^{intercept} = e^{28.5}$ **M1**

(c) $A = 2.38 \times 10^{12}$ awrt **A1**

(c) units: s-1 (since the reaction is first order, A has the same units as k) **B1**

(c) Answer: $A = 2.38 \times 10^{12}$ s-1

Question 13

(a) the profile rises from the reactants to a maximum (the transition state), then falls to the products, which lie at a lower enthalpy than the reactants (since the reaction is exothermic), oe **B1**

(a) Ea(forward) is the (positive) enthalpy difference from the reactants up to the maximum; delta H is the (negative) enthalpy difference between the reactants and the products, oe **B1**

(a) Answer: Enthalpy rises from reactants to a peak (transition state), then falls to products below the reactants' enthalpy.

(b) recognise that delta H = Ea(forward) - Ea(reverse), rearranged to Ea(reverse) = Ea(forward) - delta H **M1**

(b) correct substitution: Ea(reverse) = 75 - (-58) **M1**

(b) 133 kJ/mol, cao **A1**

(b) Answer: 133 kJ/mol

(c) the transition state (peak) is at the same absolute enthalpy whichever direction the reaction is considered, but the products lie at a lower enthalpy than the reactants (exothermic reaction), oe **B1**

(c) so the reverse reaction must climb a larger enthalpy gap, from the lower-enthalpy products up to the peak, than the forward reaction climbs from the higher-enthalpy reactants, oe **B1**

(c) Answer: The reverse reaction climbs from the lower-enthalpy products, a larger gap to the same peak.

(d) correct substitution: Ea(reverse, catalysed) = 52 - (-58) **M1**

(d) 110 kJ/mol, cao **A1**

(d) a catalyst provides a single alternative pathway (with one, lower-energy transition state) used by both the forward and reverse reactions, lowering the activation energy for each by the same amount, so both directions speed up equally and the position of equilibrium (Kc) is unaffected, oe **B1**

(d) Answer: 110 kJ/mol

Question 14

(a) the concentration halves in each successive 10 minute interval (0.800 -> 0.400 -> 0.200 -> 0.100), i.e. a constant half-life **B1**

(a) a constant half-life, independent of concentration, is characteristic of a first order reaction, oe **B1**

(a) Answer: Constant half-life of 10 minutes confirms first order.

(b) correct substitution: k = ln2/10 **M1**

(b) 0.0693 min^{-1} (accept 0.069) **A1**

(b) units: min^{-1} (a first order rate constant has units of 1/time only) **B1**

(b) Answer: 0.0693 min^{-1}

(c) correct method: 0.0693/60 **M1**

(c) 1.16 x 10^{-3} s^{-1} (accept 1.15-1.16 x 10^{-3}) **A1**

(c) Answer: 1.16 x 10^{-3} s^{-1}

(d) correct substitution: $[X] = 0.800 \times e^{-0.0693 \times 45}$ **M1**

(d) 0.0354 mol/dm3 (accept 0.035-0.036), cao **A1**

(d) Answer: 0.0354 mol/dm3

Question 15

(a) ln(k2/k1) = (Ea/R)(1/T1 - 1/T2), oe (accept ln k = ln A - Ea/RT as the base form) **B1**

(a) Answer: ln(k2/k1) = (Ea/R)(1/T1 - 1/T2)

(b) correct calculation of ln(k2/k1) = ln(13.25) = 2.58 **M1**

(b) correct calculation of (1/T1 - 1/T2) = 3.07×10^{-4} K^{-1} **M1**

(b) correct substitution: Ea = R x ln(k2/k1) / (1/T1 - 1/T2) **M1**

(b) Ea = 70000 J/mol **A1**

(b) Ea = 70.0 kJ/mol (correct conversion and to 3 sf) **B1**

(b) Answer: 70.0 kJ/mol

(c) correct rearrangement: $A = k1 / e^{-Ea/(RT1)} = k1 \times e^{Ea/(RT1)}$ **M1**

(c) correct substitution: $A = 4.00 \times 10^{-4} \times e^{70000/(8.31 \times 298)}$ **M1**

(c) 7.4×10^{8} s^{-1} (accept $7.0\text{-}7.8 \times 10^{8}$), ft **A1**

(c) Answer: 7.4×10^{8} s^{-1}

Question 16

(a) a small, fixed amount of I_2 is produced (and immediately consumed by the fixed amount of thiosulfate added) before the blue-black colour appears, so the same fixed extent of reaction occurs in every experiment, oe **B1**

(a) since this fixed amount of reaction corresponds to a fixed amount of product formed, a shorter time means a faster average rate over that period, so rate is proportional to 1/t, oe **B1**

(a) Answer: A fixed extent of reaction occurs before the colour change, so rate is proportional to 1/t.

(b) calculate 1/t (proportional to rate) for each experiment: 0.0250, 0.0500, 0.0752 s^{-1} **M1**

(b) comparing Experiments 1 and 2: $[S_2O_8^{2-}]$ doubles and 1/t (rate) doubles **M1**

(b) comparing Experiments 1 and 3: $[S_2O_8^{2-}]$ triples and 1/t (rate) triples, confirming a directly proportional relationship **A1**

(b) order with respect to $S_2O_8^{2-}$ = 1 (first order) **A1**

(b) Answer: First order with respect to $S_2O_8^{2-}$.

(c) a straight line through the origin, oe **B1**

(c) a straight line through the origin shows that 1/t (and hence rate) is directly proportional to $[S_2O_8^{2-}]$, confirming first order, oe **B1**

(c) Answer: A straight line through the origin, confirming first order.

(d) the concentration of iodide ions, $[I^-]$, oe **B1**

(d) the (small, fixed) volume/amount of sodium thiosulfate and starch indicator added, and the total volume of the reaction mixture (made up with water), oe **B1**

(d) Answer: $[I^-]$ and the amount of thiosulfate/starch (and total volume) used.

Question 17

(a) $Kp = p(SO_3)^2 / (p(SO_2)^2 \times p(O_2))$ **B1**

(a) units: atm^{-1} (since $(atm^2)/(atm^2 \times atm) = atm^{-1}$) **B1**

(a) Answer: $Kp = p(SO_3)^2 / (p(SO_2)^2 \times p(O_2))$; units atm^{-1}.

(b) correct substitution: $(1.00)^2 / ((0.40)^2 \times 0.60)$ **M1**

(b) 10.4 atm^{-1} (accept 10.4-10.5), cao **A1**

(b) units consistent with (a): atm^{-1} **B1**

(b) Answer: 10.4 atm^{-1}

(c) the position of equilibrium shifts towards the side with fewer gas moles, i.e. towards SO_3 (the products), oe **B1**

(c) because the system opposes the increase in pressure by favouring the side that reduces the total number of gas particles, oe **B1**

(c) Kp itself is unaffected by a change in pressure; Kp changes only with temperature, oe **B1**

(c) Answer: Equilibrium shifts towards SO_3; Kp is unchanged (depends only on temperature).

(d) Kp decreases **B1**

(d) increasing temperature favours the endothermic (reverse) reaction, shifting equilibrium away from products (SO_3), decreasing the equilibrium proportion of SO_3 relative to SO_2 and O_2, and hence decreasing Kp, oe **B1**

(d) Answer: Kp decreases, because increased temperature favours the endothermic reverse reaction.

Question 18

Level 3 A detailed, correct and coherent explanation linking the shape and shift of the Boltzmann distribution, the exponential term in the Arrhenius equation, and the alternative lower-Ea pathway provided by a catalyst, to the fraction of successful collisions in each case. Both the temperature effect and the catalyst effect are explained and clearly linked using appropriate terminology. **5-6**

Level 2 A mostly correct explanation of the temperature effect and/or the catalyst effect, referencing the Boltzmann distribution and activation energy, but with a gap, an underdeveloped link, or a minor inaccuracy in one part of the answer. **3-4**

Level 1 Some relevant, briefly stated points are made (e.g. 'particles have more energy' or 'a catalyst lowers activation energy') but without reference to the distribution shape or the exponential relationship, and without a coherent explanation of why the rate increase is large. **1-2**

Indicative content:

- The Boltzmann distribution shows the spread of kinetic energies of particles in a sample at a given temperature; only particles with energy equal to or greater than the activation energy, Ea, can react on collision.
- A small increase in temperature shifts the distribution only slightly (the peak moves slightly to higher energy and the curve broadens/flattens), but because Ea usually lies well out in the tail of the distribution, even this small shift causes a disproportionately large increase in the fraction of particles with energy >= Ea.
- This is reflected in the exponential term, e^(-Ea/RT), in the Arrhenius equation: because Ea/RT appears in an exponent, a small change in T produces a large, non-linear change in the rate constant k, and hence in rate.
- A catalyst provides an alternative reaction pathway/mechanism with a lower activation energy, without being used up in the overall reaction.
- Because this lower activation energy lies further to the left on the (unchanged) Boltzmann distribution for the same temperature, a much larger fraction of collisions now have sufficient energy to react, so the rate increases without any change in temperature.
- Both effects can be understood as increasing the proportion of successful (sufficiently energetic) collisions: temperature does this by shifting/broadening the energy distribution, while a catalyst does this by lowering the energy threshold that must be exceeded.

Question 19

(a) correct substitution: (0.3/40.0) x 100 **M1**

(a) 0.75%, cao **A1**

(a) Answer: 0.75%

(b) correct substitution: (0.3/13.3) x 100 **M1**

(b) 2.3% (accept 2.2-2.3%) **A1**

(b) Answer: 2.3%

(c) the fixed absolute uncertainty (± 0.3 s) is a larger proportion of the smaller measured time (13.3 s) than of the larger measured time (40.0 s), oe **B1**

(c) so, for a fixed absolute uncertainty in the timing method, percentage uncertainty is generally larger for shorter (faster) measured times, oe **B1**

(c) Answer: A fixed absolute uncertainty is a larger fraction of a shorter measured time.

(d) a valid suggestion, e.g. use a more dilute reaction mixture (lower $[S_2O_8^{2-}]$) so the reaction takes longer, oe, or use a light sensor/data logger to trigger the start and stop automatically **B1**

(d) elaboration linking the suggestion to a reduced percentage uncertainty, e.g. a longer measured time means the same fixed absolute uncertainty makes up a smaller percentage of the total time, oe, or a light sensor removes human reaction-time uncertainty, reducing the absolute uncertainty itself **B1**

(d) Answer: Use a more dilute mixture (longer time) or an automated light-sensor timer.