2.10 Chemistry: Rate Equations and Equilibrium: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 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 1 is 10 marks)

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2 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 2 is 11 marks)

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3 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 3 is 11 marks)

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4 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 4 is 8 marks)

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5 $X(g) + Y(g) \rightleftharpoons 2W(g)$

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 5 is 8 marks)

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Mark scheme · 2.10 Chemistry: Rate Equations and Equilibrium: 1-hour Pack

Question 1

(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 2

(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) $k = rate / ([S_2O_8^{2-}][I^-]) = 1.20\times10^{-5} / (0.0100 \times 0.0100)$, 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 3

(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 4

(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) $k = rate / ([CH_3COCH_3][H^+]) = 2.50\times10^{-5} / (0.500 \times 0.50)$, using any experiment **M1**

(b) k = 1.00×10^{-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 = 1.00×10^{-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).

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Question 5

(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.

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