

Units 3 and 6 are written papers about laboratory work: observations, procedures, the arithmetic of titrations and calorimetry, and the evaluation of errors. Every question is set around the core practicals, so for each one you know the method, the observation at the end point, and the error that limits it. 3 6

Glassware, readings and uncertainty

Burette – read to the nearest 0.05 cm^3 at the bottom of the meniscus; each reading $\pm 0.05 \text{ cm}^3$, so a titre is $\pm 0.10 \text{ cm}^3$

Pipette and volumetric flask – each delivers or holds one volume to a stated tolerance (e.g. $25.0 \text{ cm}^3 \pm 0.06 \text{ cm}^3$, $250.0 \text{ cm}^3 \pm 0.2 \text{ cm}^3$); use the value the question gives

Balance – use the uncertainty the question gives; a mass found by difference – the weighing bottle full, then empty after tipping – uses two readings, so its uncertainty is doubled, but solid left behind no longer matters

Thermometer – a temperature CHANGE uses two readings, so its uncertainty is twice that of one reading

Percentage uncertainty = $\text{uncertainty} \div \text{measured value} \times 100\%$. Add the percentage uncertainties of everything multiplied or divided into the answer; ignore molar masses and other given data.

Percentage error = $|\text{experimental} - \text{data-book value}| \div \text{data-book value} \times 100\%$. If it is larger than the total percentage uncertainty, there is a systematic error the measurements alone do not explain – name it and its direction.

Titrations – the routine and its arithmetic :

Rinse the burette with the solution it will hold and the pipette with its solution; the conical flask with distilled water only. Remove the funnel and fill the jet below the tap before the first reading.

Record initial and final burette readings to two decimal places, the titre for each run, and which titres are concordant (within 0.10 cm^3 or 0.20 cm^3 – the question says). Average only those.

Manganate(VII) titrations (CP13a) – self-indicating: the end point is the first permanent pale pink. $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$, so moles of $\text{Fe}^{2+} = 5 \times$ moles of MnO_4^- . Acidify with dilute sulfuric acid, not hydrochloric (MnO_4^- would oxidise Cl^-)

Iodine–thiosulfate titrations (CP13b) – titrate until the brown iodine fades to pale yellow, THEN add starch: blue-black to colourless at the end point. Added early, starch binds iodine and the end point is slow and unclear. $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$

Making a standard solution (CP4): weigh the solid, dissolve it in a beaker, transfer the solution AND the rinsings to a volumetric flask, make up to the mark with the bottom of the meniscus on the line, then stopper and invert to mix.

Energetics – calorimetry and Hess cycles :

$q = mc\Delta T$, with m the mass of the solution (density taken as 1.00 g cm^{-3}) and $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$. $\Delta H = -q \div \text{moles of the limiting reagent, in kJ mol}^{-1}$ with its sign.

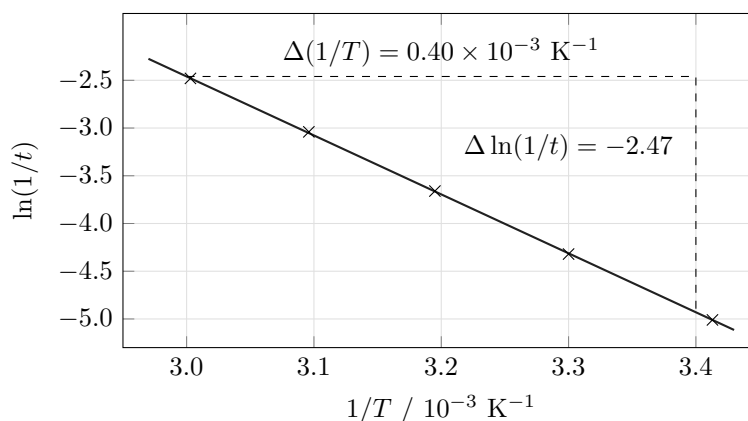
For a reaction too slow or too indirect to measure (CP2, e.g. the hydration of anhydrous copper(II) sulfate), measure the enthalpy of solution of each solid and combine them in a Hess cycle.

Heat loss to the surroundings makes ΔT , and so the magnitude of ΔH , too small. Improvements: an insulated, lidded polystyrene cup; extrapolating the cooling curve back to the time of mixing; a thermometer reading to 0.1°C .

Worked analysis: activation energy from an iodine clock (CP10) :

An iodine clock was run at five temperatures with every concentration the same, timing t from mixing until the blue-black colour appeared. The same amount of reaction has happened at that moment each time, so $1/t$ is proportional to the rate constant k . From $\ln k = \ln A - E_a/RT$, a graph of $\ln(1/t)$ against $1/T$ is a straight line of gradient $-E_a/R$.

T / K	293	303	313	323	333
t / s	150	75	39	21	12
$1/T / 10^{-3} \text{ K}^{-1}$	3.413	3.300	3.195	3.096	3.003
$\ln(1/t)$	-5.01	-4.32	-3.66	-3.04	-2.48



The triangle uses points on the line at $1/T = 3.00$ and $3.40 \times 10^{-3} \text{ K}^{-1}$.

1. Gradient $= -2.47 \div (0.40 \times 10^{-3} \text{ K}^{-1}) = -6180 \text{ K}$.
2. $E_a = -\text{gradient} \times R = 6180 \text{ K} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} = 51\,400 \text{ J mol}^{-1} = 51 \text{ kJ mol}^{-1}$.
3. Temperatures must be in kelvin; using $^\circ\text{C}$ does not give a straight line, and the gradient means nothing.

Errors to name: the temperature drifts during a run (use a water bath and record the temperature at the start and the end, then use the mean); the moment the colour appears is judged by eye (use the same observer and a white tile, or a colorimeter).

The core practicals – what each one tests

- CP1 Molar volume of a gas** – react a weighed limiting mass (e.g. of a carbonate or magnesium) with excess acid and collect the gas in a gas syringe. Gas dissolving in water, or escaping before the bung is fitted, makes the volume too small
- CP3 and CP4 Titrations** – a standard solution made up from a weighed primary standard, then used to find an unknown concentration; full burette readings and concordant titres
- CP5 Hydrolysis of halogenoalkanes** – ethanolic silver nitrate in a water bath: the time for a precipitate shows the rate, iodo fastest and chloro slowest. The C–X bond enthalpy explains it, not the polarity of the bond
- CP6 A halogenoalkane from a tertiary alcohol** – shake 2-methylpropan-2-ol with concentrated hydrochloric acid in a separating funnel, releasing the pressure often; wash with sodium hydrogencarbonate, dry with anhydrous sodium sulfate, then distil
- CP7 Oxidation of alcohols** – acidified dichromate: orange to green. Distil off as it forms for the aldehyde; heat under reflux with excess oxidant for the carboxylic acid. Test with Fehling's or Tollens' to tell them apart
- CP8 and CP15 Unknown analysis** – small portions, one test at a time, each observation written down before its deduction. Use every result, including the negative ones, to rule possibilities out
- CP9a Iodination of propanone** – withdraw samples at intervals, quench each in sodium hydrogencarbonate, and titrate the iodine left with thiosulfate. A straight line of $[I_2]$ against time shows zero order in iodine
- CP9b Iodine clock** – vary one concentration at a time with the total volume constant; $1/t$ measures the initial rate only while a small, fixed amount of reaction has happened before the colour appears
- CP11 K_a of a weak acid** K_a – calibrate the pH meter with buffers; half-neutralise the acid, where $pH = pK_a$, or use $K_a = [H^+]^2 \div [HA]$ from one concentration, assuming dissociation is small
- CP12 Electrochemical cells** – two half-cells joined by a salt bridge (filter paper soaked in potassium nitrate) and a high-resistance voltmeter; record which electrode is positive. Non-standard concentrations and temperature shift the e.m.f.
- CP14 A transition-metal complex** – prepare, filter under reduced pressure, wash with a little cold solvent and dry; calculate the percentage yield and say why it is below 100% (product left in solution, transfer losses)
- CP16 Aspirin** – recrystallise from the minimum volume of hot solvent, cool slowly, filter and dry. A pure product melts sharply close to the data-book value; an impure one melts lower and over a range

What examiners keep reporting

An observation written as a deduction: 'chloride ions present' is not what you SEE. Write 'white precipitate', then deduce.

A colour change with only one colour, or in the wrong direction. Give both, from $\rightarrow$ to: 'orange to green'.

Burette readings to one decimal place, or a mean titre that includes the rough.

An improvement that does not match the error: a lid reduces heat loss; it does nothing for a misjudged end point.