Clock reactions and initial rates

OCR A H432 · Full A-level

Show your working where needed. Check the worked answers when you finish.

Name _____ Date _____

1. When should the timer stop?

A student times how long two equal-volume mixtures take to release 5.0 cm^3 of oxygen. Why use the same small gas volume to compare initial rates?

2. Change one concentration

Two 50.0 cm^3 mixtures contain 25.0 cm^3 of other reagents and either 15.0 or 10.0 cm^3 of 0.200 mol dm^{-3} KI. Water makes up the rest. Find the water volume and initial $[I^-]$ in each mixture.

3. An indicator changes colour

An iodine clock starts with 4.00×10^{-5} mol of thiosulfate in 40.0 cm^3. $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. The starch turns blue-black after 30.0 s.

Explain the delay and calculate the mean rate of iodine production up to the endpoint in mol dm^{-3} s^{-1}. Ignore the iodine needed to colour the starch.

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4. Review four repeat timings

A clock gives 22.5, 23.7, 37.0 and 23.1 s. The student recorded stopping late in the 37.0 s run. Decide how to treat this run. Find 1/t using your mean time.

5. Find both reaction orders

A clock uses the same small endpoint change, total volume and temperature each time. The rows give initial [A], [B] in mol dm^{-3} and time in s.

Run 1: 0.100, 0.0400, 96.0. Run 2: 0.200, 0.0400, 24.0. Run 3: 0.100, 0.0800, 48.0. Deduce the rate equation.

6. Challenge a conclusion

Two iodine clock trials use the same volume, temperature and starting concentrations of the iodine-forming reactants. Run 2 has twice the thiosulfate. Times are 45 s and 91 s, both short relative to the full reaction. Assess the claim that the initial rate halved.

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7. Choose a useful measurement

A reaction consumes a coloured reactant. A student wants its rate at 90 s and can use either a clock endpoint or a colorimeter. Choose a method and explain how to obtain the rate.

8. Calculate a rate constant

In a 50.0 cm^3 mixture an endpoint occurs after 2.50×10^{-5} mol of P has formed in 40.0 s. This small change gives a good initial-rate approximation.

Rate of formation of P = k[X][Y]. Initially [X] = 0.0800 mol dm^{-3} and [Y] = 0.0250 mol dm^{-3}. Calculate k with units.

9. Extra challenge · Correct for two different observing points

Two iodine clock runs each have a final volume of 50.0 cm^3. Run 1 contains 2.00 cm^3 of 0.00500 mol dm^{-3} thiosulfate and takes 24.0 s to change colour. Run 2 contains 3.00 cm^3 of the same thiosulfate and takes 18.0 s.

The initial peroxodisulfate concentration is doubled in run 2. Temperature and initial iodide concentration are unchanged. Use $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ to calculate each average iodine production rate and infer the order in peroxodisulfate. State when this initial-rate comparison is valid.

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Worked answers

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1. When should the timer stop?

The same gas volume at the same temperature and pressure represents the same amount of oxygen. A shorter time therefore means a greater average rate over that interval.

At an early stopping point only a small fraction of the reactants has reacted. Their concentrations have changed little, so the average rate is close to the initial rate.

2. Change one concentration

Keep the final volume at 50.0 cm^3. Run 1 needs 50.0 − 25.0 − 15.0 = 10.0 cm^3 water. Run 2 needs 50.0 − 25.0 − 10.0 = 15.0 cm^3.

Run 1: $[I^-]$ = 0.200 × 15.0 ÷ 50.0 = 0.0600 mol dm^{-3}. Run 2: $[I^-]$ = 0.200 × 10.0 ÷ 50.0 = 0.0400 mol dm^{-3}.

3. An indicator changes colour

Thiosulfate reacts with iodine as it forms. Once the thiosulfate is used up, newly formed iodine can persist and give the blue-black colour with starch.

Amount of iodine produced = 4.00 × 10^{-5} ÷ 2 = 2.00 × 10^{-5} mol. Mean production rate = (2.00 × 10^{-5} ÷ 0.0400) ÷ 30.0 = 1.67 × 10^{-5} mol dm^{-3} s^{-1}.

4. Review four repeat timings

Record the 37.0 s separately and repeat it if possible. The documented late stop justifies excluding it from the mean. An unusual number on its own would be a reason to investigate.

Mean time of the other runs = (22.5 + 23.7 + 23.1) ÷ 3 = 23.1 s, so 1/t = 0.0433 s^{-1}. This is a rate proxy, not a rate in mol dm^{-3} s^{-1}.

5. Find both reaction orders

Compare reciprocals of the times. Run 2 reaches the endpoint four times as fast as run 1 when only [A] doubles. A is second order.

Run 3 reaches the endpoint twice as fast as run 1 when only [B] doubles. B is first order. Rate = $k[A]^2[B]$.

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Worked answers

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6. Challenge a conclusion

Run 2 must produce twice the amount of iodine to use up its thiosulfate. The intervals are short enough for each mean rate to approximate the initial rate.

The rate ratio (run 2 ÷ run 1) is (2 ÷ 91) ÷ (1 ÷ 45) = 90 ÷ 91 ≈ 0.99. The two initial rates are similar. The two times cannot be compared by 1/t alone because the endpoint amounts differ.

7. Choose a useful measurement

Use a colorimeter to measure absorbance repeatedly as the reaction proceeds. Convert readings to concentrations using a calibration graph.

Plot concentration against time. Draw a tangent at 90 s and take the magnitude of its gradient for the disappearance rate. A single clock time gives a mean over one interval, so it cannot isolate the rate at 90 s.

8. Calculate a rate constant

Approximate the initial production rate by $(2.50 \times 10^{-5} \div 0.0500) \div 40.0 = 1.25 \times 10^{-5}$ mol dm^{-3} s^{-1}.

$k = \text{rate} \div ([X][Y]) = 1.25 \times 10^{-5} \div (0.0800 \times 0.0250) = 0.00625$ dm^3 mol^{-1} s^{-1}. Divide the units of rate by $(\text{mol dm}^{-3})^2$.

9. Extra challenge · Correct for two different observing points

The endpoints consume 1.00×10^{-5} and 1.50×10^{-5} mol thiosulfate. Iodine at the endpoint is half these amounts: 5.00×10^{-6} and 7.50×10^{-6} mol.

Divide each amount by 0.0500 dm^3 and its time. Rates are 4.17×10^{-6} and 8.33×10^{-6} mol dm^{-3} s^{-1}. Doubling peroxodisulfate doubles the rate, so the results support first order.

In each run the endpoint must occur after only a small fraction of the reactants are consumed. The average rate then approximates the initial rate. Comparing 1/time alone would be invalid because the endpoints use different iodine amounts.

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