

Exercise walk-through

4.1.4

Unfamiliar kinetic graphs and mechanism transfer

Pearson Edexcel · International A-Level · Chemistry

Find the temperature boundary

Your turn

$\Delta H = +36.0 \text{ kJ mol}^{-1}$; $\Delta S(\text{system}) = +120 \text{ J mol}^{-1} \text{ K}^{-1}$. Which condition gives positive total entropy?

- A. T below 300 K
- B. T above 300 K
- C. Every temperature
- D. No temperature

Buffer after neutralisation

Your turn

0.0100 mol HA receives 0.00400 mol OH^- . Which HA:A⁻ ratio enters the buffer expression?

- A. 10:4
- B. 6:4
- C. 4:6
- D. 10:6

Independent structural identification

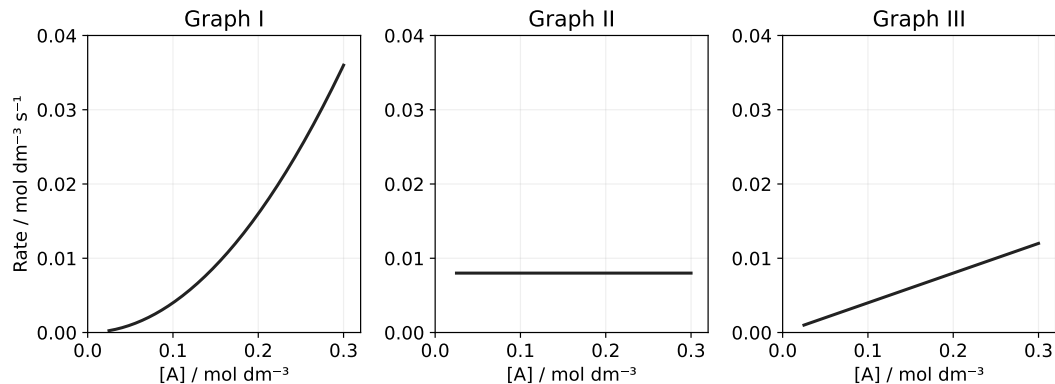
Your turn

$\text{C}_3\text{H}_6\text{O}$ has two carbon-13 signals, gives iodoform and no Tollens' silver. Which structure fits?

- A. Propanal
- B. Propanone
- C. Propan-1-ol
- D. Ethanoic acid

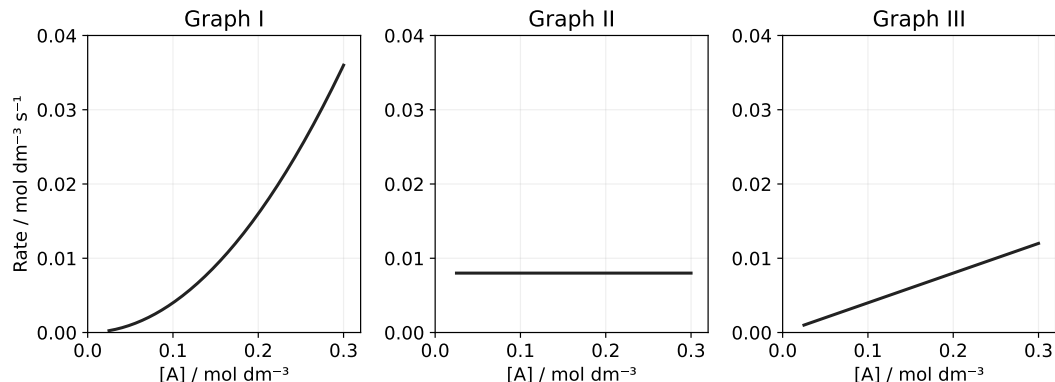
Exercise 2.1

2.1 The three graphs use original model data at fixed temperature and fixed concentrations of every other reactant. The measured concentration range is $0.025\text{--}0.300\text{ mol dm}^{-3}$. Identify the order in A for each graph and justify it using how the rate changes. State the measured range over which a zero-order claim is supported; do not extend it to an exhausted reactant. [6]



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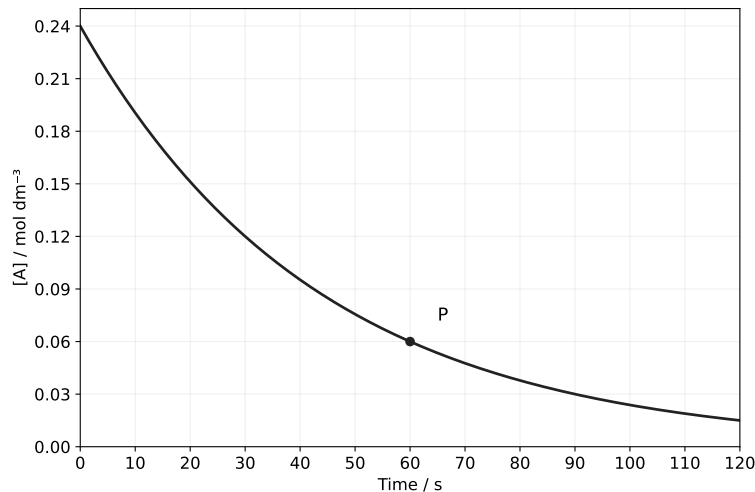
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2.1 I is second order: doubling [A] from 0.100 to 0.200 multiplies rate from 0.0040 to 0.0160 by four. II is zero order: rate remains 0.0080 over the displayed measured range, $0.025\text{--}0.300\text{ mol dm}^{-3}$, not after A is exhausted. III is first order: doubling [A] doubles rate from 0.0040 to 0.0080.

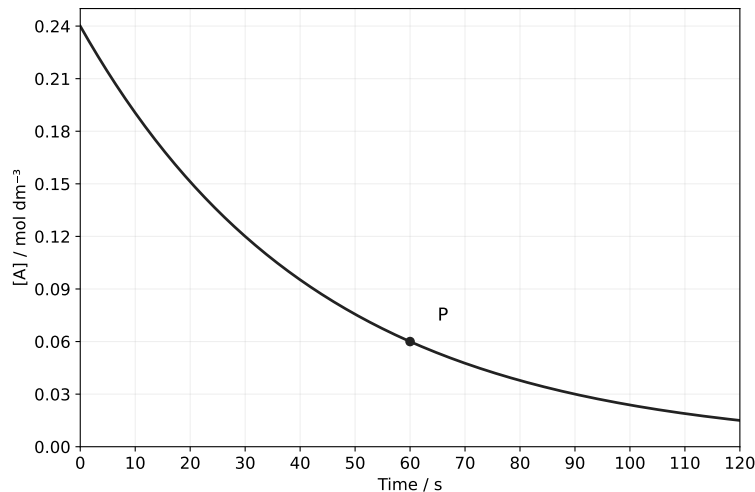
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2.2 From the concentration–time graph, read the times for $[A] = 0.120$, 0.060 and 0.030 mol dm^{-3} . Calculate two successive half-lives, state the supported order, and explain why reading only one interval would be insufficient. [4]



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Full solution 2.2

2.2 Times 30, 60 and 90 s, within graph-reading precision. Successive half-lives $60-30 = 30$ s and $90-60 = 30$ s. Constant successive half-lives support first order under the stated fixed conditions; one interval alone cannot establish their constancy or exclude every competing model.

Exercise 2.3

2.3 Draw a tangent at P on the graph above. Use two well-separated points on your tangent to estimate the instantaneous disappearance rate at 60 s. Show the gradient, sign convention and units. [4]

3 Exam-style questions

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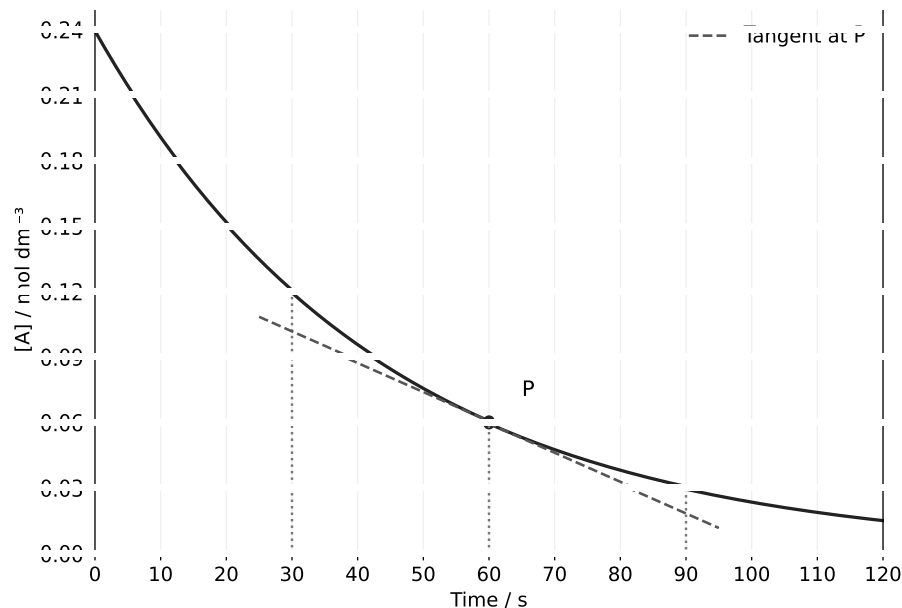
3 Exam-style questions

2.3 Draw a tangent touching P and following its local direction, not an origin-to-P chord. For example, approximate tangent points (40 s, 0.0877 mol dm⁻³) and (80 s, 0.0323 mol dm⁻³) give gradient $(0.0323 - 0.0877)/(80 - 40) = -0.001385 \text{ mol dm}^{-3} \text{ s}^{-1}$. Disappearance rate is the negative of this gradient, positive, approximately $1.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.



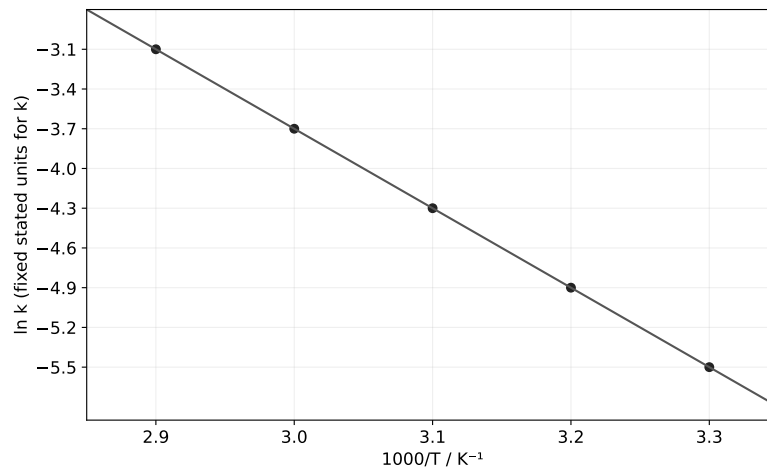
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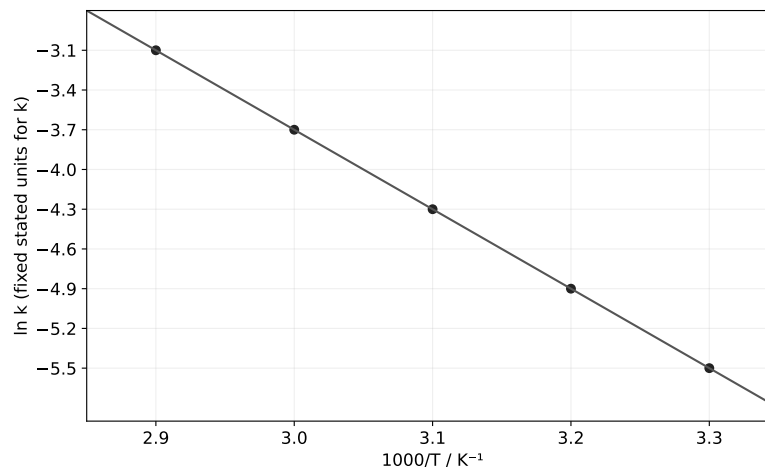
Exercise 3.1

3.1 The supplied relation is $\ln k = \ln A - E_a/(RT)$, with $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$. Use two points on the best-fit line to find its numerical gradient. Calculate E_a in kJ mol^{-1} , showing how the horizontal-axis scaling enters. Explain the error from directly multiplying this plotted gradient by $-R$. [5]



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3.1 For example (2.9, -3.1) and (3.3, -5.5) give plotted gradient $(-5.5+3.1)/(3.3-2.9) = -6.0$. Since $x = 1000/T$, this gradient is $-E_a/(1000R)$. Thus $E_a = 6.0 \times 1000 \times 8.31 = 49860 \text{ J mol}^{-1}$, or 49.9 kJ mol^{-1} . Omitting the factor 1000 underestimates E_a one thousandfold.

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Exercise 3.2

3.2 Acid-catalysed propanone iodination has measured rate $r = k[P][H^+]$, with zero order in iodine under the stated early-rate conditions. $P = \text{CH}_3\text{COCH}_3$, $\text{PH}^+ = \text{CH}_3\text{C}(=\text{OH}^+)\text{CH}_3$ and $\text{E} = \text{CH}_3\text{C}(\text{OH})=\text{CH}_2$. Propose three balanced steps using rapid reversible O-protonation, slow enol formation, then fast iodination to $\text{CH}_3\text{COCH}_2\text{I}$. Show how atoms and charges are conserved. You may use the pre-equilibrium relation $[\text{PH}^+] = K[P][H^+]$.

Derive the rate law from your steps and state the three orders. Sum the steps, explain how H^+ can be regenerated in the catalytic sequence while also being produced overall, and give one limit of the mechanistic conclusion.

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3.2 One compatible sequence is rapid $P + \text{H}^+ \rightleftharpoons \text{PH}^+$, slow $\text{PH}^+ \rightarrow E + \text{H}^+$, then ment supports a possible mechanism but does not prove it unique; early-rate comparisons require acid concentration and other kinetic factors controlled.

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3.3 Ethyl ethanoate reacts slowly with aqueous NaOH to form sodium ethanoate and ethanol. A conductivity method is proposed because highly mobile OH^- is replaced by less mobile ethanoate. Explain why this signal could follow reaction progress, give two controls/calibration requirements, and explain why gas-volume or mass-loss monitoring would not measure this reaction in a closed apparatus. [4]

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3.3 Replacing high-mobility OH^- by lower-mobility ethanoate changes conductivity as reaction progresses. Maintain/calibrate temperature and the same probe/cell geometry; calibrate conductivity against known compositions and control mixing/starting concentrations and relevant solvent background. No gas is formed or lost from the closed apparatus, so gas volume or mass loss supplies no reaction-progress signal.