AC4D Kinetics and Equilibria: Depth and Exam Drill

AQA 7405 · Calculator allowed · about 160 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question tests key definitions used throughout the kinetics and equilibria topic.

(a) State the two conditions necessary, according to collision theory, for a reaction to occur when two particles collide. **(2)**

(b) Define activation energy. **(1)**

(c) State what is meant by the order of reaction with respect to a reactant. **(1)**

(d) State the Arrhenius equation. **(1)**

(Total for Question 1 is 5 marks)

---

2 This question is about determining the rate equation for the gas-phase reaction between nitrogen monoxide and bromine.

(a) For the reaction 2NO(g) + Br2(g) -> 2NOBr(g), three experiments give: Experiment 1, [NO] = 0.10 mol/dm3, [Br2] = 0.10 mol/dm3, initial rate = 6.0 x 10^{-3} mol dm-3 s-1; Experiment 2, [NO] = 0.20 mol/dm3, [Br2] = 0.10 mol/dm3, initial rate = 24 x 10^{-3} mol dm-3 s-1; Experiment 3, [NO] = 0.10 mol/dm3, [Br2] = 0.20 mol/dm3, initial rate = 12 x 10^{-3} mol dm-3 s-1. Deduce the order of reaction with respect to NO and with respect to Br2. **(4)**

(b) Write the rate equation for this reaction, and state its overall order. **(2)**

(c) Using the data from Experiment 1, calculate the rate constant, k, including its units. **(3)**

(d) State the effect on the initial rate of this reaction of doubling both [NO] and [Br2] simultaneously. **(1)**

(Total for Question 2 is 10 marks)

3 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 3 is 9 marks)

---

4 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 4 is 9 marks)

---

5 This question is about determining the order of reaction with respect to peroxodisulfate ions using an iodine clock reaction.

(a) In the peroxodisulfate-iodide clock reaction, $S2O8^{2}$-(aq) + 2I-(aq) -> $2SO4^{2}$-(aq) + I2(aq), a small, fixed volume of sodium thiosulfate solution and starch indicator is added to the reaction mixture, and the time, t, taken for a blue-black colour to appear is measured. Explain why the initial rate of reaction can be taken as proportional to 1/t. **(2)**

(b) Three experiments give: Experiment 1, $[S2O8^{2}-] = 0.020$ mol/dm3, t = 40.0 s; Experiment 2, $[S2O8^{2}-] = 0.040$ mol/dm3, t = 20.0 s; Experiment 3, $[S2O8^{2}-] = 0.060$ mol/dm3, t = 13.3 s. Deduce the order of reaction with respect to $S2O8^{2}$-. **(4)**

(c) Describe how a graph of 1/t (y-axis) against $[S2O8^{2}-]$ (x-axis) for this data would appear, and explain how this confirms the order found in (b). **(2)**

(d) State two variables, other than temperature, that should be kept constant across the three experiments to ensure a valid comparison. **(2)**

(Total for Question 5 is 10 marks)

6 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 $2SO_2(g) + O_2(g) \leq> 2SO_3(g)$, 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 6 is 10 marks)

---

7 A small increase in temperature (for example, a rise of just 10 degrees 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 7 is 6 marks)

---

8 This question uses an ICE table to find the equilibrium composition of the water-gas shift reaction, and explores the effect of temperature on Kc.

(a) Explain why the equilibrium constant expression $K_c = [H_2O][CO] / ([H_2][CO_2])$, for the equilibrium $H_2(g) + CO_2(g) \leq> H_2O(g) + CO(g)$, has no units. **(2)**

(b) 2.00 mol of H_2 and 2.00 mol of CO_2 are mixed in a sealed 2.00 dm^3 container and allowed to reach equilibrium at a temperature where $K_c = 4.00$. Letting x be the number of moles of CO formed at equilibrium, show that $x = 1.33$ mol (to 3 sf), and hence calculate the equilibrium concentration of each species. **(6)**

(c) At a higher temperature, a new value of $K_c = 9.00$ is established. State whether increasing the temperature increased or decreased the equilibrium proportion of CO in the mixture, and explain this in terms of Le Chatelier's principle. **(3)**

(Total for Question 8 is 11 marks)

9 This question analyses the measurement uncertainty in the clock-reaction timings from Question 5.

(a) In the experiment described in Question 5, times were measured using a hand-held stopwatch, with a combined uncertainty of ± 0.3 s in each measured time. Calculate the percentage uncertainty in the time recorded in Experiment 1 (t = 40.0 s). **(2)**

(b) Calculate the percentage uncertainty in the time recorded in Experiment 3 (t = 13.3 s). **(2)**

(c) Explain why the percentage uncertainty is larger for Experiment 3 than for Experiment 1, even though the absolute uncertainty in the stopwatch timing is the same in both cases. **(2)**

(d) Suggest one change to the experimental method that would reduce the percentage uncertainty in the faster experiments, such as Experiment 3, and explain why it would help. **(2)**

(Total for Question 9 is 8 marks)

---

10 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 10 is 10 marks)

Mark scheme · AC4D Kinetics and Equilibria: Depth and Exam Drill

Question 1

- (a) **B1** the particles must collide with energy equal to or greater than the activation energy
- (a) **B1** the particles must collide with the correct orientation (geometry), oe
- **(a) Answer: Sufficient energy (≥ activation energy) and correct collision orientation.**
- (b) **B1** the minimum energy that colliding particles must have in order to react, oe
- **(b) Answer: The minimum energy needed for colliding particles to react.**
- (c) **B1** the power to which the concentration of that reactant is raised in the (experimentally determined) rate equation, oe
- **(c) Answer: The power to which that reactant's concentration is raised in the rate equation.**
- (d) **B1** $k = A\,e^{-Ea/RT}$, with terms defined (k = rate constant, A = Arrhenius constant/pre-exponential factor, Ea = activation energy, R = gas constant, T = temperature in K)
- **(d) Answer: $k = A\,e^{-Ea/RT}$**

Question 2

- (a) **M1** comparing Experiments 1 and 2: [NO] doubles ([Br2] constant) and rate increases by a factor of 4
- (a) **A1** order with respect to NO = 2
- (a) **M1** comparing Experiments 1 and 3: [Br2] doubles ([NO] constant) and rate increases by a factor of 2
- (a) **A1** order with respect to Br2 = 1
- **(a) Answer: Order 2 with respect to NO; order 1 with respect to Br2.**
- (b) **B1** rate = $k[NO]^2[Br2]$
- (b) **B1** overall order = 3
- **(b) Answer: rate = $k[NO]^2[Br2]$; overall order 3.**
- (c) **M1** correct substitution: $k = 6.0 \times 10^{-3} / (0.10^2 \times 0.10)$
- (c) **A1** k = 6.0, cao
- (c) **B1** units: $dm^6\ mol^{-2}\ s^{-1}$
- **(c) Answer: $k = 6.0\ dm^6\ mol^{-2}\ s^{-1}$**
- (d) **B1** the rate increases by a factor of 8 ($2^2 \times 2^1 = 8$), oe
- **(d) Answer: Rate increases by a factor of 8.**

Question 3

- (a) **B1** the concentration halves in each successive 10 minute interval (0.800 -> 0.400 -> 0.200 -> 0.100), i.e. a constant half-life
- (a) **B1** a constant half-life, independent of concentration, is characteristic of a first order reaction, oe
- **(a) Answer: Constant half-life of 10 minutes confirms first order.**
- (b) **M1** correct substitution: k = ln2/10
- (b) **A1** 0.0693 min^{-1} (accept 0.069)
- (b) **B1** units: min^{-1} (a first order rate constant has units of 1/time only)
- **(b) Answer: 0.0693 min^{-1}**
- (c) **M1** correct method: 0.0693/60
- (c) **A1** $1.16 \times 10^{-3}\ s^{-1}$ (accept 1.15-1.16 x 10^{-3})
- **(c) Answer: $1.16 \times 10^{-3}\ s^{-1}$**
- (d) **M1** correct substitution: $[X] = 0.800 \times e^{-0.0693 \times 45}$
- (d) **A1** 0.0354 mol/dm3 (accept 0.035-0.036), cao
- **(d) Answer: 0.0354 mol/dm3**

Question 4

- (a) **B1** ln(k2/k1) = (Ea/R)(1/T1 - 1/T2), oe (accept ln k = ln A - Ea/RT as the base form)
- **(a) Answer: ln(k2/k1) = (Ea/R)(1/T1 - 1/T2)**
- (b) **M1** correct calculation of ln(k2/k1) = ln(13.25) = 2.58
- (b) **M1** correct calculation of (1/T1 - 1/T2) = 3.07×10^{-4} K^{-1}
- (b) **M1** correct substitution: Ea = R x ln(k2/k1) / (1/T1 - 1/T2)
- (b) **A1** Ea = 70000 J/mol
- (b) **B1** Ea = 70.0 kJ/mol (correct conversion and to 3 sf)
- **(b) Answer: 70.0 kJ/mol**
- (c) **M1** correct rearrangement: $A = k1 / e^{-Ea/(RT1)} = k1 \times e^{Ea/(RT1)}$
- (c) **M1** correct substitution: $A = 4.00 \times 10^{-4} \times e^{70000/(8.31 \times 298)}$
- (c) **A1** 7.4×10^{8} s^{-1} (accept $7.0\text{-}7.8 \times 10^{8}$), ft
- **(c) Answer: 7.4×10^{8} s^{-1}**

Question 5

- (a) **B1** a small, fixed amount of I2 is produced (and immediately consumed by the fixed amount of thiosulfate added) before the blue-black colour appears, so the same fixed extent of reaction occurs in every experiment, oe
- (a) **B1** since this fixed amount of reaction corresponds to a fixed amount of product formed, a shorter time means a faster average rate over that period, so rate is proportional to 1/t, oe
- **(a) Answer: A fixed extent of reaction occurs before the colour change, so rate is proportional to 1/t.**
- (b) **M1** calculate 1/t (proportional to rate) for each experiment: 0.0250, 0.0500, 0.0752 s^{-1}
- (b) **M1** comparing Experiments 1 and 2: $[S2O8^{2-}]$ doubles and 1/t (rate) doubles
- (b) **A1** comparing Experiments 1 and 3: $[S2O8^{2-}]$ triples and 1/t (rate) triples, confirming a directly proportional relationship
- (b) **A1** order with respect to $S2O8^{2-}$ = 1 (first order)
- **(b) Answer: First order with respect to $S2O8^{2-}$.**
- (c) **B1** a straight line through the origin, oe
- (c) **B1** a straight line through the origin shows that 1/t (and hence rate) is directly proportional to $[S2O8^{2-}]$, confirming first order, oe
- **(c) Answer: A straight line through the origin, confirming first order.**
- (d) **B1** the concentration of iodide ions, [I-], oe
- (d) **B1** the (small, fixed) volume/amount of sodium thiosulfate and starch indicator added, and the total volume of the reaction mixture (made up with water), oe
- **(d) Answer: [I-] and the amount of thiosulfate/starch (and total volume) used.**

Question 6

- (a) **B1** $Kp = p(SO3)^2 / (p(SO2)^2 \times p(O2))$
- (a) **B1** units: atm^{-1} (since $(atm^2)/(atm^2 \times atm) = atm^{-1}$)
- **(a) Answer: $Kp = p(SO3)^2 / (p(SO2)^2 \times p(O2))$; units atm^{-1}.**
- (b) **M1** correct substitution: $(1.00)^2 / ((0.40)^2 \times 0.60)$
- (b) **A1** 10.4 atm^{-1} (accept 10.4-10.5), cao
- (b) **B1** units consistent with (a): atm^{-1}
- **(b) Answer: 10.4 atm^{-1}**
- (c) **B1** the position of equilibrium shifts towards the side with fewer gas moles, i.e. towards SO3 (the products), oe
- (c) **B1** because the system opposes the increase in pressure by favouring the side that reduces the total number of gas particles, oe
- (c) **B1** Kp itself is unaffected by a change in pressure; Kp changes only with temperature, oe
- **(c) Answer: Equilibrium shifts towards SO3; Kp is unchanged (depends only on temperature).**
- (d) **B1** Kp decreases
- (d) **B1** increasing temperature favours the endothermic (reverse) reaction, shifting equilibrium away from products (SO3), decreasing the equilibrium proportion of SO3 relative to SO2 and O2, and hence decreasing Kp, oe
- **(d) Answer: Kp decreases, because increased temperature favours the endothermic reverse reaction.**

Question 7

- **Level 3** (5-6): 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.
- **Level 2** (3-4): 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.
- **Level 1** (1-2): 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.
- **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.

Question 8

- (a) **B1** there are equal total powers of concentration in the numerator and denominator (2 and 2), oe
- (a) **B1** so the units of concentration cancel completely, giving Kc no units (it is dimensionless), oe
- **(a) Answer: Equal powers of concentration top and bottom cancel, so Kc is dimensionless.**
- (b) **M1** set up equilibrium moles: $H_2 = CO_2 = (2.00 - x)$, $H_2O = CO = x$
- (b) **M1** substitute into Kc, noting the volume cancels: $Kc = (x/(2.00-x))^2$
- (b) **M1** take the square root: $x/(2.00-x) = 2.00$ (since Kc = 4.00)
- (b) **A1** cso: x = 1.33 mol (3 sf), as required
- (b) **M1** calculate concentrations using V = 2.00 dm3: $[H_2] = [CO_2] = (2.00-1.33)/2.00$, $[H_2O] = [CO] = 1.33/2.00$
- (b) **A1** $[H_2] = [CO_2] = 0.333$ mol/dm3, $[H_2O] = [CO] = 0.667$ mol/dm3 (ft)
- **(b) Answer: x = 1.33 mol; $[H_2] = [CO_2] = 0.333$ mol/dm3, $[H_2O] = [CO] = 0.667$ mol/dm3.**
- (c) **B1** increasing Kc (from 4.00 to 9.00) means the equilibrium proportion of CO (and H_2O) increased, oe
- (c) **B1** an increase in Kc with increasing temperature shows that the forward reaction is endothermic, oe
- (c) **B1** by Le Chatelier's principle, increasing temperature shifts an equilibrium in the endothermic direction to oppose the change, here favouring the forward reaction (more products), consistent with the increase in Kc, oe
- **(c) Answer: The proportion of CO increased; the forward reaction is endothermic, so Le Chatelier's principle predicts a shift favouring products at higher temperature.**

Question 9

- (a) **M1** correct substitution: (0.3/40.0) x 100
- (a) **A1** 0.75%, cao
- **(a) Answer: 0.75%**
- (b) **M1** correct substitution: (0.3/13.3) x 100
- (b) **A1** 2.3% (accept 2.2-2.3%)
- **(b) Answer: 2.3%**
- (c) **B1** the fixed absolute uncertainty (± 0.3 s) is a larger proportion of the smaller measured time (13.3 s) than of the larger measured time (40.0 s), oe
- (c) **B1** so, for a fixed absolute uncertainty in the timing method, percentage uncertainty is generally larger for shorter (faster) measured times, oe
- **(c) Answer: A fixed absolute uncertainty is a larger fraction of a shorter measured time.**
- (d) **B1** a valid suggestion, e.g. use a more dilute reaction mixture (lower $[S_2O_8^{2-}]$) so the reaction takes longer, oe, or use a light sensor/data logger to trigger the start and stop automatically
- (d) **B1** elaboration linking the suggestion to a reduced percentage uncertainty, e.g. a longer measured time means the same fixed absolute uncertainty makes up a smaller percentage of the total time, oe, or a light sensor removes human reaction-time uncertainty, reducing the absolute uncertainty itself
- **(d) Answer: Use a more dilute mixture (longer time) or an automated light-sensor timer.**

Question 10

- (a) **B1** 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
- (a) **B1** 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
- **(a) Answer: Enthalpy rises from reactants to a peak (transition state), then falls to products below the reactants' enthalpy.**
- (b) **M1** recognise that delta H = Ea(forward) - Ea(reverse), rearranged to Ea(reverse) = Ea(forward) - delta H
- (b) **M1** correct substitution: Ea(reverse) = 75 - (-58)
- (b) **A1** 133 kJ/mol, cao
- **(b) Answer: 133 kJ/mol**
- (c) **B1** 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
- (c) **B1** 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
- **(c) Answer: The reverse reaction climbs from the lower-enthalpy products, a larger gap to the same peak.**
- (d) **M1** correct substitution: Ea(reverse, catalysed) = 52 - (-58)
- (d) **A1** 110 kJ/mol, cao
- (d) **B1** 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
- **(d) Answer: 110 kJ/mol**