Rate equations and reaction orders

AQA 7405 · Full A-level

Show your working where needed. Check the worked answers when you finish.

Name _____ Date _____

1. Orders and a change in concentration

A reaction follows rate = k[A][B]^2. State the order with respect to A and B and the overall order. Predict the factor by which the rate changes when only [B] doubles at fixed temperature.

2. Compare initial rates

The rows give initial [A], [B] in mol dm^{-3} and rate in mol dm^{-3} s^{-1}.

Run 1: 0.100, 0.100, 2.40 × 10^{-4}. Run 2: 0.200, 0.100, 9.60 × 10^{-4}. Run 3: 0.100, 0.200, 2.40 × 10^{-4}.

Find the rate equation and k with units.

3. A missing concentration

Rate = k[A][B]^2. At a fixed temperature, k = 0.0850 dm^6 mol^{-2} s^{-1}. The rate is 3.40 × 10^{-4} mol dm^{-3} s^{-1} when [A] = 0.250 mol dm^{-3}.

Find [B] to three significant figures.

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4. Continuous monitoring

A is the only reactant in the rate equation. A straight concentration-time graph falls from 0.850 mol dm^{-3} at 0 s to 0.550 mol dm^{-3} at 600 s.

Deduce the order with respect to A. Calculate the rate constant and give its units.

5. Interpret a concentration-time experiment

Only A is varied. Tangents to an [A]-time curve give disappearance rates of 2.00×10^{-4} at [A] = 0.100, 8.00×10^{-4} at [A] = 0.200 and 1.80×10^{-3} at [A] = 0.300. Rate is in mol dm^{-3} s^{-1} and concentration in mol dm^{-3}.

Use the data to determine the order in A and calculate k.

6. Relate two species' rates

$A \rightarrow 2B$. The tangent to an [A]-time curve at 50.0 s passes through (20.0 s, 0.380 mol dm^{-3}) and (80.0 s, 0.200 mol dm^{-3}).

Find the rate of disappearance of A and the rate of appearance of B at 50.0 s.

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7. Two proposed mechanisms

$NO_2 + CO \rightarrow NO + CO_2$ has the experimental rate equation rate = $k[NO_2]^2$.

Proposal 1: $2NO_2 \rightarrow NO_3 + NO$ (slow), then $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast). Proposal 2: $NO_2 + CO \rightarrow NO + CO_2$ in one elementary step. Decide which proposal fits both pieces of evidence.

8. Work with a reactant in excess

The rate equation is rate = k[A][B]. In one experiment B is in large excess and stays close to 0.400 mol dm^{-3}. Here the data fit rate = k(obs)[A] with k(obs) = 0.0152 s^{-1}.

Calculate k with units. Explain why the simpler fit is possible. Predict k(obs) if B instead stays close to 0.100 mol dm^{-3}.

9. Extra challenge · Two concentrations change together

The rows give initial [A] and [B] in mol dm^{-3} and rate in mol dm^{-3} s^{-1}. Run 1: 0.0800, 0.100, 1.28×10^{-4}. Run 2: 0.160, 0.200, 1.024×10^{-3}. Run 3: 0.160, 0.100, 5.12×10^{-4}.

Deduce the rate equation and k, including units. Predict the initial rate when [A] = 0.120 and [B] = 0.150 mol dm^{-3}. Is an elementary slow first step A + B → products consistent with the data?

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Worked answers

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1. Orders and a change in concentration

The order in A is one and the order in B is two. The overall order is three, the sum of the powers. Doubling [B] multiplies the rate by $2^2 = 4$.

2. Compare initial rates

Runs 1-2: doubling [A] at fixed [B] quadruples rate, so the order in A is two. Runs 1-3: doubling [B] at fixed [A] leaves rate unchanged, so the order in B is zero.

Rate = $k[A]^2$. Run 1 gives $k = 2.40 \times 10^{-4} \div 0.100^2 = 0.0240$ dm^3 mol^{-1} s^{-1}.

3. A missing concentration

$[B]^2$ = rate ÷ (k[A]) = $3.40 \times 10^{-4} \div (0.0850 \times 0.250) = 0.0160$ mol^2 dm^{-6}.

Taking the positive square root gives [B] = 0.12649… mol dm^{-3} = 0.126 mol dm^{-3} to three significant figures.

4. Continuous monitoring

A straight [A]-time line gives a constant disappearance rate as [A] changes, so the reaction is zero order in A over this range.

k = −gradient = $(0.850 - 0.550) \div 600 = 5.00 \times 10^{-4}$ mol dm^{-3} s^{-1}.

5. Interpret a concentration-time experiment

Multiplying [A] by two or three multiplies rate by four or nine, so A is second order.

k = rate/$[A]^2 = 2.00 \times 10^{-4}/0.100^2 = 0.0200$ dm^3 mol^{-1} s^{-1}.

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Worked answers

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6. Relate two species' rates

Gradient = (0.200 − 0.380) ÷ (80.0 − 20.0) = −3.00 × 10^{-3} mol dm^{-3} s^{-1}.

A disappears at 3.00 × 10^{-3} mol dm^{-3} s^{-1}. The equation makes two B per A, so B appears at 6.00 × 10^{-3} mol dm^{-3} s^{-1}.

7. Two proposed mechanisms

In proposal 1, adding the steps cancels NO_3 and one NO_2, leaving the observed overall reaction. Its slow first step consumes two NO_2, consistent with rate = k$[NO_2]^2$.

Proposal 2 gives the overall equation but predicts first order in each reactant. In proposal 1, CO is consumed in a step after the slow step.

8. Work with a reactant in excess

The nearly constant [B] is included in k(obs) = k[B], so k = 0.0152 ÷ 0.400 = 0.0380 dm^3 mol^{-1} s^{-1}. The underlying reaction is still first order in B.

At fixed [B] = 0.100 mol dm^{-3}, k(obs) = 0.0380 × 0.100 = 0.00380 s^{-1}.

9. Extra challenge · Two concentrations change together

From runs 1 and 3, doubling [A] quadruples rate, so the order in A is two. From runs 3 and 2, doubling [B] doubles rate, so B is first order.

Rate = k$[A]^2$[B]. Run 1 gives k = 1.28 × 10^{-4}/(0.0800^2 × 0.100) = 0.200 dm^6 mol^{-2} s^{-1}. The predicted rate is 0.200 × 0.120^2 × 0.150 = 4.32 × 10^{-4} mol dm^{-3} s^{-1}.

The proposed elementary slow first step would be first order in A as well as B, so it cannot explain the measurements.

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