2.10 Chemistry: Rate Equations and Equilibrium: Test Pack

Total Marks

AQA 7405 · Calculator allowed · about 60 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 Phosphorus pentachloride decomposes according to the equilibrium:
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ 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 2 is 6 marks)

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3 Ethanoic acid and ethanol react reversibly to form ethyl ethanoate and water:

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

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 3 is 11 marks)

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4 It is sometimes stated, as a rough rule of thumb, that the rate of a reaction roughly doubles for every 10°C (10 K) rise in temperature. This question tests whether that rule is generally reliable, for a reaction with an activation energy, Ea, of 50.0 kJ/mol.
You may use: ln(k2/k1) = -(Ea/R)(1/T2 - 1/T1); R = 8.31 J K-1 mol-1.

(a) Calculate the factor by which the rate constant increases (that is, the ratio k(310 K) / k(300 K)) for a temperature rise from 300 K to 310 K, given Ea = 50.0 kJ/mol. **(4)**

(b) Calculate the equivalent factor, k(510 K) / k(500 K), by which the rate constant increases for the same 10 K rise, but starting from 500 K instead, using the same value of Ea. **(3)**

(c) Using your answers to (a) and (b), evaluate the statement that the rate of a reaction roughly doubles for every 10°C rise in temperature. **(2)**

(Total for Question 4 is 9 marks)

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5 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:

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

At a temperature of 600 K, Kc 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 deltaH = -41.0 kJ/mol.

You may use: deltaG = -RT ln(Kc); deltaG = deltaH - T deltaS; R = 8.31 J K-1 mol-1.

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

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

(c) Use your answer to (b), and the value of deltaH given, to calculate deltaS 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 Kc, and explain how this is consistent with the (negative) value of deltaS 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 5 is 14 marks)

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Mark scheme · 2.10 Chemistry: Rate Equations and Equilibrium: Test Pack

Question 1

(a) 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 **B1**

(a) Answer: The constant of proportionality in the rate equation, linking rate to reactant concentration(s) raised to their orders.

(b) the power to which the concentration of that reactant is raised in the (experimentally determined) rate equation oe **B1**

(b) Answer: The power to which the concentration of that reactant is raised in the rate equation.

Question 2

(a) position of equilibrium shifts to the right (towards products, PCl_3 and Cl_2) oe **B1**

(a) because the forward reaction is endothermic, so increasing temperature favours the endothermic (forward) direction, by Le Chatelier's principle oe **B1**

(a) Answer: Equilibrium shifts right (towards PCl_3 and Cl_2), because increasing temperature favours the endothermic forward reaction.

(b) position of equilibrium shifts to the left (towards PCl_5) oe **B1**

(b) 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 **B1**

(b) Answer: Equilibrium shifts left (towards PCl_5), because increasing pressure favours the side with fewer gas moles.

(c) no effect on the position of equilibrium (or on the value of Kc/Kp) oe **B1**

(c) 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 **B1**

(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 3

(a) amount of ethanoic acid reacted = 1.00 - 0.400 = 0.600 mol **M1**

(a) amount of ethanol remaining = 1.00 - 0.600 = 0.400 mol (1:1 stoichiometry) **M1**

(a) amount of ethyl ethanoate = amount of water = 0.600 mol cao **A1**

(a) Answer: n(ethanol) = 0.400 mol; n(ethyl ethanoate) = 0.600 mol; n(water) = 0.600 mol

(b) $K_c = [CH_3COOC_2H_5][H_2O] / ([CH_3COOH][C_2H_5OH])$ **B1**

(b) Kc = (0.600 x 0.600) / (0.400 x 0.400), ft from (a) **M1**

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

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

(c) 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 **B1**

(c) 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 **B1**

(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) the amount of ethyl ethanoate increases oe **B1**

(d) because increasing [ethanol] shifts the position of equilibrium to the right (towards products), by Le Chatelier's principle, to partially oppose the increase oe **B1**

(d) the value of Kc is unchanged (unaffected), since Kc depends only on temperature oe **B1**

(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.

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Question 4

(a) correctly rearranged expression, e.g. ln(k2/k1) = (Ea/R) (1/T1 - 1/T2), with T1 = 300 K and T2 = 310 K **M1**

(a) 1/300 - 1/310 = 1.075 x 10^{-4} K-1 awrt **M1**

(a) ln(k2/k1) = (50000/8.31) x 1.075x10^{-4} = 0.647 awrt **M1**

(a) k2/k1 = $e^{0.647}$ = 1.91 awrt cao (the rate constant increases by a factor of about 1.9) **A1**

(a) Answer: k(310)/k(300) = 1.91 (awrt)

(b) 1/500 - 1/510 = 3.92 x 10^{-5} K-1 awrt **M1**

(b) ln(k2/k1) = (50000/8.31) x 3.92x10^{-5} = 0.236 awrt **M1**

(b) k2/k1 = $e^{0.236}$ = 1.27 awrt cao (ecf from method) **A1**

(b) Answer: k(510)/k(500) = 1.27 (awrt)

(c) the statement is only a rough approximation and is not generally reliable oe **B1**

(c) the actual factor depends on the absolute temperature (as well as on Ea); here it is about 1.9x (closer to doubling) for the rise from 300 K to 310 K, but only about 1.3x (well below doubling) for the same size rise from 500 K to 510 K, so the 'doubling' rule does not hold consistently oe **B1**

(c) Answer: The rule is only a rough approximation; the true factor (1.9x at 300-310 K but only 1.3x at 500-510 K here) depends on the absolute temperature, so it does not hold consistently.

Question 5

(a) 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 **B1**

(a) 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 **B1**

(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) deltaG = -RT ln(Kc) = -8.31 x 600 x ln(9.00) **M1**

(b) ln(9.00) = 2.197, so deltaG = -8.31 x 600 x 2.197 = -10,955 J/mol awrt **M1**

(b) deltaG = -11.0 kJ/mol awrt cao **A1**

(b) Answer: deltaG = -11.0 kJ/mol

(c) rearranges deltaG = deltaH - T deltaS to give deltaS = (deltaH - deltaG) / T **M1**

(c) converts deltaH and deltaG to the same units (J/mol): deltaH = -41,000 J/mol, deltaG = -10,955 J/mol (ft from (b)) **M1**

(c) deltaS = (-41,000 - (-10,955)) / 600 = -30,045/600 **M1**

(c) deltaS = -50.1 J K-1 mol-1 awrt cao (ecf from (b)) **A1**

(c) Answer: deltaS = -50.1 J K-1 mol-1

(d) Kc decreases as temperature increases oe **B1**

(d) because the forward reaction is exothermic, so increasing temperature favours the endothermic reverse reaction, by Le Chatelier's principle, decreasing Kc oe **B1**

(d) 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 **B1**

(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) a higher temperature would increase the rate constant (via the Arrhenius equation), so equilibrium would be reached faster oe **B1**

(e) 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 **B1**

(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.

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