

4.1.4 Unfamiliar kinetic graphs and mechanism transfer

Name: _____ Class: _____ Date: _____

Total: 31 marks

KEY WORDS rate-determining step

Objective

Read unfamiliar rate graphs and test a complete proposed mechanism. Questions, model data and marking guidance are original; written method reasoning does not certify practical performance.

1 Key knowledge and worked examples

Order is measured. A horizontal rate–concentration graph supports zero order over its valid range; a line through the origin supports first order; a square-law curve supports second order. Compare more than one concentration change. Successive equal half-lives support first order under fixed conditions.

■ Worked method

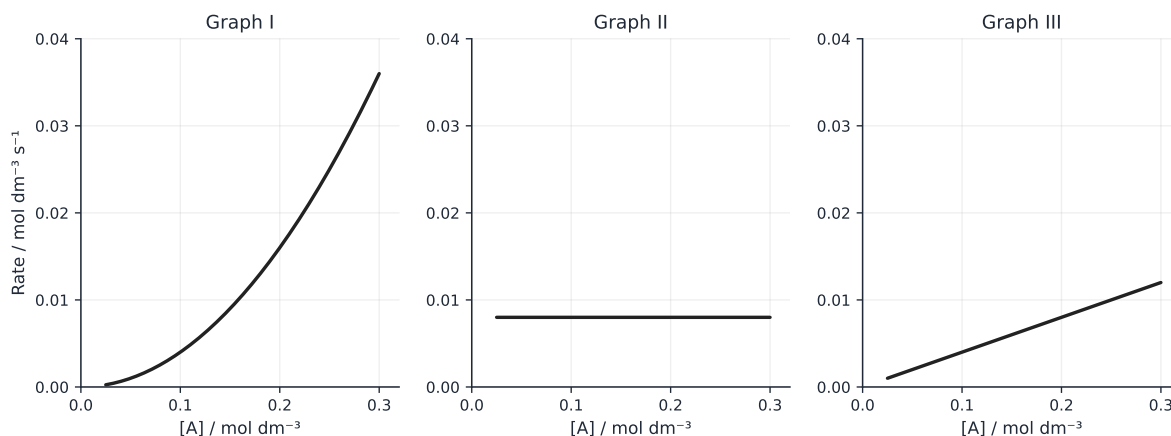
A concentration–time tangent has gradient $-0.0030 \text{ mol dm}^{-3} \text{ s}^{-1}$. The positive disappearance rate is $-d[A]/dt = +0.0030 \text{ mol dm}^{-3} \text{ s}^{-1}$. A chord gives an interval average.

For a supplied Arrhenius plot, identify the horizontal variable before using gradient $= -E_a/R$. If the horizontal variable is $1000/T$, its numerical gradient is one thousandth of the gradient against $1/T$. A plotted gradient -4.0 therefore gives $E_a = -8.31(1000)(-4.0) = 33240 \text{ J mol}^{-1} = 33.2 \text{ kJ mol}^{-1}$.

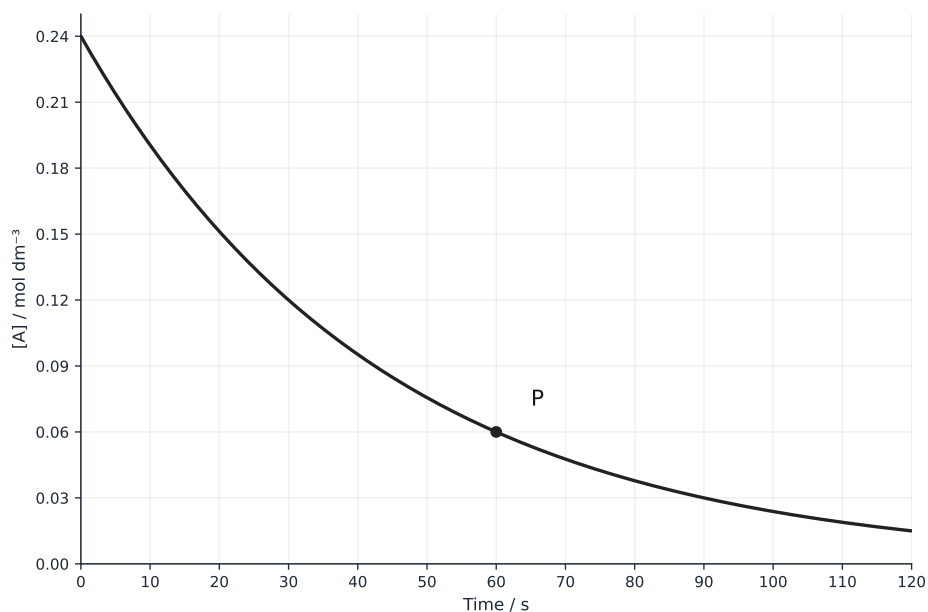
In a proposed fast pre-equilibrium $P + H^+ \rightleftharpoons PH^+$ followed by slow $PH^+ \rightarrow \text{products}$, $[PH^+] = K[P][H^+]$ and $r = k_2[PH^+] = k_2K[P][H^+]$. An intermediate may appear in the slow step without appearing in the final measured law. Check charges, atoms and the summed steps too.

2 Practice

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]



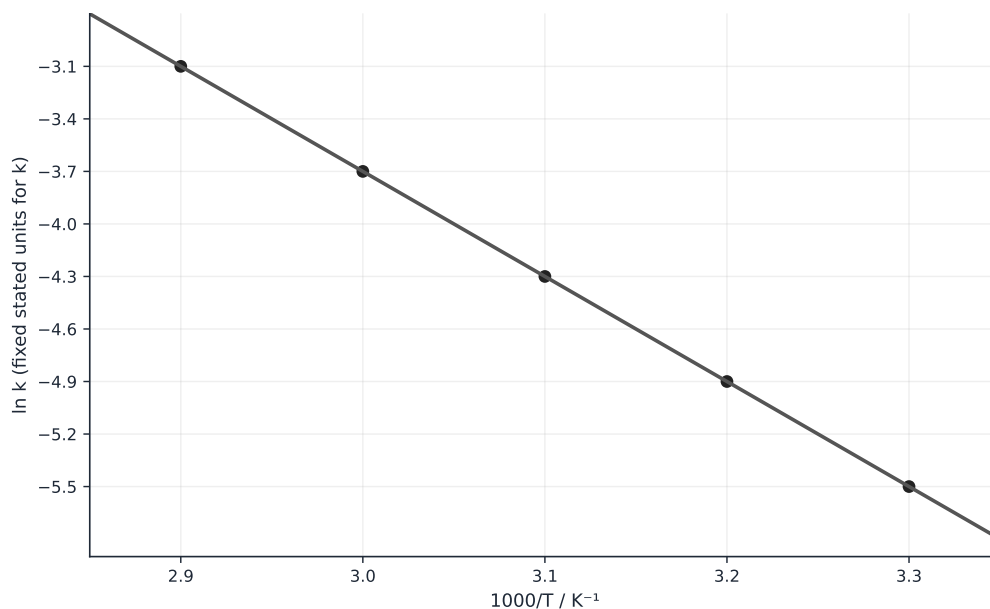
2.2 From the concentration–time graph, read the times for $[A] = 0.120$, 0.060 and 0.030 mol dm^{-3} . Calculate two successive half-lives, state the supported order, and explain why reading only one interval would be insufficient. [4]



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

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]



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. [8]

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]
