

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; CO_2 leaving a reaction mixture; a dissolved acid changing with time. Give one limitation of each choice. [6]

2.2 A quenched 5.00 cm^3 aliquot uses 8.00 cm^3 of $0.00500\text{ mol dm}^{-3}$ 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]
