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

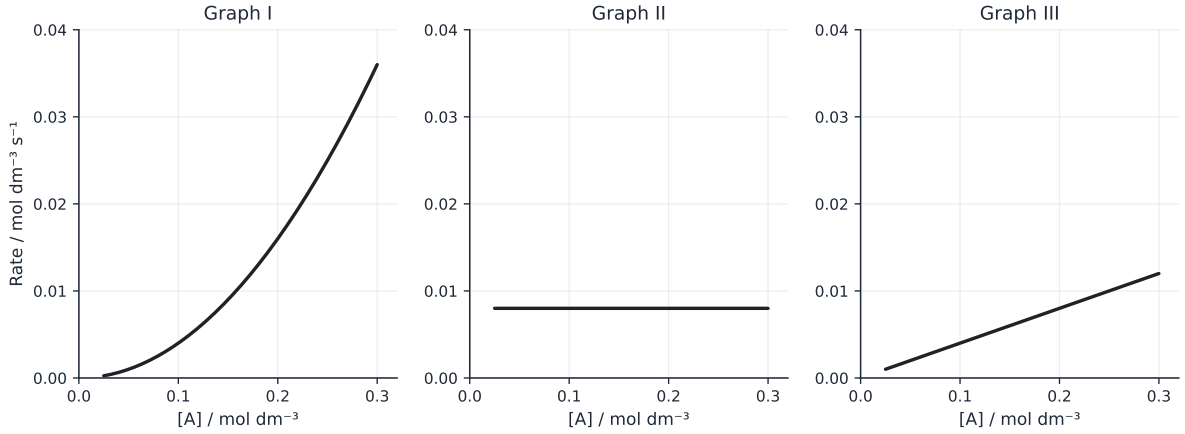
A concentration–time tangent has gradient -0.0030 mol dm^{-3} s^{-1}. The positive disappearance rate is $-d[A]/dt = +0.0030$ mol dm^{-3} s^{-1}. A chord gives an interval average.

For a supplied Arrhenius plot, identify the horizontal variable before using gradient = −Ea/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 $E_a = -8.31(1000)(-4.0) = 33240$ J mol^{-1} = 33.2 kJ mol^{-1}.

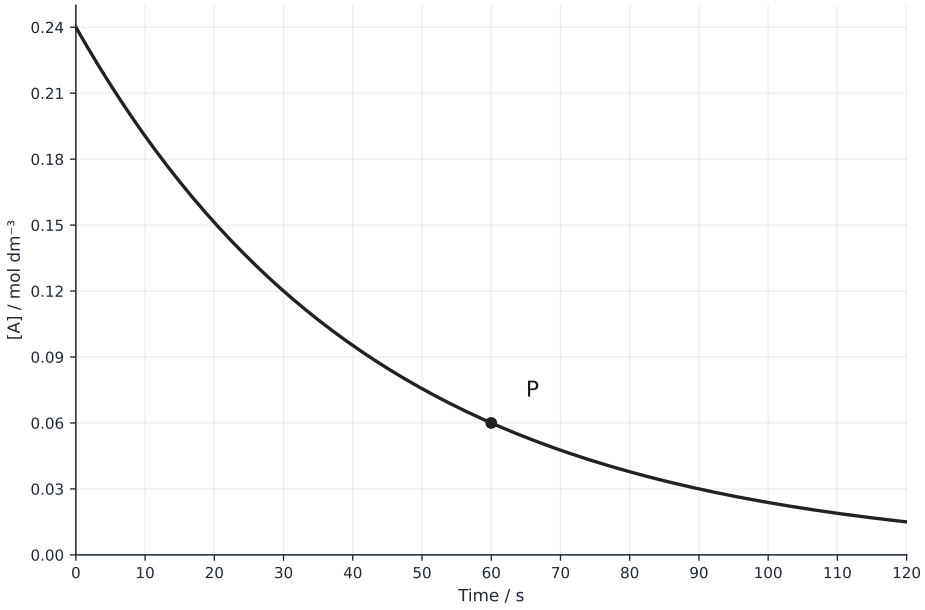
In a proposed fast pre-equilibrium $P + H^+ \rightleftharpoons PH^+$ followed by slow $PH^+ \rightarrow$ products, $[PH^+] = K[P][H^+]$ and $r = k_2[PH^+] = k_2K[P][H^+]$. An intermediate may appear in the slow step without appearing in the final measured law. Check charges, atoms and the summed steps 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 0.025–0.300 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]



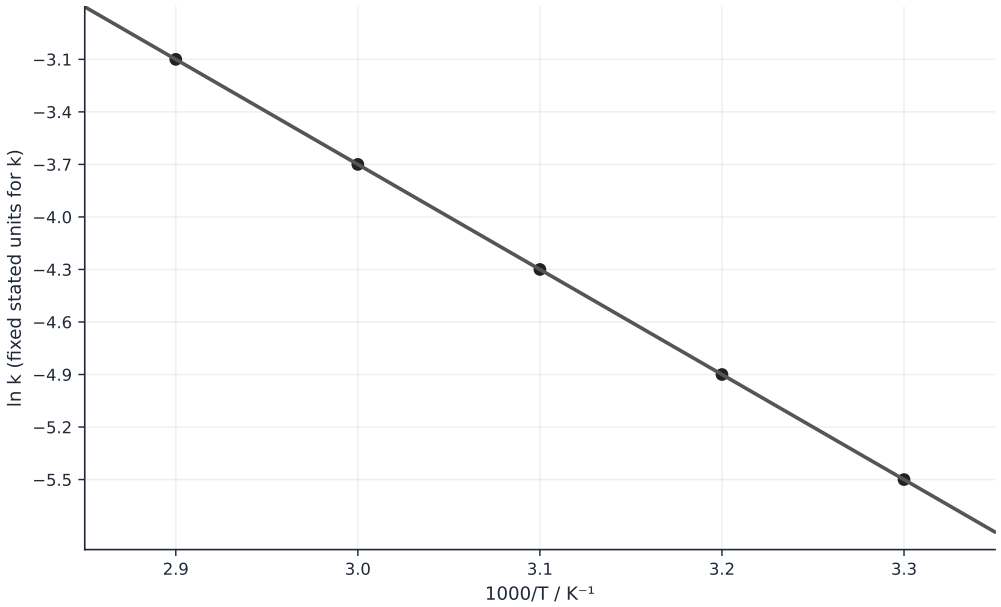
2.2 From the concentration–time graph, read the times for [A] = 0.120, 0.060 and 0.030 mol dm^{-3}. Calculate two successive half-lives, state the supported order, and explain why reading only one interval would be insufficient. [4]



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 − Ea/(RT), with R = 8.31 J mol^{-1} K^{-1}. Use two points on the best-fit line to find its numerical gradient. Calculate Ea 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 = CH_3COCH_3, PH^+ = $CH_3C(=OH^+)CH_3$ and E = $CH_3C(OH)=CH_2$. Propose three balanced steps using rapid reversible O-protonation, slow enol formation, then fast iodination to CH_3COCH_2I. Show how atoms and charges are conserved. You may use the pre-equilibrium relation $[PH^+] = K[P][H^+]$.

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]

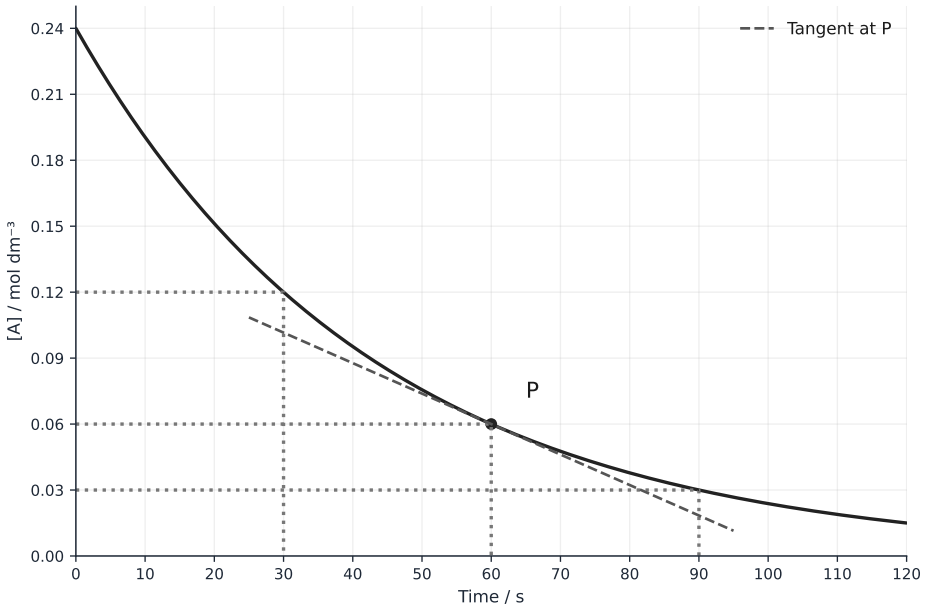
Solutions

Original marking guidance: M1 method, A1 accuracy, B1 reasoning. Accept suitably drawn graphical estimates within reading precision.

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, 0.025–0.300 mol dm^{-3}, not after A is exhausted. III is first order: doubling [A] doubles rate from 0.0040 to 0.0080.

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.

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 $(0.0323 - 0.0877)/(80 - 40) = -0.001385$ mol dm^{-3} s^{-1}. Disappearance rate is the negative of this gradient, positive, approximately 1.4×10^{-3} mol dm^{-3} s^{-1}.



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 $E_a = 6.0 \times 1000 \times 8.31 = 49860$ J mol^{-1}, or 49.9 kJ mol^{-1}. Omitting the factor 1000 underestimates Ea one thousandfold.

3.2 One compatible sequence is rapid $P + H^+ \rightleftharpoons PH^+$, slow $PH^+ \rightarrow E + H^+$, then fast $E + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$. Atoms and net charge are conserved in each; accept a chemically equivalent balanced sequence consistent with the stated conditions. Slow-step rate $r = k_2[PH^+]$ and substitution give $r = k_2K[P][H^+] = k[P][H^+]$. This is first order in propanone and H^+, zero order in iodine. Cancel PH^+ and E, and one consumed/regenerated H^+: $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$. The H^+ used in protonation is regenerated during enol formation; iodination creates another H^+ overall, so catalytic regeneration and net acid production both occur. Rate/stoichiometric agree-

ment supports a possible mechanism but does not prove it unique; early-rate comparisons require acid concentration and other kinetic factors controlled.

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.