2.10 Chemistry: Rate Equations and Equilibrium

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 core definitions used throughout the study of chemical equilibrium.

(a) State what is meant by the equilibrium constant, Kc, for a reversible reaction. **(1)**

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

(Total for Question 1 is 2 marks)

2 A reversible reaction can be catalysed to speed up the rate at which it reaches equilibrium.

(a) State how a catalyst affects the rate of a reaction, and explain why, in terms of activation energy. **(2)**

(b) Explain why the addition of a catalyst does not change the value of Kc for a reversible reaction. **(2)**

(Total for Question 2 is 4 marks)

3 The units of a rate constant, k, depend on the overall order of reaction. For a reaction with rate = $k[A]^n$, the units of k can be found by dimensional analysis, since rate always has units of mol dm-3 s-1 and concentration [A] always has units of mol dm-3.

(a) A reaction is overall second order, with rate equation rate = $k[A]^2$. Show, using dimensional analysis, that the units of k for this reaction are dm3 mol-1 s-1. **(2)**

(b) State, without further working, the units of the rate constant for a reaction that is (i) zero order overall and (ii) third order overall. **(2)**

(Total for Question 3 is 4 marks)

4 A reaction between three species, P, Q and R, was investigated using the initial rates method. The table shows the results of four experiments carried out at the same constant temperature.

Experiment	[P] (mol dm-3)	[Q] (mol dm-3)	[R] (mol dm-3)	Initial rate (mol dm-3 s-1)
1	0.020	0.010	0.010	4.0×10^{-4}
2	0.040	0.010	0.010	8.0×10^{-4}
3	0.040	0.020	0.010	8.0×10^{-4}
4	0.040	0.020	0.020	1.6×10^{-3}

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

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

(c) Using experiments 3 and 4, determine the order of reaction with respect to R. **(2)**
Show your reasoning.

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

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

(f) Predict the initial rate of reaction when [P] = 0.060 mol dm-3, [Q] = 0.050 mol dm-3 and [R] = 0.030 mol dm-3, at the same temperature. **(2)**

(Total for Question 4 is 13 marks)

5 Dinitrogen pentoxide decomposes according to the equation:

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

The concentration of N_2O_5 was monitored during this decomposition at a constant temperature. The results are shown in the table.

Time (min)	0	15	30	45
$[N_2O_5]$ (mol dm-3)	0.640	0.320	0.160	0.0800

You may use: for a first order reaction, $k = \ln 2 / t(1/2)$.

(a) Explain, using the data, why this reaction is first order with respect to N_2O_5. **(2)**

(b) State the half-life of this reaction. **(1)**

(c) Calculate the rate constant, k, for this reaction, in units of s-1. Give your answer to 3 significant figures. **(3)**

(d) Calculate the total time, from t = 0, taken for the concentration of N_2O_5 to fall to 0.0400 mol dm-3. **(2)**

(Total for Question 5 is 8 marks)

6 Sulfur dioxide is oxidised to sulfur trioxide in the Contact process:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ deltaH(forward) = -197 kJ/mol
1.00 mol of SO_2 and 0.60 mol of O_2 were mixed in a sealed 2.0 dm3 container and allowed to reach equilibrium at a constant temperature. At equilibrium, 0.20 mol of O_2 remained.

(a) Construct an ICE (initial, change, equilibrium) summary for this reaction, and hence determine the amount, in mol, of SO_2 and of SO_3 at equilibrium. **(3)**

(b) Calculate the equilibrium concentration of SO_2, O_2 and SO_3. **(2)**

(c) Write the expression for Kc for this equilibrium and use your answer to (b) to calculate its value, stating units. **(3)**

(d) State and explain the effect on the value of Kc of increasing the temperature of this system. **(2)**

(Total for Question 6 is 10 marks)

7 The reaction between peroxydisulfate(VI) ions and iodide ions was investigated using the initial rates method:

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

The table shows the results of three experiments carried out at the same constant temperature.

Experiment	$[S_2O_8^{2-}]$ (mol dm-3)	$[I^-]$ (mol dm-3)	Initial rate (mol dm-3 s-1)
1	0.0100	0.0100	1.20×10^{-5}
2	0.0200	0.0100	2.40×10^{-5}
3	0.0200	0.0200	4.80×10^{-5}

(a) Using experiments 1 and 2, determine the order of reaction with respect to $S_2O_8^{2-}$. Show your reasoning. **(2)**

(b) Using experiments 2 and 3, determine the order of reaction with respect to I^-. 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)**

(e) Predict the initial rate of reaction when $[S_2O_8^{2-}]$ = 0.0400 mol dm-3 and $[I^-]$ = 0.0150 mol dm-3, at the same temperature. **(2)**

(Total for Question 7 is 11 marks)

8 Hydrogen peroxide decomposes in the presence of a manganese(IV) oxide catalyst:
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
A student follows the reaction by collecting the oxygen gas produced in a gas syringe. When the reaction is complete, the total volume of oxygen collected is V(infinity) = 48.0 cm^3. The volume of oxygen collected, V(t), was also recorded at intervals:

Time (min)	0	5.00	10.00	15.00	20.00
V(t) (cm3)	0.00	24.0	36.0	42.0	45.0

Since oxygen is produced as H_2O_2 is used up, the quantity [V(infinity) - V(t)] is directly proportional to the concentration of H_2O_2 remaining in the solution at time t.

(a) Explain why the quantity [V(infinity) - V(t)] is directly proportional to the concentration of H_2O_2 remaining at time t, rather than V(t) itself. **(2)**

(b) Calculate the value of [V(infinity) - V(t)] at each of the five times given, and hence show that this reaction is first order with respect to H_2O_2. **(3)**

(c) State the half-life of this reaction. **(1)**

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

(e) Calculate the total time, from t = 0, taken for [V(infinity) - V(t)] to fall to 1.50 cm^3. **(2)**

(Total for Question 8 is 11 marks)

9 In a follow-up investigation of the same acid-catalysed iodination of propanone (CH_3COCH_3 + I_2 -(H^+ catalyst)-> CH_3COCH_2I + HI), the initial rate was found (using the colorimetry method described previously) for four different starting concentrations of hydrochloric acid, with [propanone] kept constant at 0.500 mol dm-3 and [I_2] also kept constant throughout.

[HCl] (mol dm-3)	0.50	1.00	1.50	2.00
Initial rate (x10^{-5} mol dm-3 s-1)	2.50	5.00	7.50	10.00

(a) Using the data, deduce the order of reaction with respect to H^+ (the catalyst). Explain your reasoning. **(2)**

(b) Given that [propanone] was 0.500 mol dm-3 throughout, and that the reaction is zero order with respect to iodine, write the overall rate equation and use the data to calculate the rate constant, k, stating its units. **(4)**

(c) State two variables, other than the concentrations already discussed, that must be kept constant across this series of experiments for the comparison to be valid. **(2)**

(Total for Question 9 is 8 marks)

10 $X(g) + Y(g) \rightleftharpoons 2W(g)$

At a certain temperature, Kc for this equilibrium = 4.0 (no units). A mixture initially containing 1.00 mol dm-3 of X and 1.00 mol dm-3 of Y, with no W present, is allowed to reach equilibrium at constant volume and temperature.

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

(b) Using x mol dm-3 as the fall in concentration of X at equilibrium, complete an ICE table for this reaction in terms of x. **(2)**

(c) Use the value of Kc to calculate x, and hence the equilibrium concentration of X, Y and W. **(4)**

(d) Verify your answer to part (c) by substituting your equilibrium concentrations back into the Kc expression. **(1)**

(Total for Question 10 is 8 marks)

11 The concentration of a reactant, V, was monitored during a reaction at a constant temperature:

Time (min)	0	1.000	3.000	7.000
[V] (mol dm-3)	1.000	0.500	0.250	0.125

You may use, for a second order reaction: $1/[V] = 1/[V]0 + kt$

(a) Using the data, calculate the time taken for each of the three successive halvings of [V] shown (that is, from 1.000 to 0.500, from 0.500 to 0.250, and from 0.250 to 0.125 mol dm-3). **(2)**

(b) Describe the pattern in these successive half-lives. **(1)**

(c) Deduce the order of reaction with respect to V. Justify your answer using the pattern identified in part (b). **(2)**

(d) Using two of the data points and the integrated rate equation for a second order reaction, calculate the rate constant, k, for this reaction, stating its units. **(3)**

(Total for Question 11 is 8 marks)

12 2-bromo-2-methylpropane, $(CH_3)_3CBr$, undergoes hydrolysis with aqueous sodium hydroxide:
$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$
The rate equation for this reaction, found by experiment, is:
rate = $k[(CH_3)_3CBr]$

(a) State the overall order of this reaction and the order with respect to hydroxide ions, OH^-. Justify both answers using the rate equation given. **(3)**

(b) Deduce whether the mechanism for this reaction is SN1 or SN2. Explain your reasoning. **(2)**

(c) Write an equation for the rate-determining step of this mechanism. **(2)**

(Total for Question 12 is 7 marks)

13 The overall equation for a reaction is:

$2E(g) + F(g) \rightarrow 2EF(g)$

The experimentally determined rate equation is rate = k[E][F].

Two possible mechanisms have been suggested.

Mechanism 1:

Step 1 (slow): $E + F \rightarrow EF + G$

Step 2 (fast): $E + G \rightarrow EF$

Mechanism 2:

Step 1 (slow): $2E \rightarrow E2$

Step 2 (fast): $E2 + F \rightarrow 2EF$

(a) Show that Mechanism 1 is consistent with both the overall equation and the experimental rate equation. **(2)**

(b) Deduce the rate equation that Mechanism 2 predicts, and explain why Mechanism 2 can be ruled out. **(3)**

(c) State the role of species G (in Mechanism 1) and of species E2 (in Mechanism 2), and explain how you can identify each as playing this role. **(2)**

(Total for Question 13 is 7 marks)

14 Nitrosyl chloride decomposes according to the equation:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

2.00 mol of NOCl(g) was introduced into an evacuated container and allowed to reach equilibrium at a constant temperature; the total pressure at equilibrium was 100 kPa. At equilibrium, 1.00 mol of NOCl remained unreacted.

(a) Calculate the amount, in mol, of NO and of Cl_2 present at equilibrium, and hence the total number of moles of gas present. **(3)**

(b) Calculate the mole fraction of each of the three gases at equilibrium. **(2)**

(c) Hence calculate the partial pressure of each gas at equilibrium. **(2)**

(d) Write the expression for Kp for this equilibrium and calculate its value, stating units. **(3)**

(e) Explain the effect, if any, of increasing the total pressure on this system, at constant temperature, on (i) the position of equilibrium and (ii) the value of Kp. **(3)**

(Total for Question 14 is 13 marks)

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15 Increasing the temperature of a reversible, exothermic reaction increases the rate at which equilibrium is reached, but decreases the equilibrium yield of product.

(a) Explain, in terms of rate constants and activation energy, why both of these observations occur. **(6)**

(Total for Question 15 is 6 marks)

16 Propanone reacts with iodine in the presence of a hydrochloric acid catalyst:

$CH_3COCH_3 + I_2$ -(H^+ catalyst)-> $CH_3COCH_2I + HI$

Iodine solution is coloured, but propanone, hydrochloric acid and the organic products are colourless, so the reaction can be monitored using a colorimeter. A calibration curve for this colorimeter gives the relationship: Absorbance = 20.0 x $[I_2]$, where $[I_2]$ is in mol dm-3.

In one experiment, the absorbance of the reaction mixture was recorded every 60 seconds:

Time (s)	0	60	120	180	240
Absorbance	0.800	0.680	0.560	0.440	0.320

(a) Explain why a colorimeter can be used to monitor the concentration of iodine during this reaction, but cannot be used to monitor the concentration of propanone or hydrochloric acid. **(2)**

(b) State and explain what the shape of the absorbance-time graph shows about the order of reaction with respect to iodine. **(3)**

(c) Using the calibration relationship and the gradient of the absorbance-time graph, calculate the rate of this reaction, in mol dm-3 s-1. **(3)**

(d) Given that this reaction is also known to be first order with respect to propanone and first order with respect to H^+ ions, write the overall rate equation for this reaction. **(2)**

(e) Suggest why it is convenient, when using this method to find the rate, that the reaction is zero order with respect to iodine. **(2)**

(Total for Question 16 is 12 marks)

17 Ammonia is manufactured industrially by the Haber process:

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

Industrially, this reaction is typically carried out at a compromise temperature of about 450°C and a compromise pressure of about 200 atm, using an iron catalyst, rather than at a lower temperature (which would give a higher equilibrium yield) or a much higher pressure (which would give an even higher yield).

Evaluate this choice of industrial conditions, in terms of the rate at which equilibrium is reached, the equilibrium yield (percentage conversion) of ammonia, and economic and practical factors. You should refer to the effects of temperature, pressure and the iron catalyst in your answer.

(Total for Question 17 is 6 marks)

18 The rate constant for a gas-phase reaction was measured at two temperatures: k1 = 3.50×10^{-4} s-1 at T1 = 298 K, and k2 = 1.75×10^{-3} s-1 at T2 = 318 K.
You may use: ln(k2/k1) = -(Ea/R)(1/T2 - 1/T1); R = 8.31 J K-1 mol-1.

(a) Calculate the activation energy, Ea, for this reaction, in kJ/mol, to 3 significant figures. **(4)**

(b) Using this value of Ea and the rate constant k2 at T2 = 318 K, calculate the rate constant, k3, at T3 = 338 K. **(4)**

(c) Explain, using the Maxwell-Boltzmann distribution, why an increase in temperature increases the value of the rate constant. **(2)**

(Total for Question 18 is 10 marks)

19 The reaction between nitrogen dioxide and carbon monoxide has the overall equation:
$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$
The rate equation for this reaction, found by experiment, is rate = $k[NO_2]^2$ (the reaction is zero order with respect to CO).
Two mechanisms have been suggested.
Mechanism 1:
Step 1 (slow): $2NO_2 \rightarrow NO_3 + NO$
Step 2 (fast): $NO_3 + CO \rightarrow NO_2 + CO_2$
Mechanism 2 (a single-step mechanism):
Step 1 (slow): $NO_2 + CO \rightarrow NO + CO_2$

(a) Show that Mechanism 1 is consistent with the overall equation, identifying any species that does not appear in the overall equation and stating its role. **(3)**

(b) Deduce the rate equation predicted by each mechanism, and explain which mechanism is consistent with the experimental rate equation. **(4)**

(c) Suggest why increasing [CO] has no effect on the rate of this reaction. **(1)**

(Total for Question 19 is 8 marks)

20 A student studies the reaction between hydrogen peroxide and iodide ions in acidic solution:
$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$
At intervals, a 10.0 cm^3 sample of the reaction mixture is removed and immediately quenched (to stop the reaction), then titrated with 0.0500 mol dm-3 sodium thiosulfate solution, using the reaction $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$, to determine the amount of iodine formed in the sample.

Time (s)	0	60.0	120	180	240
Titre of thiosulfate (cm3)	0.00	8.20	14.60	19.40	23.00

Each titre has an uncertainty of ± 0.10 cm^3 (from an initial and a final burette reading, each accurate to ± 0.05 cm^3).

(a) Use the titre at t = 60.0 s to calculate the amount, in mol, of iodine, I_2, present in the 10.0 cm^3 sample at this time, and hence the concentration of I_2 in the reaction mixture at t = 60.0 s. **(3)**

(b) The concentration of I_2 in the reaction mixture, calculated in the same way, was found to be 0.0365 mol dm-3 at t = 120 s. Estimate the initial rate of formation of I_2, using the gradient between t = 0 and t = 60.0 s. **(2)**

(c) Calculate the percentage uncertainty in the titre at t = 60.0 s and at t = 240 s, and hence comment on how the percentage uncertainty in the titre changes as the reaction proceeds. **(3)**

(d) Suggest why quenching the sample immediately on removal is essential for this method, and suggest one practical way the reaction could be quenched. **(2)**

(Total for Question 20 is 10 marks)

Mark scheme · 2.10 Chemistry: Rate Equations and Equilibrium

Question 1

(a) the ratio of the concentrations of products to reactants at equilibrium, each raised to the power of its balancing number, at a constant (fixed) temperature oe **B1**

(a) Answer: The ratio of product to reactant concentrations at equilibrium, each raised to its balancing number, at a fixed temperature.

(b) a state, in a closed system, in which the rate of the forward reaction equals the rate of the reverse reaction, so the concentrations of reactants and products remain constant, but both reactions continue to occur oe **B1**

(b) Answer: A state in a closed system where the forward and reverse reaction rates are equal, so concentrations remain constant even though both reactions continue.

Question 2

(a) a catalyst increases the rate of reaction by providing an alternative reaction pathway with a lower activation energy oe **B1**

(a) a greater proportion of particles now have energy greater than or equal to this lower activation energy, so more collisions are successful, increasing the rate constant, k, for both the forward and reverse reactions oe **B1**

(a) Answer: A catalyst provides an alternative pathway of lower activation energy, so more particles have sufficient energy to react, increasing k for both the forward and reverse reactions.

(b) a catalyst increases the rate constants of the forward and reverse reactions, kf and kr, by the same factor oe **B1**

(b) since Kc = kf/kr, this ratio is unchanged, so the value of Kc is unaffected; equilibrium is reached faster, but its position is unchanged oe **B1**

(b) Answer: Because the catalyst increases kf and kr by the same factor, the ratio Kc = kf/kr is unchanged; only the time taken to reach equilibrium is reduced.

Question 3

(a) mol dm-3 s-1 = k x (mol dm-3)^2, so k = (mol dm-3 s-1) / (mol dm-3)^2 oe **M1**

(a) k units = dm3 mol-1 s-1 cao **A1**

(a) Answer: k units = dm3 mol-1 s-1

(b) zero order: units of k = mol dm-3 s-1 **B1**

(b) third order: units of k = mol-2 dm6 s-1 (dm6 mol-2 s-1) **B1**

(b) Answer: Zero order: mol dm-3 s-1. Third order: mol-2 dm6 s-1.

Question 4

(a) [P] doubles (0.020 to 0.040) with [Q] and [R] both constant, and the initial rate doubles (4.0×10^{-4} to 8.0×10^{-4}) oe **M1**

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

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

(b) [Q] doubles (0.010 to 0.020) with [P] and [R] both constant, but the initial rate is unchanged (8.0×10^{-4} in both experiments) oe **M1**

(b) order with respect to Q = 0 (zero order) cao **A1**

(b) Answer: Order with respect to Q = 0

(c) [R] doubles (0.010 to 0.020) with [P] and [Q] both constant, and the initial rate doubles (8.0×10^{-4} to 1.6×10^{-3}) oe **M1**

(c) order with respect to R = 1 cao **A1**

(c) Answer: Order with respect to R = 1

(d) overall order = 1 + 0 + 1 = 2, ft from (a) to (c) **M1**

(d) rate = k[P][R] (Q does not appear, since it is zero order) **A1**

(d) Answer: Overall order = 2; rate = k[P][R]

(e) k = rate / ([P][R]) = 4.0×10^{-4} / (0.020 x 0.010), ft from (d) **M1**

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

(e) units: dm3 mol^{-1} s^{-1} (mol^{-1} dm3 s-1) **A1**

(e) Answer: k = 2.0 dm3 mol^{-1} s^{-1}

(f) rate = k[P][R] = 2.0 x 0.060 x 0.030, ft from (e) ([Q] is not used, since the reaction is zero order in Q) **M1**

(f) rate = 3.6 x 10^{-3} mol dm-3 s-1 cao **A1**

(f) Answer: 3.6 x 10^{-3} mol dm-3 s-1

Question 5

(a) the time taken for [N_2O_5] to halve is the same (15 minutes) for each interval shown in the table oe **B1**

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

(a) Answer: The half-life is constant at 15 minutes throughout, which is characteristic of first order kinetics.

(b) 15 minutes cao **B1**

(b) Answer: 15 minutes

(c) t(1/2) = 15 min = 900 s **M1**

(c) k = ln2 / 900 **M1**

(c) k = 7.70 x 10^{-4} s-1 awrt **A1**

(c) Answer: k = 7.70 x 10^{-4} s-1

(d) recognises that 0.0400 mol dm-3 is reached after one further half-life beyond t = 45 minutes (0.0800 halves to 0.0400) **M1**

(d) 60 minutes cao **A1**

(d) Answer: 60 minutes

Question 6

(a) change in moles of O_2 = -0.40 mol; change in moles of SO_2 = -0.80 mol (using 2:1 stoichiometry with O_2) **M1**

(a) change in moles of SO_3 = +0.80 mol (using 2:1 stoichiometry with O_2) **M1**

(a) $n(SO_2)$ at equilibrium = 0.20 mol and $n(SO_3)$ at equilibrium = 0.80 mol cao **A1**

(a) Answer: $n(SO_2)$ = 0.20 mol; $n(SO_3)$ = 0.80 mol at equilibrium

(b) concentration = moles / volume (dividing each amount by 2.0 dm3), ft from (a) **M1**

(b) $[SO_2] = [O_2]$ = 0.10 mol dm-3 and $[SO_3]$ = 0.40 mol dm-3 cao **A1**

(b) Answer: $[SO_2]$ = 0.10 mol dm-3; $[O_2]$ = 0.10 mol dm-3; $[SO_3]$ = 0.40 mol dm-3

(c) $Kc = [SO_3]^2 / ([SO_2]^2 [O_2])$ **B1**

(c) $Kc = (0.40)^2 / ((0.10)^2 \times 0.10)$, ft from (b) **M1**

(c) Kc = 160 dm3 mol^{-1} awrt cao **A1**

(c) Answer: Kc = 160 dm3 mol^{-1}

(d) Kc decreases **B1**

(d) because the forward reaction is exothermic, increasing temperature favours the endothermic (reverse) reaction, shifting the position of equilibrium to the left (reducing $[SO_3]$ and increasing $[SO_2]$ and $[O_2]$), so the value of Kc decreases oe **B1**

(d) Answer: Kc decreases, because increasing temperature favours the endothermic reverse reaction, shifting equilibrium away from SO_3.

Question 7

(a) $[S_2O_8^{2-}]$ doubles (0.0100 to 0.0200) with $[I^-]$ constant, and the initial rate doubles (1.20×10^{-5} to 2.40×10^{-5}) oe **M1**

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

(a) Answer: Order with respect to $S_2O_8^{2-}$ = 1

(b) $[I^-]$ doubles (0.0100 to 0.0200) with $[S_2O_8^{2-}]$ constant, and the initial rate doubles (2.40×10^{-5} to 4.80×10^{-5}) oe **M1**

(b) order with respect to I^- = 1 cao **A1**

(b) Answer: Order with respect to I^- = 1

(c) overall order = 1 + 1 = 2, ft from (a) and (b) **M1**

(c) rate = $k[S_2O_8^{2-}][I^-]$ **A1**

(c) Answer: Overall order = 2; rate = $k[S_2O_8^{2-}][I^-]$

(d) k = rate / $([S_2O_8^{2-}][I^-]) = 1.20 \times 10^{-5} / (0.0100 \times 0.0100)$, ft from (c) **M1**

(d) k = 0.120 cao **A1**

(d) units: dm3 mol-1 s-1 **A1**

(d) Answer: k = 0.120 dm3 mol-1 s-1

(e) rate = $k[S_2O_8^{2-}][I^-]$ = 0.120 x 0.0400 x 0.0150, ft from (d) **M1**

(e) rate = 7.20×10^{-5} mol dm-3 s-1 cao **A1**

(e) Answer: 7.20×10^{-5} mol dm-3 s-1

Question 8

(a) V(t) is the (cumulative) volume of oxygen already released, which is proportional to the amount of H_2O_2 already reacted, not the amount remaining oe **B1**

(a) so the volume of oxygen still to be released, [V(infinity) - V(t)], is proportional to the amount (concentration) of H_2O_2 that has not yet reacted oe **B1**

(a) Answer: V(t) is proportional to H_2O_2 already reacted; [V(infinity) - V(t)] is the oxygen still to be released, so it is proportional to the H_2O_2 remaining.

(b) correct values of [V(infinity) - V(t)]: 48.0, 24.0, 12.0, 6.00, 3.00 cm^3 at t = 0, 5.00, 10.00, 15.00, 20.00 min respectively **M1**

(b) identifies that this quantity halves in each successive 5.00 minute interval (a constant half-life of 5.00 min) oe **M1**

(b) a constant half-life, independent of concentration, is characteristic of a first order reaction, so the reaction is first order with respect to H_2O_2 cao **A1**

(b) Answer: [V(infinity) - V(t)] = 48.0, 24.0, 12.0, 6.00, 3.00 cm^3; the constant 5.00 min half-life shows the reaction is first order in H_2O_2.

(c) 5.00 minutes cao **B1**

(c) Answer: 5.00 minutes

(d) t(1/2) = 5.00 min = 300 s **M1**

(d) k = ln2 / 300 **M1**

(d) k = 2.31 x 10^{-3} s-1 awrt **A1**

(d) Answer: k = 2.31 x 10^{-3} s-1

(e) recognises 1.50 cm^3 is reached one further half-life after t = 20.00 min (3.00 cm^3 halves to 1.50 cm^3) **M1**

(e) 25.0 minutes cao **A1**

(e) Answer: 25.0 minutes

Question 9

(a) the initial rate is directly proportional to [HCl] (e.g. doubling [HCl] from 0.50 to 1.00 mol dm-3 doubles the initial rate from 2.50×10^{-5} to 5.00×10^{-5} mol dm-3 s-1) oe **M1**

(a) order with respect to H^+ = 1 (first order) cao **A1**

(a) Answer: Order with respect to H^+ = 1

(b) rate = $k[CH_3COCH_3][H^+]$ (no $[I_2]$ term, since zero order in I_2) **B1**

(b) k = rate / $([CH_3COCH_3][H^+]) = 2.50 \times 10^{-5} / (0.500 \times 0.50)$, using any experiment **M1**

(b) k = 1.00 x 10^{-4} cao **A1**

(b) units: dm3 mol^{-1} s^{-1} (mol^{-1} dm3 s-1), consistent with an overall second order reaction **B1**

(b) Answer: rate = $k[CH_3COCH_3][H^+]$; k = 1.00 x 10^{-4} dm3 mol^{-1} s^{-1}

(c) temperature **B1**

(c) the total volume of the reaction mixture (so the concentrations calculated remain accurate), or the colorimeter/calibration settings used to convert absorbance to concentration **B1**

(c) Answer: Temperature, and the total volume of the reaction mixture (or the colorimeter calibration used).

Question 10

(a) $K_c = [W]^2 / ([X][Y])$ **B1**

(a) Answer: $K_c = [W]^2 / ([X][Y])$

(b) equilibrium concentrations of X and Y in terms of x: [X] = [Y] = (1.00 - x) mol dm-3 **M1**

(b) equilibrium concentration of W in terms of x: [W] = 2x mol dm-3 (using 1:1:2 stoichiometry) **A1**

(b) Answer: [X] = [Y] = (1.00 - x); [W] = 2x, all in mol dm-3

(c) substitutes into the Kc expression, ft from (a) and (b): $4.0 = (2x)^2 / (1.00 - x)^2$ **M1**

(c) takes the square root of both sides (valid since [X] = [Y]): 2.0 = 2x / (1.00 - x), or equivalent full expansion/solution **M1**

(c) correct rearrangement and solution: x = 0.50 **M1**

(c) [X] = [Y] = 0.50 mol dm-3 and [W] = 1.00 mol dm-3 cao **A1**

(c) Answer: x = 0.50; [X] = [Y] = 0.50 mol dm-3; [W] = 1.00 mol dm-3

(d) $K_c = (1.00)^2 / (0.50 \times 0.50) = 1.00/0.25 = 4.0$, which matches the given value, confirming the answer cso **B1**

(d) Answer: $K_c = (1.00)^2 / (0.50 \times 0.50) = 4.0$, matching the given value.

Question 11

(a) correctly identifies each interval: 1.000 min, (3.000 - 1.000) = 2.000 min, (7.000 - 3.000) = 4.000 min **M1**

(a) all three values correct: 1.000 min, 2.000 min, 4.000 min cao **A1**

(a) Answer: 1.000 min, 2.000 min, 4.000 min

(b) each successive half-life is double the one before it; the half-life is not constant, it increases oe **B1**

(b) Answer: Each half-life is double the previous one (the half-life increases, it is not constant).

(c) second order (with respect to V) **B1**

(c) because the half-life doubling each time [V] halves (half-life inversely proportional to concentration) is characteristic of second order kinetics oe (a constant half-life would indicate first order; a halving half-life would indicate zero order) **B1**

(c) Answer: Second order, because the half-life doubles each time the concentration halves, which is characteristic of second order kinetics.

(d) correct substitution using two data points, e.g. 1/0.500 = 1/1.000 + k(1.000) **M1**

(d) correct rearrangement: k = (2.000 - 1.000)/1.000 **M1**

(d) k = 1.00 dm3 mol^{-1} min^{-1} cao **A1**

(d) Answer: k = 1.00 dm3 mol^{-1} min^{-1}

Question 12

(a) overall order = 1 (first order overall) **B1**

(a) order with respect to OH^- = 0 (zero order) **B1**

(a) because $[OH^-]$ does not appear in the rate equation, so changing $[OH^-]$ has no effect on the rate oe **B1**

(a) Answer: Overall order = 1; order with respect to OH^- = 0, because $[OH^-]$ is absent from the rate equation.

(b) SN1 (unimolecular nucleophilic substitution) **B1**

(b) because the rate depends only on the concentration of the halogenoalkane, independent of $[OH^-]$, showing the rate-determining step involves only one species (the halogenoalkane) oe **B1**

(b) Answer: SN1, because the rate is independent of $[OH^-]$, showing the rate-determining step involves only the halogenoalkane.

(c) $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ **M1**

(c) correct species and charges shown, with this identified as the (slow) rate-determining step, involving only the halogenoalkane (OH^- is not involved until the second, fast step) **A1**

(c) Answer: $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ (rate-determining step; OH^- reacts with the carbocation in a second, fast step)

Question 13

(a) adding the two steps of Mechanism 1 together, species G cancels (formed in step 1, used up in step 2), giving the overall equation 2E + F -> 2EF oe **M1**

(a) the rate-determining step (step 1) involves one molecule of E and one molecule of F reacting, matching the experimental rate equation, rate = k[E][F] cso **A1**

(a) Answer: Adding the steps of Mechanism 1 gives 2E + F -> 2EF (G cancels); step 1 (the RDS) involves one E and one F, matching rate = k[E][F].

(b) the rate-determining step in Mechanism 2 (2E -> E2) involves two molecules of E only, with no F **M1**

(b) Mechanism 2 predicts rate = $k[E]^2$ (second order in E, zero order in F) **A1**

(b) this does not match the experimental rate equation, rate = k[E][F] (which is first order in F), so Mechanism 2 can be ruled out cso **A1**

(b) Answer: Mechanism 2 predicts rate = $k[E]^2$, which does not match the experimental rate = k[E][F], so it is ruled out.

(c) G is a reaction intermediate in Mechanism 1, since it is formed in step 1 and used up in step 2, so it does not appear in the overall equation **B1**

(c) E2 is (similarly) a reaction intermediate in Mechanism 2, formed in step 1 and used up in step 2, so it also does not appear in the overall equation oe **B1**

(c) Answer: Both G and E2 are reaction intermediates: each is formed in the first step of its mechanism and consumed in the second, so neither appears in the overall equation.

Question 14

(a) moles of NOCl reacted = 2.00 - 1.00 = 1.00 mol **M1**

(a) moles NO formed = 1.00 mol (1:1 with NOCl reacted); moles Cl_2 formed = 0.50 mol (1:2 with NOCl reacted) **M1**

(a) total moles at equilibrium = 1.00 + 1.00 + 0.50 = 2.50 mol cao **A1**

(a) Answer: n(NO) = 1.00 mol; n(Cl_2) = 0.50 mol; total = 2.50 mol

(b) mole fraction = moles of component / total moles, ft from (a) **M1**

(b) x(NOCl) = 0.400; x(NO) = 0.400; x(Cl_2) = 0.200 cao **A1**

(b) Answer: x(NOCl) = 0.400; x(NO) = 0.400; x(Cl_2) = 0.200

(c) partial pressure = mole fraction x total pressure, ft from (b) **M1**

(c) p(NOCl) = 40.0 kPa; p(NO) = 40.0 kPa; p(Cl_2) = 20.0 kPa cao **A1**

(c) Answer: p(NOCl) = 40.0 kPa; p(NO) = 40.0 kPa; p(Cl_2) = 20.0 kPa

(d) $Kp = (p(NO))^2 \times p(Cl_2) / (p(NOCl))^2$ **B1**

(d) $Kp = (40.0)^2 \times 20.0 / (40.0)^2$, ft from (c) **M1**

(d) Kp = 20.0 kPa cao **A1**

(d) Answer: Kp = 20.0 kPa

(e) the position of equilibrium shifts towards NOCl (to the left), the side with fewer moles of gas (2 mol compared with 3 mol) oe **B1**

(e) because this opposes the increase in pressure (Le Chatelier's principle) by reducing the total number of gas particles oe **B1**

(e) the value of Kp is unaffected (unchanged), because Kp depends only on temperature oe **B1**

(e) Answer: Equilibrium shifts left, towards NOCl (fewer gas moles), opposing the pressure increase; Kp itself is unchanged, since Kp depends only on temperature.

Question 15

(a) **L3** A logical, coherent explanation that links the effect of temperature on the rate constants of both the forward and reverse reactions to the observed change in both rate and equilibrium yield, using the Arrhenius equation and/or the Maxwell-Boltzmann distribution. The answer shows clear understanding of why the reverse (endothermic) rate constant increases proportionally more than the forward (exothermic) rate constant, and links this correctly to the shift in equilibrium position. **5-6**

(a) **L2** Some relevant, mostly correct explanation of why rate increases with temperature (e.g. more particles with energy greater than or equal to Ea) is given, with limited or no valid link to why the equilibrium yield decreases. **3-4**

(a) **L1** Basic, isolated relevant statement(s), e.g. that rate increases with temperature or that yield decreases, without valid supporting explanation. **1-2**

(a) **L0** No relevant content. **0**

(a) Indicative content:

- Increasing temperature increases the average kinetic energy of the particles, shifting the Maxwell-Boltzmann distribution of molecular energies to the right.
- A greater proportion of particles/collisions have energy greater than or equal to the activation energy, Ea.
- This means more successful (effective) collisions occur per unit time, so the rate of reaction increases, for both the forward and the reverse reactions.
- The Arrhenius equation, k = A e^(-Ea/RT), shows that the rate constant, k, increases exponentially as T increases.
- Since the forward reaction is exothermic, the reverse reaction is endothermic and so has a higher activation energy than the forward reaction.
- Because of the exponential term in the Arrhenius equation, the rate constant of the reaction with the higher Ea (the reverse, endothermic reaction) increases by a proportionally greater amount for the same rise in temperature.
- As a result, the rate of the reverse reaction increases more than the rate of the forward reaction.
- Equilibrium is re-established when the forward and reverse rates become equal again; because the reverse rate has increased more, this happens with less product present, so the position of equilibrium shifts towards the reactants.
- This is consistent with Le Chatelier's principle: the system responds to the temperature rise by favouring the endothermic (reverse) direction.
- Both rate constants increase, so equilibrium is reached faster (a kinetic effect), but Kc/Kp for the exothermic forward reaction decreases with increasing temperature, so the equilibrium yield of product is lower (a thermodynamic/equilibrium effect).

(a) Answer: Levels-of-response essay; see indicative content.

Question 16

(a) iodine solution is coloured and absorbs visible light, so its concentration is related (proportional) to the absorbance measured oe **B1**

(a) propanone, hydrochloric acid and the organic products are colourless, so they do not absorb visible light and their concentration cannot be found this way oe **B1**

(a) Answer: Iodine is coloured and absorbs light, so its concentration can be linked to absorbance; the other species are colourless and cannot be monitored this way.

(b) the absorbance (and therefore $[I_2]$) decreases by an equal amount, 0.120, in each successive 60 s interval, i.e. the graph is a straight line of constant negative gradient **M1**

(b) this shows that the rate of reaction is constant and does not depend on (does not slow down as) $[I_2]$ falls **A1**

(b) so the reaction is zero order with respect to iodine cao **A1**

(b) Answer: The absorbance falls linearly (constant gradient), showing the rate is independent of $[I_2]$, i.e. zero order with respect to iodine.

(c) gradient of absorbance-time graph = (0.320 - 0.800) / (240 - 0) = -2.00×10^{-3} s-1 **M1**

(c) converts to a concentration gradient by dividing by the calibration constant, 20.0: $-2.00 \times 10^{-3} / 20.0$ **M1**

(c) rate = 1.00×10^{-4} mol dm-3 s-1 awrt cao **A1**

(c) Answer: Rate = 1.00×10^{-4} mol dm-3 s-1

(d) rate = $k[CH_3COCH_3][H^+]$ **B1**

(d) no $[I_2]$ term is included, since the reaction is zero order with respect to iodine oe **B1**

(d) Answer: rate = $k[CH_3COCH_3][H^+]$

(e) because the rate (and therefore the gradient of the absorbance-time graph) is constant throughout the reaction, not just at t = 0 oe **B1**

(e) so the rate can be found accurately using any two points on the (straight-line) graph, rather than needing to draw a tangent at t = 0 oe **B1**

(e) Answer: Because the rate is constant throughout (the graph is a straight line), the rate can be found from any two points, without needing to draw a tangent at t = 0.

Question 17

Level 3 A logical, coherent evaluation that correctly links the effect of temperature on both rate and equilibrium yield (via Le Chatelier's principle, since the forward reaction is exothermic), the effect of pressure on rate and yield (since there are fewer moles of gas on the product side), and the role of the iron catalyst in increasing rate without affecting the equilibrium yield or Kc, to explain why 450°C and 200 atm represent an economically sensible compromise rather than the conditions that would maximise equilibrium yield alone. **5-6**

Level 2 Some relevant, mostly correct points about the effect of temperature and/or pressure on rate and/or yield, with limited or no clear link to why a compromise is used, or with only partial reference to cost/practical factors or the catalyst's role. **3-4**

Level 1 Basic, isolated relevant statement(s), e.g. that higher temperature increases rate, or that a catalyst is used to speed up the reaction, without a developed link to the equilibrium yield or to the reasoning behind the compromise conditions. **1-2**

Level 0 No relevant content. **0**

Indicative content:

- Increasing temperature increases the rate constant (and so the rate) of both the forward and reverse reactions, so equilibrium is reached faster at 450°C than at a lower temperature.
- Since the forward reaction is exothermic, increasing temperature shifts the position of equilibrium to the left, by Le Chatelier's principle, decreasing the equilibrium yield (percentage conversion) of ammonia.
- 450°C is therefore a compromise: high enough to give an economically acceptable rate (equilibrium reached in a reasonable time), but not so high that the equilibrium yield becomes too low to be worthwhile.
- Increasing pressure increases both the rate (higher concentrations of gas molecules increase collision frequency) and the equilibrium yield, since there are fewer moles of gas on the product side (2 mol NH_3) than the reactant side (4 mol $N_2 + H_2$ in total), so increasing pressure shifts equilibrium to the right, by Le Chatelier's principle.
- 200 atm is a compromise pressure: very high pressures would give an even greater yield and rate, but require much stronger (thicker walled) reaction vessels and pipework, and more energy to compress the gases, greatly increasing capital and running costs.
- The iron catalyst increases the rate of both the forward and reverse reactions by providing a lower activation energy pathway, allowing equilibrium to be reached quickly at 450°C.
- The catalyst does not affect the position of equilibrium or the value of Kc/Kp, so it allows a lower temperature to be used than would otherwise be needed to reach equilibrium quickly, helping to preserve a reasonable yield.
- Unreacted N_2 and H_2 are recycled back into the reactor, so even though the equilibrium yield (single pass) is well below 100 percent (typically around 10-15 percent), the overall conversion over time is much higher, which is another reason very high pressure and low temperature are not needed to make the process economically viable.
- Overall conclusion: the chosen conditions do not maximise the equilibrium yield alone, but instead balance rate, yield, capital/running costs and safety to maximise the economically viable rate of ammonia production per unit cost.

Question 18

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

(a) ln(k2/k1) = ln(5.00) = 1.609, and 1/T1 - 1/T2 = 1/298 - 1/318 = 2.11 x 10^{-4} K-1 awrt **M1**

(a) Ea = 8.31 x 1.609 / (2.11x10^{-4}) = 63,400 J/mol awrt **M1**

(a) Ea = 63.4 kJ/mol awrt cao **A1**

(a) Answer: Ea = 63.4 kJ/mol

(b) ln(k3/k2) = (Ea/R)(1/T2 - 1/T3), ft from (a) **M1**

(b) 1/T2 - 1/T3 = 1/318 - 1/338 = 1.86 x 10^{-4} K-1 awrt **M1**

(b) ln(k3/k2) = (63400/8.31) x 1.86x10^{-4} = 1.42 awrt, so k3/k2 = $e^{1.42}$ = 4.14 awrt **M1**

(b) k3 = 1.75x10^{-3} x 4.14 = 7.24 x 10^{-3} s-1 awrt cao (ecf from method) **A1**

(b) Answer: k3 = 7.24 x 10^{-3} s-1

(c) increasing temperature increases the average kinetic energy of the particles, shifting the Maxwell-Boltzmann distribution to the right (broadening and flattening it) oe **B1**

(c) a greater proportion of particles/collisions have energy greater than or equal to the activation energy, Ea, so more collisions are successful (effective) per unit time, increasing the rate constant oe **B1**

(c) Answer: Increasing temperature shifts the Maxwell-Boltzmann distribution to higher energies, so a greater proportion of particles exceed Ea, increasing the rate constant.

Question 19

(a) adding the two steps of Mechanism 1 together, NO_3 cancels (formed in step 1, used up in step 2), giving the overall equation NO_2 + CO -> NO + CO_2 oe **M1**

(a) NO_3 does not appear in the overall equation cao **A1**

(a) NO_3 is a reaction intermediate, since it is formed in one step and used up in a later step oe **B1**

(a) Answer: Adding the steps of Mechanism 1 gives NO_2 + CO -> NO + CO_2 (NO_3 cancels); NO_3 is a reaction intermediate.

(b) the rate-determining step of Mechanism 1 ($2NO_2$ -> NO_3 + NO) involves two molecules of NO_2 and no CO **M1**

(b) Mechanism 1 predicts rate = k[NO_2]^2, which matches the experimental rate equation cao **A1**

(b) the rate-determining (only) step of Mechanism 2 involves one molecule of NO_2 and one molecule of CO **M1**

(b) Mechanism 2 predicts rate = k[NO_2][CO], which does not match the experimental rate equation (since it is first, not zero, order in CO), so Mechanism 2 can be ruled out cao **A1**

(b) Answer: Mechanism 1 predicts rate = k[NO_2]^2, matching experiment; Mechanism 2 predicts rate = k[NO_2][CO], which does not match, so Mechanism 2 is ruled out.

(c) CO does not take part in the rate-determining (slow) step, only in the fast step after it, so changing [CO] does not affect the (slow) rate-determining step and therefore does not affect the overall rate oe **B1**

(c) Answer: CO only takes part in the fast step, after the rate-determining step, so changing [CO] does not affect the overall rate.

Question 20

(a) moles of thiosulfate = 0.0500 x (8.20/1000) = 4.10 x 10^{-4} mol **M1**

(a) moles of I_2 = half the moles of thiosulfate (1:2 stoichiometry) = 2.05 x 10^{-4} mol **M1**

(a) [I_2] = 2.05x10^{-4} / (10.0/1000) = 0.0205 mol dm-3 cao **A1**

(a) Answer: [I_2] = 0.0205 mol dm-3 at t = 60.0 s

(b) gradient = (0.0205 - 0) / (60.0 - 0), ft from (a) **M1**

(b) initial rate = 3.42 x 10^{-4} mol dm-3 s-1 awrt cao **A1**

(b) Answer: Initial rate of formation of I_2 = 3.42 x 10^{-4} mol dm-3 s-1

(c) percentage uncertainty at t = 60.0 s = (0.10/8.20) x 100 = 1.22% awrt **M1**

(c) percentage uncertainty at t = 240 s = (0.10/23.00) x 100 = 0.435% awrt **M1**

(c) the percentage uncertainty decreases as the reaction proceeds (as the titre volume increases), since the same fixed ± 0.10 cm^3 uncertainty is a smaller fraction of a larger titre oe **A1**

(c) Answer: 1.22% at t = 60.0 s; 0.435% at t = 240 s; percentage uncertainty decreases as the titre volume increases.

(d) the reaction must be stopped essentially instantly so that the titre measured corresponds accurately to the concentration of I_2 present at that exact sampling time, not to a later time oe **B1**

(d) e.g. add an excess of sodium hydrogencarbonate to neutralise (remove) the H^+ catalyst, stopping the reaction (or plunge the sample into an ice bath to sharply reduce the rate) oe **B1**

(d) Answer: Quenching stops the reaction instantly so the titre reflects the true [I_2] at that sampling time; this can be done by adding excess sodium hydrogencarbonate to neutralise the H^+ catalyst.