Edexcel International A Level (IAL) Chemistry

Your notes

Advanced Physical Chemistry Core Practicals

Contents

Your notes

Core Practical 9a: Titrimetric Methods

- This practical uses a titrimetric method (a technique involving titration) to determine the **order of reaction with respect to iodine** in its acid-catalysed reaction with propanone
- Propanone reacts with iodine in the presence of an acid catalyst:

$$CH_3COCH_3\,(aq) + I_2\,(aq) \rightarrow CH_3COCH_2I\,(aq) + H^+\,(aq) + I^-\,(aq)$$

Aim

- To determine how the concentration of iodine, $[I_2]$, affects the rate of the reaction

Experimental design

- The concentrations of the other reactants, propanone and H^+, do not change
- A **large excess** of both propanone and the acid catalyst is used
  - This means that their concentrations will remain effectively constant throughout the experiment

Method (sampling and quenching)

- We need to find the concentration of iodine at various points in time, so we use a sampling and titration method

1. Mix 25 cm^3 of 1.0 mol dm^{-3} aqueous propanone with 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid in a beaker
2. Add 50 cm^3 of 0.02 mol dm^{-3} iodine solution
   - **Start the timer as soon this is added to the beaker**
3. At regular intervals, use a pipette to withdraw 10 cm^3 portion of the reaction mixture and transfer this to a conical flask
4. **Quench** / stop the sample reacting further by adding a spatula of sodium hydrogen carbonate
5. Titrate the sample against 0.01 mol dm^{-3} sodium thiosulfate(VI) solution using starch as an indicator
   - Starch is used as an indicator is used to determine the concentration of iodine

$$2S_2O_3^{2-}\,(aq) + I_2\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

6. Record the result for each titration in a suitable table

Time (mins)	Titre (cm^3)

0	
5	
10	

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Practical tips

- Have everything ready and set up before beginning the procedure
- Keep the timer running throughout the practical rather than stopping the clock
- Record the time when the sodium hydrogencarbonate is added to the samples of reaction mixture
  - This is when the reaction actually stopped
  - This means that the concentration of iodine can be calculated accurately

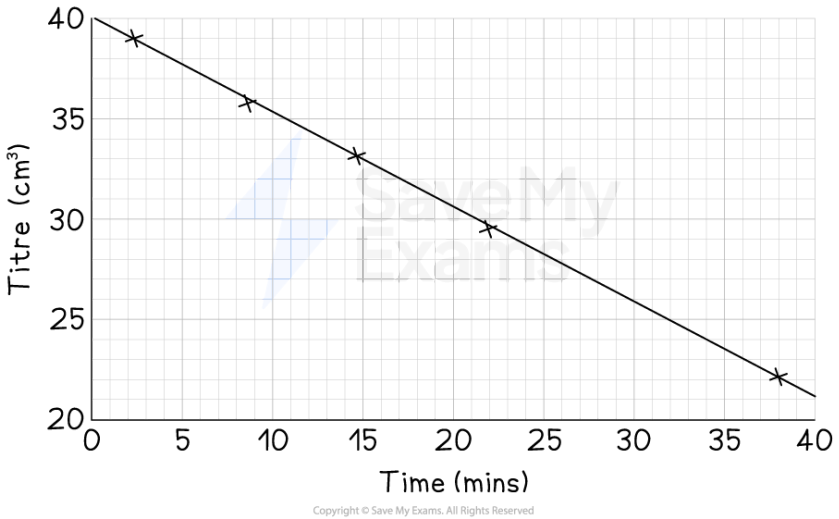
Results

- Here is an example set of results

Time (mins)	Titre (cm^3)
2.3	39.10
8.6	35.80
14.7	33.15
21.9	29.55
38.0	22.10

Analysis and conclusion

- Plot a graph of **titre (y-axis)** against **time (x-axis)**



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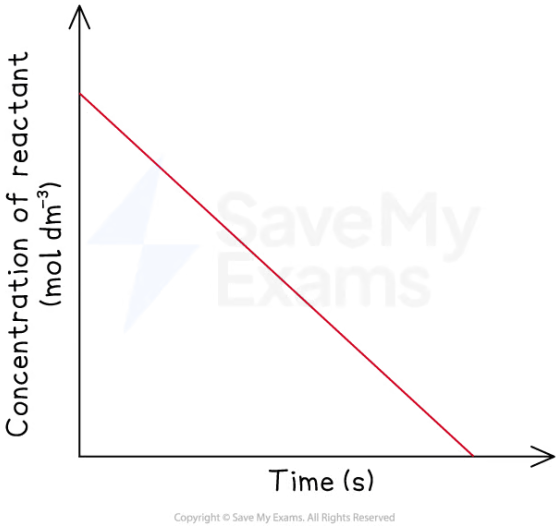
- For this reaction, the graph is a **straight line with a negative gradient**
  - A straight, descending line on a concentration-time graph means the rate of reaction is **constant**.
  - This shows that the rate is **independent** of the concentration of iodine.
  - Therefore, the reaction is **zero order** with respect to iodine



Concentration-time graphs of a zero-order reaction

- The reaction is first order with respect to propanone and H^+
- This experiment determines that the reactions is zero order with respect to iodine
- So, the overall rate equation is:

$$\text{Rate} = k[CH_3COCH_3(aq)][H^+(aq)]$$

- $[I_2]$ does not appear in the rate equation because its order is zero

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Core Practical 9b: Investigating a Clock Reaction

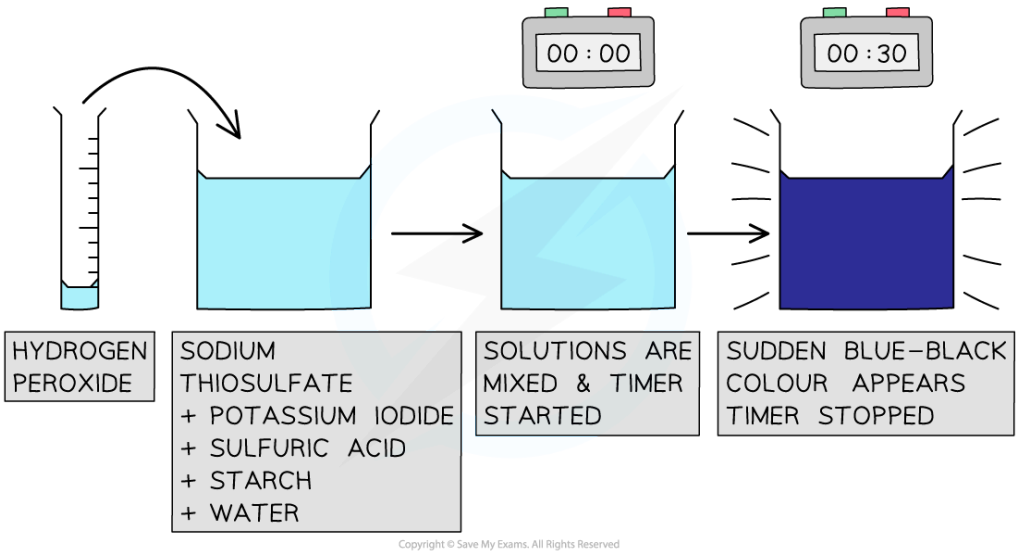
- Clock reactions are so called because they show a sharp dramatic colour change after a period of time has elapsed
- They make ideal reactions for studying kinetics
- Iodine clock reactions come in a number of variations, but they generally all use starch to show a sudden purple-black colour at the end of the reaction
- A common iodine clock reaction uses the reaction between hydrogen peroxide and iodine

$$H_2O_2\,(aq) + 2I^-\,(aq) + 2H^+(aq) \rightarrow I_2\,(aq) + 2H_2O\,(l)$$

- Adding sodium thiosulfate to the reaction mixture uses up the iodine and acts as the reaction timer

$$2S_2O_3^{2-}\,(aq) + I_2\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

- The amounts chosen are such that the iodine produced is in **excess** compared to the other reagents
  - Therefore, as soon as the iodine is in excess the blue-black colour of iodine in starch is seen



The iodine clock reaction provides a good way to study reaction kinetics

Steps in the procedure

- The solutions are measured in burettes and placed in a small beaker

- The sulfuric acid is in excess so can be measured in a measuring cylinder rather than burette
- The reaction is started by adding 1cm^3 of 0.25 mol dm^{-3} hydrogen peroxide and starting a timer
- The timer is stopped when the blue black colour appears
- Suitable volume compositions to use could be as follows:

Iodine Clock Volume Compositions Table

Run	0.01 mol dm^{-3} $Na_2S_2O_3$(aq)/cm^3	H_2O / cm^3	0.5 mol dm^{-3} KI(aq) / cm^3	0.05 mol dm^{-3} H_2SO_4 /cm^3	Starch solution / cm^3
1	1	4	1	25	1
2	1	3	2	25	1
3	1	2	3	25	1
4	1	1	4	25	1
5	1	0	5	25	1

Practical tips

- Hydrogen peroxide is typically found in 'volume' concentrations, based on the volume of oxygen given of when it decomposes:

$$2H_2O_2\,(aq) \rightarrow O_2\,(g) + 2H_2O\,(l)$$

- For example in school laboratories, a suitable concentration of hydrogen peroxide may be listed as 3% or '10 vol'
  - '10 vol' means that when 1cm^3 of hydrogen peroxide decomposes it generates 10 cm^3 of oxygen
  - '10 vol' or 3% hydrogen peroxide has a concentration of 0.979 mol dm^3

Specimen Results

- Here is a set of typical results for the iodine clock reaction

Specimen Results for the Iodine Clock Reaction Table

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Concentration of potassium iodide / mol dm^{-3} × 10^{-2}	Time for blue colour to appear / s	Rate, 1/t s^{-1}
1.515	40	0.025
3.030	20	0.050
4.545	13	0.075
6.060	10	0.100
7.576	8	0.120

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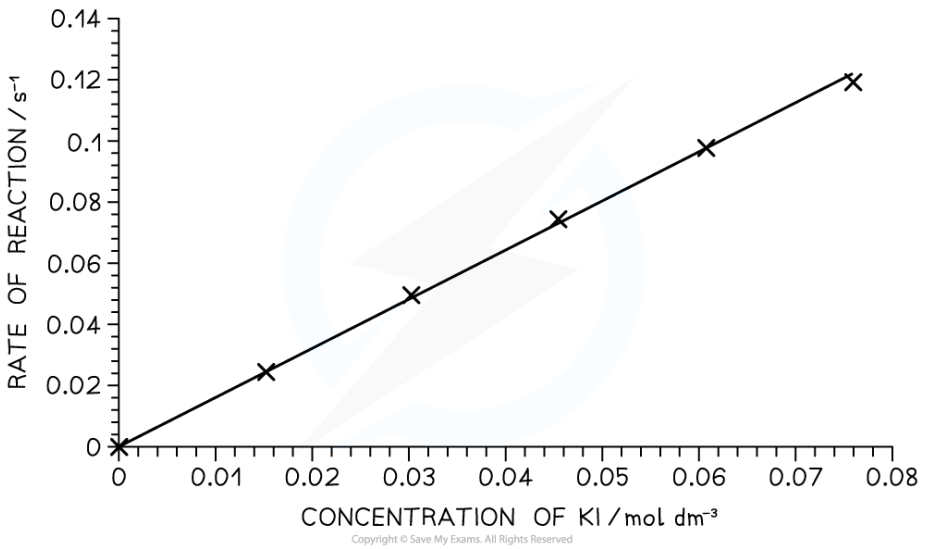
Analysis

- The time of reaction is converted to rate of reaction by calculating the reciprocal value
- A graph is plotted of rate versus concentration



A rate- concentration graph for the iodine clock reaction

- From this graph we can see that the rate of reaction is directly proportional to the concentration of potassium iodide:
  - As concentration doubles; the rate of reaction also doubles
- This tells us that the reaction is first order with respect to potassium iodide

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Core Practical 10: Finding the Activation Energy of a Reaction

- In this practical the activation energy for the reaction between bromide ions and bromate(V) ions will be determined

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$$

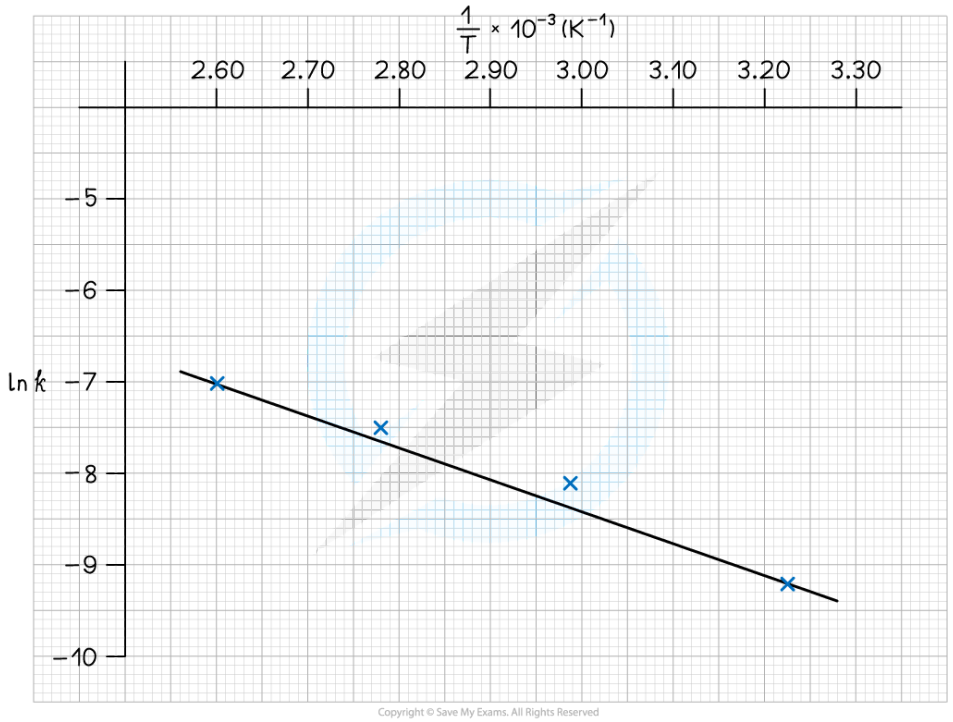
- The bromine produced in the first reaction reacts with the phenol
- When the phenol is 'used up', the bromine is no longer removed
- The bromine then bleaches the indicator at the 'end of the reaction'
  - Common indicators for this reaction are methyl red and methyl orange

Steps in procedure

- Pipette 10.0 cm^3 of phenol solution and 10.0 cm^3 of a bromide / bromate solution into one boiling tube
- Add four drops of methyl red indicator to the mixture
- Pipette 5.0 cm^3 of sulfuric acid solution into a separate boiling tube
- Use a kettle and a beaker to prepare a water bath with a temperature of 37 °C (±1 °C) and stand the two boiling tubes in the water bath
- When the contents of the boiling tubes have reached the water temperature, mix the contents of the two tubes by pouring rapidly from one tube into the other and then pouring the mixture back into the empty test tube
- Start the stop clock at the same time
- Leave the boiling tube containing the reaction mixture in the water and time until the methyl red indicator disappears
- Record the results
- Repeat the whole experiment at different temperatures
  - Use ice to achieve the lowest temperature if required

Sample Data

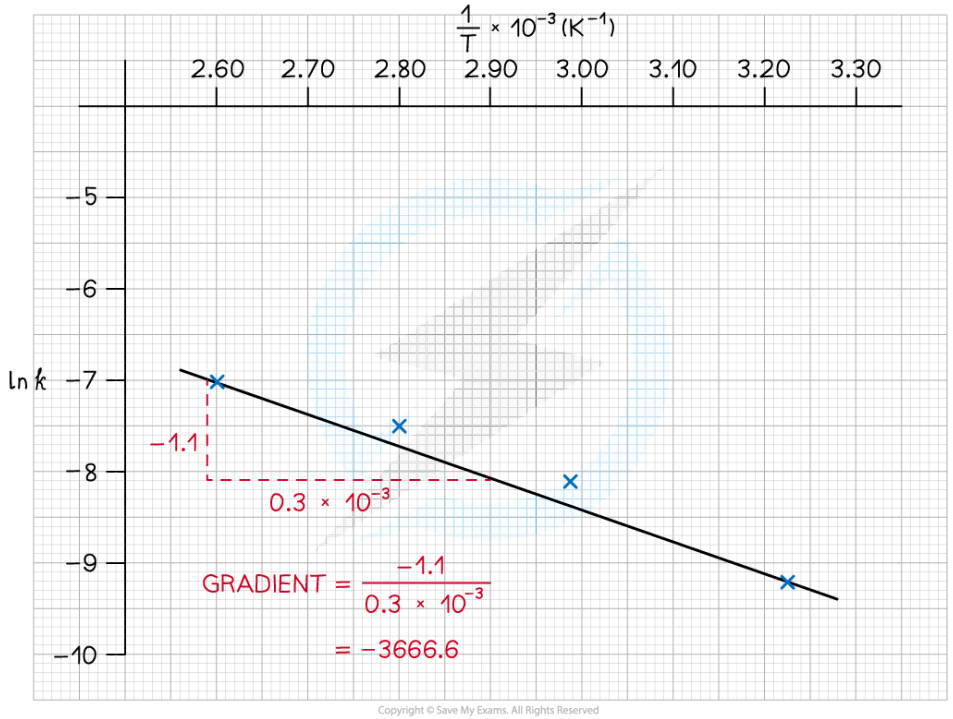
Temperature / K	$\frac{1}{T}$ / K^{-1}	Time (t) / s	Rate constant (k) / s^{-1}	ln k
310	3.23×10^{-3}	57	1.01×10^{-4}	−9.2
335	2.99×10^{-3}	31	3.01×10^{-4}	−8.1
360	2.78×10^{-3}	19	5.37×10^{-4}	−7.5
385	2.60×10^{-3}	7	9.12×10^{-4}	−7.0



Graph plotted from data

Your notes

CALCULATE THE ACTIVATION ENERGY:



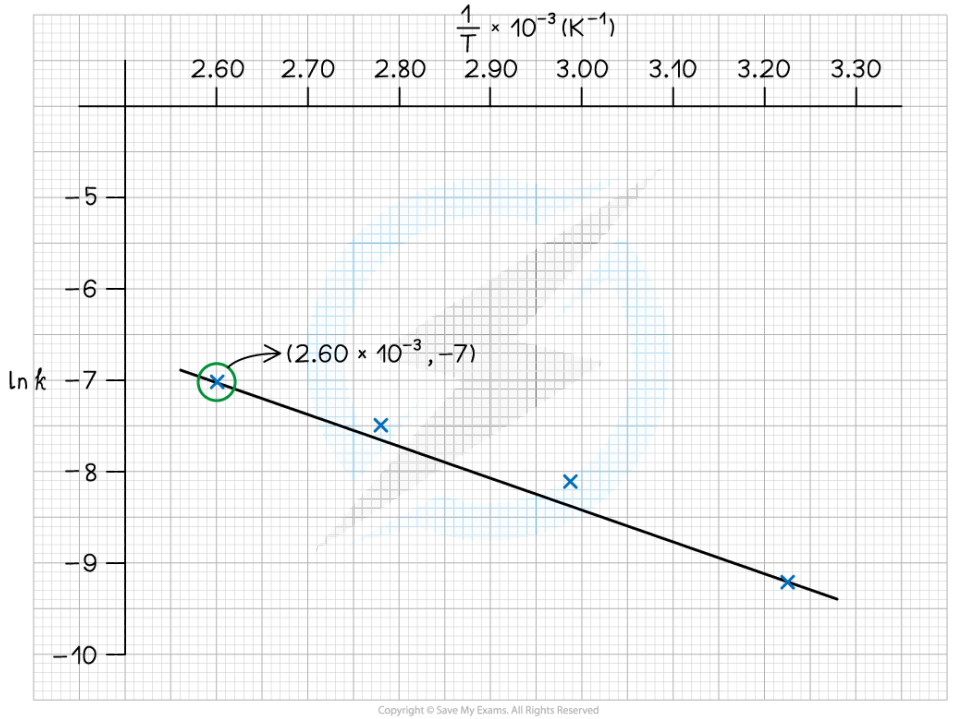
$$\text{GRADIENT} = \frac{-E_a}{R} = -3666.6$$

$$E_a = -(-3666.6 \times 8.31)$$
$$= 30{,}469 \text{ J mol}^{-1}$$
$$= 30.5 \text{ kJ mol}^{-1}$$

Your notes

Your notes

CALCULATE A:



CHOOSE A POINT ON THE GRAPH
$(2.60 \times 10^{-3}, -7.0)$

USE THE FOLLOWING EQUATION:

$y = m x + c$

$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$

$\ln k = -7.0$

$\frac{1}{T} = 2.60 \times 10^{-3}$

} FROM THE POINT CHOSEN ON THE GRAPH

$\frac{-E_a}{R} = \frac{-1.1}{0.3 \times 10^{-3}}$

$= -3666.6$

SO: $-7.0 = (-3666.6 \times 2.60 \times 10^{-3}) + \ln A$

$-7.0 = -9.53 + \ln A$

$\therefore \ln A = -7.0 + 9.53$

$= 2.53$

$A = e^{2.53}$

$A = 12.55$

Your notes

Core Practical 11: Finding Ka for a Weak Acid

- The K_a of a weak acid may be determined by finding the pH at the half equivalence point
- At the half equivalence point $K_a = [H^+]$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = [H^+]$$

Key steps in the procedure

- A pH probe or meter is calibrated before use
- 25 cm^3 of 0.1 mol dm^{-3} ethanoic acid is pipetted into a conical flask and a few drops of phenolphthalein indicator are added
- A burette is filled with 0.1 mol dm^{-3} sodium hydroxide solution
- The contents of the conical flask are titrated against the sodium hydroxide until the indicator just turns pink
- A further pipette containing 25 cm^3 of the acid is then added to the flask and the pH is measured

Specimen Results

- pH at half equivalence point = 4.75

Analysis

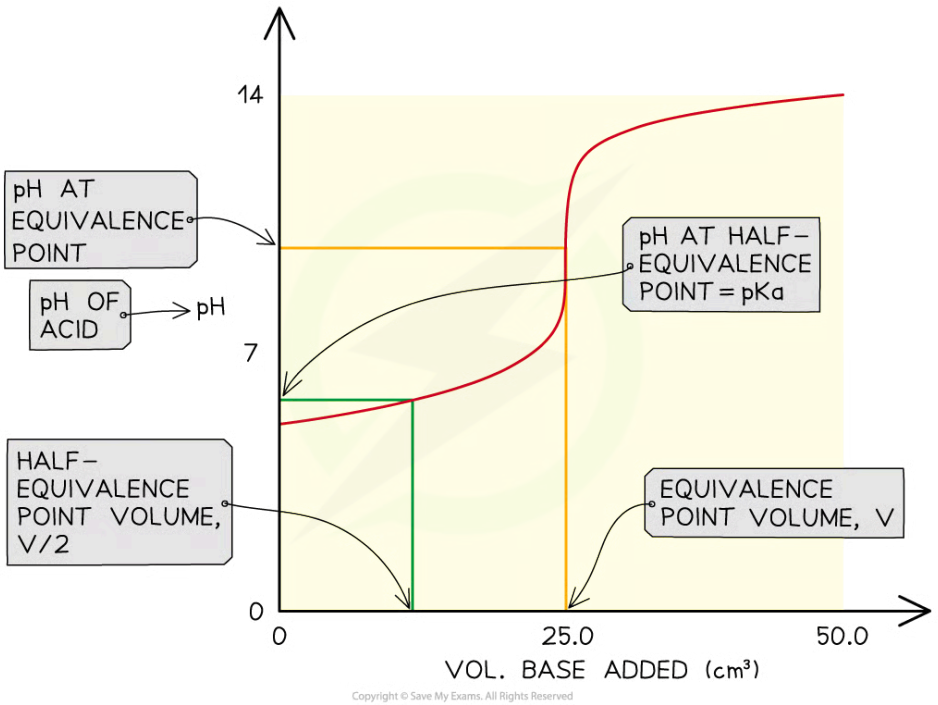
- After the addition of the second portion of acid, the solution is effectively a half-neutralised sample of acid
- This is the half-equivalence point at which the $K_a = [H^+]$
- By measuring the pH at that point you can convert it to $[H^+]$ and hence find the K_a of the acid

$$pH = 4.75$$

$$[H^+] = 10^{-pH} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\therefore K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

- You can also say that the pK_a = pH at the half-equivalence point



The pH at the half-equivalence point in a weak acid titration gives the pKa of the weak acid

Examiner Tips and Tricks

The sources of uncertainty in this experiment include the measurements made by the pipette and burette, and the judgement of the end-point of the titration.Be careful, there is a single uncertainty in the pipette measurements as one reading was taken but there is double the uncertainty for the burette reading as there was the initial and final readings.

Your notes

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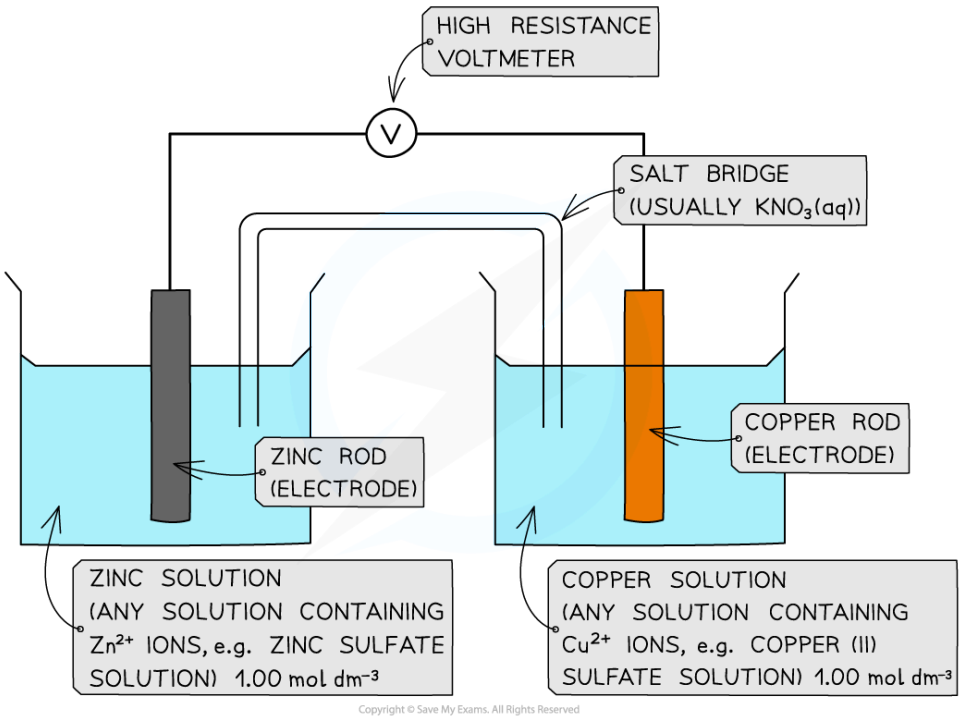
Core Practical 12: Investigating Electrochemical Cells

Measuring the EMF of a cell

- To measure a cell EMF you will need
  - Two small beakers, around 75 cm^3 capacity
  - Strips of suitable metals such as copper, zinc, iron and silver
  - 1.0 mol dm^{-3} solutions of the metal ions (nitrates, chlorides or sulfates depending on their solubility)
  - A high resistance voltmeter (usually a digital multimeter has this)
  - Two sets of wires with crocodile clips
  - A salt bridge consisting of a strip of filter paper soaked in saturated potassium nitrate



The experimental set up for measuring the EMF of a cell made of two metal / metal ion half cells

The procedure

- The strips of metals need to be freshly cleaned to remove any oxide coatings

- This can be done with a piece of sandpaper

- To support the metals, it is easiest to have long strips that can be folded over the side of the beaker and held in place with the crocodile clips
- Fill up the beakers to about two thirds of the way with the metal ion solutions
- Using tongs, dip a strip of filter paper into a beaker of saturated potassium nitrate solution and then place it between the two beakers making sure the ends of the strip are well immersed in the solutions
- Connect the crocodile clips to the voltmeter, wait for a steady reading and record the measurement


Your notes

Practical tips

- If you don't get a positive reading on the voltmeter swap the terminals around
- Voltmeters will have marked positive and negative terminals (usually in red and black, respectively), so when you get a positive reading this tells you the relative polarity of the metals in the cell
- Change the salt bridge each time, to prevent cross contamination of ions between half cells

Calculating the Theoretical EMF of a Cell

- The voltage you measure in your experiment can be compared to a theoretical value calculated using **standard electrode potentials (E°)**
  - These values are found in the electrochemical series in your data book.
- The EMF of a cell is the difference between the E° values of the two half-cells
- The formula is:

$$E°(cell) = E°(positive\ electrode) - E°(negative\ electrode)$$

- A simple way to remember this is "most positive E° value minus most negative E° value

Worked Example

Calculate the theoretical EMF for a cell made of zinc and iron.

1. **Find the E° values from a data book:**
   - $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ has an E° = **-0.44 V**
   - $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ has an E° = **-0.76 V**
2. **Identify the positive and negative electrodes:**
   - The half-cell with the **more positive** (less negative) E° value will be the **positive electrode**
     - In this case, that is the **Fe^{2+}/Fe** half-cell.

- The half-cell with the **more negative** E° value will be the **negative electrode**
  - This is the **Zn^{2+}/Zn** half-cell.

3. **Apply the formula:**
   - E°(cell) = E°(positive) - E°(negative)
   - E°(cell) = (-0.44) - (-0.76)
   - E°(cell) = **+0.32 V**

This calculation is how the theoretical values in the specimen results table are determined.

Your notes

Specimen Results

- Here is a set of typical results for this experiment:

Negative electrode	Positive electrode	EMF / V
Zn (s) / Zn^{2+} (aq)	Cu^{2+} (aq) / Cu (s)	1.10
Zn (s) / Zn^{2+} (aq)	Fe^{2+} (aq) / Fe (s)	0.32
Fe (s) / Fe^{2+} (aq)	Cu^{2+} (aq) / Cu (s)	0.78
Zn (s) / Zn^{2+} (aq)	Ag^{+} (aq) / Ag (s)	1.56
Cu (s) / Cu^{2+} (aq)	Ag^{+} (aq) / Ag (s)	0.46

Analysis

- It is unlikely you will get very close to the theoretical results as these would be obtained under **standard conditions** (1.0 mol dm^{-3} concentration, 298 K temperature)
  - This is because these conditions are hard to achieve in a school laboratory
- However, the **relative** EMF of cells you construct should match the theoretical values
- The higher the EMF, the larger the difference in reactivity ('electron pushing power') between the metals