2.4 Kinetics and Equilibria: 2-hour Pack

AQA 7405 · Calculator allowed · about 120 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Ammonia is manufactured industrially by the Haber process:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ deltaH = -92 kJ/mol

Industrially, a compromise temperature of about 450°C and a pressure of about 200 atm are used, together with an iron catalyst.

(a) State and explain the effect of increasing the pressure on the position of this equilibrium, and on the equilibrium yield of ammonia. **(2)**

(b) Explain, in terms of the frequency of collisions, why increasing the pressure also increases the rate at which this equilibrium is reached. **(2)**

(c) The iron catalyst is essential for making this process economically viable. Explain why the catalyst has no effect on the position of equilibrium or on the equilibrium yield of ammonia. **(2)**

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(d) Explain why a compromise temperature of about 450°C, rather than a much lower temperature, is used industrially in the Haber process, given that the forward reaction is exothermic. Your answer should refer to the effect of temperature on both the position of equilibrium and the rate of reaction. **(6)**

(Total for Question 1 is 12 marks)

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2 The rate constant for a first order reaction is 2.00×10^{-5} s-1 at 300 K and 3.51×10^{-4} s-1 at 350 K.

You may use: $\ln(k2/k1) = (Ea/R)(1/T1 - 1/T2)$; $k = A \times e^{-Ea/(RT)}$; R = 8.31 J K-1 mol-1.

(a) Calculate the activation energy, Ea, of this reaction in kJ/mol. Give your answer to 3 significant figures. **(5)**

(b) Using your value of Ea (or Ea = 50.0 kJ/mol if you did not obtain an answer to (a)), calculate the Arrhenius constant, A, for this reaction, stating its units. **(3)**

(Total for Question 2 is 8 marks)

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3 The Arrhenius equation can be written in the linear form:

$\ln k = -(Ea/R)(1/T) + \ln A$

so a graph of ln k (y-axis) against 1/T (x-axis) gives a straight line. For a particular first order reaction, this graph has a gradient of -9640 K and a y-intercept of 28.5. (R = 8.31 J K-1 mol-1.)

(a) State the units of the quantity plotted on each axis of this graph. **(2)**

(b) Use the gradient of the graph to calculate the activation energy, Ea, of the reaction in kJ/mol. Give your answer to 3 significant figures. **(3)**

(c) Use the y-intercept of the graph to calculate the Arrhenius constant, A, for this reaction, stating its units. **(3)**

(Total for Question 3 is 8 marks)

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4 This synoptic question links the activation energies of the forward and reverse reactions, the reaction enthalpy profile, and the effect of a catalyst.

(a) For a reversible, exothermic reaction, the activation energy of the forward reaction is Ea(forward) = 75 kJ/mol, and the overall enthalpy change is delta H = -58 kJ/mol. Describe the shape of the reaction (enthalpy) profile for this reaction, and how Ea(forward) and delta H are represented on it. **(2)**

(b) Calculate the activation energy of the reverse reaction, Ea(reverse), explaining your method. **(3)**

(c) Explain, in terms of the reaction profile, why Ea(reverse) is greater than Ea(forward) for this exothermic reaction. **(2)**

(d) A catalyst is added, lowering Ea(forward) to 52 kJ/mol without changing delta H. Calculate the new activation energy of the reverse reaction, and explain why a catalyst affects the rate of the forward and reverse reactions equally. **(3)**

(Total for Question 4 is 10 marks)

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5 This question is about the first-order decomposition kinetics of a compound X, determined from concentration-time data.

(a) A compound X decomposes; its concentration is monitored over time: t = 0 min, [X] = 0.800 mol/dm3; t = 10 min, [X] = 0.400 mol/dm3; t = 20 min, [X] = 0.200 mol/dm3; t = 30 min, [X] = 0.100 mol/dm3. Using this data, show that the reaction is first order with respect to X. **(2)**

(b) Calculate the rate constant, k, for this reaction using k = ln2 / t(1/2), stating its units. **(3)**

(c) Convert your answer to (b) into units of s^{-1}. **(2)**

(d) Using your rate constant from (b), calculate the concentration of X remaining after 45 minutes, using $[X] = [X]_0 e^{-kt}$. **(2)**

(Total for Question 5 is 9 marks)

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6 This question uses rate constants at two temperatures to calculate an activation energy using the Arrhenius equation.

(a) State the form of the Arrhenius equation used to calculate an activation energy from rate constants measured at two different temperatures. **(1)**

(b) For a reaction, $k1 = 4.00 \times 10^{-4}\ s^{-1}$ at T1 = 298 K and $k2 = 5.30 \times 10^{-3}\ s^{-1}$ at T2 = 328 K. Calculate the activation energy, Ea, in kJ/mol. **(5)**

(c) Use your value of Ea from (b) to calculate the Arrhenius constant, A, given $k1 = 4.00 \times 10^{-4}\ s^{-1}$ at 298 K. **(3)**

(Total for Question 6 is 9 marks)

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7 This question is about the equilibrium constant, Kp, for the contact process equilibrium used in industrial sulfuric acid manufacture.

(a) Write the expression for Kp for the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, and state its units. **(2)**

(b) At equilibrium in a sealed container at a total pressure of 2.00 atm, the partial pressures are $p(SO_2) = 0.40$ atm, $p(O_2) = 0.60$ atm, $p(SO_3) = 1.00$ atm. Calculate Kp, including units. **(3)**

(c) State and explain, using Le Chatelier's principle, the effect of increasing the total pressure on the position of equilibrium, and on the value of Kp. **(3)**

(d) The forward reaction is exothermic. State and explain the effect of increasing temperature on the value of Kp. **(2)**

(Total for Question 7 is 10 marks)

8 A small increase in temperature (for example, a rise of just 10°C) can approximately double the rate of many reactions, even though the average kinetic energy of the particles increases by a relatively small amount. Using the Boltzmann distribution and the Arrhenius equation, explain why a small increase in temperature causes such a large increase in reaction rate, and explain how a catalyst increases reaction rate without any increase in temperature.

(Total for Question 8 is 6 marks)

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Mark scheme · 2.4 Kinetics and Equilibria: 2-hour Pack

Question 1

(a) the position of equilibrium shifts towards NH_3 (to the right), because this side has fewer moles of gas (4 mol of gaseous reactants forming 2 mol of gaseous product) oe **B1**

(a) so increasing the pressure increases the equilibrium yield of ammonia oe **B1**

(a) Answer: Equilibrium shifts right (towards NH_3, the side with fewer gas moles), increasing the yield of ammonia.

(b) increasing the pressure increases the concentration of the gas particles (they are pushed closer together in the same volume) oe **B1**

(b) this increases the frequency of collisions between particles, increasing the rate of both the forward and reverse reactions oe **B1**

(b) Answer: Higher pressure increases gas particle concentration, so collisions happen more often, increasing both forward and reverse reaction rates.

(c) the catalyst provides an alternative reaction pathway of lower activation energy, increasing the rate of both the forward and reverse reactions by the same factor oe **B1**

(c) equilibrium is reached more quickly, but the equilibrium position (and therefore the equilibrium yield) is unchanged oe **B1**

(c) Answer: The catalyst speeds up the forward and reverse reactions equally, so equilibrium is reached faster but its position (and yield) is unaffected.

(d) **L3** A detailed, coherent and logically structured explanation that correctly links the effect of temperature on the position of equilibrium (via Le Chatelier's principle, since the forward reaction is exothermic) with its effect on the rate of reaction (via collision theory/the Maxwell-Boltzmann distribution), and clearly explains why a compromise is needed for economic reasons. Accurate scientific terminology is used throughout. **5-6**

(d) **L2** Some relevant scientific points relating to either the equilibrium yield or the rate of reaction are made, with some correct reasoning, but the discussion is not fully developed, may focus mainly on one aspect (yield or rate) with limited linkage between them, or contains minor inaccuracies. **3-4**

(d) **L1** Basic, isolated relevant statements are made (e.g. only that the reaction is exothermic, or only that a lower temperature gives a slower rate), with little structure, linkage or use of scientific reasoning. **1-2**

(d) **L0** No relevant content, or the answer does not relate to the question. **0**

(d) Indicative content:

- The forward reaction is exothermic (deltaH = -92 kJ/mol); by Le Chatelier's principle, decreasing the temperature shifts the position of equilibrium to the right (towards NH_3), increasing the equilibrium yield of ammonia.
- However, decreasing the temperature also decreases the rate of both the forward and reverse reactions, because fewer particles have energy greater than or equal to the activation energy (from the Maxwell-Boltzmann distribution), so fewer collisions are successful.
- At a very low temperature, although the equilibrium yield would be high, the rate of reaction would be far too slow for the process to be economically viable, since it would take too long to reach equilibrium.
- At a very high temperature, the rate of reaction would be fast (equilibrium reached quickly), but the equilibrium would shift to the left (towards N_2 and H_2), lowering the equilibrium yield of ammonia.
- A compromise temperature (around 450°C) is therefore chosen to give a reasonably fast rate of reaction while still achieving an acceptable equilibrium yield of ammonia, balancing rate and yield to maximise overall economic efficiency.
- Any unreacted N_2 and H_2 can be recycled through the reactor, so a lower yield per single pass is an acceptable trade-off if the overall rate of production is high enough, reinforcing why rate is weighed against yield rather than yield alone being maximised.

(d) Answer: Levels-of-response answer; see indicative content.

Question 2

(a) calculates the ratio k2/k1 = $3.51 \times 10^{-4} / 2.00 \times 10^{-5} = 17.6$ awrt **M1**

(a) ln(17.6) = 2.87 awrt **M1**

(a) calculates $1/T1 - 1/T2 = 1/300 - 1/350 = 4.76 \times 10^{-4}$ K-1 awrt **M1**

(a) rearranges to Ea = R x ln(k2/k1) / (1/T1 - 1/T2) and substitutes values **M1**

(a) Ea = 50.0 kJ/mol awrt **A1**

(a) Answer: Ea = 50.0 kJ/mol

(b) rearranges $k = A e^{-Ea/RT}$ to $A = k \times e^{Ea/RT}$, using the data at T = 300 K, ft from (a) **M1**

(b) Ea/(RT) = 50000/(8.31x300) = 20.1 awrt; $A = 2.00 \times 10^{-5} \times e^{20.1}$ **M1**

(b) $A = 1.03 \times 10^4$ s-1 awrt (units s-1, same as k, since the reaction is first order) **A1**

(b) Answer: $A = 1.03 \times 10^4$ s-1

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Question 3

(a) y-axis (ln k): no units (dimensionless) **B1**

(a) x-axis (1/T): K-1 **B1**

(a) Answer: ln k has no units; 1/T has units K-1.

(b) Ea = -gradient x R = 9640 x 8.31 **M1**

(b) Ea = 80100 J/mol awrt **A1**

(b) Ea = 80.1 kJ/mol cao **A1**

(b) Answer: Ea = 80.1 kJ/mol

(c) $A = e^{intercept} = e^{28.5}$ **M1**

(c) $A = 2.38 \times 10^{12}$ awrt **A1**

(c) units: s-1 (since the reaction is first order, A has the same units as k) **B1**

(c) Answer: $A = 2.38 \times 10^{12}$ s-1

Question 4

(a) the profile rises from the reactants to a maximum (the transition state), then falls to the products, which lie at a lower enthalpy than the reactants (since the reaction is exothermic), oe **B1**

(a) Ea(forward) is the (positive) enthalpy difference from the reactants up to the maximum; delta H is the (negative) enthalpy difference between the reactants and the products, oe **B1**

(a) Answer: Enthalpy rises from reactants to a peak (transition state), then falls to products below the reactants' enthalpy.

(b) recognise that delta H = Ea(forward) - Ea(reverse), rearranged to Ea(reverse) = Ea(forward) - delta H **M1**

(b) correct substitution: Ea(reverse) = 75 - (-58) **M1**

(b) 133 kJ/mol, cao **A1**

(b) Answer: 133 kJ/mol

(c) the transition state (peak) is at the same absolute enthalpy whichever direction the reaction is considered, but the products lie at a lower enthalpy than the reactants (exothermic reaction), oe **B1**

(c) so the reverse reaction must climb a larger enthalpy gap, from the lower-enthalpy products up to the peak, than the forward reaction climbs from the higher-enthalpy reactants, oe **B1**

(c) Answer: The reverse reaction climbs from the lower-enthalpy products, a larger gap to the same peak.

(d) correct substitution: Ea(reverse, catalysed) = 52 - (-58) **M1**

(d) 110 kJ/mol, cao **A1**

(d) a catalyst provides a single alternative pathway (with one, lower-energy transition state) used by both the forward and reverse reactions, lowering the activation energy for each by the same amount, so both directions speed up equally and the position of equilibrium (Kc) is unaffected, oe **B1**

(d) Answer: 110 kJ/mol

Question 5

(a) the concentration halves in each successive 10 minute interval (0.800 -> 0.400 -> 0.200 -> 0.100), i.e. a constant half-life **B1**

(a) a constant half-life, independent of concentration, is characteristic of a first order reaction, oe **B1**

(a) Answer: Constant half-life of 10 minutes confirms first order.

(b) correct substitution: k = ln2/10 **M1**

(b) 0.0693 min^{-1} (accept 0.069) **A1**

(b) units: min^{-1} (a first order rate constant has units of 1/time only) **B1**

(b) Answer: 0.0693 min^{-1}

(c) correct method: 0.0693/60 **M1**

(c) 1.16×10^{-3} s^{-1} (accept 1.15-1.16 x 10^{-3}) **A1**

(c) Answer: 1.16×10^{-3} s^{-1}

(d) correct substitution: $[X] = 0.800 \times e^{-0.0693 \times 45}$ **M1**

(d) 0.0354 mol/dm3 (accept 0.035-0.036), cao **A1**

(d) Answer: 0.0354 mol/dm3

Question 6

(a) ln(k2/k1) = (Ea/R)(1/T1 - 1/T2), oe (accept ln k = ln A - Ea/RT as the base form) **B1**

(a) Answer: ln(k2/k1) = (Ea/R)(1/T1 - 1/T2)

(b) correct calculation of ln(k2/k1) = ln(13.25) = 2.58 **M1**

(b) correct calculation of (1/T1 - 1/T2) = 3.07×10^{-4} K^{-1} **M1**

(b) correct substitution: Ea = R x ln(k2/k1) / (1/T1 - 1/T2) **M1**

(b) Ea = 70000 J/mol **A1**

(b) Ea = 70.0 kJ/mol (correct conversion and to 3 sf) **B1**

(b) Answer: 70.0 kJ/mol

(c) correct rearrangement: $A = k1 / e^{-Ea/(RT1)} = k1 \times e^{Ea/(RT1)}$ **M1**

(c) correct substitution: $A = 4.00 \times 10^{-4} \times e^{70000/(8.31 \times 298)}$ **M1**

(c) 7.4×10^{8} s^{-1} (accept 7.0-7.8 x 10^{8}), ft **A1**

(c) Answer: 7.4×10^{8} s^{-1}

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Question 7

(a) Kp = $p(SO_3)^2 / (p(SO_2)^2 \times p(O_2))$ **B1**

(a) units: atm^{-1} (since $(atm^2)/(atm^2 \times atm) = atm^{-1}$) **B1**

(a) Answer: Kp = $p(SO_3)^2 / (p(SO_2)^2 \times p(O_2))$; units atm^{-1}.

(b) correct substitution: $(1.00)^2 / ((0.40)^2 \times 0.60)$ **M1**

(b) 10.4 atm^{-1} (accept 10.4-10.5), cao **A1**

(b) units consistent with (a): atm^{-1} **B1**

(b) Answer: 10.4 atm^{-1}

(c) the position of equilibrium shifts towards the side with fewer gas moles, i.e. towards SO_3 (the products), oe **B1**

(c) because the system opposes the increase in pressure by favouring the side that reduces the total number of gas particles, oe **B1**

(c) Kp itself is unaffected by a change in pressure; Kp changes only with temperature, oe **B1**

(c) Answer: Equilibrium shifts towards SO_3; Kp is unchanged (depends only on temperature).

(d) Kp decreases **B1**

(d) increasing temperature favours the endothermic (reverse) reaction, shifting equilibrium away from products (SO_3), decreasing the equilibrium proportion of SO_3 relative to SO_2 and O_2, and hence decreasing Kp, oe **B1**

(d) Answer: Kp decreases, because increased temperature favours the endothermic reverse reaction.

Question 8

Level 3 A detailed, correct and coherent explanation linking the shape and shift of the Boltzmann distribution, the exponential term in the Arrhenius equation, and the alternative lower-Ea pathway provided by a catalyst, to the fraction of successful collisions in each case. Both the temperature effect and the catalyst effect are explained and clearly linked using appropriate terminology. **5-6**

Level 2 A mostly correct explanation of the temperature effect and/or the catalyst effect, referencing the Boltzmann distribution and activation energy, but with a gap, an underdeveloped link, or a minor inaccuracy in one part of the answer. **3-4**

Level 1 Some relevant, briefly stated points are made (e.g. 'particles have more energy' or 'a catalyst lowers activation energy') but without reference to the distribution shape or the exponential relationship, and without a coherent explanation of why the rate increase is large. **1-2**

Indicative content:

- The Boltzmann distribution shows the spread of kinetic energies of particles in a sample at a given temperature; only particles with energy equal to or greater than the activation energy, Ea, can react on collision.
- A small increase in temperature shifts the distribution only slightly (the peak moves slightly to higher energy and the curve broadens/flattens), but because Ea usually lies well out in the tail of the distribution, even this small shift causes a disproportionately large increase in the fraction of particles with energy >= Ea.
- This is reflected in the exponential term, e^(-Ea/RT), in the Arrhenius equation: because Ea/RT appears in an exponent, a small change in T produces a large, non-linear change in the rate constant k, and hence in rate.
- A catalyst provides an alternative reaction pathway/mechanism with a lower activation energy, without being used up in the overall reaction.
- Because this lower activation energy lies further to the left on the (unchanged) Boltzmann distribution for the same temperature, a much larger fraction of collisions now have sufficient energy to react, so the rate increases without any change in temperature.
- Both effects can be understood as increasing the proportion of successful (sufficiently energetic) collisions: temperature does this by shifting/broadening the energy distribution, while a catalyst does this by lowering the energy threshold that must be exceeded.

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