AC9D Chemistry: Rate Equations and Equilibrium: Depth and Exam Drill

Total Marks

AQA 7405 · Calculator allowed · about 150 minutes

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question tests core definitions used throughout the study of reaction kinetics.

(a) State what is meant by the rate constant, k, of a reaction. **(1)**

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

(Total for Question 1 is 2 marks)

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2 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 2 is 2 marks)

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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)

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4 Phosphorus pentachloride decomposes according to the equilibrium:
PCl5(g) ≤> PCl3(g) + Cl2(g) deltaH = +92.5 kJ/mol (the forward reaction is endothermic)
This equilibrium is set up in a sealed, rigid container.

(a) Predict and explain the effect on the position of equilibrium of increasing the temperature of the system, at constant volume. **(2)**

(b) Predict and explain the effect on the position of equilibrium of increasing the total pressure of the system, at constant temperature. **(2)**

(c) State the effect, if any, of adding a catalyst on (i) the position of this equilibrium and (ii) the time taken to reach equilibrium. **(2)**

(Total for Question 4 is 6 marks)

5 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 5 is 11 marks)

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6 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 cm3. 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 cm3. **(2)**

(Total for Question 6 is 11 marks)

7 The rate constant for a gas-phase reaction was measured at two temperatures: $k1 = 3.50 \times 10^{-4}$ s-1 at T1 = 298 K, and $k2 = 1.75 \times 10^{-3}$ 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 7 is 10 marks)

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8 The reaction between nitrogen dioxide and carbon monoxide has the overall equation:
$NO2(g) + CO(g) \rightarrow NO(g) + CO2(g)$
The rate equation for this reaction, found by experiment, is rate = $k[NO2]^2$ (the reaction is zero order with respect to CO).
Two mechanisms have been suggested.
Mechanism 1:
Step 1 (slow): $2NO2 \rightarrow NO3 + NO$
Step 2 (fast): $NO3 + CO \rightarrow NO2 + CO2$
Mechanism 2 (a single-step mechanism):
Step 1 (slow): $NO2 + CO \rightarrow NO + CO2$

(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 8 is 8 marks)

9 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 cm3 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 cm3 (from an initial and a final burette reading, each accurate to ± 0.05 cm3).

(a) Use the titre at t = 60.0 s to calculate the amount, in mol, of iodine, I_2, present in the 10.0 cm3 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 9 is 10 marks)

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10 Ethanoic acid and ethanol react reversibly to form ethyl ethanoate and water:
$CH_3COOH(l) + C_2H_5OH(l) \leq\!> CH_3COOC_2H_5(l) + H_2O(l)$
1.00 mol of ethanoic acid and 1.00 mol of ethanol were mixed with a trace of concentrated sulfuric acid catalyst and allowed to reach equilibrium at a constant temperature. At equilibrium, titration of a sample showed that 0.400 mol of ethanoic acid remained unreacted.

(a) Determine the amount, in mol, of ethanol, ethyl ethanoate and water present at equilibrium. **(3)**

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

(c) Explain why, for this particular equilibrium, Kc can be calculated directly from the amounts in mol of each species, without first converting to concentrations. **(2)**

(d) A large excess of ethanol is added to the equilibrium mixture, at constant temperature. State and explain the effect on (i) the amount of ethyl ethanoate at the new equilibrium and (ii) the value of Kc. **(3)**

(Total for Question 10 is 11 marks)

11 Ammonia is manufactured industrially by the Haber process:

$N_2(g) + 3H_2(g) \leq> 2NH_3(g)$ ΔH(forward) = -92 kJ/mol

Industrially, this reaction is typically carried out at a compromise temperature of about 450 degrees 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 11 is 6 marks)

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12 This question links the equilibrium and kinetics content of this topic with thermodynamics from elsewhere in the specification. The water-gas shift reaction is used industrially in the production of hydrogen:

$CO(g) + H_2O(g) \leq> CO_2(g) + H_2(g)$

At a temperature of 600 K, K_c for this equilibrium = 9.00 (no units, since the total number of moles of gas is the same on both sides of the equation). The standard enthalpy change for this reaction is ΔH = -41.0 kJ/mol.

You may use: $\Delta G = -RT \ln(K_c)$; $\Delta G = \Delta H - T\Delta S$; R = 8.31 J K-1 mol-1.

(a) Without any calculation, explain why this reaction, although thermodynamically favourable at 600 K ($K_c > 1$), is carried out industrially in the presence of a catalyst. **(2)**

(b) Calculate ΔG for this reaction at 600 K, in kJ/mol, to 3 significant figures. **(3)**

(c) Use your answer to (b), and the value of ΔH given, to calculate ΔS for this reaction, in J K-1 mol-1, to 3 significant figures. **(4)**

(d) The forward reaction is exothermic. Using Le Chatelier's principle, predict the effect of increasing the temperature above 600 K on the value of K_c, and explain how this is consistent with the (negative) value of ΔS you calculated in (c). **(3)**

(e) Evaluate whether operating this process at a much higher temperature, such as 900 K instead of 600 K, would be a sensible industrial strategy, considering both the rate at which equilibrium is reached and the equilibrium yield of hydrogen. **(2)**

(Total for Question 12 is 14 marks)

Mark scheme · AC9D Chemistry: Rate Equations and Equilibrium: Depth and Exam Drill

Question 1

- (a) **B1** the constant of proportionality in the rate equation, linking the rate of reaction to the concentration(s) of the reactant(s) raised to their respective orders oe
- **(a) Answer: The constant of proportionality in the rate equation, linking rate to reactant concentration(s) raised to their orders.**
- (b) **B1** the power to which the concentration of that reactant is raised in the (experimentally determined) rate equation oe
- **(b) Answer: The power to which the concentration of that reactant is raised in the rate equation.**

Question 2

- (a) **B1** 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
- **(a) Answer: The ratio of product to reactant concentrations at equilibrium, each raised to its balancing number, at a fixed temperature.**
- (b) **B1** 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
- **(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 3

- (a) **M1** mol dm-3 s-1 = k x (mol dm-3)^2, so k = (mol dm-3 s-1) / (mol dm-3)^2 oe
- (a) **A1** k units = dm3 mol-1 s-1 cao
- **(a) Answer: k units = dm3 mol-1 s-1**
- (b) **B1** zero order: units of k = mol dm-3 s-1
- (b) **B1** third order: units of k = mol-2 dm6 s-1 (dm6 mol-2 s-1)
- **(b) Answer: Zero order: mol dm-3 s-1. Third order: mol-2 dm6 s-1.**

Question 4

- (a) **B1** position of equilibrium shifts to the right (towards products, PCl3 and Cl2) oe
- (a) **B1** because the forward reaction is endothermic, so increasing temperature favours the endothermic (forward) direction, by Le Chatelier's principle oe
- **(a) Answer: Equilibrium shifts right (towards PCl3 and Cl2), because increasing temperature favours the endothermic forward reaction.**
- (b) **B1** position of equilibrium shifts to the left (towards PCl5) oe
- (b) **B1** because there are fewer moles of gas on the reactant side (1 mol) than the product side (2 mol), so increasing pressure favours the side with fewer gas moles, opposing the increase, by Le Chatelier's principle oe
- **(b) Answer: Equilibrium shifts left (towards PCl5), because increasing pressure favours the side with fewer gas moles.**
- (c) **B1** no effect on the position of equilibrium (or on the value of Kc/Kp) oe
- (c) **B1** the time taken to reach equilibrium is reduced (equilibrium is reached faster), since the catalyst increases the rate of both the forward and reverse reactions equally oe
- **(c) Answer: No effect on the position of equilibrium; the time taken to reach equilibrium is reduced, since the catalyst speeds up both forward and reverse reactions equally.**

Question 5

- (a) **M1** [$S_2O_8^{2-}$] doubles (0.0100 to 0.0200) with [I-] constant, and the initial rate doubles (1.20×10^{-5} to 2.40×10^{-5}) oe
- (a) **A1** order with respect to $S_2O_8^{2-}$ = 1 cao
- **(a) Answer: Order with respect to $S_2O_8^{2-}$ = 1**
- (b) **M1** [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
- (b) **A1** order with respect to I- = 1 cao
- **(b) Answer: Order with respect to I- = 1**
- (c) **M1** overall order = 1 + 1 = 2, ft from (a) and (b)
- (c) **A1** rate = k[$S_2O_8^{2-}$][I-]
- **(c) Answer: Overall order = 2; rate = k[$S_2O_8^{2-}$][I-]**
- (d) **M1** k = rate / ([$S_2O_8^{2-}$][I-]) = 1.20×10^{-5} / (0.0100 x 0.0100), ft from (c)
- (d) **A1** k = 0.120 cao
- (d) **A1** units: dm3 mol-1 s-1
- **(d) Answer: k = 0.120 dm3 mol-1 s-1**
- (e) **M1** rate = k[$S_2O_8^{2-}$][I-] = 0.120 x 0.0400 x 0.0150, ft from (d)
- (e) **A1** rate = 7.20×10^{-5} mol dm-3 s-1 cao
- **(e) Answer: 7.20×10^{-5} mol dm-3 s-1**

Question 6

- (a) **B1** V(t) is the (cumulative) volume of oxygen already released, which is proportional to the amount of H2O2 already reacted, not the amount remaining oe
- (a) **B1** so the volume of oxygen still to be released, [V(infinity) - V(t)], is proportional to the amount (concentration) of H2O2 that has not yet reacted oe
- **(a) Answer: V(t) is proportional to H2O2 already reacted; [V(infinity) - V(t)] is the oxygen still to be released, so it is proportional to the H2O2 remaining.**
- (b) **M1** correct values of [V(infinity) - V(t)]: 48.0, 24.0, 12.0, 6.00, 3.00 cm3 at t = 0, 5.00, 10.00, 15.00, 20.00 min respectively
- (b) **M1** identifies that this quantity halves in each successive 5.00 minute interval (a constant half-life of 5.00 min) oe
- (b) **A1** a constant half-life, independent of concentration, is characteristic of a first order reaction, so the reaction is first order with respect to H2O2 cao
- **(b) Answer: [V(infinity) - V(t)] = 48.0, 24.0, 12.0, 6.00, 3.00 cm3; the constant 5.00 min half-life shows the reaction is first order in H2O2.**
- (c) **B1** 5.00 minutes cao
- **(c) Answer: 5.00 minutes**
- (d) **M1** t(1/2) = 5.00 min = 300 s
- (d) **M1** k = ln2 / 300
- (d) **A1** k = 2.31 x 10^{-3} s-1 awrt
- **(d) Answer: k = 2.31 x 10^{-3} s-1**
- (e) **M1** recognises 1.50 cm3 is reached one further half-life after t = 20.00 min (3.00 cm3 halves to 1.50 cm3)
- (e) **A1** 25.0 minutes cao
- **(e) Answer: 25.0 minutes**

Question 7

- (a) **M1** rearranges to Ea = R ln(k2/k1) / (1/T1 - 1/T2)
- (a) **M1** 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
- (a) **M1** Ea = 8.31 x 1.609 / (2.11x10^{-4}) = 63,400 J/mol awrt
- (a) **A1** Ea = 63.4 kJ/mol awrt cao
- **(a) Answer: Ea = 63.4 kJ/mol**
- (b) **M1** ln(k3/k2) = (Ea/R)(1/T2 - 1/T3), ft from (a)
- (b) **M1** 1/T2 - 1/T3 = 1/318 - 1/338 = 1.86 x 10^{-4} K-1 awrt
- (b) **M1** ln(k3/k2) = (63400/8.31) x 1.86x10^{-4} = 1.42 awrt, so k3/k2 = $e^{1.42}$ = 4.14 awrt
- (b) **A1** k3 = 1.75x10^{-3} x 4.14 = 7.24 x 10^{-3} s-1 awrt cao (ecf from method)
- **(b) Answer: k3 = 7.24 x 10^{-3} s-1**
- (c) **B1** increasing temperature increases the average kinetic energy of the particles, shifting the Maxwell-Boltzmann distribution to the right (broadening and flattening it) oe
- (c) **B1** 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
- **(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 8

- (a) **M1** adding the two steps of Mechanism 1 together, NO3 cancels (formed in step 1, used up in step 2), giving the overall equation NO2 + CO -> NO + CO2 oe
- (a) **A1** NO3 does not appear in the overall equation cao
- (a) **B1** NO3 is a reaction intermediate, since it is formed in one step and used up in a later step oe
- **(a) Answer: Adding the steps of Mechanism 1 gives NO2 + CO -> NO + CO2 (NO3 cancels); NO3 is a reaction intermediate.**
- (b) **M1** the rate-determining step of Mechanism 1 (2NO2 -> NO3 + NO) involves two molecules of NO2 and no CO
- (b) **A1** Mechanism 1 predicts rate = k$[NO2]^2$, which matches the experimental rate equation cao
- (b) **M1** the rate-determining (only) step of Mechanism 2 involves one molecule of NO2 and one molecule of CO
- (b) **A1** Mechanism 2 predicts rate = k[NO2][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
- **(b) Answer: Mechanism 1 predicts rate = k$[NO2]^2$, matching experiment; Mechanism 2 predicts rate = k[NO2][CO], which does not match, so Mechanism 2 is ruled out.**
- (c) **B1** 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
- **(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 9

- (a) **M1** moles of thiosulfate = 0.0500 x (8.20/1000) = 4.10 x 10^{-4} mol
- (a) **M1** moles of I2 = half the moles of thiosulfate (1:2 stoichiometry) = 2.05 x 10^{-4} mol
- (a) **A1** [I2] = 2.05x10^{-4} / (10.0/1000) = 0.0205 mol dm-3 cao
- **(a) Answer: [I2] = 0.0205 mol dm-3 at t = 60.0 s**
- (b) **M1** gradient = (0.0205 - 0) / (60.0 - 0), ft from (a)
- (b) **A1** initial rate = 3.42 x 10^{-4} mol dm-3 s-1 awrt cao
- **(b) Answer: Initial rate of formation of I2 = 3.42 x 10^{-4} mol dm-3 s-1**
- (c) **M1** percentage uncertainty at t = 60.0 s = (0.10/8.20) x 100 = 1.22% awrt
- (c) **M1** percentage uncertainty at t = 240 s = (0.10/23.00) x 100 = 0.435% awrt
- (c) **A1** the percentage uncertainty decreases as the reaction proceeds (as the titre volume increases), since the same fixed ± 0.10 cm3 uncertainty is a smaller fraction of a larger titre oe
- **(c) Answer: 1.22% at t = 60.0 s; 0.435% at t = 240 s; percentage uncertainty decreases as the titre volume increases.**
- (d) **B1** the reaction must be stopped essentially instantly so that the titre measured corresponds accurately to the concentration of I2 present at that exact sampling time, not to a later time oe
- (d) **B1** 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
- **(d) Answer: Quenching stops the reaction instantly so the titre reflects the true [I2] at that sampling time; this can be done by adding excess sodium hydrogencarbonate to neutralise the H+ catalyst.**

Question 10

- (a) **M1** amount of ethanoic acid reacted = 1.00 - 0.400 = 0.600 mol
- (a) **M1** amount of ethanol remaining = 1.00 - 0.600 = 0.400 mol (1:1 stoichiometry)
- (a) **A1** amount of ethyl ethanoate = amount of water = 0.600 mol cao
- **(a) Answer: n(ethanol) = 0.400 mol; n(ethyl ethanoate) = 0.600 mol; n(water) = 0.600 mol**
- (b) **B1** Kc = [CH3COOC2H5][H2O] / ([CH3COOH][C2H5OH])
- (b) **M1** Kc = (0.600 x 0.600) / (0.400 x 0.400), ft from (a)
- (b) **A1** Kc = 2.25 cao
- **(b) Answer: Kc = 2.25 (no units)**
- (c) **B1** the total number of moles of reactants (1 + 1 = 2) equals the total number of moles of products (1 + 1 = 2), i.e. the stoichiometric coefficients are equal on both sides oe
- (c) **B1** so the volume (V) terms in the Kc expression, [n/V] for each of the two species on top and the two species on the bottom, cancel exactly, leaving Kc as a ratio of amounts in mol (and dimensionless) oe
- **(c) Answer: Because there are equal numbers of moles on both sides, the volume terms in the Kc expression cancel, so Kc can be found directly from the mole amounts and is dimensionless.**
- (d) **B1** the amount of ethyl ethanoate increases oe
- (d) **B1** because increasing [ethanol] shifts the position of equilibrium to the right (towards products), by Le Chatelier's principle, to partially oppose the increase oe
- (d) **B1** the value of Kc is unchanged (unaffected), since Kc depends only on temperature oe
- **(d) Answer: The amount of ethyl ethanoate increases, as equilibrium shifts right to oppose the increase in [ethanol]; Kc itself is unchanged, since it depends only on temperature.**

Question 11

- **Level 3** (5-6): 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 degrees C and 200 atm represent an economically sensible compromise rather than the conditions that would maximise equilibrium yield alone.
- **Level 2** (3-4): 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.
- **Level 1** (1-2): 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.
- **Level 0** (0): No relevant content.
- **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 degrees 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 degrees 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 degrees 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 12

- (a) **B1** the (uncatalysed) reaction has a high activation energy, so even though the equilibrium favours products (Kc > 1), the rate at which equilibrium is reached would be very slow without a catalyst oe
- (a) **B1** a catalyst provides an alternative pathway of lower activation energy, increasing the rate (allowing equilibrium, and so useful conversion, to be reached in an economically practical time), without changing the position of equilibrium or the value of Kc oe
- **(a) Answer: Without a catalyst the activation energy is too high for the reaction to reach equilibrium quickly; a catalyst lowers the activation energy, increasing the rate without changing Kc.**
- (b) **M1** deltaG = -RT ln(Kc) = -8.31 x 600 x ln(9.00)
- (b) **M1** ln(9.00) = 2.197, so deltaG = -8.31 x 600 x 2.197 = -10,955 J/mol awrt
- (b) **A1** deltaG = -11.0 kJ/mol awrt cao
- **(b) Answer: deltaG = -11.0 kJ/mol**
- (c) **M1** rearranges deltaG = deltaH - T deltaS to give deltaS = (deltaH - deltaG) / T
- (c) **M1** converts deltaH and deltaG to the same units (J/mol): deltaH = -41,000 J/mol, deltaG = -10,955 J/mol (ft from (b))
- (c) **M1** deltaS = (-41,000 - (-10,955)) / 600 = -30,045/600
- (c) **A1** deltaS = -50.1 J K-1 mol-1 awrt cao (ecf from (b))
- **(c) Answer: deltaS = -50.1 J K-1 mol-1**
- (d) **B1** Kc decreases as temperature increases oe
- (d) **B1** because the forward reaction is exothermic, so increasing temperature favours the endothermic reverse reaction, by Le Chatelier's principle, decreasing Kc oe
- (d) **B1** since deltaS is negative, the term -T deltaS becomes more positive as T increases, so deltaG becomes less negative (less thermodynamically favourable) as T increases, consistent with a smaller (decreasing) Kc at higher temperature oe
- **(d) Answer: Kc decreases as temperature increases; since deltaS is negative, -T deltaS becomes more positive at higher T, making deltaG less negative, consistent with a smaller Kc.**
- (e) **B1** a higher temperature would increase the rate constant (via the Arrhenius equation), so equilibrium would be reached faster oe
- (e) **B1** but since Kc decreases with increasing temperature for this exothermic reaction (from (d)), the equilibrium yield of hydrogen would be lower, so 900 K is not straightforwardly better; a compromise temperature (as with a catalyst at a moderate temperature) is likely to give a better balance of rate and yield oe
- **(e) Answer: A higher temperature would increase the rate but decrease the equilibrium yield of hydrogen (since Kc falls), so 900 K is not simply better; a moderate, catalysed temperature gives a better balance of rate and yield.**