2.10 Chemistry: Rate Equations and Equilibrium: 2-hour Pack

Total Marks

AQA 7405 · Calculator allowed · about 120 minutes

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 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 1 is 8 marks)

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2 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 2 is 7 marks)

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3 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 3 is 7 marks)

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4 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 4 is 13 marks)

5 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 5 is 6 marks)

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6 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 6 is 12 marks)

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7 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 7 is 6 marks)

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8 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 8 is 10 marks)

9 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 9 is 8 marks)

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10 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 10 is 10 marks)

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Mark scheme · 2.10 Chemistry: Rate Equations and Equilibrium: 2-hour Pack

Question 1

(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 2

(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 3

(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.

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Question 4

(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 5

(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.

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Question 6

(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 7

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.

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Question 8

(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 9

(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 10

(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 cm³ 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.

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