2.4 Kinetics and Equilibria: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

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

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

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

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

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

(Total for Question 1 is 8 marks)

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2 This question is about the equilibrium constant, Kc, for homogeneous equilibria.
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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

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

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

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

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

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

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

(Total for Question 2 is 9 marks)

3 A sealed container holds an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$:
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
At equilibrium, the total pressure is 2.00 atm, and the mole fractions are 0.400 for N_2O_4 and 0.600 for NO_2.

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

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

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

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

(Total for Question 3 is 9 marks)

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4 2.00 mol of PCl_5 gas is placed in a sealed 5.00 dm3 container and allowed to reach equilibrium at a constant temperature:

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

At equilibrium, 1.20 mol of PCl_5 remains.

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

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

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

(Total for Question 4 is 9 marks)

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

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

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

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

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

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

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

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

(Total for Question 5 is 11 marks)

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Mark scheme · 2.4 Kinetics and Equilibria: 1-hour Pack

Question 1

(a) NO_3 **B1**

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

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

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

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

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

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

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

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

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

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

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

Question 2

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

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

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

(b) Answer: No units.

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

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

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

(c) Answer: Kc = 32.0

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

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

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

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

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

(f) B **B1**

(f) Answer: B

Question 3

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

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

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

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

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

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

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

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

(c) units: atm **B1**

(c) Answer: Kp = 1.80 atm

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

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

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

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Question 4

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

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

(a) Answer: PCl_3 = Cl_2 = 0.80 mol

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

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

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

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

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

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

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

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

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

Question 5

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

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

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

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

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

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

(c) Answer: 0.0400 mol CH_3COOH

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

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

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

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

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

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

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

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

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

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