not a transition metal

transition metal compound ∴ coloured.

1. Zinc reacts with copper(II) sulfate solution, $CuSO_4(aq)$.

Which apparatus could be used to determine the effect of the concentration of $CuSO_4(aq)$ on the rate of reaction?

~~**A**~~ balance

~~**B**~~ gas syringe

[✓ **C**] colorimeter

~~**D**~~ pH meter

$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

Blue sol. colourless sol.

Displacement reaction: Zn is more reactive than Cu.

Your answer C

[1]

2. Using the graph, what is the value of the pre-exponential factor, *A*, for the decomposition of N_2O_5?

$2N_2O_5(g) \rightarrow 4NO(g) + O_2(g)$

Arrhenius equation:
(linear form)

$\ln k = \frac{-E_A}{RT} + \ln A$

$y = mx + c$

y-intercept = 31.5 = ln A

$A = e^{31.5} = 4.79 \times 10^{13}$ s^{-}

A 3.45 s^{-1}

B 31.5 s^{-1}

C 1.04×10^{5} s^{-1}

[✓ **D**] 4.79×10^{13} s^{-1}

Your answer D

[1]

3. Iodine monochloride, ICl, can react with hydrogen to form iodine.

$$2ICl + H_2 \rightarrow 2HCl + I_2$$

This reaction was carried out several times using different concentrations of ICl or H_2. The initial rate of each experiment was calculated and the results are shown below. Initial concentrations are shown for each experiment.

	[ICl] / mol dm^{-3}	[H_2] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
Experiment 1	0.250	0.500	2.04×10^{-2}
Experiment 2	0.500 ×2	0.500 ×1	4.08×10^{-2} ×2
Experiment 3	0.125 ÷4	0.250 ÷2	5.10×10^{-3} ÷8

(a) **(i)** Calculate the rate constant, *k*, for this reaction. Include units in your answer.

Show **all** your working.

rate = $k[ICl]^x[H_2]^y$

x and y indicate order of reaction

[H_2] and [ICl] are both first order reactions as their increase in concentration is mirrored by the change in rate of reaction.

rate = $k[ICl][H_2]$

$$\frac{2.04 \times 10^{-2}}{0.250 \times 0.500} = 0.163 \text{ mol}^{-1}\text{ dm}^{3}\text{ s}^{-1}$$

$$\frac{\cancel{mol\ dm^{-3}}\ s^{-1}}{mol^{\cancel{2}}\ dm^{-\cancel{6}\,3}}$$

k = ...0.163.............. units mol^{-1} dm^{3} s^{-1}.......... **[4]**

(ii) Calculate the rate of reaction when ICl has a concentration of 3.00×10^{-3} mol dm^{-3} and H_2 has a concentration of 2.00×10^{-3} mol dm^{-3}.

Show **all** your working.

rate = $0.163[ICl][H_2]$

rate = $0.163[3 \times 10^{-3}][2 \times 10^{-3}]$

rate = 9.78×10^{-7} mol dm^{-3} s^{-1}

rate = ...9.78×10^{-7}........ mol dm^{-3} s^{-1} **[1]**

(b) Reaction rates can be increased or decreased by changing the temperature of the reaction. **Fig. 17.1** below shows the energy distribution of the reactant molecules at 25 °C.

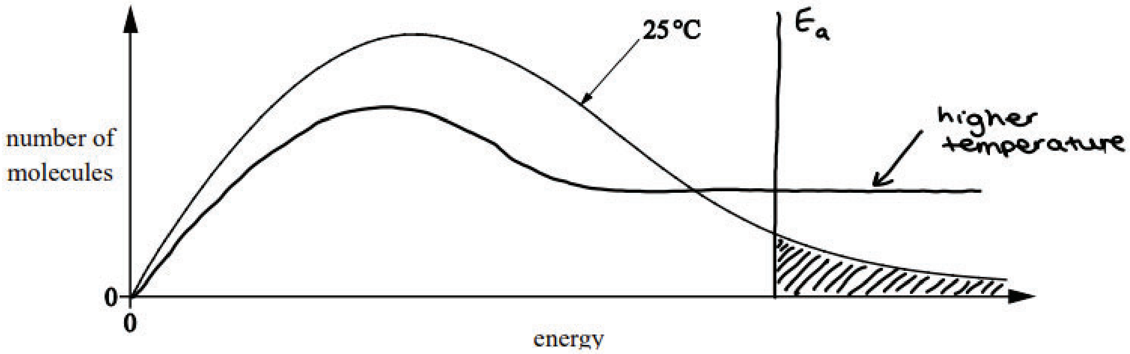


Fig. 17.1

Draw a second curve on **Fig. 17.1**, to represent the distribution of the same number of molecules at a higher temperature.

Use your curve to explain how increasing the temperature increases the rate of reaction.

The graph shows that at a higher temperature more molecules have energy $> E_a$.

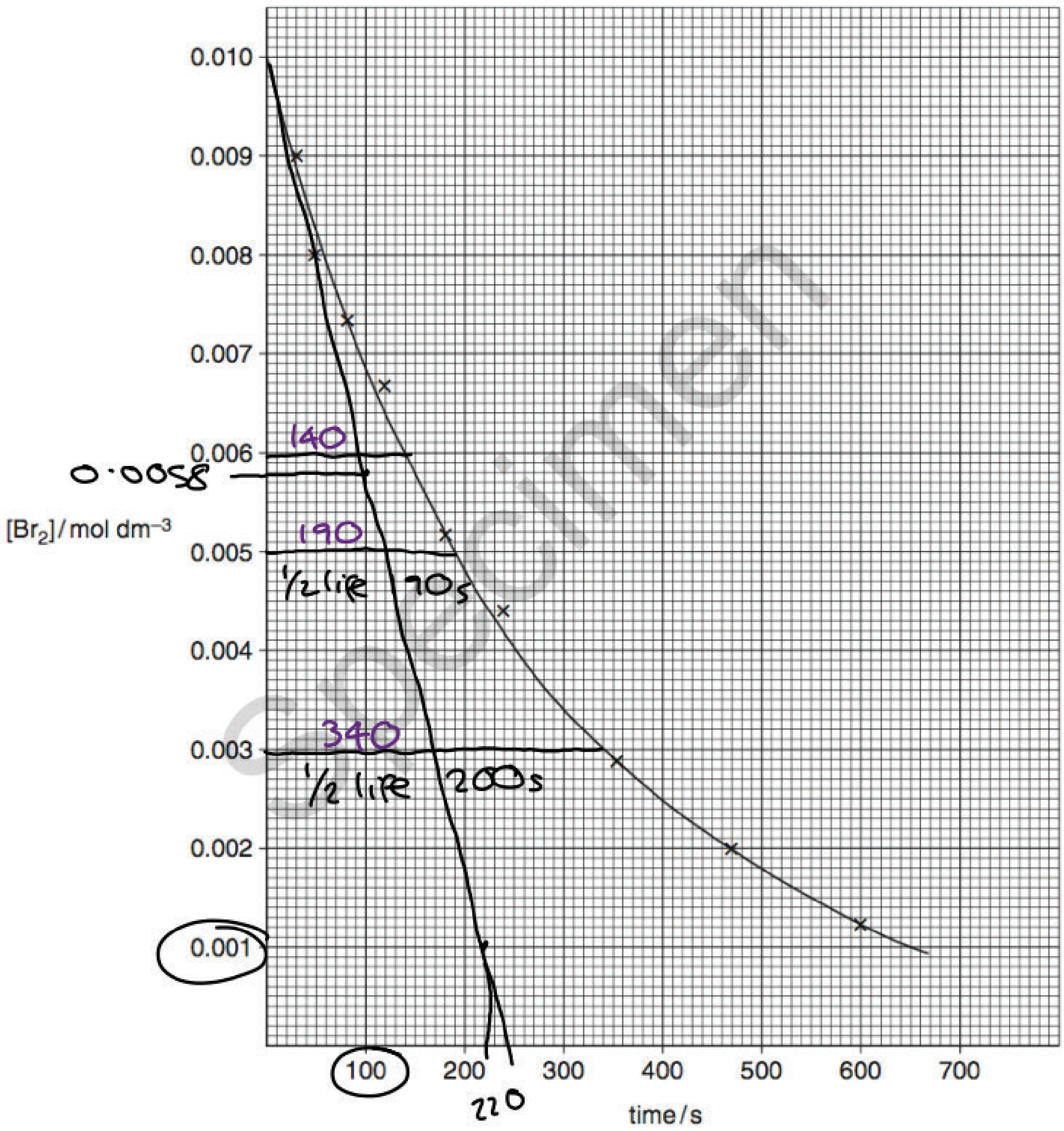
[2]

4. Methanoic acid and bromine react as in the equation below.

$$Br_2(aq) + HCOOH(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

A student investigates the rate of this reaction by monitoring the concentration of bromine over time. The student uses a large excess of HCOOH to ensure that the order with respect to HCOOH will be effectively zero.

From the experimental results, the student plots the graph below.



(a) Suggest how the concentration of the bromine could have been monitored.

measure reduction of colour of bromine

[1]

(b) Suggest a different experimental method that would allow the rate of this reaction to be followed over time.

measure volume of CO_2 produced

[1]

(c) Why would use of excess HCOOH ensure that the order with respect to HCOOH is effectively zero?

concentration of HCOOH would be constant

[1]

(d)* Using the graph, determine

- the initial rate of reaction
- the rate constant.

gradient of tangent at $t = 0\,s$

Your answer must show full working using the graph and the lines below as appropriate.

$$\frac{0.0058 - 0.001}{220 - 100} = 4\times10^{-5}\ mol\,dm^{-3}\,s^{-1}$$

divided concentration by time

Constant ½ life of 190s

so Br_2 is 1st order

$$k = \frac{rate}{[Br_2]} = \frac{4\times10^{-5}}{0.01} = 4\times10^{-3}\ s^{-1}$$

$$\frac{\cancel{mol\,dm^{-3}}\ s^{-1}}{\cancel{mol\,dm^{-3}}}$$

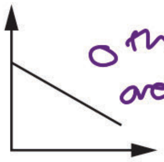
concentration at $t = 0\,s$

[6]

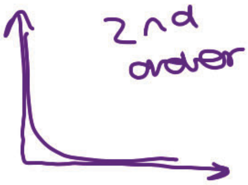
5. A reaction is zero order with respect to a reactant **A**.

Which concentration–time graph for reactant **A** is the correct shape?

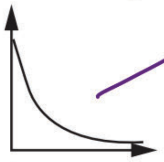
A



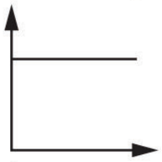
0th order



B

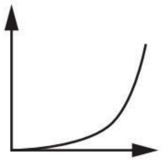


C



0th order for rate-concentration graph

~~**D**~~



concentration decreases over time

Your answer A **[1]**

6. Aqueous solutions of hydrogen peroxide, $H_2O_2(aq)$, decompose as in the equation below.

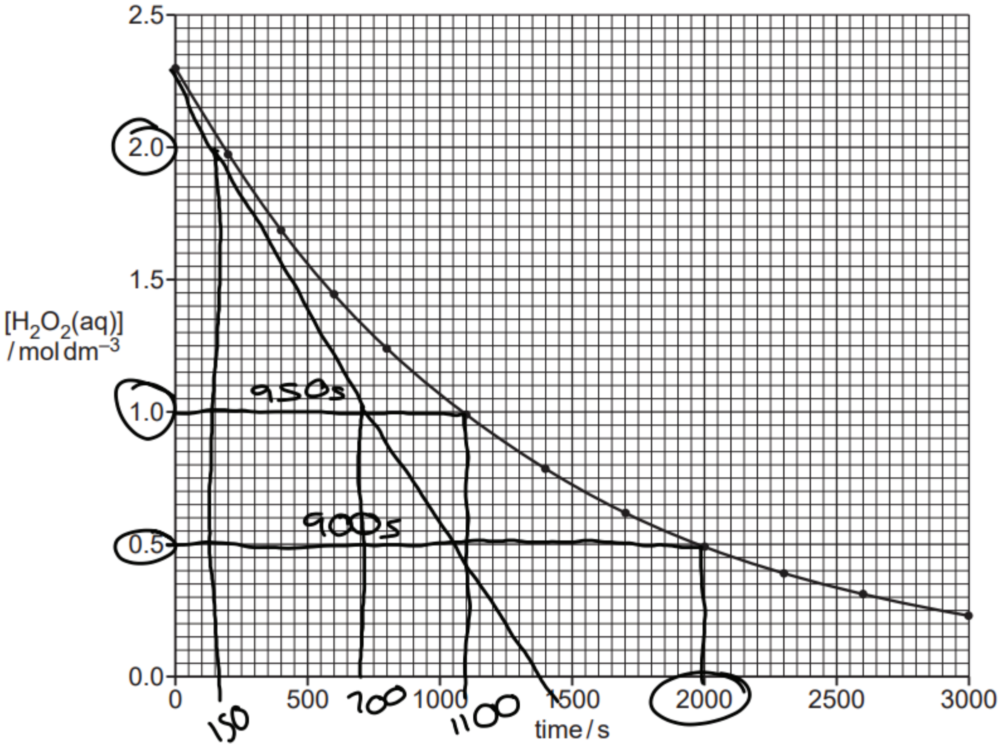
2 : 1 molar ratio

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

A student investigates the decomposition of $H_2O_2(aq)$ by measuring the volume of oxygen gas produced over time. All gas volumes are measured at room temperature and pressure.

The student uses 25.0 cm^3 of 2.30 mol dm^{-3} H_2O_2. $\frac{n}{V \times C}$ R $\frac{\text{vol}}{\text{molar vol}} = \text{mol}$

From the results, the student determines the concentration of $H_2O_2(aq)$ at each time. The student then plots a concentration–time graph.



(a) Determine the total volume of oxygen, measured at room temperature and pressure, that the student should be prepared to collect in this investigation.

Suggest apparatus that would allow this gas volume to be collected, indicating clearly the scale of working.

moles of H_2O_2 : $2.3 \times 25 \times 10^{-3} = 0.0575$ mol

moles of O_2 : $0.0575 \div 2 = 0.02875$ mol

molar volume

$0.02875 \times 24000 = 690 cm^3$

collect in 1000 cm^3 / 1 dm^3 measuring cylinder **[3]** reaction on mass balance measure every 5/10s →

(b) Suggest a different experimental method that would allow the rate of this reaction to be followed over time.

measure mass loss

[1]

(c)* Determine the initial rate of reaction, the order with respect to H_2O_2, and the rate constant.

Your answer must show full working on the graph and on the lines below.

$$\frac{\Delta y}{\Delta x} = \frac{2 - 1}{700 - 150} = 1.8 \times 10^{-3}\ \text{moldm}^{-3}\ \text{s}^{-1}$$

constant ½ lives: 900s and 950s (± 50s) so 1st order

$$k = \frac{\text{rate}}{[H_2O_2]} = \frac{1.8 \times 10^{-3}}{2.3} = 7.8 \times 10^{-4}\ \text{s}^{-1}$$

[6]

7. This question is about reactions of hydrogen peroxide, H_2O_2.

(a) Hydrogen peroxide, H_2O_2, iodide ions, I^-, and acid, H^+, react as shown in the equation below.

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

A student carries out several experiments at the same temperature, using the initial rates method, to determine the rate constant, *k*, for this reaction.

The results are shown below.

1st order

0th order

Experiment	**Initial concentrations**			**Rate**
	$[H_2O_2(aq)]$ / mol dm^{-3}	**$[I^-(aq)]$ / mol dm^{-3}**	**$[H^+(aq)]$ / mol dm^{-3}**	**/ 10^{-6} mol dm^{-3} s^{-1}**
1	0.0100 ×1	0.0100 ×2	0.100 ×1	2.00 ×2
2	0.0100 ×2	0.0200 ÷2	0.100 ×1	4.00 ×1
3	0.0200 ×1	0.0100 ×1	0.100 ×2	4.00 ×1
4	0.0200	0.0100	0.200	4.00

(i) Determine the rate equation and calculate the rate constant, *k*, including units.

$$rate = k[H_2O_2]^1[I^-]^1[H^+]^0$$

$$rate = k[H_2O_2][I^-]$$

$$\frac{2\times10^{-6}}{0.01 \times 0.01} = 0.02$$

$$\frac{mol\,dm^{-3}\,s^{-1}}{mol\,dm^{-3} \times mol\,dm^{-3}}$$

↑

k = 0.02 units $mol^{-1}\,dm^{3}\,s^{-1}$ **[3]**

(ii) The rate constant, *k*, for this reaction is determined at different temperatures, *T*.

Explain how the student could determine the activation energy, E_a, for the reaction graphically using values of *k* and *T*.

plot a graph of ln k against 1/T and measure the gradient.

E_a = gradient × $-R$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

[3]

(b) Solutions of hydrogen peroxide decompose slowly into water and oxygen:

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

This reaction is catalysed by manganese dioxide, $MnO_2(s)$.

Standard electrode potentials are shown below.

I $O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ $E^\ominus = +0.70\,V$

II $MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$ $E^\ominus = +1.51\,V$

III $H_2O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.78\,V$

Using the electrode potentials, explain how MnO_2 is able to act as a catalyst for the decomposition of hydrogen peroxide.

You answer should include relevant equations.

I+II:

$H_2O_2 + MnO_2 + \overset{2}{\cancel{4}}H^+ + \cancel{2e^-} \rightarrow O_2 + \cancel{2H^+} + \cancel{2e} + Mn^{2+} + 2H_2O$

$H_2O_2 + MnO_2 + 2H^+ \rightarrow O_2 + Mn^{2+} + 2H_2O$

II + III:

$Mn^{2+} + \cancel{2H_2O} + H_2O_2 + \cancel{2H^+} + \cancel{2e^-} \rightarrow MnO_2 + \overset{2}{\cancel{4}}H^+ + \cancel{2e^-} + \cancel{2H_2O}$

$Mn^{2+} + H_2O_2 \longrightarrow MnO_2 + 2H^+$

I more -ve E than II so I moves left. II more -ve E than III moves left. MnO_2 is regenerated so acts as a catalyst.

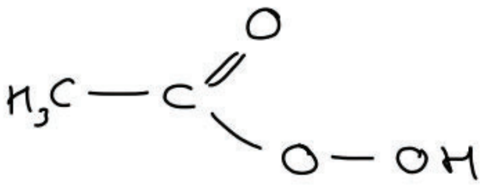
[4]

(c) Peroxycarboxylic acids are organic compounds with the COOOH functional group.

Peroxyethanoic acid, CH_3COOOH, is used as a disinfectant.

(i) Suggest the structure for CH_3COOOH.

The COOOH functional group must be clearly displayed.



[1]

(ii) Peroxyethanoic acid can be prepared by reacting hydrogen peroxide with ethanoic acid. This is a heterogeneous equilibrium.

different states

$$H_2O_2(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COOOH(aq) + H_2O(l) \quad K_c = 0.37\,dm^3\,mol^{-1}$$

A 250 cm^3 equilibrium mixture contains concentrations of 0.500 mol dm^{-3} H_2O_2(aq) and 0.500 mol dm^{-3} CH_3COOH(aq).

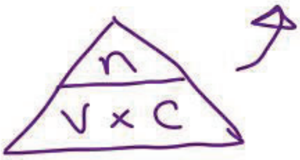
Calculate the amount, in mol, of peroxyethanoic acid in the equilibrium mixture.

square brackets means concentration

$$0.37 = K_c = \frac{\boxed{[CH_3COOOH]}}{[H_2O_2][CH_3COOH]} = \frac{[CH_3COOOH]}{[0.5][0.5]}$$

$$0.37 \times [0.5][0.5] = [CH_3COOOH] = 0.0925 \text{ moldm}^{-3}$$

$$0.0925 \times 250 \times 10^{-3} = 0.023125 \text{ mol}$$

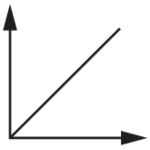


amount = 0.023 mol **[3]**

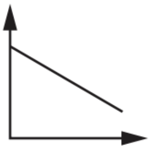
8. A reaction is first order with respect to a reactant **X**.

Which rate–concentration graph for reactant **X** is the correct shape?

[✓ **A**]

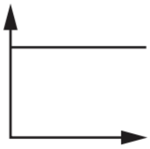


B



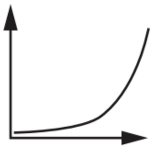
1st order concentration-time graph

C



0 order rate-concentration graph

D



2nd order rate-concentration graph

Your answer A **[1]**

9. This question is about reaction rates.

Aqueous iron(III) ions, $Fe^{3+}(aq)$, react with aqueous iodide ions, $I^-(aq)$, as shown below.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

A student carries out three experiments to investigate how different concentrations of $Fe^{3+}(aq)$ and $I^-(aq)$ affect the initial rate of this reaction. The results are shown below.

first order second order

Experiment	$[Fe^{3+}(aq)]$ / mol dm^{-3}	$[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.00×10^{-2}	3.00×10^{-2}	8.10×10^{-4}
2 ×1	8.00×10^{-2} ×2	3.00×10^{-2} ×1	×2 1.62×10^{-3} ×2 ×4
3	4.00×10^{-2}	6.00×10^{-2}	3.24×10^{-3}

(a)* Determine the rate constant and a possible two-step mechanism for this reaction that are consistent with these results. **[6]**

$$rate = k[Fe^{3+}][I^-]^2$$

$$k = \frac{8.10\times10^{-4}}{(4\times10^{-2})(3\times10^{-2})^2} = 22.5\ mol^{-2}\,dm^{6}\,s^{-1}$$

$$\frac{mol\,dm^{-3}\,s^{-1}}{(mol\,dm^{-3})^3} = \frac{\cancel{mol\,dm^{-3}}\,s^{-1}}{mol^{\cancel{3}\,2}\,dm^{-\cancel{9}\,6}}$$

cancel out

$$\text{Slow: } Fe^{3+}(aq) + 2I^-(aq) \rightarrow \overbrace{[FeI_2]^+}$$

$$\text{Fast: } \underbrace{[FeI_2]^+} + Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + I_{2}(aq)$$

overall equation:

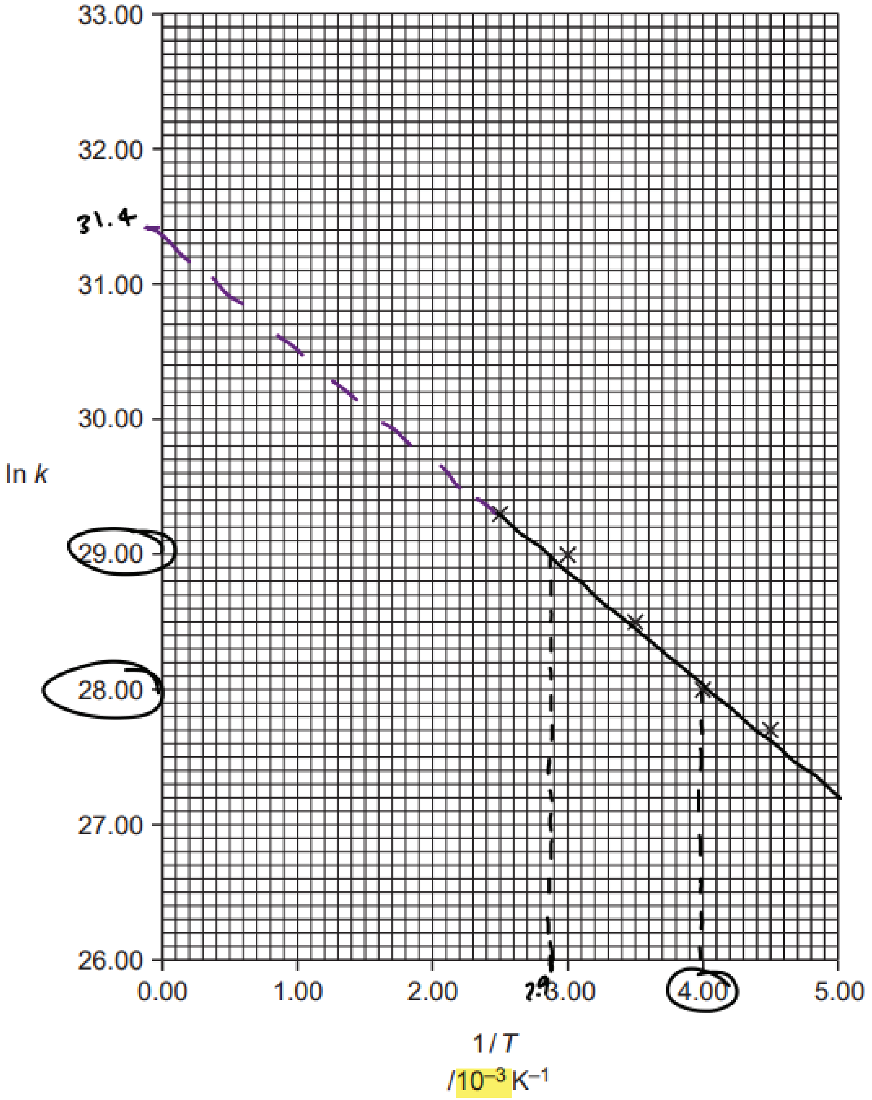
$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

Additional answer space if required

(b) A student carries out an investigation to find the activation energy, E_a, and the pre-exponential factor, A, of a reaction.

$\ln k = -\frac{E_a}{RT} + \ln A$

The student determines the rate constant, k, at different temperatures, T.
The student then plots a graph of $\ln k$ against $1/T$ as shown below.



(i) Draw a best-fit straight line and calculate the activation energy, in J mol^{-1}. Give your answer to **three** significant figures.

Show your working.

gradient: $\frac{29 - 28}{2.9\times10^{-3} - 4\times10^{-3}} = -909 = \frac{-Ea}{R}$

$Ea = +909 \times 8.314 = 7557.4$

$= 7560$ (3sf.)

activation energy, E_a = + ...7560........ J mol^{-1} **[3]**

(ii) Use the graph to calculate the value of the pre-exponential factor, *A*.

y intercept = ln A

Show your working.

$\ln A = 31.4$

$A = e^{31.4} = 4.33\times10^{13}$

pre-exponential factor, *A* = ...4.33×10^{13}........ **[2]**

10. A graph of ln *k* against $\frac{1}{T}$ (T in K) for a reaction has a gradient with the numerical value of −4420.

What is the activation energy, in kJ mol^{-1}, for this reaction?

A −532

B −36.7

[✓ **C**] +36.7

D +5.32 × 10^{5}

Your answer C

[1]

$$\ln K = \frac{E_a}{RT} + \ln A$$

↑ gradient

↑ y intercept

if ln k agains $\frac{1}{T}$

$$\text{gradient} = -\frac{E_a}{R}$$

$$-4420 \times -8.314 = 36747.88\ \text{J mol}^{-1}$$

$$= 36.74788\ \text{kJ mol}^{-1}$$

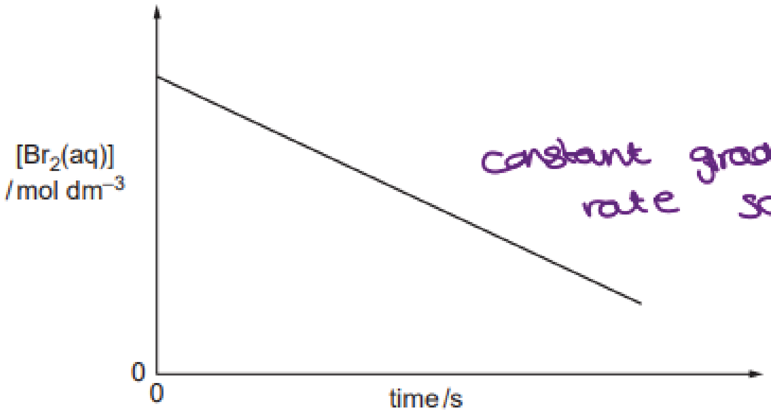
11. Three students carry out a rates investigation on the reaction between bromine and propanone in the presence of hydrochloric acid.

$CH_3COCH_3(aq) + Br_2(aq) \rightarrow CH_3COCH_2Br(aq) + HBr(aq)$

Each student investigates the effect of changing the concentration of one of the reactants whilst keeping the other concentrations constant.

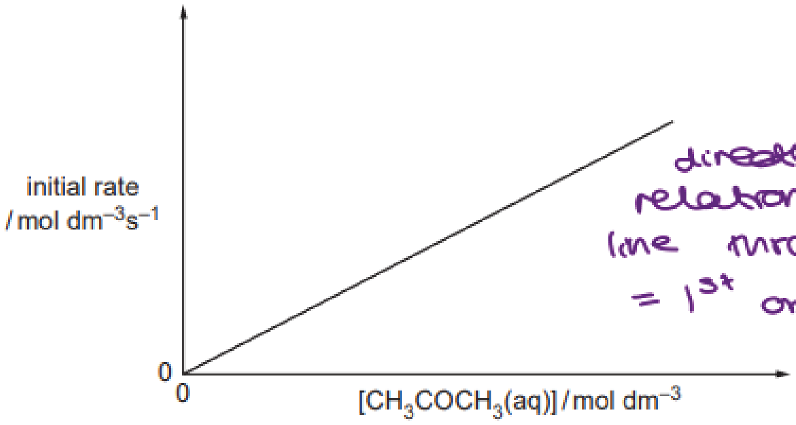
Their results are shown below.

Results of student 1



constant gradient = constant rate so zero order

Results of student 2



directly proportional relationship: straight line through the origin = 1st order

Results of student 3

Experiment	[Br_2(aq)] / mol dm^{-3}	[CH_3COCH_3(aq)] / mol dm^{-3}	[H^+(aq)] / mol dm^{-3}	Initial rate / 10^{-5} mol dm^{-3} s^{-1}
1	0.004	1.60	0.20	1.25
2	0.004	1.60	0.40	2.50

×1 ×1 ×2 ×2

directly proportional relationship = 1st order

Explain how the reaction orders can be determined from the students' results, and determine the rate equation and rate constant. **[6]**

Zero order with respect to $[Br_2]$ because constant gradient / rate

1st order with respect to $[CH_3COCH_3]$ because straight line through (0,0)

1st order with respect to $[H^+]$ because as $[H^+] \times 2$ = initial rate × 2

$$\text{rate} = k[CH_3COCH_3]^1[H^+]^1[Br_2]^0$$

= 1 so don't need to write it

data from experiment 1

$$k = \frac{\text{rate}}{[CH_3COCH_3][H^+]} = \frac{1.25\times10^{-5}}{1.6\times0.2}$$

$$= 3.9\times10^{-5}\ mol^{-1}\,dm^{3}\,s^{-1}$$

Additional answer space if required

units : $$\frac{mol\,dm^{-3}\,s^{-1}}{mol\,dm^{-3}\times mol\,dm^{-3}} = \frac{\cancel{mol\,dm^{-3}}\,s^{-1}}{mol^{\cancel{2}}\,dm^{-\cancel{6}3}}$$

12. These short questions are from different areas of chemistry.

(a) Explain why a CF_4 molecule has polar bonds but does **not** have an overall dipole.

F is more electronegative than C but CF_4 is symmetrical so the dipoles cancel out **[2]**

(b) Explain why a small proportion of molecules in water have a relative molecular mass of 20.

molecules contain : ^2H (deuterium)
^3H (tritium)

[1]

(c) What is the partial pressure of O_2 (in Pa) in a gas mixture containing 21% O_2 by volume and with a total pressure of 1.0×10^5 Pa?

partial pressure = mol fraction × total pressure

$0.21 \times 1.00 \times 10^5 = 2.1 \times 10^4$ Pa

21% = 0.21 = mol fraction

partial pressure of O_2 = 2.1×10^4 Pa **[1]**

(d) What mass of carbon dioxide (in g) is formed by the complete combustion of $42.0\,m^3$ (measured at RTP) of propane?

$$mol = \frac{vol\ (dm^3)}{molar\ volume}$$

molar volume = $24 dm^3$ at RTP

$$\frac{42 \times 10^3}{24} = 1750 \text{ mol of } C_3H_8$$

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

$(1750 \times 3) \times (12 + (16 \times 2)) = 2.31 \times 10^5$ g

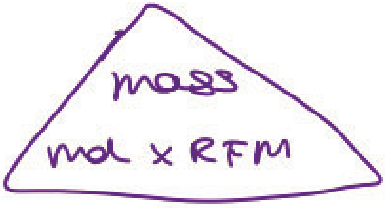
mass = 2.31×10^5 g **[2]**

(e) A reaction is first order with respect to H^+. At a pH of 1, the initial rate is $2.4 \times 10^{-3}\, mol\, dm^{-3}\, s^{-1}$.

What is the initial rate at a pH of 3?

$$\frac{2.4 \times 10^{-3}}{10^2} = 2.4 \times 10^{-5}\, mol\, dm^{-3}\, s^{-1}$$

initial rate = 2.4×10^{-5} $mol\, dm^{-3}\, s^{-1}$ **[1]**



(f) What is the number of oxygen atoms in 4.26 g of P_2O_5?

$$\frac{4.26}{(31\times2)+(16\times5)} = 0.03\text{mol of } P_2O_5$$

$$(5\times0.03)\times6.02\times10^{23} = 9.03\times10^{22}$$

number of oxygen atoms = 9.03×10^{22} **[2]**

13. A graph is plotted of ln(k) against 1/T.
(k = rate constant, T = temperature in K)

The gradient has the numerical value of −55 000.

What is the activation energy, in kJ mol^{-1}?

A +1.5 × 10^{-7}

B +2.22 × 10^{-6}

C +6.62

D +457

Your answer D

[1]

$k = Ae^{-\frac{Ea}{RT}}$

$\ln k = -\frac{Ea}{R}\left(\frac{1}{T}\right) + \ln A$

$y = m \quad x + c$

$-55000 = -\frac{Ea}{R}$

$55000 \times 8.314 = Ea = 457270$ J mol^{-1}

$= 457.270$ kJ mol^{-1}

14. The equation for the reaction of ICl and H_2 is shown below.

$2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$

The rate constant *k* for this reaction is 1.63 × 10^{-6} $dm^3\,mol^{-1}\,s^{-1}$.

overall 2nd order

What is the overall order of the reaction?

$\text{rate} = k[A]^1[B]^1$

$\frac{\text{rate}}{[A][B]} = k = \frac{\cancel{mol\,dm^{-3}}\,s^{-1}}{\cancel{mol\,dm^{-3}}\,mol\,dm^{-3}}$

A 0

B 1

C 2

D 3

Your answer C **[1]**

15. A student investigates the reaction between ethanoic acid, $CH_3COOH(l)$ and methanol, $CH_3OH(l)$, in the presence of an acid catalyst. The equation is shown below.

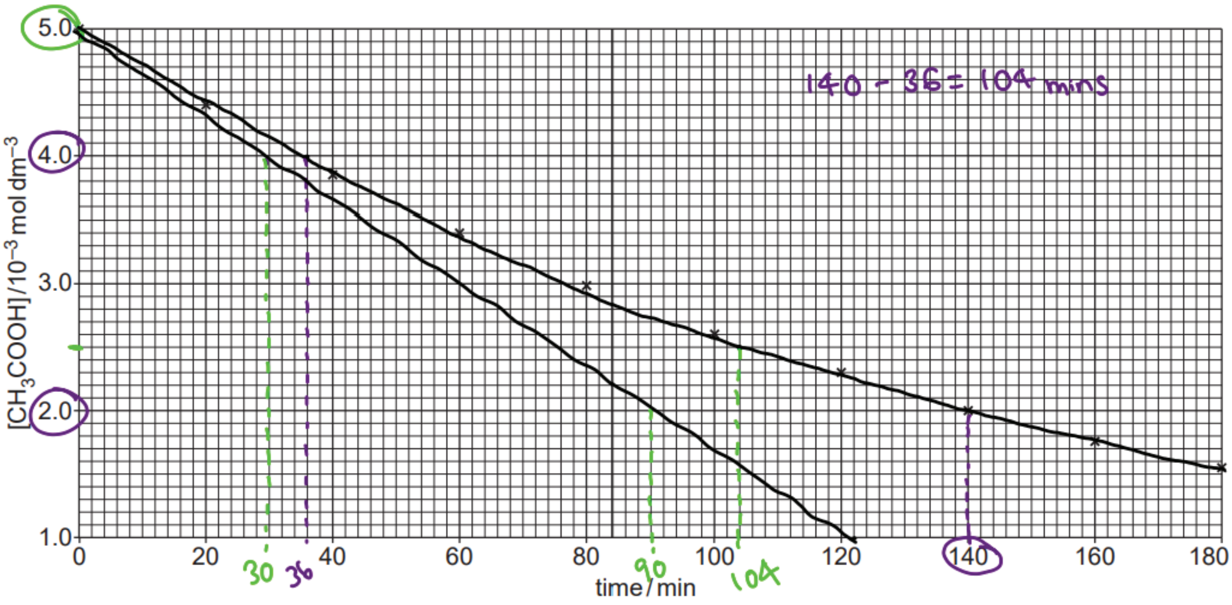
$$CH_3COOH(l) + CH_3OH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$$

(a) The student carries out an experiment to determine the order of reaction with respect to CH_3COOH.

The student uses a large excess of CH_3OH. The temperature is kept constant throughout the experiment.

The student takes a sample from the mixture every 20 minutes, and then determines the concentration of the ethanoic acid in each sample.

From the experimental results, the student plots the graph below.



(i) Explain why the student uses a large excess of methanol in this experiment.

- To keep $[CH_3OH]$ constant
- Zero order with respect to CH_3OH **[1]**
- To ensure equilibrium is far to the right.

(ii) Use the half-life of this reaction to show that the reaction is first order with respect to CH_3COOH.

Show your working on the graph and below.

constant ½ lives of 104 mins so first order **[2]**

(iii) Determine the initial rate of reaction.

$$k = \frac{\ln 2}{t_{1/2}}$$

(I) $k = \frac{\ln 2}{104} = 6.66\times10^{-3}\ \text{min}^{-1}$

$6.66\times10^{-3}\times5\times10^{-3} = 3.33\times10^{-5}$ mol dm^{-3} min^{-1}

(II) $\frac{(4-2)\times10^{-3}}{90-30} = 3.33\times10^{-5}$ mol dm^{-3} min^{-1}

initial rate = 3.33×10^{-5} mol dm^{-3} min^{-1} **[2]**

(b) The student carries out a second experiment to determine the value of K_c for this reaction.

The student mixes 9.6 g of CH_3OH with 12.0 g of CH_3COOH and adds the acid catalyst.

When the mixture reaches equilibrium, 0.030 mol of CH_3COOH remains.

Calculate K_c for this equilibrium.

$$K_c = \frac{[CH_3COOCH_3][H_2O]}{[CH_3OH][CH_3COOH]}$$

$\frac{9.6}{12+3+16+1} = 0.3$ mol CH_3OH

$\frac{12}{12+3+12+(16\times2)+1} = 0.2$ mol CH_3COOH

	CH_3OH	CH_3COOH	CH_3COOCH_3	H_2O
I	0.3	0.2	0	0
C	−0.17	−0.17	+0.17	+0.17
E	0.13	0.03	0.17	0.17

$$K_c = \frac{[0.17/V][0.17/V]}{[0.13/V][0.03/V]} = 7.4$$

K_c = 7.4 **[4]**