MEGA LECTURE · A LEVEL CHEMISTRY

Chapter 19: Rate Equations

OCR A Level Chemistry A (H432) — Structured Practice Worksheet

SPECIFICATION	TOTAL MARKS	SUGGESTED TIME
3.3.1 Rate equations: orders, rate constant, initial rates, rate-determining step, effect of temperature on k	90	1 hour 50 minutes

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Instructions to candidates

- Answer **all** questions in the spaces provided. Show all working in calculations.
- Marks are shown in brackets [ ] at the end of each part.

Question 1 — The rate equation and orders of reaction 3.3.1

a. State what is meant by the *rate of a reaction*. **[1]**

b. Define the term *order of reaction* with respect to a reactant. **[2]**

c. Write the general form of the rate equation for a reaction between reactants A and B, defining each term. **[2]**

d. Explain what it means for a reaction to be *zero order* with respect to a reactant. **[2]**

e. Explain what it means for a reaction to be *first order* with respect to a reactant. **[2]**

f. For a reaction with rate equation rate = $k[A]^2[B]$, state the order with respect to A, the order with respect to B, and the overall order of reaction. **[3]**

Question 1 total: 12 marks

Question 2 — Units of the rate constant, k

3.3.1

a. For a reaction that is zero order overall, state the units of the rate constant k. Show your reasoning. **[2]**

b. For a reaction that is first order overall (rate = k[A]), derive the units of k. **[3]**

c. For a reaction that is second order overall (rate = $k[A]^2$), derive the units of k. **[3]**

d. For a reaction that is third order overall (rate = $k[A][B]^2$), derive the units of k. **[3]**

Question 2 total: 11 marks

Question 3 — Determining orders from initial rates data

3.3.1

The initial rate of the reaction A + B → products was measured in three experiments at constant temperature.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	4.0×10^{-3}
3	0.20	0.20	1.6×10^{-2}

a. Using experiments 1 and 2, determine the order of reaction with respect to A. **[2]**

b. Using experiments 2 and 3, determine the order of reaction with respect to B. **[2]**

c. Write the rate equation for this reaction and state the overall order. **[2]**

d. Using data from experiment 1, calculate the value of the rate constant k, including its units. **[4]**

e. Calculate the initial rate of reaction when [A] = 0.30 mol dm^{-3} and [B] = 0.15 mol dm^{-3}. **[3]**

Question 3 total: 13 marks

Question 4 — Concentration–time graphs and the half-life method 3.3.1

The concentration of reactant A was monitored over time during a reaction at constant temperature.

Time / s	**0**	**20**	**40**	**60**	**80**
[A] / mol dm^{-3}	0.800	0.400	0.200	0.100	0.0500

a. Define the *half-life* of a reactant. **[2]**

b. Using the data in the table, determine each successive half-life of A, showing your working. **[3]**

c. State what your answer to (b) indicates about the order of reaction with respect to A. **[1]**

d. Explain, in terms of the rate equation, why a constant half-life indicates this order of reaction. **[3]**

e. Sketch, on the axes below, the shape of a concentration–time graph for a reactant that is instead *zero order*, and briefly describe its shape. **[2]**

Sketch: [A] (y-axis) against time (x-axis) for a zero-order reactant

Question 4 total: 11 marks

Question 5 — Rate-determining step and the rate equation 3.3.1

A reaction between A, B and C proceeds by the following two-step mechanism:
Step 1 (slow): A + B → X
Step 2 (fast): X + C → P
Overall equation: A + B + C → P
The experimentally determined rate equation is: rate = k[A][B]

a. Identify which step is the rate-determining step, explaining how the rate equation shows this. **[2]**

b. Explain why only species that take part in, or before, the rate-determining step appear in the rate equation. **[3]**

c. Explain why C does not appear in the rate equation, even though it is a reactant in the overall equation. **[3]**

d. Suggest the molecularity (number of species reacting) of the rate-determining step. **[1]**

Question 5 total: 9 marks

Question 6 — Temperature, the Boltzmann distribution and k 3.3.1

a. State the effect of increasing temperature on the rate constant, k, of a reaction. **[1]**

b. Explain, in terms of the Boltzmann distribution of molecular energies and the activation energy, E_a, why k increases as temperature increases. **[4]**

c. Sketch, on the axes below, the Boltzmann distribution at two temperatures T_1 and T_2 ($T_2 > T_1$), labelling E_a. **[2]**

Sketch: number of molecules (y-axis) against energy (x-axis), curves for T_1 and T_2

d. Explain, in terms of activation energy, why adding a catalyst increases the rate constant, k, at a fixed temperature. **[2]**

Question 6 total: 9 marks

Question 7 — Half-life and the rate constant 3.3.1

a. State the relationship linking the rate constant, k, and the half-life, $t_{½}$, for a first-order reaction. **[1]**

b. A first-order reaction has a rate constant $k = 4.62 \times 10^{-2}\ s^{-1}$ at 25 °C. Calculate its half-life. **[2]**

c. A different first-order reaction has a half-life of 18.0 minutes. Calculate the rate constant, k, in s^{-1}. **[3]**

d. State the units of k found in part (c), and explain how these units confirm that the reaction is first order. **[2]**

Question 7 total: 8 marks

Question 8 — Initial rates with a zero-order reactant

3.3.1

The initial rate of the reaction 2A + B → products was measured in three experiments at constant temperature.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.050	0.050	3.0×10^{-4}
2	0.100	0.050	3.0×10^{-4}
3	0.100	0.100	6.0×10^{-4}

a. Using experiments 1 and 2, determine the order of reaction with respect to A. **[2]**

b. Using experiments 2 and 3, determine the order of reaction with respect to B. **[2]**

c. Write the rate equation for this reaction and state the overall order. **[2]**

d. Using data from experiment 1, calculate the value of the rate constant k, including its units. **[3]**

e. Explain, in terms of the rate equation, why increasing [A] has no effect on the initial rate of this reaction. **[2]**

Question 8 total: 11 marks

Question 9 — Extended response

Synoptic

A student claims that increasing the concentration of a reactant increases the rate constant, k, for a reaction. Using ideas about the rate equation, collision theory and activation energy, explain why the student is incorrect, and explain what actually determines the value of k. [6]

This question is marked using a level of response.

Question 9 total: 6 marks

PAPER TOTAL: 90 MARKS

MARK SCHEME — Chapter 19: Rate Equations

Award marks independently unless stated. ECF applies to calculations.

Q1 (a) [1]

- The rate of reaction is the change in concentration of a reactant or product per unit time. (1)

Q1 (b) [2]

- The order of reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the rate equation. (1)
- It shows how the rate of reaction is affected by (depends on) the concentration of that reactant. (1)

Q1 (c) [2]

- rate = $k[A]^m[B]^n$ (1)
- k is the rate constant; m and n are the orders of reaction with respect to A and B respectively. (1)

Q1 (d) [2]

- Zero order means the rate is independent of the concentration of that reactant. (1)
- Changing the concentration of that reactant has no effect on the rate (since $[A]^0 = 1$). (1)

Q1 (e) [2]

- First order means the rate is directly proportional to the concentration of that reactant. (1)
- E.g. doubling the concentration of that reactant doubles the rate. (1)

Q1 (f) [3]

- Order with respect to A = 2. (1)
- Order with respect to B = 1. (1)
- Overall order = 2 + 1 = 3. (1)

Q2 (a) [2]

- rate = k, so units of k = units of rate. (1)
- Units of k = mol dm^{-3} s^{-1}. (1)

Q2 (b) [3]

- k = rate / [A]. (1)
- Units = (mol dm^{-3} s^{-1}) ÷ (mol dm^{-3}). (1)
- = s^{-1}. (1)

Q2 (c) [3]

- $k = \text{rate} / [A]^2$. (1)
- Units = (mol dm^{-3} s^{-1}) ÷ (mol dm^{-3})^2. (1)
- = mol^{-1} dm^3 s^{-1}. (1)

Q2 (d) [3]

- $k = \text{rate} / ([A][B]^2)$, overall order = 3. (1)
- Units = (mol dm^{-3} s^{-1}) ÷ (mol dm^{-3})^3. (1)
- = mol^{-2} dm^6 s^{-1}. (1)

Q3 (a) [2]

- Comparing experiments 1 and 2: [B] is constant, [A] doubles (0.10 → 0.20) and the rate doubles ($2.0 \rightarrow 4.0 \times 10^{-3}$). (1)
- Order with respect to A = 1 (first order). (1)

Q3 (b) [2]

- Comparing experiments 2 and 3: [A] is constant, [B] doubles (0.10 → 0.20) and the rate increases four-fold ($4.0 \times 10^{-3} \rightarrow 1.6 \times 10^{-2}$). (1)
- Order with respect to B = 2 (second order). (1)

Q3 (c) [2]

- rate = $k[A][B]^2$. (1)
- Overall order = 1 + 2 = 3. (1)

Q3 (d) [4]

- Rearranging: k = rate ÷ ([A][B]^2). (1)
- Using experiment 1: k = (2.0 × 10^{-3}) ÷ (0.10 × 0.10^2) = (2.0 × 10^{-3}) ÷ (1.0 × 10^{-3}). (1)
- k = 2.0. (1)
- Units: mol^{-2} dm^6 s^{-1}. (1)

ECF: units must be consistent with the overall order of 3 found in (c).

Q3 (e) [3]

- rate = k[A][B]^2 = 2.0 × 0.30 × (0.15)^2. (1)
- = 2.0 × 0.30 × 0.0225 = 0.0135. (1)
- rate = 1.35 × 10^{-2} mol dm^{-3} s^{-1}. (1)

Q4 (a) [2]

- The half-life is the time taken for the concentration of a reactant to fall (decrease) to half of its initial value. (2)

Q4 (b) [3]

- 0.800 → 0.400 mol dm^{-3} takes 20 s (0 → 20 s); 0.400 → 0.200 mol dm^{-3} takes 20 s (20 → 40 s). (1)
- 0.200 → 0.100 mol dm^{-3} takes 20 s (40 → 60 s); 0.100 → 0.0500 mol dm^{-3} takes 20 s (60 → 80 s). (1)
- Each successive half-life is the same, 20 s (constant half-life). (1)

Q4 (c) [1]

- The reaction is first order with respect to A. (1)

Q4 (d) [3]

- For a first-order reaction, rate = k[A], so rate is directly proportional to [A]. (1)
- As [A] halves, the rate also halves, so the time taken for the concentration to halve again is unchanged. (1)
- This gives a constant half-life, independent of concentration, which is a specific feature of first-order kinetics ($t_{½}$ = ln2 / k, a constant). (1)

Q4 (e) [2]

- A straight line with a constant (negative) gradient, starting at the initial concentration and decreasing linearly. (1)
- The line reaches [A] = 0 and then remains at zero (concentration cannot go negative). (1)

Q5 (a) [2]

- Step 1 is the rate-determining step. (1)
- The rate equation, rate = k[A][B], contains only A and B, which are the species that react in step 1. (1)

Q5 (b) [3]

- The rate of the overall reaction is limited (determined) by the slowest step, the RDS. (1)
- Species that react in, or before, the RDS affect how quickly the RDS can occur, so their concentrations appear in (affect) the rate equation. (1)
- Species that react only after the RDS, in a faster subsequent step, do not affect the overall rate, since the RDS is already the bottleneck. (1)

Q5 (c) [3]

- C reacts in step 2, which occurs after the rate-determining step (step 1). (1)
- Step 2 is fast, so changing [C] does not affect the overall rate of reaction, as step 2 is not the bottleneck. (1)
- Therefore C's concentration does not appear in the rate equation, even though C is a reactant in the overall stoichiometric equation. (1)

Q5 (d) [1]

- Bimolecular (two species, A and B, react together in the RDS). (1)

Q6 (a) [1]

- k increases as temperature increases. (1)

Q6 (b) [4]

- As temperature increases, the Boltzmann distribution shifts/broadens, so more molecules have energy greater than or equal to the activation energy, E_a. (1)
- The fraction (proportion) of molecules with $E \geq E_a$ increases. (1)
- This increases the frequency of successful (effective) collisions between reacting particles. (1)
- Since k reflects the proportion of collisions that result in reaction, k increases as temperature increases. (1)

Q6 (c) [2]

- Both curves start at the origin, rise to a single peak and do not touch the x-axis, with the same area under each curve. (1)
- The T_2 curve has a lower, broader peak shifted to higher energy, with a greater area beyond E_a than the T_1 curve. (1)

Q6 (d) [2]

- A catalyst provides an alternative reaction pathway with a lower activation energy. (1)
- At the same temperature, a greater fraction of molecules now have $E \geq E_a$ (the new, lower E_a), so k increases. (1)

Q7 (a) [1]

- $t_{½} = \ln 2 / k$ (1)

Q7 (b) [2]

- $t_{½} = \ln 2 \div (4.62 \times 10^{-2}) = 0.693 \div 0.0462$. (1)
- $t_{½} = 15.0$ s. (1)

Q7 (c) [3]

- $t_{½} = 18.0$ min $= 1080$ s. (1)
- $k = \ln 2 \div t_{½} = 0.693 \div 1080$. (1)
- $k = 6.42 \times 10^{-4}$ s^{-1}. (1)

Q7 (d) [2]

- Units of k = s^{-1}. (1)
- A rate constant with units of s^{-1} (time^{-1}, no concentration term) confirms an overall order of 1 (first order), consistent with Q2(b). (1)

Q8 (a) [2]

- Comparing experiments 1 and 2: [B] is constant, [A] doubles (0.050 → 0.100) but the rate is unchanged (3.0×10^{-4} in both). (1)
- Order with respect to A = 0 (zero order). (1)

Q8 (b) [2]

- Comparing experiments 2 and 3: [A] is constant, [B] doubles (0.050 → 0.100) and the rate doubles ($3.0 \times 10^{-4} \rightarrow 6.0 \times 10^{-4}$). (1)
- Order with respect to B = 1 (first order). (1)

Q8 (c) [2]

- rate = k[B]. (1)
- Overall order = 0 + 1 = 1. (1)

Q8 (d) [3]

- $k = \text{rate} \div [B] = (3.0 \times 10^{-4}) \div 0.050$. (1)
- $k = 6.0 \times 10^{-3}$. (1)
- Units: s^{-1}. (1)

Q8 (e) [2]

- The rate equation, rate = k[B], shows the reaction is zero order with respect to A. (1)
- A is not involved up to and including the rate-determining step, so changing [A] has no effect on the frequency of the collisions that determine the rate. (1)

Q9 [6] — Level of response

- **Level 3 (5–6):** Correctly explains, using collision theory and E_a, why increasing concentration increases rate but not k, and correctly states/explains that k depends only on temperature (and the presence of a catalyst), with clear, logical reasoning throughout.
- **Level 2 (3–4):** Explains that the student is incorrect and gives a broadly correct explanation, but with one aspect (e.g. what does determine k) incomplete or lacking detail.
- **Level 1 (1–2):** States that the student is incorrect with limited or generic supporting reasoning; little reference to collision theory, E_a, or what actually determines k.

Indicative content: *Increasing the concentration of a reactant increases the rate of reaction because there are more particles per unit volume, increasing the frequency of collisions between reactant particles, and so the frequency of successful collisions (with $E \geq E_a$) also increases — but the rate constant, k, itself is unchanged. k is a constant for a given reaction at a given temperature: it reflects the fraction of collisions that have sufficient energy to react (and are correctly orientated), which depends on the activation energy and the temperature, not on how many particles are present. The rate equation, rate = $k[A]^m[B]^n$, already accounts for the effect of concentration separately through the concentration terms; k is only changed by a change in temperature (via the Boltzmann distribution/fraction of molecules with $E \geq E_a$) or by the addition of a catalyst (which lowers E_a). The student has confused the effect of concentration on the overall rate with the effect of temperature/catalysis on the rate constant.*

END OF MARK SCHEME · 90 marks