

4.1.3 Rate measurements, iodine evidence and activation energy

Name: _____ Class: _____ Date: _____ **Total: 26 marks**

KEY WORDS aliquot • initial rate

Objective

Select and evaluate rate measurements for core practicals 9a, 9b and 10. Questions and marking guidance are original; use the approved supervised laboratory method.

1 Key knowledge and worked examples

Choose an observable linked to reaction progress. Gas volume or mass loss can follow an escaping gas; colorimetry can follow a suitable coloured species; quenched aliquots can be titrated. Sampling must stop or greatly slow the reaction without changing the amount being measured. Use the same aliquot volume, temperature and timing procedure.

■ Worked titration method

Iodine reacts with thiosulfate: $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. A quenched 5.00 cm³ reaction aliquot uses 10.00 cm³ of 0.00500 mol dm⁻³ thiosulfate.

$$n(S_2O_3^{2-}) = cV = 0.00500 \times 0.01000 = 5.00 \times 10^{-5} \text{ mol}$$

$$n(I_2) = \frac{1}{2}n(S_2O_3^{2-}) = 2.50 \times 10^{-5} \text{ mol}$$

$$[I_2]_{\text{sample}} = n/V = 2.50 \times 10^{-5} / 0.00500 = 0.00500 \text{ mol dm}^{-3}$$

If quenching dilutes the whole aliquot, titrating all that diluted sample still gives the iodine amount originally in 5.00 cm³. Do not divide by the quench volume to report the original reaction concentration.

■ Clock and temperature comparisons

In an iodine clock, a fixed small amount of iodine must form before the indicator endpoint. A fixed thiosulfate amount removes iodine until it is exhausted. Then starch detects the remaining iodine. When the same small extent is reached each time, initial rate is proportional to 1/t. Keep endpoint reagents, total volume and temperature fixed while changing one initial reactant concentration.

For acid-catalysed propanone iodination, usual rate data support first order in propanone and H⁺, zero order in iodine. Iodine can therefore react after the slow sequence while still appearing in the overall reaction. For activation energy, compare a justified common rate proxy at several measured reaction temperatures. A bath reading alone does not establish the mixture temperature. Plot ln k against 1/T only after using kelvin and identifying the actual axis scaling.

2 Practice

2.1 Select a suitable measurement for each: a coloured iodine reactant disappearing; CO₂ leaving a reaction mixture; a dissolved acid changing with time. Give one limitation of each choice. [6]

2.2 A quenched 5.00 cm³ aliquot uses 8.00 cm³ of 0.00500 mol dm⁻³ thiosulfate. Calculate iodine concentration in the original reaction aliquot. [3]

2.3 A controlled clock takes 20 s in trial A and 40 s in trial B. Compare their initial rates and state two conditions needed for that comparison. [3]

3 Exam-style questions

3.1 Equal quenched 5.00 cm^3 aliquots from one reaction require 10.00, 8.00, 6.00 and 4.00 cm^3 of $0.00500 \text{ mol dm}^{-3}$ thiosulfate at 0, 20, 40 and 60 s. Calculate the iodine disappearance rate over 0–60 s. Explain the order with respect to iodine that the trace supports under these conditions, and why it does not establish the orders in propanone and H^+ . [6]

3.2 Separate trials give: doubling propanone doubles rate; doubling H^+ doubles rate; doubling iodine leaves rate unchanged. Write the law and predict the factor change when propanone doubles and H^+ halves. Explain the role iodine may have in a compatible mechanism. [4]

3.3 A student plots $\ln(1/t)$ against $1/T$ for clock data at several temperatures. State two assumptions needed to infer activation energy from the gradient. If the gradient is -5000 K and $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, calculate the activation energy. [4]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 Calibrated colorimetry for iodine, with suitable wavelength/path length and no interfering colour/turbidity. Mass loss or collected gas volume for escaping CO₂, limited by leaks or CO₂ remaining dissolved. Timed quenched aliquots followed by titration for acid, requiring justified effective quenching and allowance for sampling delay. Accept another suitable explained technique.

2.2 $n(S_2O_3^{2-}) = 0.00500 \times 0.00800 = 4.00 \times 10^{-5}$ mol. Iodine is half this, 2.00×10^{-5} mol. Original $[I_2] = 2.00 \times 10^{-5} / 0.00500 = 0.00400$ mol dm⁻³.

2.3 A has twice B's initial rate, since inverse time compares the same endpoint extent. Keep the endpoint amount small and identical and temperature/total volume and other reactant conditions controlled. Only the intentionally varied concentration should differ.

3.1 Initial iodine concentration 0.00500 mol dm⁻³, final 0.00200 mol dm⁻³. Disappearance rate = $(0.00500 - 0.00200) / 60 = 5.00 \times 10^{-5}$ mol dm⁻³ s⁻¹. Constant iodine loss in equal time intervals supports zero order in iodine over this measured range, provided the other kinetic factors stay sufficiently constant. Separate controlled variations of propanone and H⁺ are needed to determine their individual orders.

3.2 $r = k[\text{propanone}][H^+]$. Factor $2 \times \frac{1}{2} = 1$, unchanged. Iodine can react after the rate-determining sequence; zero order is not absence from the overall reaction or a unique mechanism proof.

3.3 The fixed small endpoint makes 1/t proportional to the initial rate with a comparable proportionality factor across temperatures; reactant concentrations/other conditions are controlled so the change reflects k, with actual mixture temperatures measured in kelvin. $E_a = -R \times \text{gradient} = 8.31 \times 5000 = 41550$ J mol⁻¹, or 41.6 kJ mol⁻¹.