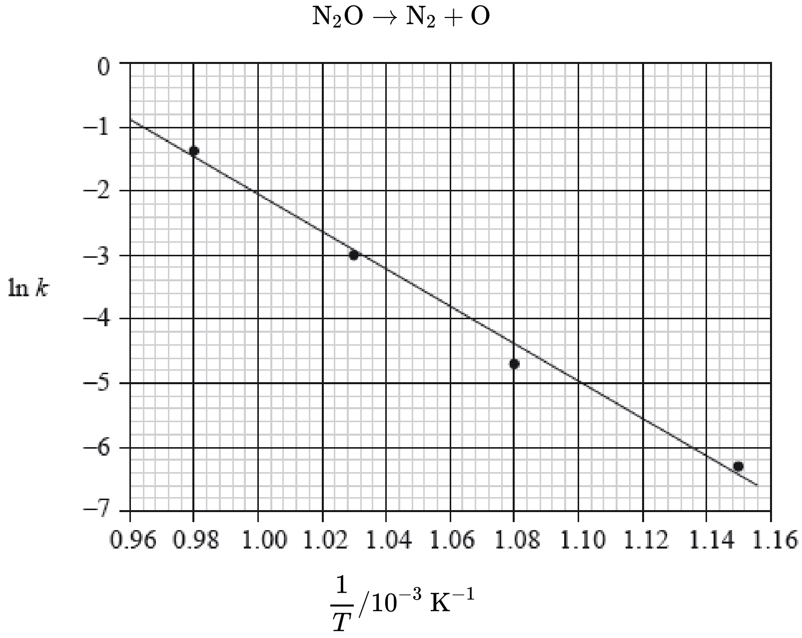
HL Paper 2

Consider the following graph of $\ln k$ against $\frac{1}{T}$ (temperature in Kelvin) for the second order decomposition of N_2O into N_2 and O.



a. State how the rate constant, k varies with temperature,T. [1]

b. Determine the activation energy, E_a, for this reaction. [3]

c. The rate expression for this reaction is rate $= k[N_2O]^2$ and the rate constant is $0.244\ dm^3 mol^{-1} s^{-1}$ at 750 °C. [2]

A sample of N_2O of concentration $0.200\ mol\ dm^{-3}$ is allowed to decompose. Calculate the rate when 10% of the N_2O has reacted.

Markscheme

a. k increases with increase in T/k decreases with decrease in T;

Do not allow answers giving just the Arrhenius equation or involving lnk relationships.

b. $\text{gradient} = -E_a/R$;

$-30000\ (K) = -E_a/R$;

Allow value in range –28800–31300 (K).

c. $0.9 \times 0.200 = 0.180\ (mol\ dm^{-3})$;

$\text{rate} = \left(0.244 \times (0.180)^2 =\right)\ 7.91 \times 10^{-3}\ mol\ dm^{-3} s^{-1}$;

*Award **[2]** for correct final answer.*

*Award **[1 max]** for either 9.76×10^{-3} mol dm^{-3}s^{-1} or 9.76×10^{-5} mol dm^{-3}s^{-1}.*

Examiners report

a. This question on chemical kinetics was very poorly answered by candidates. In (a), many candidates simply gave the Arrhenius equation and failed to describe the explicit relationship between k and T.

b. (b) was answered very poorly and although some candidates had an idea about the gradient expression, most were out by a factor of 100 in their final answer and many totally ignored units.

c. In (c), the most common error related to the 10% reduction and units also proved challenging.

Consider the following reaction studied at 263 K.

$$2\mathrm{NO(g)} + \mathrm{Cl_2(g)} \rightleftharpoons 2\mathrm{NOCl(g)}$$

It was found that the forward reaction is first order with respect to $\mathrm{Cl_2}$ and second order with respect to NO. The reverse reaction is second order with respect to NOCl.

Consider the following equilibrium reaction.

$$\mathrm{Cl_2(g)} + \mathrm{SO_2(g)} \rightleftharpoons \mathrm{SO_2Cl_2(g)} \quad \Delta H^{\ominus} = -84.5\ \mathrm{kJ}$$

In a $1.00\ \mathrm{dm^3}$ closed container, at 375 °C, $8.60 \times 10^{-3}\ \mathrm{mol}$ of $\mathrm{SO_2}$ and $8.60 \times 10^{-3}\ \mathrm{mol}$ of $\mathrm{Cl_2}$ were introduced. At equilibrium, $7.65 \times 10^{-4}\ \mathrm{mol}$ of $\mathrm{SO_2Cl_2}$ was formed.

a.i. State the rate expression for the forward reaction. [1]

a.ii. Predict the effect on the rate of the forward reaction and on the rate constant if the concentration of NO is halved. [2]

a.iii. 1.0 mol of $\mathrm{Cl_2}$ and 1.0 mol of NO are mixed in a closed container at constant temperature. Sketch a graph to show how the concentration of NO and NOCl change with time until after equilibrium has been reached. Identify the point on the graph where equilibrium is established. [4]

b. Consider the following reaction. [2]

$$\mathrm{NO_2(g)} + \mathrm{CO(g)} \rightarrow \mathrm{NO(g)} + \mathrm{CO_2(g)}$$

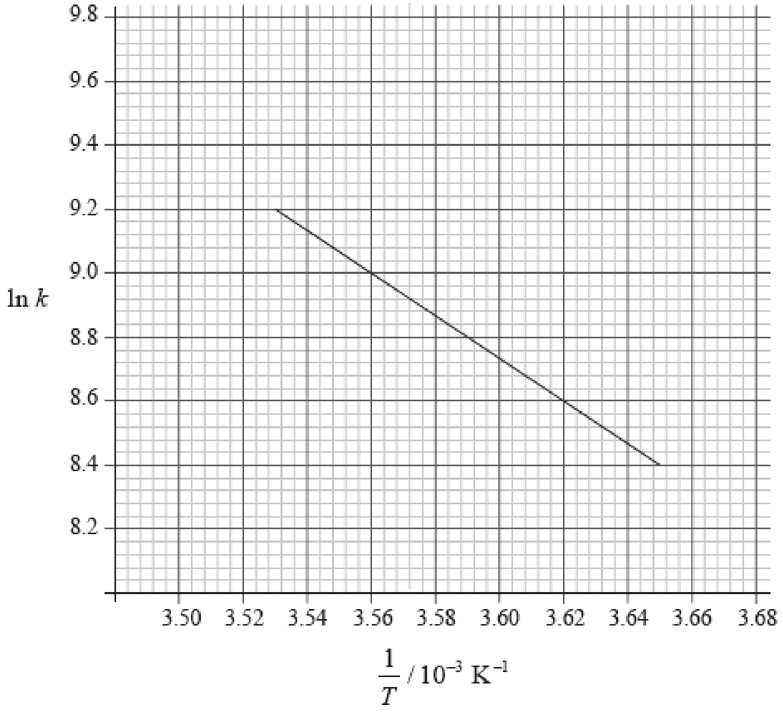
Possible reaction mechanisms are:

$$\begin{array}{lll} \text{Above 775 K:} & \mathrm{NO_2 + CO \rightarrow NO + CO_2} & \text{slow} \\ \text{Below 775 K:} & \mathrm{2NO_2 \rightarrow NO + NO_3} & \text{slow} \\ & \mathrm{NO_3 + CO \rightarrow NO_2 + CO_2} & \text{fast} \end{array}$$

Based on the mechanisms, deduce the rate expressions above and below 775 K.

c. State **two** situations when the rate of a chemical reaction is equal to the rate constant. [2]

d. Consider the following graph of $\ln k$ against $\frac{1}{T}$ for the first order decomposition of $\mathrm{N_2O_4}$ into $\mathrm{NO_2}$. Determine the activation energy in $\mathrm{kJ\,mol^{-1}}$ for this reaction. [2]



e.i. Deduce the equilibrium constant expression, K_c, for the reaction. [1]

e.ii. Determine the value of the equilibrium constant, K_c. [3]

e.iii. If the temperature of the reaction is changed to 300 °C, predict, stating a reason in each case, whether the equilibrium concentration of SO_2Cl_2 and the value of K_c will increase or decrease. [3]

e.iv. If the volume of the container is changed to $1.50\ dm^3$, predict, stating a reason in each case, how this will affect the equilibrium concentration of SO_2Cl_2 and the value of K_c. [3]

e.v. Suggest, stating a reason, how the addition of a catalyst at constant pressure and temperature will affect the equilibrium concentration of SO_2Cl_2. [2]

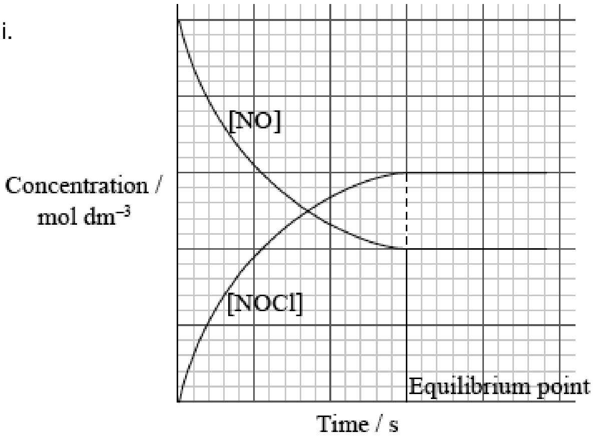
Markscheme

a.i. $rate = k[NO]^2[Cl_2]$;

a.ii. rate of reaction will decrease by a factor of 4;

no effect on the rate constant;

a.iii.



y axis labelled concentration/mol dm^{-3} and *x* axis is labelled time/s;

gradient for [NO];

gradient for [NOCl] will be equal and opposite;

equilibrium point identified / two curves level off at same time;

b. Above 775 K: $\text{rate} = k[\text{NO}_2][\text{CO}]$;

Below 775 K: $\text{rate} = k[\text{NO}_2]^2$;

c. zero order reaction;

all concentrations are $1.0\ \text{mol dm}^{-3}$;

d. $\text{slope} = \frac{9.2-8.4}{(3.53-3.65)\times 10^{-3}} = -6.67 \times 10^3$;

$(E_a = 6.67 \times 10^3 \times 8.31)$

$55.4\ (\text{kJ mol}^{-1})$;

Accept in range 55.0 – 56.0

*Award **[1]** if 55454 (J) stated*

*Award **[2]** for the correct final answer*

e.i. $(K_c) = \frac{[\text{SO}_2\text{Cl}_2]}{[\text{Cl}_2][\text{SO}_2]}$;

Ignore state symbols.

Square brackets [ ] required for the equilibrium expression.

e.ii. $7.84 \times 10^{-3}\ \text{mol of SO}_2$ and $7.84 \times 10^{-3}\ \text{mol of Cl}_2$;

$7.84 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{of SO}_2$, $7.84 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{of Cl}_2$ **and**
$7.65 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{of SO}_2\text{Cl}_2$;

12.5;

*Award **[1]** for 10.34*

*Award **[3]** for the correct final answer*

e.iii value of K_c increases;

$[\text{SO}_2\text{Cl}_2]$ increases;

decrease in temperature favours (forward) reaction which is exothermic;

Do not allow ECF.

e.iv no effect on the value of K_c / depends only on temperature;

$[\text{SO}_2\text{Cl}_2]$ decreases;

increase in volume favours the reverse reaction which has more gaseous moles;

Do not allow ECF.

e.v. no effect;

catalyst increases the rate of forward and reverse reactions (equally) / catalyst decreases activation energies (equally);

Examiners report

a.i. In part (a) the rate expression was correctly stated although some confused this with an equilibrium constant expression.

a.ii.Only the better candidates realized that the rate of reaction will decrease by a factor of four and there will be no effect on the rate constant.

a.iii.Although most candidates were able to correctly sketch the concentration versus time graph many forgot to label the axes or include units.

b. Part (b) was well answered and candidates demonstrated a good understanding of rate expressions based on reaction mechanism.

c. The better candidates were able to figure out that the rate of a chemical reaction is equal to the rate constant when all concentrations are $1.0\ \text{mol dm}^{-3}$ or for a zero order reaction.

d. Most candidates had difficulty in calculating activation energy from the graph in part (d) and some gave the answer in J mol^{-1} instead of kJ mol^{-1} which showed that they missed this instruction in the question.

e.i. In part (e), the equilibrium constant expression was correctly stated by the majority but calculating the value of K_c proved to be difficult.

e.ii.A large number of candidates obtained the incorrect answer of 10.34 as a result of using the initial concentrations of the reactants instead of equilibrium concentrations.

e.iii.[N/A]

e.iv.The application of Le Chatelier's principle was handled well by the majority with minor omissions such as not using the term gaseous particles in part (iv).

e.v.Some candidates stated that the addition of a catalyst does not affect the value of K_c or the position of equilibrium, which did not answer the question and scored no marks because they had not commented on the concentration of $SOCl_2$. Some candidates correctly stated that a catalyst increases the rate of forward and reverse reactions equally.

Nitrogen(II) oxide reacts with hydrogen according to the equation below.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

A suggested mechanism for this reaction is:

Step 1: $NO + H_2 \rightleftharpoons X$ fast

Step 2: $X + NO \rightarrow Y + H_2O$ slow

Step 3: $Y + H_2 \rightarrow N_2 + H_2O$ fast

a. Define the term *rate of reaction*. [1]

b. Explain why increasing the particle size of a solid reactant decreases the rate of reaction. [2]

c.i. Identify the rate-determining step. [1]

c.ii.A student hypothesized that the order of reaction with respect to H_2 is 2. [2]

Evaluate this hypothesis.

Markscheme

a. change in concentration of reactant/product with time / rate of change of concentration;

Accept “increase” instead of “change” for product and “decrease” instead of “change” for reactant.

Accept “mass/amount/volume” instead of “concentration”.

Do not accept substance.

b. surface area decreases;

frequency/probability of collisions decreases;

Accept number of collisions per unit time decreases.

c.i. step 2 / $X + NO \rightarrow Y + H_2O$ / slow;

c.ii. invalid / unlikely as order most likely one (with respect to hydrogen);

$\text{rate} = k[NO]^2[H_2]$ / H_2 only involved once in the formation of the intermediate before the slow step / *OWTTE*;

Award M2 only if M1 is correct.

Examiners report

a. Although most candidates were able to define the rate of reaction, some of weaker candidates gave imprecise answers which did not refer to concentration of the reactants or products and the “the time for the reaction to go to completion” was not an uncommon response. Most candidates realized that the surface area would decrease but, as in previous sessions, lost marks as they did not refer to the reduced “frequency” of collisions. Most candidates were able to identify the rate determining step and correctly state that the reaction would be first order with respect to hydrogen however only a minority could explain their answer in sufficient detail *i.e.* that H_2 was involved only once in the formation of the intermediate before the rate determining step.

b. Although most candidates were able to define the rate of reaction, some of weaker candidates gave imprecise answers which did not refer to concentration of the reactants or products and the “the time for the reaction to go to completion” was not an uncommon response. Most candidates realized that the surface area would decrease but, as in previous sessions, lost marks as they did not refer to the reduced “frequency” of collisions. Most candidates were able to identify the rate determining step and correctly state that the reaction would be first order with respect to hydrogen however only a minority could explain their answer in sufficient detail *i.e.* that H_2 was involved only once in the formation of the intermediate before the rate determining step.

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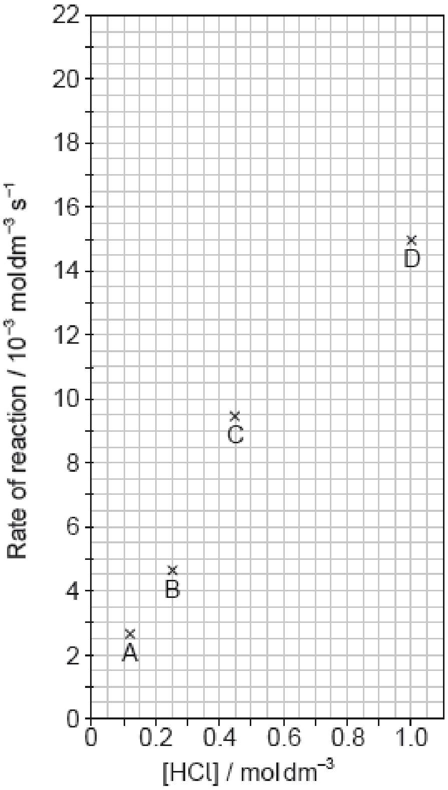
of collisions. Most candidates were able to identify the rate determining step and correctly state that the reaction would be first order with respect to hydrogen however only a minority could explain their answer in sufficient detail *i.e.* that $\mathrm{H_2}$ was involved only once in the formation of the intermediate before the rate determining step.

Calcium carbonate reacts with hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The results of a series of experiments in which the concentration of HCl was varied are shown below.



a. Outline **two** ways in which the progress of the reaction can be monitored. No practical details are required. [2]

b.i. Suggest why point D is so far out of line assuming human error is not the cause. [1]

b.ii. Draw the best fit line for the reaction excluding point D. [1]

b.iii. Suggest the relationship that points A, B and C show between the concentration of the acid and the rate of reaction. [1]

b.iv. Deduce the rate expression for the reaction. [1]

b.v. Calculate the rate constant of the reaction, stating its units. [2]

c. Predict from your line of best fit the rate of reaction when the concentration of HCl is 1.00 mol dm^{-3}. [1]

d. Describe how the activation energy of this reaction could be determined. [3]

Markscheme

a. *Any two of:*

loss of mass «of reaction mixture/CO_2»

«increase in» volume of gas produced

change of conductivity

change of pH

change in temperature

*Do **not** accept "disappearance of calcium carbonate".*

*Do **not** accept "gas bubbles".*

*Do **not** accept "colour change" or "indicator".*

[2 marks]

b.i. reaction is fast at high concentration ***AND*** may be difficult to measure accurately

OR

so many bubbles of CO_2 produced that inhibit contact of HCl(aq) with $CaCO_3$(s)

OR

insufficient change in conductivity/pH at high concentrations

OR

calcium carbonate has been used up/is limiting reagent/ there is not enough calcium carbonate «to react with the high concentration of HCl»

OR

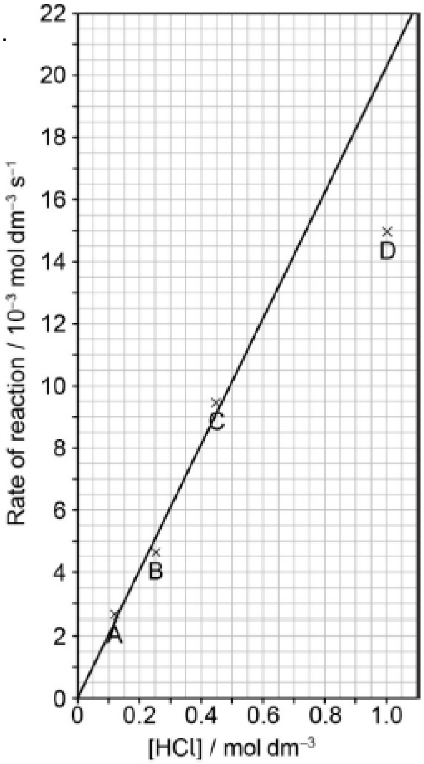
HCl is in excess

OR

so many bubbles of CO_2 produced that inhibit contact of HCl(aq) with $CaCO_3$(s)

[1 mark]

b.ii.



straight line going through the origin ***AND*** as close to A, B, C as is reasonably possible

[1 mark]

b.iii. «directly» proportional

Accept “first order” or “linear”.

*Do **not** accept “rate increases as concentration increases” or “positive correlation”.*

[1 mark]

b.iv. rate = *k* $[H^+]$

Accept “rate = k [HCl]”.

[1 mark]

b.v. 0.02

s^{-1}

[2 marks]

c. 20.5×10^{-3} «mol dm^{-3} s^{-1}»

Accept any answer in the range 19.5–21.5.

[1 mark]

d. ***ALTERNATIVE 1:***

carry out reaction at several temperatures

plot $\frac{1}{T}$ against log rate constant

E_a = – gradient × R

ALTERNATIVE 2:

carry out reaction at two temperatures

determine two rate constants

OR

determine the temperature coefficient of the rate

use the formula $\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Accept "gradient = $\frac{-E_a}{R}$*" for M3.*

Award both M2 and M3 for the formula $\ln\frac{rate_1}{rate_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$.

Accept any variation of the formula, such as $\frac{rate_1}{rate_2} = e^{-\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$.

[3 marks]

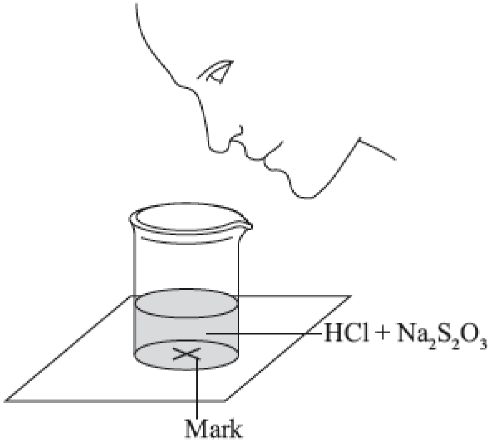
Examiners report

a. [N/A]
b.i. [N/A]
b.ii. [N/A]
b.iii. [N/A]
b.iv. [N/A]
b.v. [N/A]
c. [N/A]
d. [N/A]

A group of students investigated the rate of the reaction between aqueous sodium thiosulfate and hydrochloric acid according to the equation below.

$$\mathrm{Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l\,)}$$

The two reagents were rapidly mixed together in a beaker and placed over a mark on a piece of paper. The time taken for the precipitate of sulfur to obscure the mark when viewed through the reaction mixture was recorded.



Initially they measured out $10.0\ \mathrm{cm}^3$ of $0.500\ \mathrm{mol\,dm}^{-3}$ hydrochloric acid and then added $40.0\ \mathrm{cm}^3$ of $0.0200\ \mathrm{mol\,dm}^{-3}$ aqueous sodium thiosulfate. The mark on the paper was obscured 47 seconds after the solutions were mixed.

One proposed mechanism for this reaction is:

$\mathrm{S_2O_3^{2-}(aq) + H^+(aq) \rightleftharpoons HS_2O_3^-(aq)}$ Fast

$\mathrm{HS_2O_3^-(aq) + H^+(aq) \rightarrow SO_2(g) + S(s) + H_2O(l)}$ Slow

The teacher asked the students to devise another technique to measure the rate of this reaction.

Another group suggested collecting the sulfur dioxide and drawing a graph of the volume of gas against time.

a. (i) State the volumes of the liquids that should be mixed. [3]

Liquid	$0.500\ \mathrm{mol\,dm^{-3}\ HCl}$	$0.0200\ \mathrm{mol\,dm^{-3}\ Na_2S_2O_3}$	Water
Volume / cm^3			

(ii) State why it is important that the students use a similar beaker for both reactions.

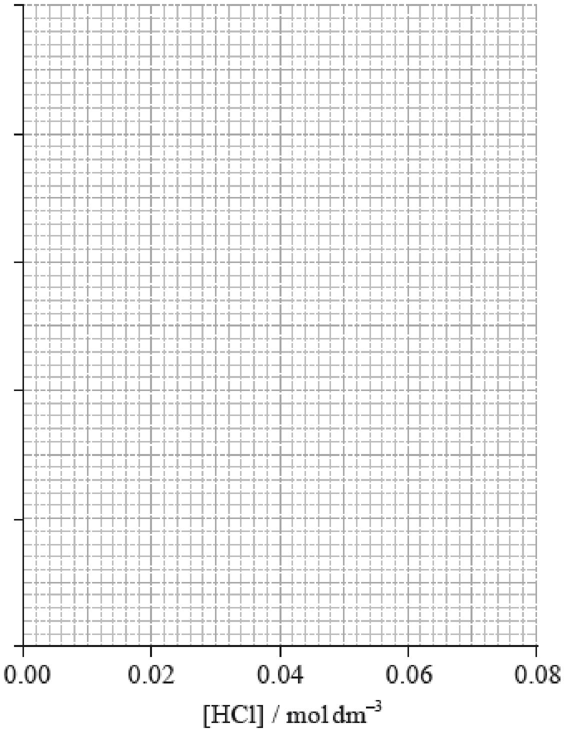
(iii) If the reaction were first order with respect to the thiosulfate ion, predict the time it would take for the mark on the paper to be obscured when the concentration of sodium thiosulfate solution is halved.

b. (i) Deduce the rate expression of this mechanism. [6]

(ii) The results of an experiment investigating the effect of the concentration of hydrochloric acid on the rate, while keeping the concentration of thiosulfate at the original value, are given in the table below.

[HCl] / mol dm^{-3}	0.020	0.040	0.060	0.080
Time / s	89.1	72.8	62.4	54.2

On the axes provided, draw an appropriate graph to investigate the order of the reaction with respect to hydrochloric acid.



(iii) Identify **two** ways in which these data **do not** support the rate expression deduced in part (i).

c. (i) Sketch and label, indicating an approximate activation energy, the Maxwell–Boltzmann energy distribution curves for two temperatures, T_1 and $T2$ $(T_2 > T_1)$, at which the rate of reaction would be significantly different. [6]

(ii) Explain why increasing the temperature of the reaction mixture would significantly increase the rate of the reaction.

d. (i) One group suggested recording how long it takes for the pH of the solution to change by one unit. Calculate the initial pH of the original reaction mixture. [3]

(ii) Deduce the percentage of hydrochloric acid that would have to be used up for the pH to change by one unit.

e.i. Calculate the volume of sulfur dioxide, in cm^3, that the original reaction mixture would produce if it were collected at 1.00×10^5 Pa and 300 K. [3]

e.ii.Sulfur dioxide, a major cause of acid rain, is quite soluble in water and the equilibrium shown below is established. [3]

$$SO_2(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$$

Given that the K_a for this equilibrium is 1.25×10^{-2} mol dm^{-3}, determine the pH of a 2.00 mol dm^{-3} solution of sulfur dioxide.

e.iiiUsing Table 15 of the Data Booklet, identify an organic acid that is a stronger acid than sulfur dioxide. [1]

Markscheme

a. (i)

Liquid	0.500 mol dm^{-3} HCl	0.0200 mol dm^{-3} $Na_2S_2O_3$	Water
Volume / cm^3	10(.0)	20(.0)	20(.0)

;

Accept other volumes in a 1:2:2 ratio.

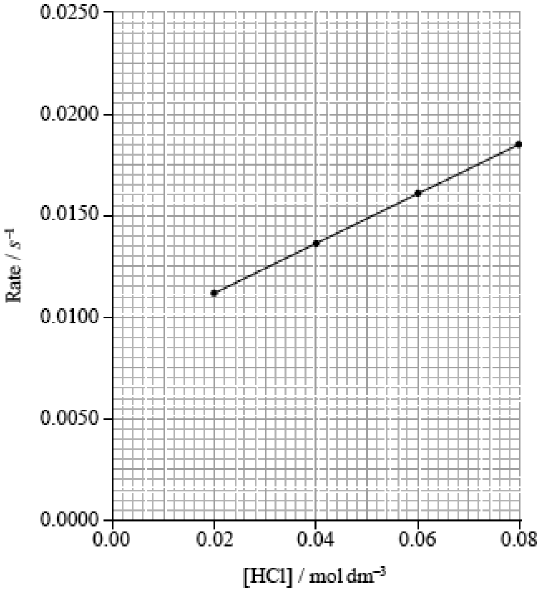
(ii) depth of liquid in the beaker must remain constant / *OWTTE*;

Accept "same thickness of glass" and any other valid point, such as answers framed around minimizing uncontrolled variables / making it a "fair test".

(iii) 94 (s) / 1 min 34 s;

b. (i) $\text{rate} = k[S_2O_3^{2-}][H^+]^2 / \text{rate} = k[Na_2S_2O_3][HCl]^2$;

(ii)



correct scale and units on *y*-axis;

Accept other suitable scales (such as 1/t) and units (such as ms^{-1}).

Axes do not have to show origin/start at zero.

correct calculation of rate in s^{-1};

[HCl] / mol dm^{-3}	0.02	0.04	0.06	0.08
Time / *s*	89.1	72.8	62.4	54.2
Rate / *s*$^{-1}$	0.0112	0.0137	0.0161	0.0185

If graph correct, assume this has been done on calculator and not written down.

correct plotting of points that the student decides to use **and** a connecting line;

Award final mark if 3 or more points are correct, irrespective of what is plotted on y-axis.

If line goes through the correct values at given concentrations of HCl, assume that points are marked there.

(iii) linear dependence on [HCl] (so not second order in $[H^+]$);

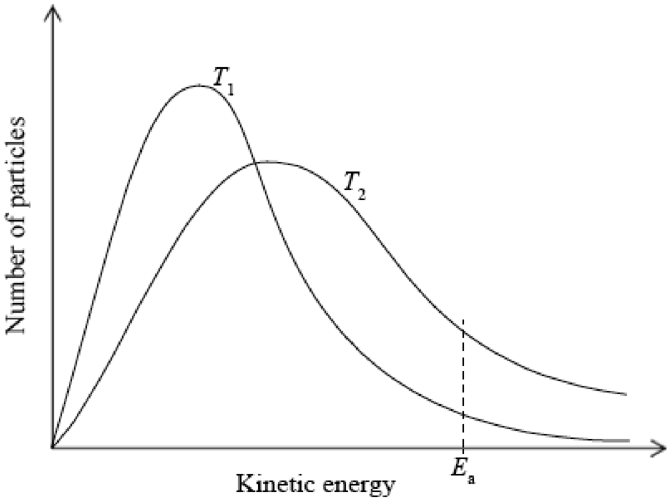
Accept that doubling of concentration does not result in quadrupling of rate / OWTTE.

does not go through origin;

Remember to allow ECF from (b) (i).

c.

(i)



labelled y-axis: number of particles / probability of particles (with that kinetic energy) **and** *labelled x-axis:* (kinetic) energy;

Allow fraction/proportion/amount of particles (with kinetic energy) for y-axis label.

Allow speed/velocity for x-axis label.

T_2 curve broader **and** with maximum lower **and** to right of T_1 curve;

Do not award this mark if both curves not asymmetric.

Curves must pass through the origin and be asymptotic to x axis.

Do not award this mark if curves not labelled.

E_{a} marked on graph;

(ii) kinetic energy of molecules increases;

This may be answered implicitly in the final marking point.

frequency of collision/number of collisions per unit time increases;

*Do **not** accept "number of collisions increases".*

greater proportion of molecules have energy greater than/equal to activation energy / rate related to temperature by the Arrhenius equation;

*Award **[1 max]** for statements such as "there will be more successful collisions" if neither of last two marking points awarded.*

d. (i) $[\mathrm{H^+}] = 0.5 \times \frac{10}{50} = 0.1\ (\mathrm{mol\,dm^{-3}})$;

$\mathrm{pH}\ (= -\log{[\mathrm{Hr^+}]} = -\log(0.10)) = 1$;

(ii) 90%;

e.i. $\mathrm{mol\ Na_2S_2O_3} = \mathrm{mol\ SO_2} = 0.0400 \times 0.0200 = 0.000800$;

$V = \frac{n \times R \times T}{p} / \frac{0.000800 \times 8.31 \times 300}{10^5}$;

$(1.99 \times 10^{-5}\ \mathrm{m^3}) = 19.9\ (\mathrm{cm^3})$;

*Note that two errors involving a factor of 1000 can also produce the correct answer. If this is the case award **[1]** not **[3]**.*

Accept 20.0 cm^3 if R =8.314 is used.

*Award **[2]** for 17.9 cm^3 or 19.2 cm^3 (result from using molar volume at standard temperature and pressure or at room temperature and pressure).*

OR

$\mathrm{mol\ Na_2S_2O_3} = \mathrm{mol\ SO_2} = 0.0400 \times 0.0200 = 0.000800$;

$V = 0.00080 \times 2.24 \times 10^{-2} \times \left[\frac{1.00 \times 10^5}{1.01 \times 10^5}\right] \times \frac{300}{273}$;

$(1.95 \times 10^{-5}\ \mathrm{m}^3) = 19.5\ (\mathrm{cm}^3)$;

Note that two errors involving a factor of 1000 can also produce the correct answer. If this is the case award [1] not [3].

*Deduct **[1]** for answers based on amount of HCl, so correct calculation would score **[2 max]**.*

e.ii. $K_\mathrm{a} = \frac{[\mathrm{H}^+][\mathrm{HSO}_3^-]}{[\mathrm{H_2SO_3}]} = \frac{x^2}{2-x} \approx \frac{x^2}{2} \approx 1.25 \times 10^{-2}\ (\mathrm{mol\,dm^{-3}})$;

$[\mathrm{H}^+] = \sqrt{2.50 \times 10^{-2}} = 0.158\ (\mathrm{mol\,dm^{-3}})$;

$\mathrm{pH} = -\log(0.158) = 0.80$;

*Award **[3]** for correct final answer.*

e.iii dichloroethanoic acid / trichloroethanoic acid / 2,4,6-trinitrophenol;

Examiners report

a. This was quite a popular question, though generally not well answered. In the first part students again appeared to display a lack of expertise in a practical context with very few able to devise a mixture that would halve the concentration of thiosulfate, whilst keeping other concentrations constant, and answers predicting that this would halve the reaction time were far more commonly encountered than those doubling it. Many candidates did however suggest valid reasons why the reaction vessel should remain unchanged and a significant number of students were able to correctly deduce the rate equation that the mechanism given would predict. Again a lack of ability to interpret experimental data was evident in the fact that it was very rare to find students who realised that a graph of (time)-1 against concentration was required to be able to deduce the reaction order, with almost all simply plotting time-concentration graphs and, as a result, very few could evaluate the mechanism in the light of the experimental data. Part (c) was a fairly standard question on the effect of temperature on reaction rate, hence it was a surprise that students did not score better on it, with many of the oft repeated mistakes (number of collisions rather than collision frequency) again coming to the surface. Again it was probably inability to interpret experimental data that led to only very few students being able to correctly state the initial pH of the mixture (I am certain almost all would have gained the mark if the pH of $0.1\ \mathrm{mol\,dm^{-3}}$ HCl had been asked for) and the percentage that would have to be consumed to increase the pH by one unit (which is independent of the previous answer) proved too much for almost all candidates. In part (e) most students could quote and substitute into the ideal gas equation, but converting from m^3 to cm^3 posed a problem for most candidates. Quite a number of candidates were however able to calculate the pH of the sulfur dioxide solution and identify a stronger acid.

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Nitrogen monoxide reacts at 1280 °C with hydrogen to form nitrogen and water. All reactants and products are in the gaseous phase.

The gas-phase decomposition of dinitrogen monoxide is considered to occur in two steps.

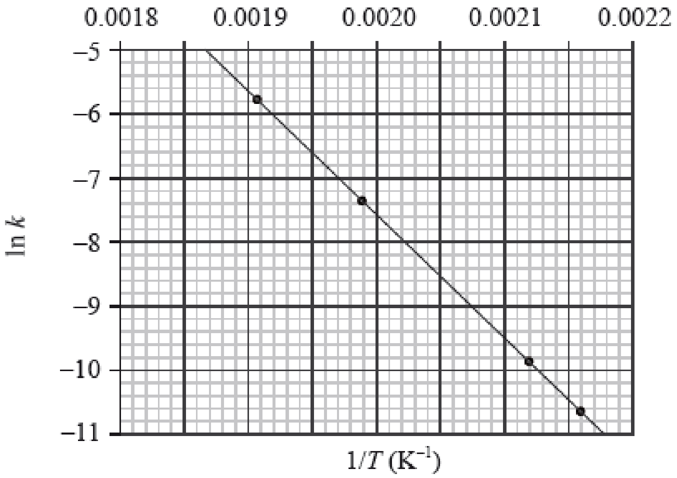
$$\begin{aligned} &\text{Step 1:}\quad N_2O(g) \xrightarrow{k_1} N_2(g) + O(g) \\ &\text{Step 2:}\quad N_2O(g) + O(g) \xrightarrow{k_2} N_2(g) + O_2(g) \end{aligned}$$

The experimental rate expression for this reaction is rate $= k[N_2O]$.

The conversion of CH_3NC into CH_3CN is an exothermic reaction which can be represented as follows.

$$CH_3{-}N{\equiv}C \rightarrow \text{transition state} \rightarrow CH_3{-}C{\equiv}N$$

This reaction was carried out at different temperatures and a value of the rate constant, k, was obtained for each temperature. A graph of $\ln k$ against $1/T$ is shown below.



a.i. Define the term *rate of reaction*. [1]

a.ii. State an equation for the reaction of magnesium carbonate with dilute hydrochloric acid. [1]

a.iii. The rate of this reaction in (a) (ii), can be studied by measuring the volume of gas collected over a period of time. Sketch a graph which shows how the volume of gas collected changes with time. [1]

a.iv. The experiment is repeated using a sample of hydrochloric acid with double the volume, but half the concentration of the original acid. Draw a second line on the graph you sketched in part (a) (iii) to show the results in this experiment. Explain why this line is different from the original line. [4]

b.i. The kinetics of the reaction were studied at this temperature. The table shows the initial rate of reaction for different concentrations of each reactant. [4]

Deduce the order of the reaction with respect to NO and H_2, and explain your reasoning.

b.ii. Deduce the rate expression for the reaction. [1]

b.iii. Determine the value of the rate constant for the reaction from Experiment 3 and state its units. [2]

c.i. Identify the rate-determining step. [1]

c.ii. Identify the intermediate involved in the reaction. [1]

d.i. Define the term *activation energy*, E_a. [1]

d.ii. Construct the enthalpy level diagram and label the activation energy, E_a, the enthalpy change, ΔH, and the position of the transition state. [3]

d.iii. Describe qualitatively the relationship between the rate constant, k, and the temperature, T. [1]

d.iv. Calculate the activation energy, E_a, for the reaction, using Table 1 of the Data Booklet. [4]

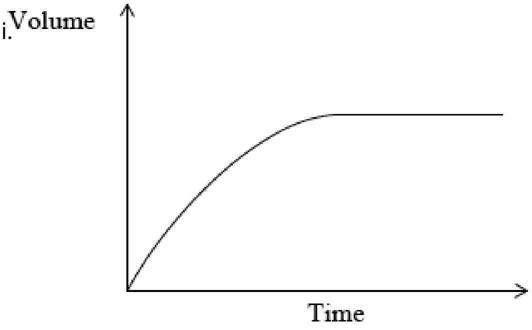
Markscheme

a.i. decrease in concentration/mass/amount/volume of reactant with time / increase in concentration/mass/amount/volume of product with time / change in concentration/mass/amount/volume of reactant/product with time;

a.ii. $MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + CO_2(g) + H_2O(l)$;

Ignore state symbols.

a.iii.



;

Plot starts at the origin and levels off.

No mark awarded if axes are not labelled.

a.iv. new curve reaches same height as original curve;

new curve less steep than original curve;

volume of gas produced is the same because the same amount of acid is used;

reaction is slower because concentration is decreased;

b.i.(from experiments 1 and 2 at constant $[H_2]$), [NO] doubles, rate quadruples;

hence, second order with respect to NO;

(from experiments 2 and 3 at constant [NO]), $[H_2]$doubles, rate doubles;

first order with respect to H_2;

Allow alternative mathematical deductions also.

b.ii$\text{rate} = k[\text{NO}]^2[H_2]$;

b.iii$k\left(= (10.00 \times 10^{-5})/(10.00 \times 10^{-3})^2(4.00 \times 10^{-3})\right) = 2.50 \times 10^2$;

Do not penalize if Experiments 1 or 2 are used to determine k.

$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$;

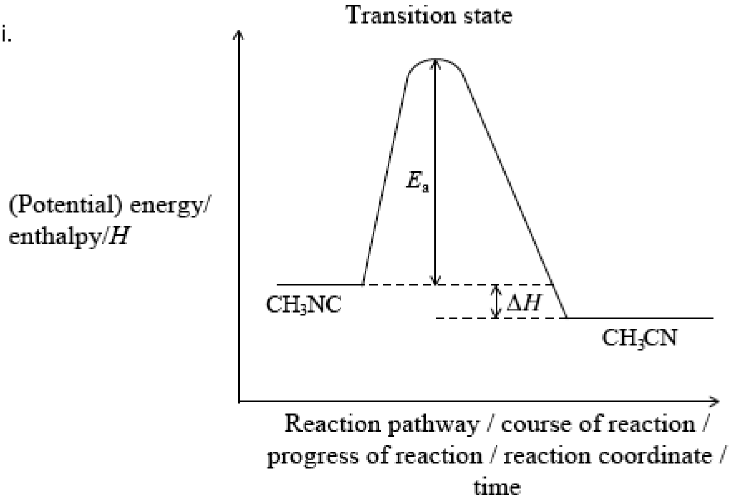
c.i.step 1 / equation showing step 1;

c.ii.O (atom) / oxygen atom;

Do not allow oxygen or O₂.

d.i.(minimum) energy needed for a reaction to occur / difference in energy between the reactants and transition state;

d.ii.



correct position of activation energy;

correct position of ΔH **and** $H(CH_3NC)$/reactant line above $H(CH_3CN)$ product line;

Accept ΔE instead of ΔH on diagram if y-axis is labelled as energy.

Do not penalize if CH_3NC and CH_3CN are not labelled on diagram.

correct position of transition state;

*Allow **[2 max]** if axes are not labelled on diagram.*

d.iiias temperature/T increases rate constant/*k* increases (exponentially);

d.ivfrom graph gradient $m = -\frac{E_a}{R}$;

measurement of gradient from chosen points on graph;

Units of m are K. Do not penalize if not given, but do not award mark for incorrect units.

Value of m is based on any two suitable points well separated on the plot.

correct answer for E_a;

correct units corresponding to answer;

***Note:** A typical answer for E_a = 1.6 × 10^2 kJ / kJ mol^{-1}.*

Examiners report

a.i. Surprisingly, the rate of reaction was only correctly defined by approximately 50% of candidates in (a) (i).

a.ii. The equation for the reaction of magnesium carbonate with dilute hydrochloric acid was not well answered (part (ii)), and often candidates did not write correct formula or forgot to include water as a product.

a.iii Part (iii) was well answered by most candidates.

a.iv Part (iv) was well answered by most candidates, although the weaker candidates often only scored two or three marks.

b.i. Part (b) (i) was well answered and many candidates scored all four marks. Some candidates used a simple mathematical approach and those that followed this method typically were able to deduce the order correctly.

b.ii. For (ii) most candidates were able to write the rate expression for the reaction.

b.iii In (iii), determining the value of the rate constant and its corresponding units was difficult for many candidates and only the better candidates scored both marks. Many mistakes were seen in the units.

c.i. Part (c) (i) was usually well answered.

c.ii. A common mistake for (ii) involved candidates writing O_2 instead of O.

d.i. The definition of activation energy was well answered.

d.ii. Part (ii) was a question where most candidates scored at least one/two marks although perfect answers were less common. Reasons leading to the loss of marks included: absence of axes, incomplete libelling of axes and the incorrect identification of the position of the transition state.

d.iii Parts (iii) and (iv) were very poorly answered for such a fundamental topic. All sorts of errors were evident, including incorrect gradients, inability to rearrange the Arrhenius Equation etc.

d.iv Even the better candidates struggled greatly with this question, even though this comes straight from AS 16.3.2.

But-2-ene belongs to the homologous series of the alkenes.

The time taken to produce a certain amount of product using different initial concentrations of C_4H_9Br and NaOH is measured. The results are shown in the following table.

Reaction	[C_4H_9Br] / 10^{-2} mol dm^{-3}	[NaOH] / 10^{-3} mol dm^{-3}	t / s
A	1.0	2.0	46
B	2.0	2.0	23
C	2.0	4.0	23

a.i. Outline **three** features of a homologous series. [3]

a.ii. Describe a test to distinguish but-2-ene from butane, including what is observed in **each** case. [2]

a.iii. 2-bromobutane can be produced from but-2-ene. State the equation of this reaction using structural formulas. [1]

a.iv. State what is meant by the term *stereoisomers*. [1]

a.v. Explain the existence of geometrical isomerism in but-2-ene. [2]

c.i. Deduce the order of reaction with respect to $\mathrm{C_4H_9Br}$ and NaOH, using the data above. [3]

$\mathrm{C_4H_9Br}$

NaOH:

c.ii. Deduce the rate expression. [1]

c.iii. Based on the rate expression obtained in (c) (ii) state the units of the rate constant, k. [1]

d.ii. Halogenalkanes can react with NaOH via $\mathrm{S_N1}$ and $\mathrm{S_N2}$ type mechanisms. Explain why $\mathrm{C_4H_9Br}$ reacts via the mechanism described in (d) (i). [1]

d.iii. Identify the rate-determining step of this mechanism. [1]

Markscheme

a.i. same functional group / same general formula;

difference between successive members is $\mathrm{CH_2}$;

similar chemical properties;

Do not accept "same" chemical properties.

gradually changing physical properties;

a.ii. adding bromine (water);

but-2-ene: brown/orange to colourless / decolourizes bromine water **and**

butane: does not change colour;

OR

adding <u>acidified</u> potassium permanganate solution/$KMnO_4$(aq);

but-2-ene: purple to colourless/brown **and**

butane: does not change colour;

OR

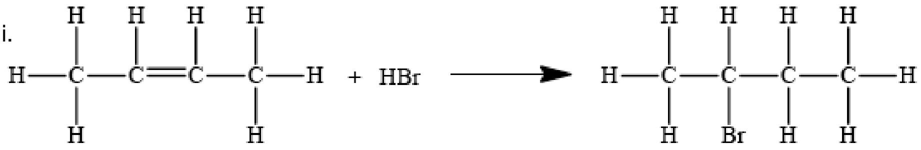
adding Baeyer's reagent;

but-2-ene: purple/pink to brown **and**

butane: does not change colour;

Do not accept “clear” or “transparent” for “colourless”.

a.iii.

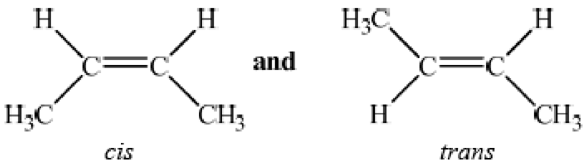


Accept condensed structural formula.

Penalise missing H atoms or incorrect bonds (such as C–HO, C–H_2C) once only in the whole paper.

a.iv.compounds with the same structural formula but different arrangement of atoms (in space);

a.v.(but-2-ene exists as) *cis*-but-2-ene **and** *trans*-but-2-ene /



restricted rotation of C=C/double bond;

c.i. *C_4H_9Br:*

[C_4H_9Br] doubles **and** time halves/rate doubles/rate proportional to [C_4H_9Br];

Do not accept rate increases when [C_4H_9Br] increases.

NaOH:

[NaOH] doubles **and** time/rate does not change/rate independent of [NaOH];

C_4H_9Br: first order **and** *NaOH:* zero order;

c.ii.rate $= k[\mathrm{C_4H_9Br}]$;

Accept ECF.

c.iii.s^{-1};

Accept ECF.

d.ii.greater stability of tertiary carbocation;

steric hindrance for $\mathrm{S_N2}$ mechanism;

positive inductive effect (of alkyl groups);

Do not allow ECF.

d.iii.the first step / Br^- leaving / formation of carbocation;

Do not allow ECF.

Examiners report

a.i. Features of an homologous series need to be learnt; this was answered relatively poorly.

a.ii.The most common reagent was bromine (some indeed used liquid bromine!) and the common errors were using HBr and describing “colourless” as “clear”.

a.iii.In (iii), some gave the equation backwards, a consequence, perhaps, of misreading the question.

a.iv.In (iv) many referred to “same molecular formula” rather than “same structural formula”.

a.v.The lack of rotation about the double bond in (v) was not well described.

c.i. In (c) (i) the explanations were a little vague, some candidates perhaps being fooled by the data of *time* rather than *rate*. Many expected to be given marks for a series of numbers and calculations without explanations.

c.ii.Answers to (ii) were usually consistent with (i).

c.iii.Answers to (iii) were usually consistent with (i).

d.ii.(ii) was rarely answered correctly while the answer to (iii) was patchy.

d.iii.(ii) was rarely answered correctly while the answer to (iii) was patchy.

$\mathrm{BF_3(g)}$ reacts with $\mathrm{NH_3(g)}$ to form $\mathrm{F_3BNH_3(g)}$ according to the equation below.

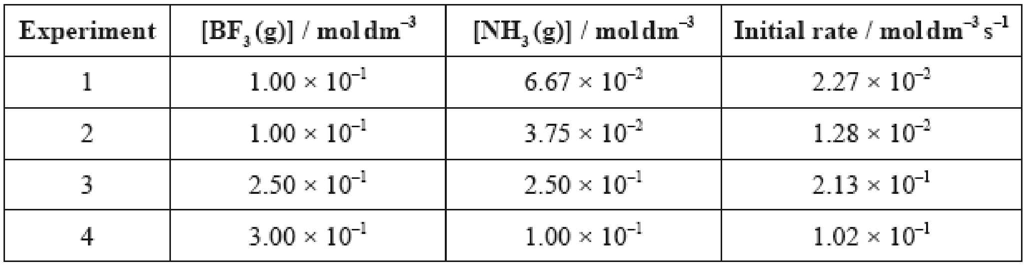
$$\mathrm{BF_3(g) + NH_3(g) \rightarrow F_3BNH_3(g)}$$

The following is a proposed mechanism for the reaction of NO(g) with $\mathrm{H_2(g)}$.

$$\begin{aligned} &\text{Step 1:} \quad \mathrm{2NO(g) \rightarrow N_2O_2(g)} \\ &\text{Step 2:} \quad \mathrm{N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)} \end{aligned}$$

e.i. Identify the type of bond present between $\mathrm{BF_3}$ and $\mathrm{NH_3}$ in $\mathrm{F_3BNH_3(g)}$ and state another example of a compound with this type of bonding. [2]

e.ii.The table below shows initial rates of reaction for different concentrations of each reactant for this reaction at temperature, T. [3]



Experiment	[$\mathrm{BF_3}$(g)] / mol dm^{-3}	[$\mathrm{NH_3}$(g)] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.00×10^{-1}	6.67×10^{-2}	2.27×10^{-2}
2	1.00×10^{-1}	3.75×10^{-2}	1.28×10^{-2}
3	2.50×10^{-1}	2.50×10^{-1}	2.13×10^{-1}
4	3.00×10^{-1}	1.00×10^{-1}	1.02×10^{-1}

Deduce the rate expression, the overall order of the reaction and determine the value of k, the rate constant, with its units, using the data from Experiment 4.

f.i. Identify the intermediate in the reaction. [1]

f.ii. The observed rate expression is $\mathrm{rate} = k[\mathrm{NO}]^2[\mathrm{H_2}]$. Assuming that the proposed mechanism is correct, comment on the relative speeds of the two steps. [1]

g. The following two-step mechanism has been suggested for the reaction of $\mathrm{NO_2(g)}$ with CO (g), where $k_2 \gg k_1$. [2]

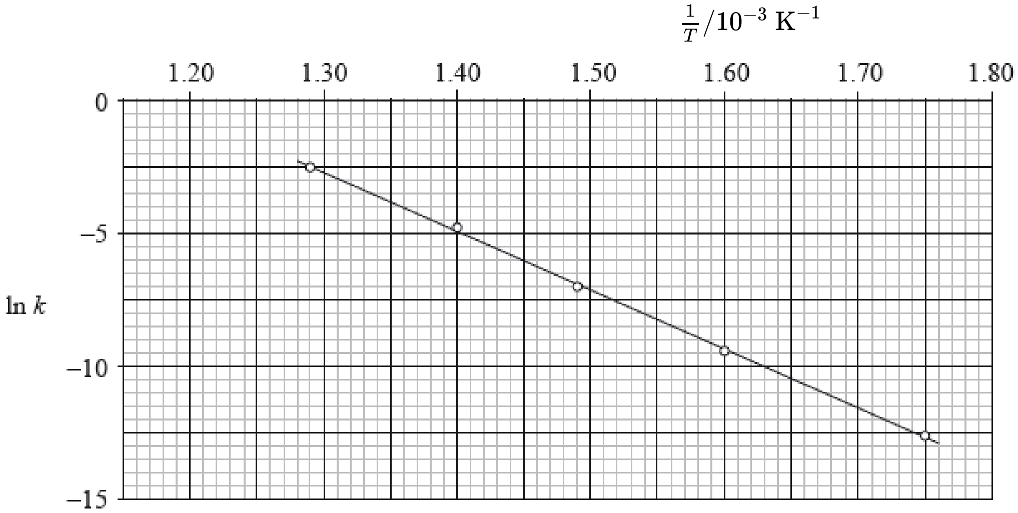
$$\begin{aligned} &\text{Step 1} \quad \mathrm{NO_2(g) + NO_2(g)} \xrightarrow{k_1} \mathrm{NO(g) + NO_3(g)} \\ &\text{Step 2:} \quad \mathrm{NO_3(g) + CO(g)} \xrightarrow{k_2} \mathrm{NO_2(g) + CO_2(g)} \\ &\text{Overall:} \quad \mathrm{NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)} \end{aligned}$$

The experimental rate expression is $\text{rate} = k[NO_2]^2$. Explain why this mechanism produces a rate expression consistent with the experimentally observed one.

h. HI(g) decomposes into $H_2(g)$ and $I_2(g)$ according to the reaction below. [4]

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The reaction was carried out at different temperatures and a value of the rate constant, k, was obtained for each temperature. A graph of $\ln k$ against $\frac{1}{T}$ is shown below.



Calculate the activation energy, E_a, for the reaction using these data and Table 1 of the Data Booklet showing your working.

Markscheme

e.i. dative (covalent)/coordinate;

carbon monoxide/CO / hydronium (ion)/ H_3O^+ / ammonium (ion)/NH_4^+ / aluminium chloride/Al_2Cl_6 / any relevant transition metal complex (*e.g.* $[Ni(NH_3)_6]^{2+}$);

Accept AlCl$_3$.

e.ii. $\text{rate} = k[BF_3][NH_3]$;

second (order)/2°;

$k = 3.40\ dm^3 mol^{-1} s^{-1}$;

Allow units of L mol^{-1}s^{-1} or M^{-1}s^{-1}.

Units required for mark.

f.i. N_2O_2;

f.ii. ($[H_2]$ appears in rate expression so) step 2 rate-determining/rds/slow step;

Allow "since step 1 involves 2NO and step 2 involves H$_2$ and as all 3 molecules are involved in rate expression, then two steps must have approximately same rate" / OWTTE.

g. ($k_2 \gg k_1$ so) step 1 rate-determining/rds/slow step;

two molecules of NO_2 involved in step 1 consistent with rate expression / rate of overall reaction must equal rate of step 1 which is $\text{rate} = k_1[NO_2]^2$ / *OWTTE;*

h. $E_a = -R \times m$;

measurement of gradient from **two** points on line;

Accept a gradient in range –2.14 × 10^4 K to –2.27 × 10^4 (K).

correct answer for E_a;

correct units $kJ\,mol^{-1}/J\,mol^{-1}$ corresponding to answer;

Allow kJ or J.

A typical answer for E_a = 1.85 × 10^2 $kJ\,mol^{-1}$.

Allow answers for E_a in range 1.75 × 10^2 $kJ\,mol^{-1}$ to 1.91 × 10^2 $kJ\,mol^{-1}$.

*Award **[4]** for correct final answer with some working shown.*

*Award **[2 max]** for correct final answer without any working shown.*

Examiners report

e.i. (i) was usually well done.

e.ii. some did not answer the question which asked for the overall order of the reaction. Some candidates also got their units incorrect. A few G2 comments mentioned the fact that the data was quite complicated as there was no experiment with $[NH_3]$ constant. It is true that the maths here may appear more challenging than normal, but candidates should be able to handle this type of data and in fact a significant number of the better candidates did score full marks on this question.

f.i. This was well answered.

f.ii. This was well answered.

g. Although most candidates stated that the rds was step 1, many struggled with the explanation.

h. Although this question has been asked on a number of recent papers, candidates really struggled with this graphical based format. All sorts of mistakes were made, including gradients, units etc. Some did not even know how to approach the question.

Sodium thiosulfate solution, $Na_2S_2O_3(aq)$, and hydrochloric acid, $HCl(aq)$, react to produce solid sulfur as in the equation below.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$$

The following results to determine the initial rate were obtained:

Experiment	**$[S_2O_3^{2-}(aq)]$ / $mol\,dm^{-3}$**	**$[H^+(aq)]$ / $mol\,dm^{-3}$**	**Initial rate / $mol\,dm^{-3}\,s^{-1}$**
1	0.200	2.00	0.036
2	0.200	1.00	0.036
3	0.100	1.00	0.018

a. Deduce, with a reason, the order of reaction with respect to each reactant. [2]

b. State the rate expression for this reaction. [1]

c. Determine the value of the rate constant, k, and state its units. [2]

d. State an equation for a possible rate-determining step for the reaction. [1]

e. Suggest how the activation energy, E_a, for this reaction may be determined. [3]

Markscheme

a. experiments 1 and 2 ($[\mathrm{S_2O_3^{2-}}]$ remains constant) change in $[\mathrm{H^+}]$ does not affect the rate so zero order with respect to $\mathrm{H^+(aq)}$ / *OWTTE*;

experiment 1/2 and 3 ($[\mathrm{H^+}]$ has no effect) $[\mathrm{S_2O_3^{2-}}]$ is halved and rate is also halved so first order with respect to $[\mathrm{S_2O_3^{2-}}]$ / *OWTTE*;

Accept explanation given in mathematical terms.

*Award **[1 max]** if both [$S_2O_3^{2-}$] is first order, **and** [H^+] is zero order are stated without reason.*

b. rate $= k[\mathrm{S_2O_3^{2-}}]$;

c. 0.18;

$\mathrm{s^{-1}}$;

d. $\mathrm{S_2O_3^{2-} \rightarrow S + SO_3^{2-}}$;

Accept any balanced equation that starts with only one $S_2O_3^{2-}$.

Equations must be balanced in terms of number of atoms and charge.

e. determine rate at a range of temperatures (while keeping concentrations constant);

calculate k for each temperature;

plot graph of $\ln k$ against T^{-1};

gradient is $\frac{-E_\mathrm{a}}{R}$/*OWTTE*;

Examiners report

a. The interpretation of orders of rate from experimental data was well understood, and explained. Calculations of both the value and units of K_c were also done well. Very few candidates produced an acceptable equation for the rate determining step, many did not realise the importance of balancing both the number of atoms and charge on both sides. The required careful explanation of how E_a is determined from experimental data was lacking, too often a vague description of using gradient and R without context was considered sufficient by many candidates.

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Reaction kinetics can be investigated using the iodine clock reaction. The equations for two reactions that occur are given below.

Reaction A: $\mathrm{H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)}$

Reaction B: $\mathrm{I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)}$

Reaction B is much faster than reaction A, so the iodine, $\mathrm{I_2}$, formed in reaction A immediately reacts with thiosulfate ions, $\mathrm{S_2O_3^{2-}}$, in reaction B, before it can react with starch to form the familiar blue-black, starch-iodine complex.

In one experiment the reaction mixture contained:

5.0 ± 0.1 $\mathrm{cm^3}$ of 2.00 $\mathrm{mol\,dm^{-3}}$ hydrogen peroxide ($\mathrm{H_2O_2}$)

5.0 ± 0.1 $\mathrm{cm^3}$ of 1% aqueous starch

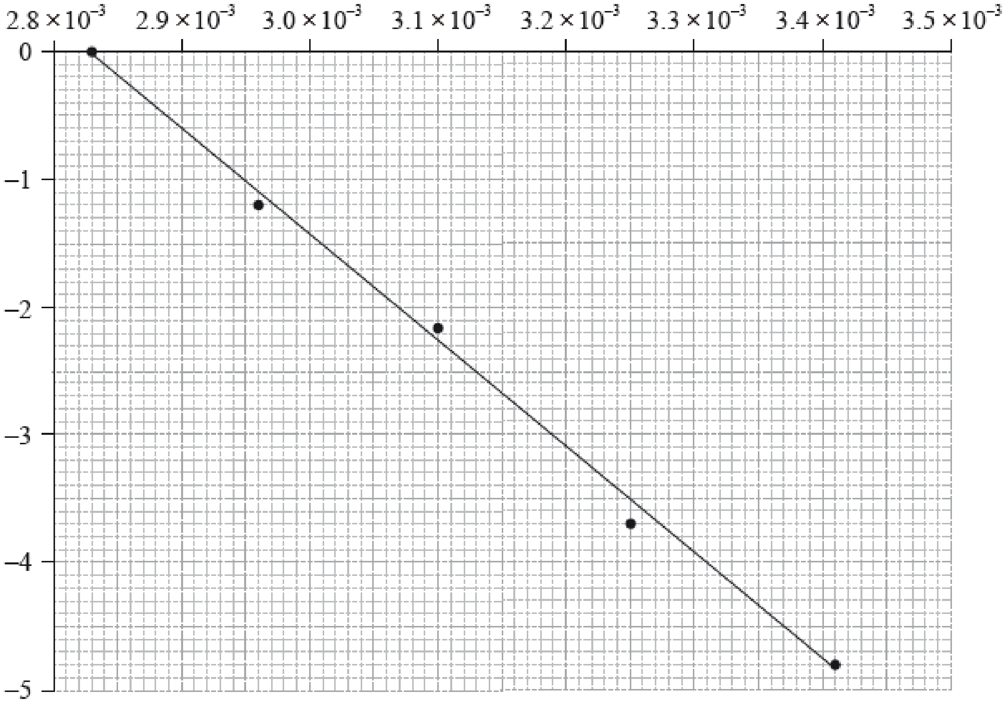
20.0 ± 0.1 $\mathrm{cm^3}$ of 1.00 $\mathrm{mol\,dm^{-3}}$ sulfuric acid ($\mathrm{H_2SO_4}$)

20.0 ± 0.1 $\mathrm{cm^3}$ of 0.0100 $\mathrm{mol\,dm^{-3}}$ sodium thiosulfate ($\mathrm{Na_2S_2O_3}$)

50.0 ± 0.1 $\mathrm{cm^3}$ of water with 0.0200 ± 0.0001 g of potassium iodide (KI) dissolved in it.

After 45 seconds this mixture suddenly changed from colourless to blue-black.

The activation energy can be determined using the Arrhenius equation, which is given in Table 1 of the Data Booklet. The experiment was carried out at five different temperatures. An incomplete graph to determine the activation energy of the reaction, based on these results, is shown below.



a. The concentration of iodide ions, I^-, is assumed to be constant. Outline why this is a valid assumption. [1]

b. For this mixture the concentration of hydrogen peroxide, H_2O_2, can also be assumed to be constant. Explain why this is a valid assumption. [2]

c. Explain why the solution suddenly changes colour. [2]

d.i. Calculate the total uncertainty, in $\mathrm{cm^3}$, of the volume of the reaction mixture. [1]

d.ii. Calculate the percentage uncertainty of the concentration of potassium iodide solution added to the overall reaction mixture. [1]

d.iii. Determine the percentage uncertainty in the concentration of potassium iodide in the final reaction solution. [1]

e. The colour change occurs when $1.00 \times 10^{-4}\ \mathrm{mol}$ of iodine has been formed. Use the total volume of the solution and the time taken, to calculate the rate of the reaction, including appropriate units. [4]

f.i. State the labels for each axis. [2]

x-axis:

y-axis:

f.ii. Use the graph to determine the activation energy of the reaction, in $\mathrm{kJ\ mol^{-1}}$, correct to **three** significant figures. [3]

g. In another experiment, 0.100 g of a black powder was also added while all other concentrations and volumes remained unchanged. The time taken for the solution to change colour was now 20 seconds. Outline why you think the colour change occurred more rapidly and how you could confirm your hypothesis. [2]

Markscheme

a. KI/$\mathrm{I^-}$/potassium iodide/iodide (ion) (rapidly) reformed (in second stage of reaction);

b. amount (in mol) of $\mathrm{H_2O_2}$/hydrogen peroxide $\gg$ amount (in mol) $\mathrm{Na_2S_2O_3/S_2O_3^{2-}}$/sodium thiosulfate/ thiosulfate (ion);

Accept amount (in mol) of H_2O_2/hydrogen peroxide $\gg$ amount (in mol) KI/I^-/potassium iodide/iodide (ion).

Accept "H_2O_2/hydrogen peroxide is in (large) excess/high concentration".

(at end of reaction) $[\mathrm{H_2O_2}]$ is only slightly decreased/virtually unchanged;

c. all $\mathrm{Na_2S_2O_3}$/sodium thiosulfate/$\mathrm{S_2O_3^{2-}}$/thiosulfate consumed/used up;

Accept "iodine no longer converted to iodide".

(free) iodine is formed / iodine reacts with starch / forms iodine-starch complex;

d.i. $(5 \times 0.1) = (\pm)0.5\ (\mathrm{cm^3})$;

d.ii. $(\pm)0.7(\%)$;

Comprises both mass of KI = ± 0.5% and volume of KI = ± 0.2%.

d.iii. $0.5 + 0.7 = (\pm)1.2\%$;

Sum of (i) and (ii) (percentage uncertainty of total volume = absolute uncertainty as 100 cm^3).

e. total volume $0.100\ (\mathrm{dm^3})/100\ (\mathrm{cm^3})$;

$\left(\text{change in concentration } = \frac{1.00\times10^{-4}}{0.100} =\right)\ 1.00 \times 10^{-3}\ (\mathrm{mol\,dm^3})$;

$\left(\text{rate} = \frac{1.00\times10^{-3}}{45} =\right)\ 2.2 \times 10^{-5}$;

*Award **[3]** for the correct final answer.*

$\mathrm{mol\,dm^{-3}s^{-1}}$;

f.i. *x-axis:* $\frac{1}{\text{Temperature}}/\frac{1}{T}/\mathrm{T^{-1}}$;

Ignore units.

y-axis: ln rate/$\log_e$ rate / ln rate constant/$\log_e$ rate constant / ln k/$\log_e k$;

f.ii. gradient $= \frac{-E_a}{R}$;

gradient $= \frac{-4.00}{(3.31\times10^{-3} - 2.83\times10^{-3})} = -8333/ = \frac{-4.80}{(3.41\times10^{-3} - 2.83\times10^{-3})} = -8276$;

$E_a = \left(\frac{8.31\times8333}{1000}\right) = 69.3\ (\mathrm{kJ\,mol^{-1}})/ = \left(\frac{8.31\times8276}{1000}\right) = 68.8\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer.*

Accept values from 65.0 to 73.0 kJ mol^{-1}.

*Deduct **[1]** for final answer in J mol^{-1}.*

*Deduct **[1]** for final answer not to 3 significant figures.*

g. acting as a catalyst / black powder reacts with thiosulfate ions / solid dissolves to give blue-black solution;

Accept any other valid suggestion which will make colour change more rapid.

For catalyst: amount/mass of black powder remains constant / no new/different products formed / activation energy decreased;

For other suggestions: any appropriate way to test the hypothesis;

*Award **[1]** for valid hypothesis, **[1]** for appropriate method of testing the stated hypothesis.*

Examiners report

a. This question explored basic chemical concepts in the context of a practical situation. Whilst this is one frequently carried out during practical courses, none of the questions depended on prior knowledge. Students varied significantly in their ability to interpret the information given to answer parts (a) to (c), but very few could correctly carry out the propagation of uncertainties required in part (d). An encouraging number were able to carry out the rate calculation required in part (e). It was surprising how many students, though unable to identify the axes of the Arrhenius graph given in part (f), were still able to interpret it to correctly calculate the activation energy. Part (g) was deliberately open ended and elicited a number of interesting responses, though frequently the tests proposed would not in fact confirm the suggested hypothesis.

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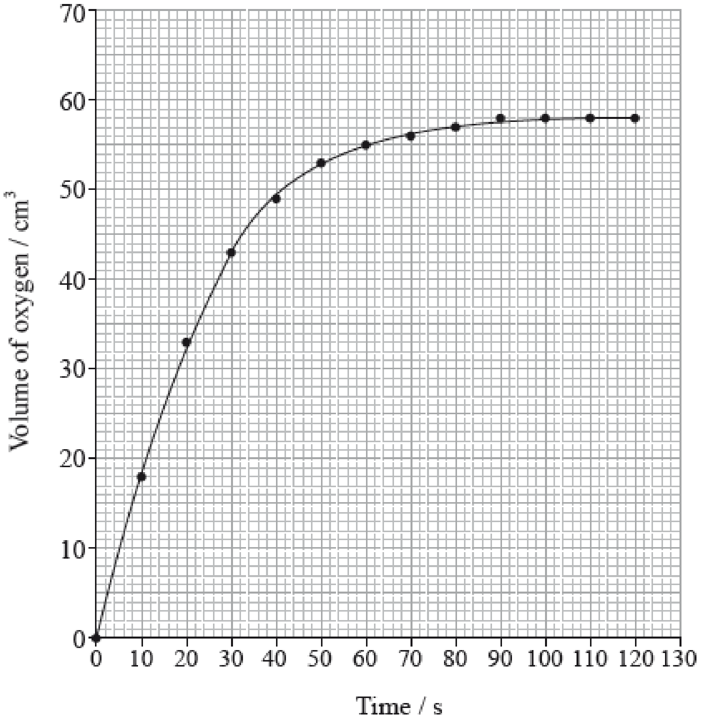
Hydrogen peroxide decomposes according to the equation below.

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

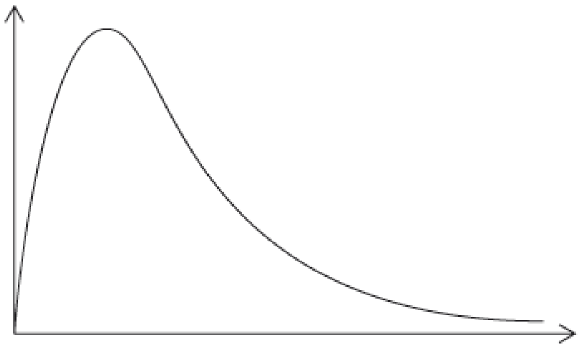
The rate of the decomposition can be monitored by measuring the volume of oxygen gas released. The graph shows the results obtained when a solution of hydrogen peroxide decomposed in the presence of a CuO catalyst.



a.i. Outline how the initial rate of reaction can be found from the graph. [2]

a.ii. Explain how and why the rate of reaction changes with time. [3]

b. A Maxwell-Boltzmann energy distribution curve is drawn below. Label both axes and explain, by annotating the graph, how catalysts increase the rate of reaction. [3]



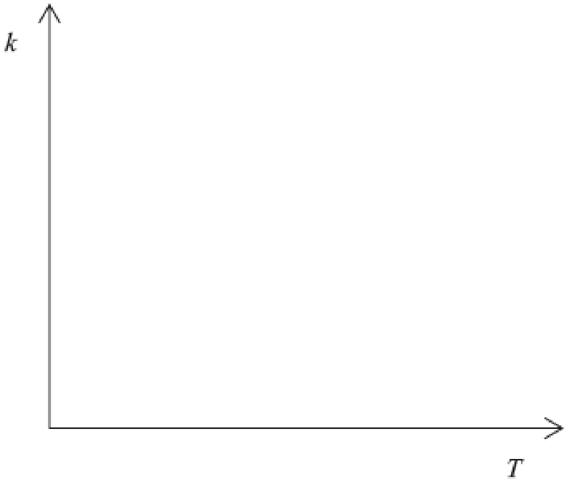
c. (i) In some reactions, increasing the concentration of a reactant does not increase the rate of reaction. Describe how this may occur. [2]

(ii) Consider the reaction

$$2A + B \rightarrow C + D$$

The reaction is first order with respect to **A**, and zero order with respect to **B**. Deduce the rate expression for this reaction.

d. Sketch a graph of rate constant (k) versus temperature. [1]



e. Hydrochloric acid neutralizes sodium hydroxide, forming sodium chloride and water. [9]

$$\mathrm{NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)} \quad \Delta H^{\ominus} = -57.9\ \mathrm{kJ\,mol^{-1}}$$

(i) Define *standard enthalpy change of reaction*, $\Delta H^{\ominus}$.

(ii) Determine the amount of energy released, in kJ, when $50.0\ \mathrm{cm^3}$ of $1.00\ \mathrm{mol\,dm^{-3}}$ sodium hydroxide solution reacts with $50.0\ \mathrm{cm^3}$ of $1.00\ \mathrm{mol\,dm^{-3}}$ hydrochloric acid solution.

(iii) In an experiment, 2.50 g of solid sodium hydroxide was dissolved in $50.0\ \mathrm{cm^3}$ of water. The temperature rose by 13.3 °C. Calculate the standard enthalpy change, in $\mathrm{kJ\,mol^{-1}}$, for dissolving one mole of solid sodium hydroxide in water.

$$\mathrm{NaOH(s) \rightarrow NaOH(aq)}$$

(iv) Using relevant data from previous question parts, determine $\Delta H^{\ominus}$, in $\mathrm{kJ\,mol^{-1}}$, for the reaction of solid sodium hydroxide with hydrochloric acid.

$$\mathrm{NaOH(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

f. (i) Zinc is found in the d-block of the periodic table. Explain why it is not considered a transition metal. [5]

(ii) Explain why $\mathrm{Fe^{3+}}$ is a more stable ion than $\mathrm{Fe^{2+}}$ by reference to their electron configurations.

Markscheme

a.i. (draw a) tangent to the curve at origin/time = 0/start of reaction;

(calculate) the gradient/slope (of the tangent);

a.ii. rate decreases (with time);

concentration/number of (reactant) molecules per unit volume decreases (with time);

Do not accept "number of molecules decreases" or "amount of reactant decreases".

collisions (between reactant molecules/reactant and catalyst) become less frequent;

Do not accept "fewer collisions" without reference to frequency (eg, no. collisions per second).

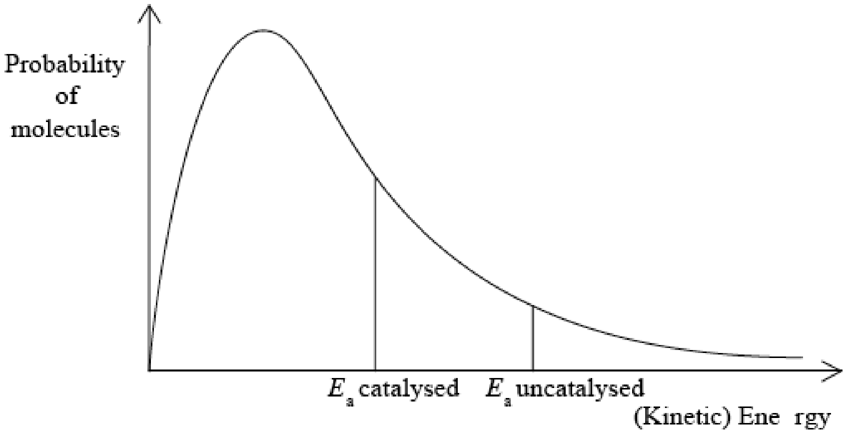
b. *y-axis*: probability / fraction of molecules/particles / probability density

Allow "number of particles/molecules" on y-axis.

and

x-axis: (kinetic) energy;

Accept "speed/velocity" on x-axis.



correct relative position of E_a catalysed and E_a uncatalysed;

more/greater proportion of molecules/collisions have the lower/required/catalysed E_a (and can react upon collision);

M3 can be scored by stating ***or*** *shading and annotating the graph.*

Accept "a greater number/proportion of successful collisions as catalyst reduces E_a".

c. (i) reactant not involved in (or before) the slowest/rate-determining step/RDS;

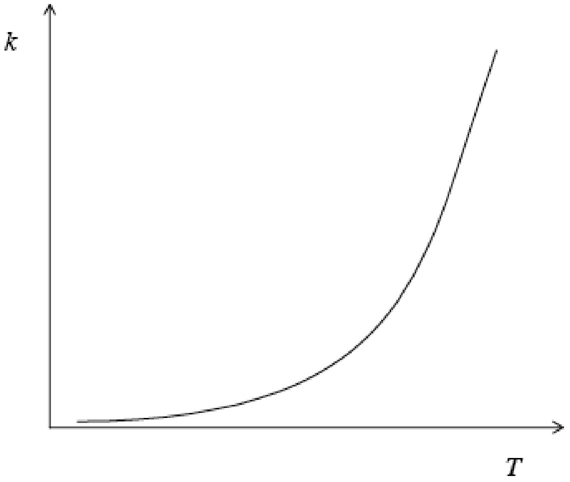
reactant is in (large) excess;

(ii) $(\text{rate} =)\ k[\text{A}]$;

Accept rate = $k[A]^1[B]^0$.

d. curve with a positive slope curving upwards;

Do not penalize if curve passes through the origin.



e. (i) heat transferred/absorbed/released/enthalpy/<u>potential</u> energy change when 1 mol/molar amounts of reactant(s) react (to form products) / *OWTTE*;

under standard conditions / at a pressure 100 kPa/101.3 kPa/1 atm **and** temperature 298 K/25 °C;

Award ***[2]*** *for difference between standard enthalpies of products and standard enthalpies of reactants / $H^\ominus$ (products) – $H^\ominus$ (reactants).*

Award ***[2]*** *for difference between standard enthalpies of formation of products and standard enthalpies of formation of reactants / $\Sigma\Delta H_f^\ominus$ (products) – $\Sigma\Delta H_f^\ominus$ (reactants).*

(ii) $(1.00 \times 0.0500 =)\ 0.0500\ (\text{mol})$;

$(0.0500 \times 57.9 =)\ 2.90\ (\text{kJ});$

Ignore any negative sign.

*Award **[2]** for correct final answer.*

*Award **[1 max]** for 2900 J.*

(iii) $\left(\frac{2.50}{40.00} =\right)\ 0.0625\ (\text{mol NaOH});$

$0.0500 \times 4.18 \times 13.3 = 2.78\ (\text{kJ})/50.0 \times 4.18 \times 13.3 = 2780\ (\text{J});$

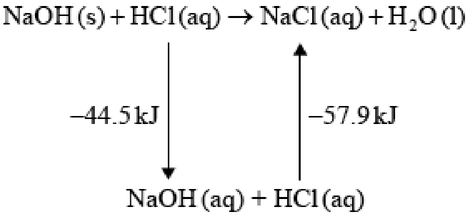
$\left(\frac{2.78}{0.0625}\right) = -44.5\ (\text{kJ mol}^{-1});$

*Award **[3]** for correct final answer.*

Negative sign is necessary for M3.

Award M2 and M3 if is used to obtain an enthalpy change of –46.7 (kJ mol^{-1}).

(iv) $-44.5 - 57.9$ / correct Hess's Law cycle (as below) / correct manipulation of equations;



$-102.4\ \text{kJ};$

*Award **[2]** for correct final answer.*

f. (i) zinc (only) forms the ion Zn^{2+} / has the oxidation state $+2$;

Allow forms only one ion / has only one oxidation state.

has full d-subshell/orbitals / does not have a partially filled d-subshell/orbitals (needed to exhibit transition metal properties);

(ii) $\text{Fe}^{2+}\text{: 1s}^2\text{2s}^2\text{2p}^6\text{3s}^2\text{3p}^6\text{3d}^6/[\text{Ar}]\ \text{3d}^6$ **and** $\text{Fe}^{3+}\text{: 1s}^2\text{2s}^2\text{2p}^6\text{3s}^2\text{3p}^6\text{3d}^5/[\text{Ar}]\ \text{3d}^5$;

half-full sub-level/3d^5 has extra stability;

less repulsion between electrons / electrons singly occupy orbitals / electrons do not have to pair with other electrons;

Accept converse points for Fe^{2+}.

Examiners report

a.i. Most candidates related the rate of reaction to the gradient of the curve, but only a few suggested drawing a tangent at $t = 0$.

a.ii. Answers were often disappointing and only a few candidates gained full marks.

Candidates often talked about the number of reactant molecules decreasing but neglected to relate this to a lower concentration. Also some candidates still fail to highlight frequency rather than the number of collisions.

b. Well answered by more than half of the candidates. The labelling of the axes was a challenge for some candidates. The annotation of the diagram with the energy of activation with and without a catalyst was mostly correct, though some weaker students confused it with the effect of temperature and constructed a second curve. Some candidates could not offer an explanation for the third mark.

c. (i) Only a few candidates scored this mark. Many candidates stated that a reactant concentration having no effect indicated that the reaction that was zero order in that species, rather than describing the underlying mechanistic reason for the zero order dependence.

(ii) More than half of the candidates could construct a correct rate expression from information about the order of the reactants.

d. A number of candidates gave a linear relationship, rather than an exponential one, between reaction rate and temperature.

e. (i) Defining the standard enthalpy change of reaction was not well answered.

(ii) More than half of the candidates calculated the amount of energy released correctly.

(iii) Half of the candidates were able to gain the three marks. Many candidates lost the third mark for not quoting the negative sign for the enthalpy change. Quite a few candidates used a wrong value for the mass of water.

(iv) Many good answers. A Hess's Law cycle wasn't often seen. Quite a few candidates scored through ECF from (iii).

f. (i) Most candidates knew that zinc has a full 3d sub-shell but almost all missed out on the second mark about only having one possible oxidation state in its compounds.

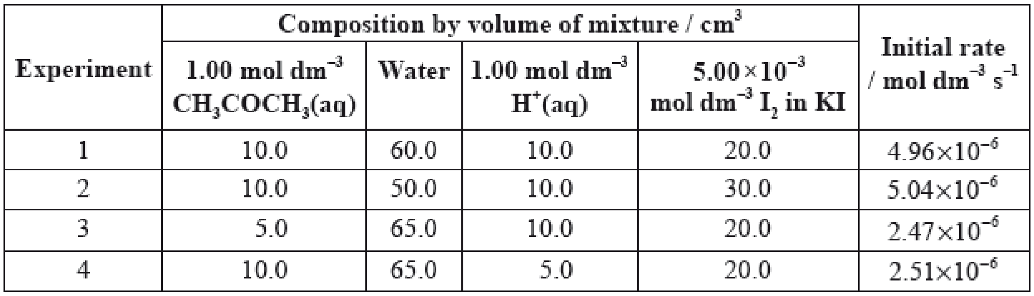
(ii) This was a challenging question for many candidates. A large number of candidates did not give the correct electron configurations for the ions, and only few mentioned the stability of the half-full d-sub-shell. Very few scored the third mark.

Alex and Hannah were asked to investigate the kinetics involved in the iodination of propanone. They were given the following equation by their teacher.

$$\mathrm{CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_2ICOCH_3(aq) + HI(aq)}$$

Alex's hypothesis was that the rate will be affected by changing the concentrations of the propanone and the iodine, as the reaction can happen without a catalyst. Hannah's hypothesis was that as the catalyst is involved in the reaction, the concentrations of the propanone, iodine and the hydrogen ions will all affect the rate.

They carried out several experiments varying the concentration of one of the reactants or the catalyst whilst keeping other concentrations and conditions the same, and obtained the results below.



Experiment	Composition by volume of mixture / cm^3				Initial rate / $mol\ dm^{-3}\ s^{-1}$
	1.00 $mol\ dm^{-3}$ $CH_3COCH_3(aq)$	Water	1.00 $mol\ dm^{-3}$ $H^+(aq)$	5.00×10^{-3} $mol\ dm^{-3}$ I_2 in KI	
1	10.0	60.0	10.0	20.0	4.96×10^{-6}
2	10.0	50.0	10.0	30.0	5.04×10^{-6}
3	5.0	65.0	10.0	20.0	2.47×10^{-6}
4	10.0	65.0	5.0	20.0	2.51×10^{-6}

a. Explain why they added water to the mixtures. [1]

b. (i) Deduce the order of reaction for each substance and the rate expression from the results. [3]

(ii) Comment on whether Alex's or Hannah's hypothesis is correct.

c. Using the data from Experiment 1, determine the concentration of the substances used and the rate constant for the reaction including its units. [3]

d. (i) This reaction uses a catalyst. Sketch and annotate the Maxwell-Boltzmann energy distribution curve for a reaction with and without a catalyst on labelled axes below. [3]

(ii) Describe how a catalyst works.

Markscheme

a. to maintain a constant volume / *OWTTE*;

b. (i) $[H^+]$ order 1, $[CH_3COCH_3]$ order 1, $[I_2]$ order 0;

$(\text{rate} =)k[H^+][CH_3COCH_3]$;

*Award **[2]** for correct rate expression.*

Allow expressions including $[I_2]^0$.

(ii) neither were correct / Alex was right about propanone and wrong about iodine / Hannah was right about propanone and hydrogen ions but wrong about iodine / *OWTTE*;

c. $[CH_3COCH_3] = 0.100\ \text{mol dm}^{-3}$ **and** $[H^+] = 0.100\ \text{mol dm}^{-3}$;

$k = \frac{4.96\times10^{-6}}{(0.100\times0.100)} = 4.96 \times 10^{-4}$;

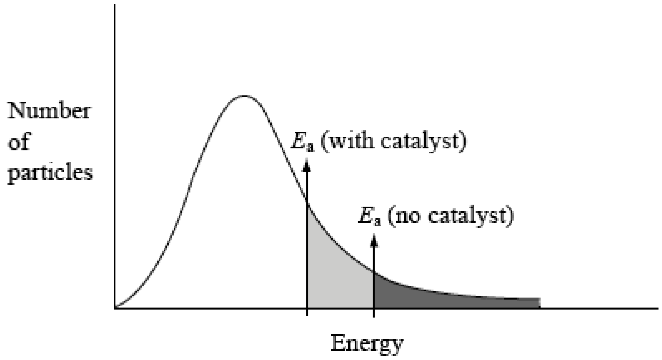
$\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$;

Ignore calculation of $[I_2]$.

No ECF here for incorrect units.

d.

(i)



axes correctly labelled *x* = energy/velocity/speed, *y* = number/% of molecules/particles;

graph showing correct curve for Maxwell-Boltzmann distribution;

If two curves are drawn, first and second mark can still be scored, but not third.

Curve(s) must begin at origin and not go up at high energy.

two activation energies shown with E_{cat} shown lower;

Award the mark for the final point if shown on an enthalpy level diagram.

(ii) catalyst provides an alternative pathway of lower energy / *OWTTE*;

Accept catalyst lowers activation energy (of reaction).

Examiners report

a. The presented data in the question proved to be quite tricky for many candidates, and answers to this question were generally disappointing. Very few stated the need to maintain a constant volume in (a) and many thought that water was added in order to provide a solvent for the reagents.

b. In (b)(i), although the question clearly told candidates to deduce the order for each substance, several did this for only two substances, often the species shown as reactants in the supplied equation. Then the orders shown in the rate expression did not always match the ones deduced. Only the better candidates got the rate expression correct and lots of guess work was seen here. A number gave K_c instead of k. The hypothesis question was also poorly answered and many candidates were not prepared for a question where both were incorrect.

c. Part (c) proved difficult and only the very best candidates got the two concentrations correct most just substituted volumes into their rate expression.

d. In (d), many candidates drew an enthalpy level diagram and not the Maxwell-Boltzmann distribution curve and others showed two curves. Those that did draw a correct curve often mislabelled the axes. However, the vast majority could explain how a catalyst worked.

Consider the following sequence of reactions.

$$\mathrm{RCH_3} \xrightarrow{reaction 1} \mathrm{RCH_2Br} \xrightarrow{reaction 2} \mathrm{RCH_2OH}$$

$\mathrm{RCH_3}$ is an unknown alkane in which R represents an alkyl group.

All the isomers can by hydrolysed with aqueous sodium hydroxide solution. When the reaction of one of these isomers, **X**, was investigated the following kinetic data were obtained.

Experiment	**Initial [X] / mol dm^{-3}**	**Initial [OH$^-$] / mol dm^{-3}**	**Initial rate of reaction / mol dm^{-3} min^{-1}**
1	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{-3}
2	2.0×10^{-2}	4.0×10^{-2}	4.0×10^{-3}
3	4.0×10^{-2}	4.0×10^{-2}	8.0×10^{-3}

a. The alkane contains 82.6% by mass of carbon. Determine its empirical formula, showing your working. [3]

b. A 1.00 g gaseous sample of the alkane has a volume of 385 cm^3 at standard temperature and pressure. Deduce its molecular formula. [2]

c. State the reagent and conditions needed for *reaction 1*. [2]

d. *Reaction 1* involves a free-radical mechanism. Describe the stepwise mechanism, by giving equations to represent the initiation, propagation and termination steps. [4]

e. The mechanism in *reaction 2* is described as S$_N$2. Explain the mechanism of this reaction using curly arrows to show the movement of electron pairs, and draw the structure of the transition state. [3]

f. There are four structural isomers with the molecular formula $\mathrm{C_4H_9Br}$. One of these structural isomers exists as two optical isomers. Draw diagrams to represent the three-dimensional structures of the two optical isomers. [2]

g. (i) Deduce the rate expression for the reaction. [9]

(ii) Determine the value of the rate constant for the reaction and state its units.

(iii) State the name of isomer **X** and explain your choice.

(iv) State equations for the steps that take place in the mechanism of this reaction and state which of the steps is slow and which is fast.

Markscheme

a. $n_C = \frac{82.6}{12.01} = 6.88$ **and** $n_H = \frac{17.4}{1.01} = 17.2$;

ratio is 1:2.5;

C_2H_5;

No penalty for using 12 and 1.

b. $\left(M = \frac{22400}{385}\right) = 58.2/\left(M = \frac{mRT}{PV}\right) = 58.3$;

C_4H_{10};

c. Br_2/bromine ;

UV/ultraviolet light;

Accept hf/hv/sunlight.

d. *initiation:*

$Br_2 \rightarrow 2Br\bullet$;

propagation:

$Br\bullet + RCH_3 \rightarrow HBr + RCH_2\bullet$;

$RCH_2\bullet + Br_2 \rightarrow RCH_2Br + Br\bullet$;

termination: [1 max]

$Br\bullet + Br\bullet \rightarrow Br_2$;

$RCH_2\bullet + Br\bullet \rightarrow RCH_2Br$;

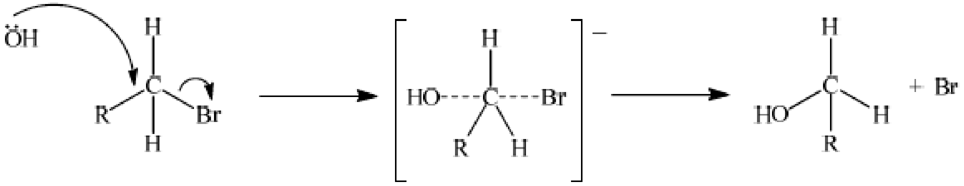
$RCH_2\bullet + RCH_2\bullet \rightarrow RCH_2CH_2R$;

*Award **[1]** for any termination step.*

Accept radical with or without throughout.

Do not penalise the use of an incorrect alkane in the mechanism.

e.



curly arrow going from lone pair/negative charge on O in OH^- to C;

Do not allow curly arrow originating on H in OH^-.

curly arrow showing Br leaving;

Accept curly arrow either going from bond between C and Br to Br in bromoethane or in the transition state.

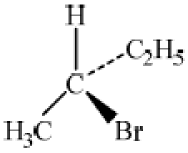
representation of transition state showing negative charge, square brackets and partial bonds;

Do not penalize if HO and Br are not at 180° to each other.

Do not award M3 if OH ---- C bond is represented unless already penalised in M1.

Do not penalise the use of an incorrect alkyl chain in the mechanism.

f.



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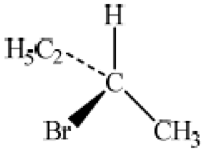

;

First and second structures should be mirror images. Tetrahedral arrangement around carbon must be shown.

g. (i) order with respect to $\mathrm{OH^-} = 0$;

order with respect to $\mathrm{X} = 1$;

rate $= k[\mathrm{X}]$;

*Award **[3]** for final correct answer.*

(ii) 0.2(0);

min^{-1};

(iii) 2-bromo-2-methyl-propane;

Do not penalize missing hyphens or added spaces.

Accept 2-methyl-2-bromopropane.

tertiary structure;

(iv) $\mathrm{C_4H_9Br \rightarrow C_4H_9^+ + Br^-}$ / in equation with curly arrows **and** slow;

$\mathrm{C_4H_9^+ + OH^- \rightarrow C_4H_9OH}$ / in equation with curly arrows **and** fast;

No penalty if primary structure is shown.

No credit for S_N2 mechanism, except by ECF.

Examiners report

a. Although this was the least popular question in Section B there was generally a good level of performance. In (a) most candidates scored at least 2 out of 3 marks for calculating the empirical formula.

b. Many managed to give a correct molecular formula based on their background knowledge once they had determined the molar mass from the density calculation.

c. The conditions of free radical substitution were well known.

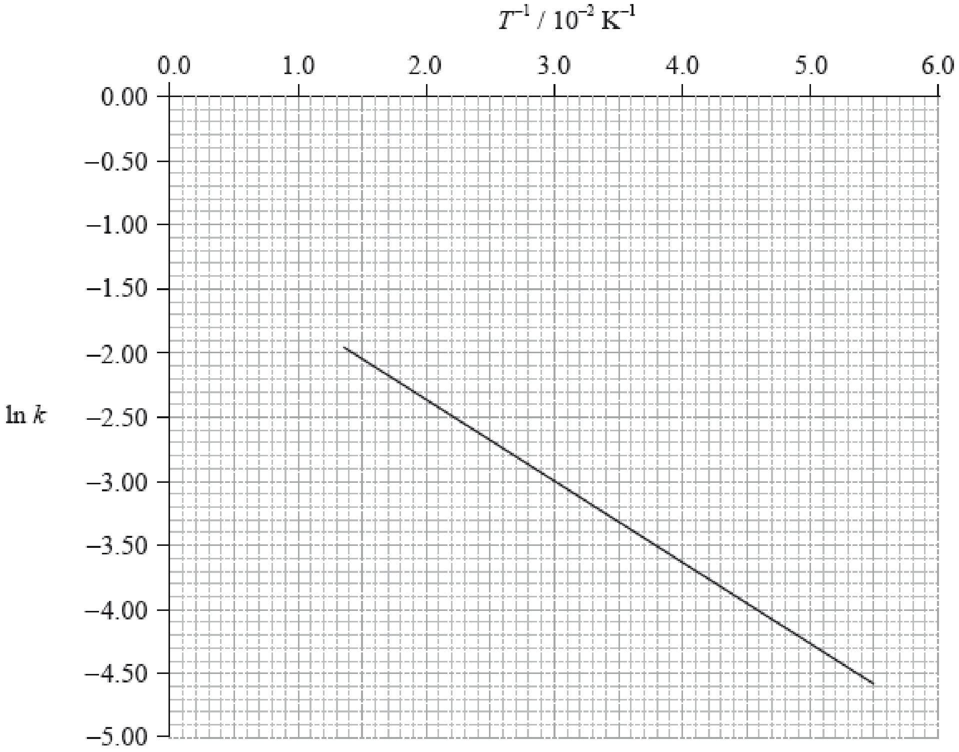
d. The mechanism of free radical substitution was well known.

e. The conditions and mechanism of free radical substitution were well known but the S_N2 mechanism in (e) caused more problems.

f. Again the use of curly arrows proved to be difficult. In some case they originated from the H not the lone pair on O of the nucelophile, or were missing from the C – Br bond. Another common mistake was the omission of a negative charge from the transition state. As the attack of the nucleophile is on the opposite side of the carbon atom to the halogen leaving, the partial bonds in the transition state should be drawn at 180 degrees. Candidates were not penalised however if they failed to do this.

g. Most candidates were able to draw accurate 3D diagrams for the stereoisomers of 2-bromobutane, to deduce the rate expression from the experimental data presented in (g), and correctly identify X as having a tertiary structure. It was also pleasing to see that most were able to describe the S_N1 mechanism.

To determine the activation energy of a reaction, the rate of reaction was measured at different temperatures. The rate constant, k, was determined and $\ln k$ was plotted against the inverse of the temperature in Kelvin, T^{-1}. The following graph was obtained.



a. Define the term *activation energy*, E_a. [1]

b. Use the graph on page 8 to determine the value of the activation energy, E_a, in $\mathrm{kJ\,mol^{-1}}$. [2]

c. On the graph on page 8, sketch the line you would expect if a catalyst is added to the reactants. [1]

Markscheme

a. minimum energy needed to react/start a reaction / energy difference between reactants and transition state;

b. *gradient of the line*: –63;

Accept –60 to –65.

$E_a\ (= -R \times \text{gradient}) = 0.52\ (\mathrm{kJ\,mol^{-1}})$;

Accept 0.50 to 0.54.

c. gradient of the line less steep (less negative);

Accept any position as long as gradient less steep.

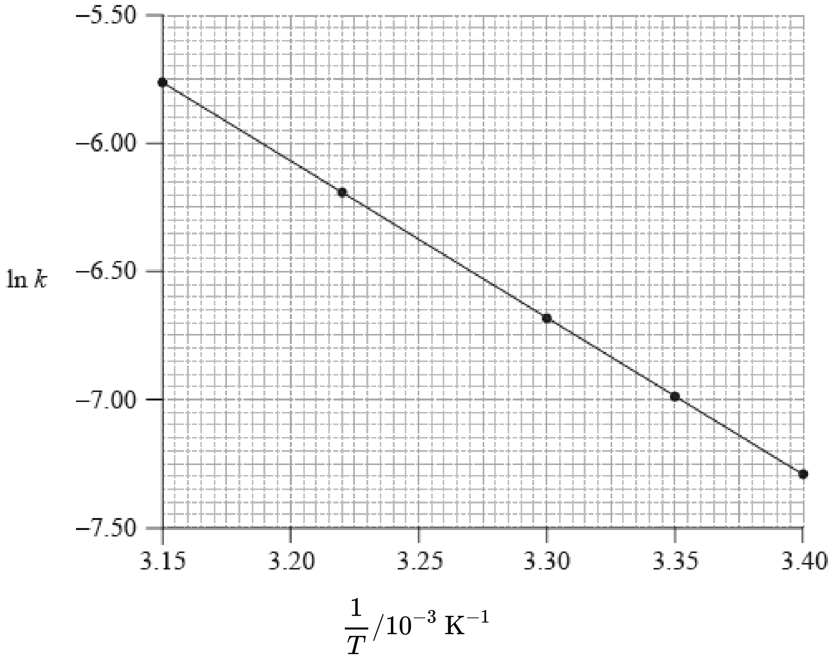
Examiners report

a. The idea of activation energy being a *minimum* was seldom communicated. Few were able to follow through all the mathematics to find E_a by a graphical method and those that did had often omitted 10^{-2} in their calculations. The answers were often poorly set out so it was difficult to assess the award of part marks; indeed, many candidates seemed to hope that a correct answer would somehow emerge from a mass of incomprehensible figures.

b. The idea of activation energy being a *minimum* was seldom communicated. Few were able to follow through all the mathematics to find E_a by a graphical method and those that did had often omitted 10^{-2} in their calculations. The answers were often poorly set out so it was difficult to assess the award of part marks; indeed, many candidates seemed to hope that a correct answer would somehow emerge from a mass of incomprehensible figures.

c. The idea of activation energy being a *minimum* was seldom communicated. Few were able to follow through all the mathematics to find E_a by a graphical method and those that did had often omitted 10^{-2} in their calculations. The answers were often poorly set out so it was difficult to assess the award of part marks; indeed, many candidates seemed to hope that a correct answer would somehow emerge from a mass of incomprehensible figures. The gradient of the graph for (c) was generously marked; all candidates had to do was to realize that the catalyst would lower the activation energy and thus the gradient would be less negative. As long as a line with less negative gradient was drawn, the mark was awarded.

Consider the following graph of $\ln k$ against $\frac{1}{T}$.



a. A catalyst provides an alternative pathway for a reaction, lowering the activation energy, E_a. Define the term *activation energy*, E_a. [1]

b. State how the rate constant, *k* , varies with temperature, *T*. [1]

c. Determine the activation energy, E_a, correct to **three** significant figures and state its units. [3]

Markscheme

a. minimum energy needed (by reactants/colliding particles) to react/start/initiate a reaction / for a successful collision;

Allow energy difference between reactants and transition state.

b. *k* increases with *T*;

Do not accept k proportional to T or statement of Arrhenius equation from Data booklet.

c. slope/gradient/$m = \frac{-E_a}{R} / -6.20 \times 10^3$;

Allow range of m from –5.96 × 10^3 to –6.44 × 10^3.

Award M1 for $m = \frac{-E_a}{R}$ *even if gradient is out of range.*

$E_a = (6.20 \times 10^3 \times 8.31) = 51.5\ \text{kJ mol}^{-1} / 5.15 \times 10^4\ \text{J mol}^{-1}$

E_a value correct;

units correct;

*Award **[3]** for correct final answer.*

Allow range of E_a from 49.5 to 53.5 kJ mol^{-1} / 4.95 × 10^4 to 5.35 × 10^4 J mol^{-1}.

Answer must be given correct to three significant figures.

M3 can be scored independently.

Examiners report

a. In (a) the most common mistake was for students to omit minimum in the definition of activation energy. Many described the relation between temperature and rate constant as linear or 'proportional'. Only a small number of students gained full marks for the determination of activation energy because many either calculated an incorrect gradient or used the wrong units.

b. In (a) the most common mistake was for students to omit minimum in the definition of activation energy. Many described the relation between temperature and rate constant as linear or 'proportional'. Only a small number of students gained full marks for the determination of activation energy because many either calculated an incorrect gradient or used the wrong units.

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The electron configuration of chromium can be expressed as $[\text{Ar}]4\text{s}^{\text{x}}3\text{d}^{\text{y}}$.

Hydrogen and nitrogen(II) oxide react according to the following equation.

$$2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$$

At time = t seconds, the rate of the reaction is

$$\text{rate} = k[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2$$

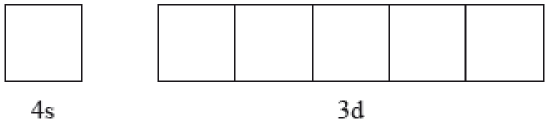
When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:

$$[\mathrm{Cu(H_2O)_6}]^{2+}\mathrm{(aq)} + 4\mathrm{Cl^-(aq)} \rightarrow [\mathrm{CuCl_4}]^{2-}\mathrm{(aq)} + 6\mathrm{H_2O(l)}$$

a.i. Explain what the square brackets around argon, [Ar], represent. [1]

a.ii. State the values of x and y. [1]

a.iii. Annotate the diagram below showing the 4s and 3d orbitals for a chromium atom using an arrow, ↿ and ⇂, to represent a spinning electron. [1]



b.i. Explain precisely what the square brackets around nitrogen(II) oxide, [NO(g)], represent in this context. [1]

b.ii. Deduce the units for the rate constant k. [1]

c.i. Explain what the square brackets around the copper containing species represent. [1]

c.ii. Explain why the $[\mathrm{Cu(H_2O)_6}]^{2+}$ ion is coloured and why the $[\mathrm{CuCl_4}]^{2-}$ ion has a different colour. [2]

d. Some words used in chemistry can have a specific meaning which is different to their meaning in everyday English. [1]

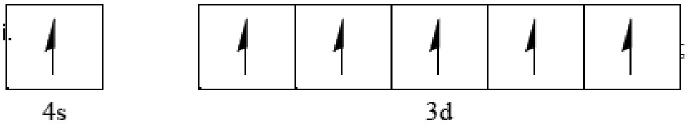
State what the term *spontaneous* means when used in a chemistry context.

Markscheme

a.i. the electron configuration (of argon) / $1s^2 2s^2 2p^6 3s^2 3p^6$;

a.ii. $x = 1$ **and** $y = 5$;

a.iii.



Accept all six arrows pointing down rather than up.

b.i. the concentration (of nitrogen(II) oxide);

Award ***[0]*** *if reference made to equilibrium.*

b.ii. $\mathrm{mol^{-2} dm^6 s^{-1}} / \mathrm{dm^6 mol^{-2} s^{-1}}$;

Accept $(\mathrm{mol^{-1}\,dm^3})2\mathrm{s^{-1}}$.

c.i. complex (ion) / the charge is delocalized over all that is contained in the brackets;

c.ii. colour is due to energy being absorbed when electrons are promoted within the split d orbitals;

the colour observed is the complementary colour to the energy absorbed / *OWTTE*;

Accept either answer for first mark.

changing the ligand / coordination number / geometry changes the amount the d orbitals are split/energy difference between the d orbitals / *OWTTE*;

d. the reaction gives out (Gibbs Free) energy that can do work;

ΔG for the reaction has a negative value;

a reaction that occurs without adding energy (beyond that required to overcome energy barrier);

Examiners report

a.i. Most candidates were familiar with the use of square brackets to represent noble gas electron configurations and concentrations in rate expressions and it was encouraging to see candidates give a correct orbital diagram with the d electrons unpaired.

a.ii. A significant number of students were unaware of the exceptional nature of the electron configuration for chromium.

a.iii. A significant number of students were unaware of the exceptional nature of the electron configuration for chromium, but were able to gain the mark in (a) (iii) with ecf.

b.i. The understanding of the use of square bracket to represent complex ions was limited.

b.ii. Many candidates omitted the s^{-1} in the units for the rate constant.

c.i. [N/A]

c.ii. (c) (ii) proved to be more challenging with many candidates mixing up sub-shells with orbitals and absorption with emission spectra.

d. Many candidates were familiar with the use of the term *spontaneous* when used in a chemical context.

A mixture of 1.00 mol SO_2(g), 2.00 mol O_2(g) and 1.00 mol SO_3(g) is placed in a 1.00 dm^3 container and allowed to reach equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

c.i. Nitrogen oxide is in equilibrium with dinitrogen dioxide. [1]

$2NO(g) \rightleftharpoons N_2O_2(g) \quad \Delta H^{\ominus} < 0$

Deduce, giving a reason, the effect of increasing the temperature on the concentration of N_2O_2.

c.ii. A two-step mechanism is proposed for the formation of NO_2(g) from NO(g) that involves an exothermic equilibrium process. [2]

First step: $2NO(g) \rightleftharpoons N_2O_2(g)$ fast

Second step: $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ slow

Deduce the rate expression for the mechanism.

d. The rate constant for a reaction doubles when the temperature is increased from 25.0 °C to 35 °C. [2]

Calculate the activation energy, E_a, in kJ mol^{-1} for the reaction using section 1 and 2 of the data booklet.

Markscheme

c.i. $[N_2O_2]$ decreases ***AND*** exothermic «thus reverse reaction favoured»

Accept "product" for [N_2O_2].

*Do **not** accept just "reverse reaction favoured/shift to left" for "[N_2O_2] decreases".*

[1 mark]

c.ii. ***ALTERNATIVE 1:***

«from equilibrium, step 1»

$$K_c = \frac{[N_2O_2]}{[NO]^2}$$

OR

$[N_2O_2] = K_c[NO]^2$

«from step 2, rate «= $k_1[N_2O_2][O_2] = k_2K[NO]^2[O_2]$»

rate = $k[NO]^2[O_2]$

ALTERNATIVE 2:

«from step 2» rate = $k_2[N_2O_2][O_2]$

«from step 1, $\text{rate}_{(1)} = k_1[NO]^2 = k_{-1}[N_2O_2]$, $[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$»

«rate = $\frac{k_1}{k_{-1}} k_2[NO]^2[O_2]$»

rate = $k[NO]^2[O_2]$

*Award **[2]** for correct rate expression.*

[2 marks]

d. «$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$»

T_2 = «273 + 35 =» 308 K ***AND*** T_1 = «273 + 25 =» 298 K

E_a = 52.9 «kJ mol^{-1}»

*Award **[2]** for correct final answer.*

[2 marks]

Examiners report

c.i. [N/A]
c.ii. [N/A]
d. [N/A]

Chemical kinetics involves an understanding of how the molecular world changes with time.

A catalyst provides an alternative pathway for a reaction, lowering the activation energy, E_a.

Sketch graphical representations of the following reactions, for X → products.

For the reaction below, consider the following experimental data.

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

Experiment	**Initial [ClO_2(aq)] / mol dm^{-3}**	**Initial [OH^-(aq)] / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	1.00×10^{-1}	1.00×10^{-1}	2.30×10^{-1}
2	5.00×10^{-2}	1.00×10^{-1}	5.75×10^{-2}
3	5.00×10^{-2}	3.00×10^{-2}	1.73×10^{-2}

Another reaction involving OH^- (aq) is the base hydrolysis reaction of an ester.

$$CH_3COOCH_2CH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + CH_3CH_2OH(aq)$$

A two-step mechanism has been proposed for the following reaction.

$$\text{Step 1:} \quad ClO^-(aq) + ClO^-(aq) \rightarrow ClO_2^-(aq) + Cl^-(aq)$$
$$\text{Step 2:} \quad ClO_2^-(aq) + ClO^-(aq) \rightarrow ClO_3^-(aq) + Cl^-(aq)$$

a. (i) Define the term *rate of reaction*. [4]

(ii) Temperature and the addition of a catalyst are two factors that can affect the rate of a reaction. State **two** other factors.

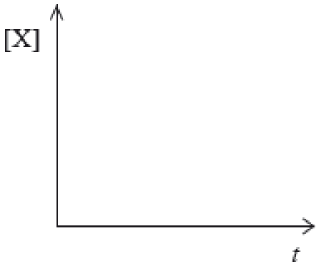
(iii) In the reaction represented below, state **one** method that can be used to measure the rate of the reaction.

$$ClO_3^-(aq) + 5Cl^-(aq) + 6H^+(aq) \rightarrow 3Cl_2(aq) + 3H_2O(l)$$

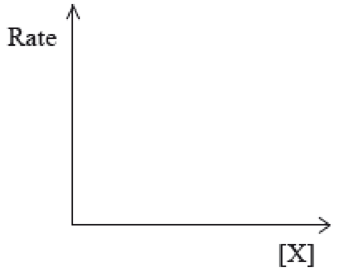
b. (i) Define the term *activation energy*, E_a. [4]

(ii) Sketch the **two** Maxwell–Boltzmann energy distribution curves for a fixed amount of gas at two different temperatures, T_1 and T_2 $(T_2 > T_1)$. Label **both** axes.

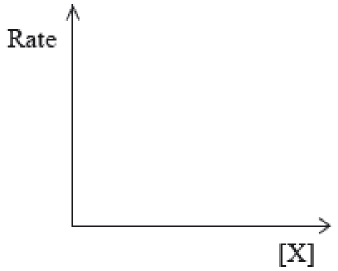
c. (i) Concentration of reactant X against time for a **zero-order** reaction. [3]



(ii) Rate of reaction against concentration of reactant X for a **zero-order** reaction.



(iii) Rate of reaction against concentration of reactant X for a **first-order** reaction.



d. (i) Deduce the rate expression. [5]

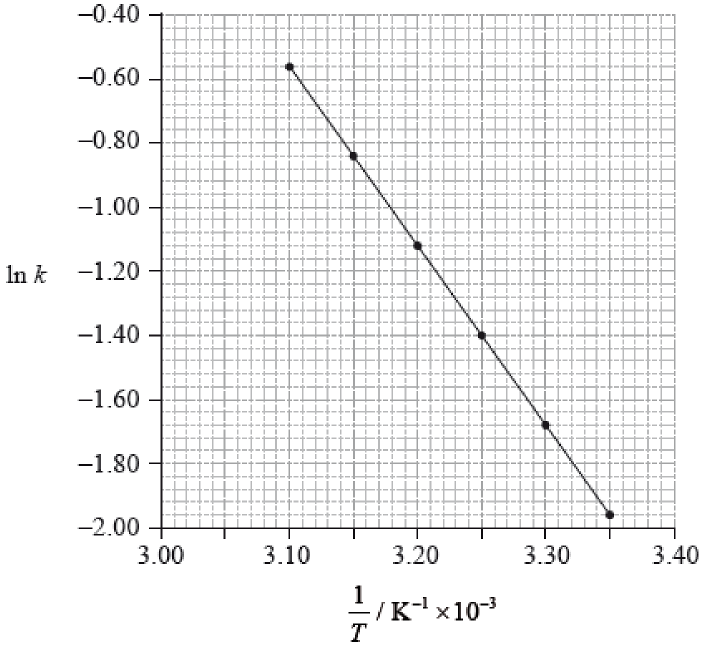
(ii) Determine the rate constant, k, and state its units, using the data from Experiment 2.

(iii) Calculate the rate, in $\mathrm{mol\,dm^{-3}s^{-1}}$, when $[\mathrm{ClO_2(aq)}] = 1.50 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ and $[\mathrm{OH^-(aq)}] = 2.35 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$.

e.i. Apply IUPAC rules to name the ester, $CH_3COOCH_2CH_3$(aq). [1]

e.ii. Describe **qualitatively** the relationship between the rate constant, *k*, and temperature, *T*. [1]

e.iii. The rate of this reaction was measured at different temperatures and the following data were recorded. [4]



Using data from the graph, determine the activation energy, E_a, correct to **three** significant figures and **state its units**.

f.i. Deduce the overall equation for the reaction. [1]

f.ii. Deduce the rate expression for each step. [2]

Step 1:

Step 2:

Markscheme

a. (i) change in concentration of reactant/product with time / rate of change of concentration;

Increase can be used instead of change for product or decrease can be used instead of change for reactant.

Allow mass/amount/volume instead of concentration.

Do not accept substance.

(ii) concentration;

particle size / surface area;

light;

pressure;

Allow pH.

(iii) (measuring electrical) conductivity / (measuring) pH;

Accept other suitable method.

b. (i) minimum/least/smallest energy needed (by reactants/colliding particles) to react/start/initiate a reaction;

Allow energy difference between reactants and transition state.

Minimum/least/smallest required for the mark.

(ii) *x-axis label*: (kinetic) energy/(K)E **and** *y-axis label*: probability/fraction of molecules/particles / probability density;

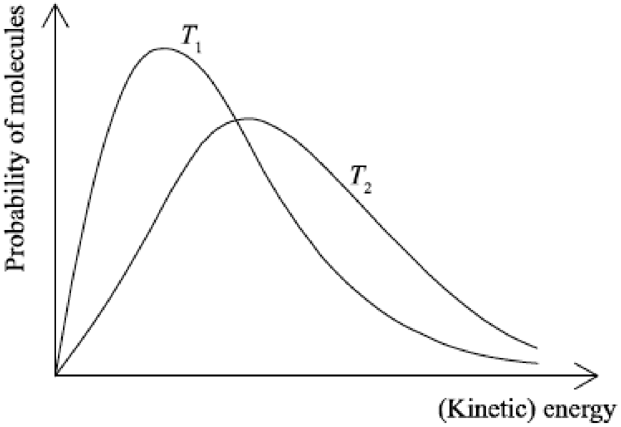
Allow number of molecules/particles for y-axis.

correct shape of a typical Maxwell–Boltzmann energy distribution curve;

Do not award mark if curve is symmetric, does not start at zero or if it crosses x-axis.

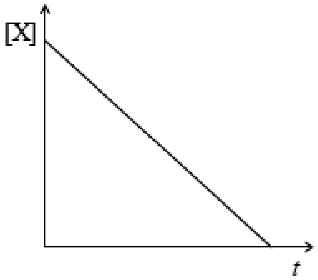
two curves represented with second curve for $T_2 > T_1$ to right of first curve, peak maximum lower than first curve and after the curves cross going to the right, T_2 curve needs to be above T_1 curve as illustrated;

M2 and M3 can be scored independently.

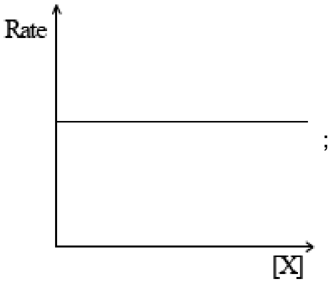


c.

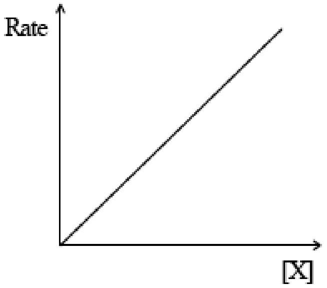
(i)



;

(ii) 

;

(iii) 

;

d. (i) second order in $\mathrm{ClO_2}$ **and** first order in $\mathrm{OH^-}$;

rate $= k[\mathrm{ClO_2}]^2[\mathrm{OH^-}]$;

*Award **[2]** for correct final answer.*

(ii) $k = 2.30 \times 10^2/230$;

$\mathrm{mol^{-2}dm^6s^{-1}}$;

(iii) $1.22 \times 10^{-3}/0.00122\ (\mathrm{mol\,dm^{-3}s^{-1}})$;

e.i. ethyl ethanoate;

Do not allow ethyl acetate.

e.ii. as temperature/*T* increases, (value of) rate constant/*k* increases (exponentially);

Do not allow answers involving ln k from the Arrhenius equation.

Do not allow T directly proportional to k.

e.iii slope $= -5.6 \times 10^3 / -5600\ (\mathrm{K})$;

$E_\mathrm{a} = -\mathrm{slope} \times \mathrm{R}/\mathrm{slope} = -E_\mathrm{a}/R$;

$E_\mathrm{a}(= 5.60 \times 10^3\ K \times 8.31\ \mathrm{J\,K^{-1}mol^{-1}}) = 4.65 \times 10^4\ (\mathrm{J\,mol^{-1}})/46.5\ (\mathrm{kJ\,mol^{-1}})$;

Accept answers in range 4.60 × 10^4 J mol^{-1} to 4.67 × 10^4 (J mol $^{-1}$).

$\mathrm{J\,mol^{-1}/kJ\,mol^{-1}}$;

Accept J or kJ.

*Unit mark can be scored independently but correct E_a values with incorrect units scores only **[3 max]** (for example 46.5 J mol $^{-1}$).*

*Award **[4]** for correct final answer.*

f.i. $3\mathrm{ClO^-(aq)} \rightarrow \mathrm{ClO_3^-(aq)} + 2\mathrm{Cl^-(aq)}$;

Ignore state symbols.

f.ii. *Step 1*: rate $= k[\mathrm{ClO^-}]^2$;

Step 2: rate $= k[\mathrm{ClO_2^-}][\mathrm{ClO^-}]$;

Penalize missing k once only.

Examiners report

a. This was the most popular question in Section B of the paper. Part (a) was very well answered.

b. In (b) (i), some candidates failed to mention minimum/least/smallest energy in the definition of activation energy. In part (ii), again candidates often dropped easy marks here for poor representations of the Maxwell-Boltzmann energy distribution curves. In some cases the curves were drawn symmetrically, which was incorrect. In addition, incorrect labels were often given for the x- and y-axes. Some candidates mixed these curves up with enthalpy level diagrams. It was nice to see more candidates giving a more precise label for the y-axis as probability/fraction of molecules rather than just number of molecules. The latter was allowed but is less precise (although does tend to be used in many IB textbooks).

c. Part (c) however was very well answered.

d. In part (d), many candidates also scored highly though the units of *k* in (ii) did cause a problem for some candidates.

e.i. In (e) (i), the most common mistake was candidates stating ethyl methanoate instead of ethyl ethanoate.

e.ii. In part (ii), a number of candidates stated incorrectly that *T* is directly proportional to *k*, which is incorrect. Proportionality is a concept embedded in AS 11.3.1 in Topic 11, and may be worth some further discussion in the light of the Arrhenius Equation.

e.iii. The most difficult part of Q6 however involved (e) (iii). Very few candidates scored full marks here and simply did not know how to manipulate the equation to get the activation energy. Others even gave incorrect units.

f.i. One respondent stated that part (f) (ii) would be difficult for candidates. (f) certainly did prove challenging and the rate expression for step two was often given incorrectly. This question became a good discriminating question in Section B. However the better students did manage to score all three marks in part (f).

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Sodium thiosulfate solution reacts with dilute hydrochloric acid to form a precipitate of sulfur at room temperature.

$$Na_2S_2O_3\ (aq) + 2HCl\ (aq) \rightarrow S\ (s) + SO_2\ (g) + 2NaCl\ (aq) + X$$

(i) Using the graph, explain the order of reaction with respect to sodium thiosulfate.

(ii) In a different experiment, this reaction was found to be first order with respect to hydrochloric acid. Deduce the overall rate expression for the reaction.

Markscheme

i

first order
«because» [$Na_2S_2O_3$] is «directly» proportional to rate of reaction «$\frac{1}{t}$»

Do not accept "linear" for M2.

ii

rate = k[$Na_2S_2O_3$][HCl]

Examiners report

[N/A]

Nitrogen dioxide and carbon monoxide react according to the following equation:

$$NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g) \qquad \Delta H = -226 \text{ kJ}$$

Experimental data shows the reaction is second order with respect to NO_2 and zero order with respect to CO.

b.i. State the rate expression for the reaction. [1]

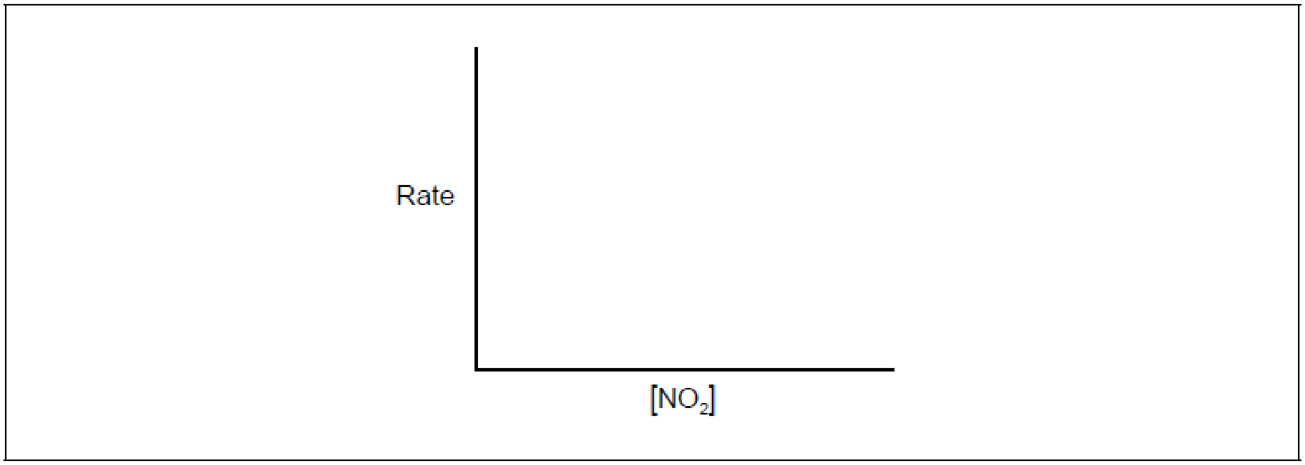
b.ii. The following mechanism is proposed for the reaction. [1]

$$\begin{array}{ll} \text{Step I} & NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g) \\ \text{Step II} & NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \end{array}$$

Identify the rate determining step giving your reason.

b.iii. State one method that can be used to measure the rate for this reaction. [1]

b.v. Sketch the relationship between the rate of reaction and the concentration of NO_2. [1]



c. The Arrhenius equation, $k = Ae^{-\frac{Ea}{RT}}$, gives the relationship between the rate constant and temperature. [1]

State how temperature affects activation energy.

Markscheme

b.i. «rate =» k [NO_2]^2

Accept rate = k $[NO_2]^2[CO]^0$.

[1 mark]

b.ii. «step» I ***AND*** CO does not appear in the rate law expression

OR

«step» I ***AND*** only «2 molecules of» NO_2 appears in rate expression

Do not allow ECF from (i).

[1 mark]

b.iii. «IR or UV-vis» spectroscopy

OR

colorimetry

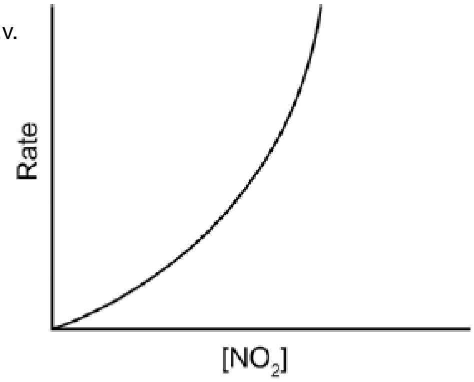
OR

colour change «over time»

Accept GC/gas chromatography.

[1 mark]

b.v.



Curve must go through origin.

[1 mark]

c. activation energy is independent of temperature

Accept "no relationship".

[1 mark]

Examiners report

b.i. [N/A]
b.ii. [N/A]
b.iii. [N/A]
b.v. [N/A]
c. [N/A]

Analytical chemistry uses instruments to separate, identify, and quantify matter.

Menthol is an organic compound containing carbon, hydrogen and oxygen.

Nitric oxide reacts with chlorine.

$$2NO\ (g) + Cl_2\ (g) \rightarrow 2NOCl\ (g)$$

The following experimental data were obtained at 101.3 kPa and 263 K.

Experiment	Initial [NO] / $mol\,dm^{-3}$	Initial [Cl_2] / $mol\,dm^{-3}$	Initial rate / $mol\,dm^{-3}\,min^{-1}$
1	1.30×10^{-1}	1.30×10^{-1}	3.95×10^{-1}
2	1.30×10^{-1}	2.60×10^{-1}	7.90×10^{-1}
3	2.60×10^{-1}	2.60×10^{-1}	3.16

b. Outline how this spectrum is related to the energy levels in the hydrogen atom. [1]

c. A sample of magnesium has the following isotopic composition. [2]

Isotope	^{24}Mg	^{25}Mg	^{26}Mg
Relative abundance / %	78.6	10.1	11.3

Calculate the relative atomic mass of magnesium based on this data, giving your answer to **two** decimal places.

d.i. Complete combustion of 0.1595 g of menthol produces 0.4490 g of carbon dioxide and 0.1840 g of water. Determine the empirical formula of the compound showing your working. [3]

d.ii. 0.150 g sample of menthol, when vaporized, had a volume of 0.0337 dm^3 at 150 °C and 100.2 kPa. Calculate its molar mass showing your working. [2]

d.iii. Determine the molecular formula of menthol using your answers from parts (d)(i) and (ii). [1]

e.i. Deduce the order of reaction with respect to Cl_2 and NO. [2]

Cl_2:

. . . .

NO:

. . . .

e.ii. State the rate expression for the reaction. [1]

e.iii. Calculate the value of the rate constant at 263 K. [1]

Markscheme

b. electron transfer/transition between high«er» energy level to low«er» energy level

OR

electron transitions into first energy level causes UV series

OR

transition into second energy level causes visible series

OR

transition into third energy level causes infrared series

Accept any of the points shown on a diagram.

c. 24 x 0.786 + 25 x 0.101 + 26 x 0.113

24.33

Award **[2]** for correct final answer.
Award **[0]** for 24.31 with no working (data booklet value).

d.i. carbon: «$\frac{0.4490\text{ g}}{44.01\text{ g mol}^{-1}}$ =» 0.01020 «mol» / 0.1225 «g»

OR

hydrogen: «$\frac{0.1840\times 2}{18.02\ g\ mol^{-1}}$ =» 0.02042 «mol» / 0.0206 «g»

oxygen: «0.1595 – (0.1225 + 0.0206)» = 0.0164 «g» / 0.001025 «mol»

empirical formula: $C_{10}H_{20}O$

*Award **[3]** for correct final answer.*

*Do **not** award M3 for a hydrocarbon.*

d.ii. «temperature =» 423 K

OR

$M = \frac{mRT}{pV}$

«$M = \frac{0.150\text{ g}\times 8.31\text{ JK}^{-1}\text{ mol}^{-1}\times 423\text{ K}}{100.2\text{ kPa}\times 0.0337\text{ dm}^3}$ =» 156 «g mol^{-1}»

*Award **[1]** for correct answer with no working shown.*

*Accept "pV = nRT **AND** n = $\frac{m}{M}$" for M1.*

d.iii. $C_{10}H_{20}O$

[1 Mark]

e.i. *Cl_2:* first

NO: second

e.ii. rate = *k* $[NO]^2\ [Cl_2]$

e.iii. 180 / 1.80 x 10^2 «$\text{dm}^6\ \text{mol}^{-2}\ \text{min}^{-1}$»

Examiners report

b. [N/A]
c. [N/A]
d.i. [N/A]

d.ii.[N/A]
d.iii.[N/A]
e.i. [N/A]
e.ii.[N/A]
e.iii.[N/A]

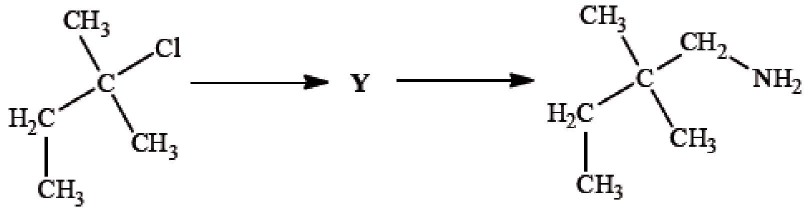
2-methylbutan-2-ol, $(CH_3)_2C(OH)CH_2CH_3$, is a liquid with a smell of camphor that was formerly used as a sedative. One way of producing it starts with 2-methylbut-2-ene.

As well as 2-methylbutan-2-ol, the reaction also produces a small quantity of an optically active isomer, **X**.

2-methylbutan-2-ol can also be produced by the hydrolysis of 2-chloro-2-methylbutane, $(CH_3)_2CClC_2H_5$, with aqueous sodium hydroxide.

2-chloro-2-methylbutane contains some molecules with a molar mass of approximately $106\ g\,mol^{-1}$ and some with a molar mass of approximately $108\ g\,mol^{-1}$.

2-chloro-2-methylbutane can also be converted into compound **Z** by a two-stage reaction via compound **Y**:



2-chloro-2-methylbutane

Z

a. State the other substances required to convert 2-methylbut-2-ene to 2-methylbutan-2-ol. [2]

b. Explain whether you would expect 2-methylbutan-2-ol to react with acidified potassium dichromate(VI). [2]

c.i. State what is meant by *optical activity*. [1]

c.ii. State what optical activity indicates about the structure of the molecule. [1]

c.iii. Optical activity can be detected using a polarimeter. Explain how this works. [3]

c.iv. Deduce the structural formula of **X**. [1]

d. Explain why 2-methylbut-2-ene is less soluble in water than 2-methylbutan-2-ol. [2]

e.i. Explain the mechanism of this reaction using curly arrows to represent the movement of electron pairs. [4]

e.ii. State the rate expression for this reaction and the units of the rate constant. [2]

e.iii. Suggest why, for some other halogenoalkanes, this hydrolysis is much more effective in alkaline rather than in neutral conditions. [1]

f.i. Outline why there are molecules with different molar masses. [1]

g.i. Draw the structure of **Y**. [1]

g.ii. State the reagent and any catalyst required for both the formation of **Y** and the conversion of **Y** into **Z**. [3]

Formation of **Y**:

Conversion of **Y** into **Z**:

Markscheme

a. water/H_2O;

Accept steam.

(concentrated) sulfuric acid/H_2SO_4 (catalyst);

Accept phosphoric acid/H_3PO_4.

*Award **[2]** for HBr and NaOH (two-stage process via the halogenoalkane).*

b. not react;

tertiary alcohol (not easily oxidized);

c.i. rotates the plane (of polarization) of plane polarized light;

*Accept answers in which **one** of the "plane"s is missing.*

c.ii. two isomers that are enantiomers/chiral/non-superimposable mirror images;

Accept "contains an asymmetric/chiral carbon" or "contains a carbon bonded to four <u>different</u> groups".

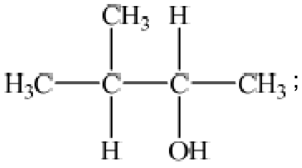
c.iii. polarizes light / polarized light source;

light passed through sample;

analyser / second polarizer detects whether plane of polarization rotated;

c.iv.

$(CH_3)_2CH—CH(OH)—CH_3$ /



$H_3C—C(CH_3)(H)—C(H)(OH)—CH_3$;

Accept $C_3H_7–CH(OH)–CH_3$, but not $CH_3–CH_2–CH_2–CH(OH)–CH_3$.

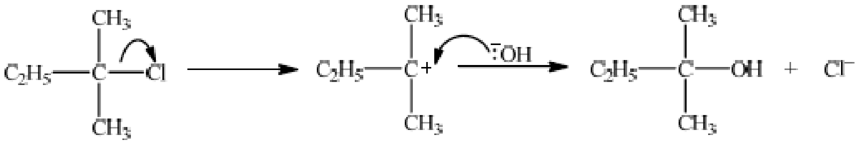
d. 2-methylbutan-2-ol has hydroxyl/OH group;

Do not accept "hydroxide group".

Allow 2-methylbutan-2-ol is an alcohol.

2-methylbutan-2-ol can form H-bonds (to water) / 2-methylbut-2-ene cannot form H-bonds (to water);

e.i.



curly arrow showing Cl^- leaving;

representation of tertiary carbocation;

curly arrow going from lone pair/negative charge on O in $\mathrm{HO^-}$ to $\mathrm{C^+}$;

Do not allow arrow originating on H in HO⁻.

formation of organic product $\mathrm{CH_3CH_2C(CH_3)_2OH}$ **and** $\mathrm{Cl^-}$/NaCl

(somewhere in mechanism);

*Award **[3 max]** if a candidate gives a fully correct S_N2 mechanism.*

e.ii $\mathrm{rate} = \mathrm{k}\times$ [2-chloro-2-methylbutane]/$[\mathrm{CH_3CH_2C(CH_3)_2Cl}]$/[halogenoalkane]

/[R–Cl];

$\mathrm{s^{-1}}$;

e.iii hydroxide ion/$\mathrm{OH^-}$ is a better nucleophile than water / hydroxide ion/$\mathrm{OH^-}$ has negative charge;

undergo $\mathrm{S_N2}$ hydrolysis / RDS depends on attack of $\mathrm{OH^-}$/hydroxide ion (nucleophile);

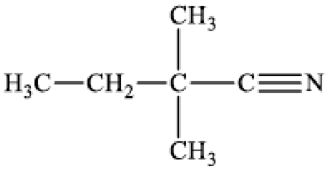
Accept other suggestions that are chemically valid.

f.i. chlorine can be $^{35}\mathrm{Cl}$/Cl–35 or $^{37}\mathrm{Cl}$/Cl–37;

Accept "chlorine can exist as two isotopes".

Answer must refer to chlorine rather than isotopes in general.

g.i.



$\mathrm{H_3C{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C{\equiv}N}$;

Do not accept condensed formulas such as $CH_3CH_2C(CH_3)_2CN$.

Accept the cyanide group as –CN without showing the triple bond.

g.ii *Formation of Y:*

cyanide ion/$\mathrm{CN^-}$ / potassium cyanide/KCN;

Accept hydrogen cyanide/HCN.

Conversion of Y into Z:

hydrogen/$\mathrm{H_2}$;

nickel/Ni / platinum/Pt / palladium/Pd (catalyst);

Examiners report

a. Many students could recall the reagents for the hydration of an alkene and recognize the alcohol as a tertiary alcohol that would not undergo oxidation. Statements regarding optical activity often lacked precision and betrayed confusion with chirality. Very few could correctly describe how a polarimeter worked, especially the second rotating sheet of polaroid, and students frequently drew the structure of 2-methylbutan-2-ol rather than its chiral isomer. Most students stated that the alcohol was more polar than the alkene, but fewer mentioned that it could form hydrogen bonds to water and even less linked this to the presence of the hydroxyl group. Almost all students recognized that the hydrolysis was $\mathrm{S_N1}$, with an encouraging number being able to write reasonable mechanisms, though many still lost marks through a lack of precision in where their curly arrows started and ended. Many candidates also stated an appropriate rate equation along with the units of the rate constant. Very few students linked the difference of two molar mass units to the presence in the molecule of chlorine, with its naturally occurring isotopes, and the discussion of any effect on the hydrolysis rate often revealed a lack of clear thinking. In contrast many students correctly identified the nitrile as the intermediate in the chain extension reaction and reagents for its formation and hydrogenation were generally well known.

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a.i. Ethanol is a primary alcohol that can be oxidized by acidified potassium dichromate(VI). Distinguish between the reaction conditions needed to produce ethanal and ethanoic acid. [2]

Ethanal:

Ethanoic acid:

a.ii. Determine the oxidation number of carbon in ethanol and ethanal. [2]

Ethanol:

Ethanal:

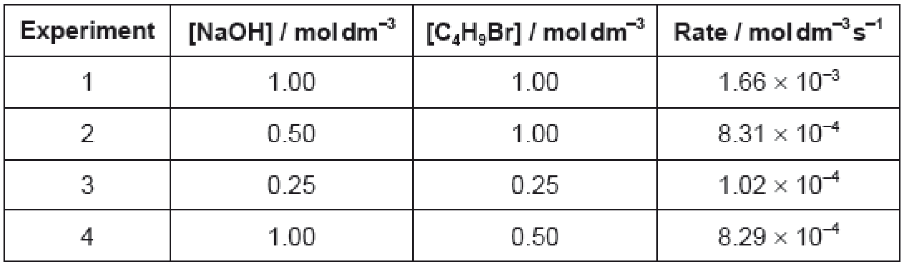
a.iii Deduce the half-equation for the oxidation of ethanol to ethanal. [1]

a.iv Deduce the overall redox equation for the reaction of ethanol to ethanal with acidified potassium dichromate(VI). [2]

b. Ethanol can be made by reacting aqueous sodium hydroxide with bromoethane. [4]

Explain the mechanism for this reaction, using curly arrows to represent the movement of electron pairs.

c.i. Determine the orders of reaction of the reactants and the overall rate expression for the reaction between 2-bromobutane and aqueous sodium hydroxide using the data in the table. [2]



Experiment	[NaOH] / mol dm^{-3}	[C_4H_9Br] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	1.00	1.00	1.66×10^{-3}
2	0.50	1.00	8.31×10^{-4}
3	0.25	0.25	1.02×10^{-4}
4	1.00	0.50	8.29×10^{-4}

c.ii. Determine the rate constant, k, with its units, using the data from experiment 3. [2]

c.iii Identify the molecularity of the rate-determining step in this reaction. [1]

d.i. 2-bromobutane exists as optical isomers. [1]

State the essential feature of optical isomers.

d.ii 2-bromobutane exists as optical isomers. [2]

Outline how a polarimeter can distinguish between these isomers.

f. Describe the formation of σ and π bonds in an alkene. [2]

g. The two most abundant isotopes of bromine have the mass numbers 79 and 81. [2]

Calculate the relative abundance of $^{79}\mathrm{Br}$ using table 5 of the data booklet, assuming the abundance of the other isotopes is negligible.

Markscheme

a.i. *Ethanal*: distill off product as it forms;

Accept distillation.

Ethanoic acid: (heat under) reflux / use excess oxidizing agent;

a.ii *Ethanol:* –2/–II;

Ethanal: –1/–I;

Do not accept 2–, 1– but penalize once only.

a.iii $\mathrm{CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-}$;

Half-equation required. Do not accept $C_2H_5OH + 2[O] \rightarrow CH_3CHO + H_2O$.

Accept e for e^-.

a.iv. $3CH_3CH_2OH(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3CH_3CHO(l) + 7H_2O(l)$

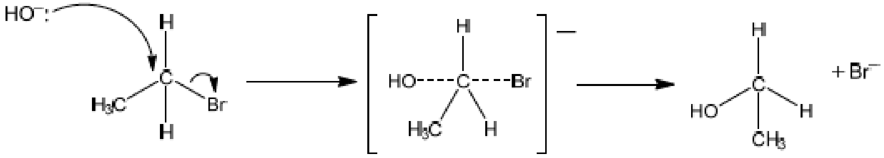
correct reactants and products;

correct balancing;

M2 can only be scored if M1 correct.

Ignore state symbols.

b.



curly arrow going from lone pair/negative charge on O in HO^- to C;

Do not allow curly arrow originating on H in HO^-.

curly arrow showing Br leaving;

Accept curly arrow either going from bond between C and Br to Br in bromoethane or in the transition state.

representation of transition state showing negative charge, square brackets and partial bonds;

Do not penalize if HO and Br are not at 180° to each other.

Do not award M3 if OH----C bond is represented.

formation of organic product CH_3CH_2OH **and** Br^-;

*Award **[3 max]** for correct S_N1 mechanism.*

c.i. $[NaOH]$ / $[OH^-]$ is 1/first order **and** $[C_4H_9Br]$ is 1/first order;

$\text{rate} = k[OH^-][C_4H_9Br]$ / $\text{rate} = k[NaOH][C_4H_9Br]$;

Square brackets must be used for M2.

c.ii. $\left(\frac{1.02\times10^{-4}}{0.25\times0.25} =\right) 0.0016/1.6 \times 10^{-3}$;

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

Accept $M^{-1}s^{-1}$.

Ignore order of units.

Must use experiment 3 data.

c.iii. bimolecular/2;

Accept dimolecular.

d.i. chiral/asymmetric carbon / carbon attached to 4 different groups / non-super imposable mirror images;

d.ii. enantiomers rotate plane of (plane-) polarized light;

in opposite directions (by equal amounts);

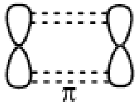
f. *Sigma bonds*:

result from head-on/end-on overlap of orbitals / *OWTTE*;

Accept axial overlap of orbitals.

Accept "symmetric orbital" with respect to same plane / OWTTE.

Pi bonds:



/

result from sideways overlap of orbitals / *OWTTE*;

Accept "antisymmetric orbitals" with respect to (defining) plane (containing at least one atom) / OWTTE.

g. $79.91 = 79x + 81(1 - x)$;

Award M1 for any suitable calculation.

(abundance $^{79}\mathrm{Br} =$) 54.5%;

*Award **[2]** for correct final answer.*

Examiners report

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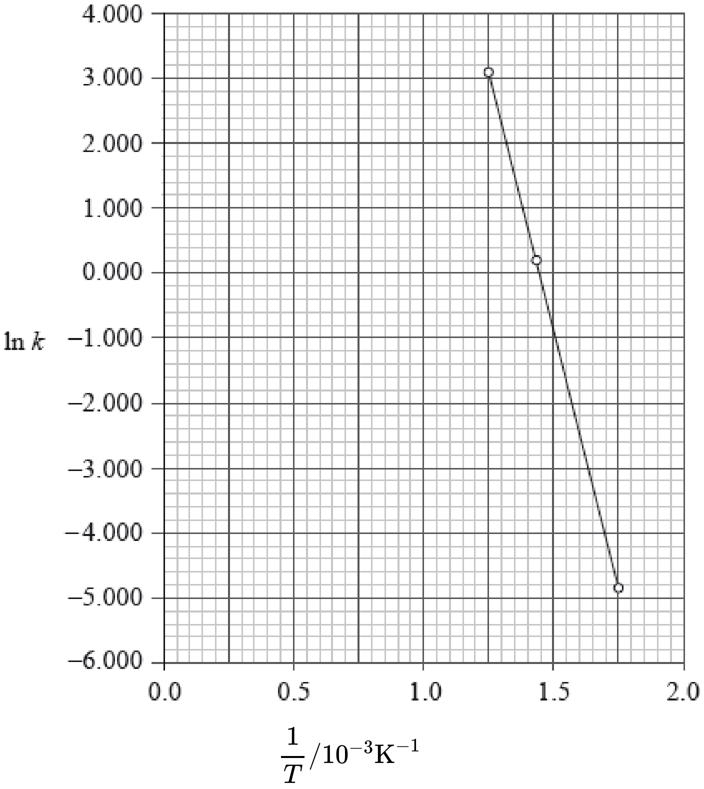
g. The idea of “reflux” was usually given for the production of ethanoic acid in (a) but ethanal was less clear. We accept that perhaps we should have phrased (a) (ii), “Determine the *average* oxidation number of carbon in …” In practice, this was one of the best answered parts and caused few difficulties. Few had any idea how to attempt the half-equation in (iii) and the overall equation in (iv). Although the mechanism in (b) has been set on numerous occasions, candidates are still not taking care over the start and finish of the curly arrows and the intermediate is drawn poorly. It must have partial bonds and the sign must be outside the square brackets. Some candidates offered an $\mathrm{S_N1}$ mechanism. In (c) (ii), the orders were usually successfully deduced but many omitted to give the overall rate expression. In part (ii), quite a number of candidates unaccountably ignored the instruction and used any experiment but No 3. The units were frequently wrong or omitted. The molecularity was answered satisfactorily. In (d), candidates frequently stated that the molecules have mirror images but not that these mirror images are non-superposable. “Chiral” was a popular correct answer. There seemed to be little understanding of a polarimeter with some suggesting that the crystals themselves rotate. In (e) the equations were poor and few were able to identify the reagent. Most descriptions in (f) would have been improved with a careful and clear diagram. Part (g), the relative abundance of $^{79}\mathrm{Br}$ was well done except by those who tried to do it “by inspection”; this usually led to the wrong answer.

The reaction between carbon monoxide, CO(g), and nitrogen dioxide, $\mathrm{NO_2(g)}$, was studied at different temperatures and a graph was plotted of $\ln k$ against $\frac{1}{T}$. The equation of the line of best fit was found to be:

$$\ln k = -1.60 \times 10^4 \left(\frac{1}{T}\right) + 23.2$$



a. (i) State the **full** electron configuration of Fe. [8]

(ii) State the **abbreviated** electron configuration of $\mathrm{Fe^{3+}}$ ions.

(iii) Cyanide ions, $\mathrm{CN^-}$, can act as ligands. One complex ion that involves the cyanide ion is $[\mathrm{Fe(CN)_6}]^{3-}$. Identify the property of a cyanide ion which allows it to act as a ligand, and explain the bonding that occurs in the complex ion in terms of acid–base theory. Describe the structure of the complex ion, $[\mathrm{Fe(CN)_6}]^{3-}$.

(iv) Explain why complexes of $\mathrm{Fe^{3+}}$ are coloured.

c. (i) The Arrhenius equation is shown in Table 1 of the Data Booklet. Identify the symbols k and A. [6]

k:

A:

(ii) Calculate the activation energy, E_a, for the reaction between CO(g) and $\mathrm{NO_2(g)}$.

(iii) Calculate the numerical value of A.

Markscheme

a. (i) $\mathrm{1s^22s^22p^63s^23p^63d^64s^2/1s^22s^22p^63s^23p^64s^23d^6}$;

(ii) $\mathrm{[Ar]3d^5}$;

(iii) lone pair of electrons (on C);

$\mathrm{CN^-}$ acts as a Lewis base / $\mathrm{Fe^{3+}}$ acts as a Lewis acid;

dative covalent/coordinate bond formed (between $\mathrm{CN^-}$ and $\mathrm{Fe^{3+}}$);

ligands occupy an octahedral shape around central metal ion / coordination number of $\mathrm{Fe^{3+}}$ is 6;

(iv) d sub-level splits (into two sets of orbitals of different energy) / $\_\,\bar{\ }\,\_\,\bar{\ }\,\_\updownarrow\Delta E$;

colour due to electron transitions between (split) d orbitals;

c. (i) k:

rate constant;

A:

Arrhenius constant / frequency/pre-exponential factor;

(ii) $\text{gradient} = \frac{-E_\mathrm{a}}{R} / E_\mathrm{a} = -\text{gradient} \times R$;

$(= -(-16) \times 8.31) = +133\ (\mathrm{kJ\,mol^{-1}}) / 1.33 \times 10^5\ (\mathrm{J\,mol^{-1}})$;

(iii) $\ln \mathrm{A} = (\text{intercept on } y\text{ - axis} =)\ 23.2$;

$\mathrm{A} = 1.190 \times 10^{10}$;

Examiners report

a. Most candidates had no difficulty with the full electron configuration of Fe in (a) but many could not write the abbreviated electron configuration of $\mathrm{Fe^{3+}}$, losing 3d electrons ahead of 4s. Some G2 comments suggested that the word abbreviated caused problems, but this is stated in the teacher‘s notes and most candidates seemed to have no difficulty with the term. Descriptions of cyanide ions acting as ligands were particularly well expressed but some candidates had difficulty explaining why $\mathrm{Fe^{3+}}$ ions are coloured, referring to excited orbitals emitting light.

c. In part (c) most candidates identified the symbols of the Arrhenius equation. Many calculated the activation energy, although several calculated the gradient from the graph rather than using the equation of the line of best fit. (This was accepted, but made the question much harder than intended.) Several candidates also calculated the numerical value of A correctly.

The rate of the acid-catalysed iodination of propanone can be followed by measuring how the concentration of iodine changes with time.

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

The general form of the rate equation is:

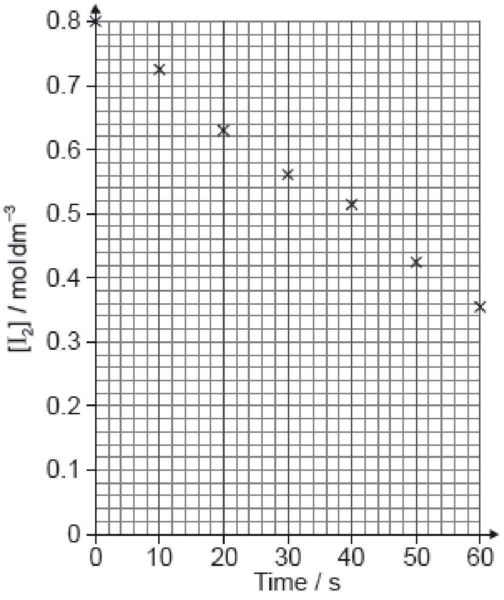
$$\text{Rate} = [H_3CCOCH_3(aq)]^m \times [I_2(aq)]^n \times [H^+(aq)]^p$$

The reaction is first order with respect to propanone.

a.i. Suggest how the change of iodine concentration could be followed. [1]

a.ii A student produced these results with $[\mathrm{H}^+] = 0.15\ \mathrm{mol\,dm^{-3}}$. Propanone and acid were in excess and iodine was the limiting reagent. [2]

Determine the relative rate of reaction when $[\mathrm{H}^+] = 0.15\ \mathrm{mol\,dm^{-3}}$.



b. The student then carried out the experiment at other acid concentrations with all other conditions remaining unchanged. [2]

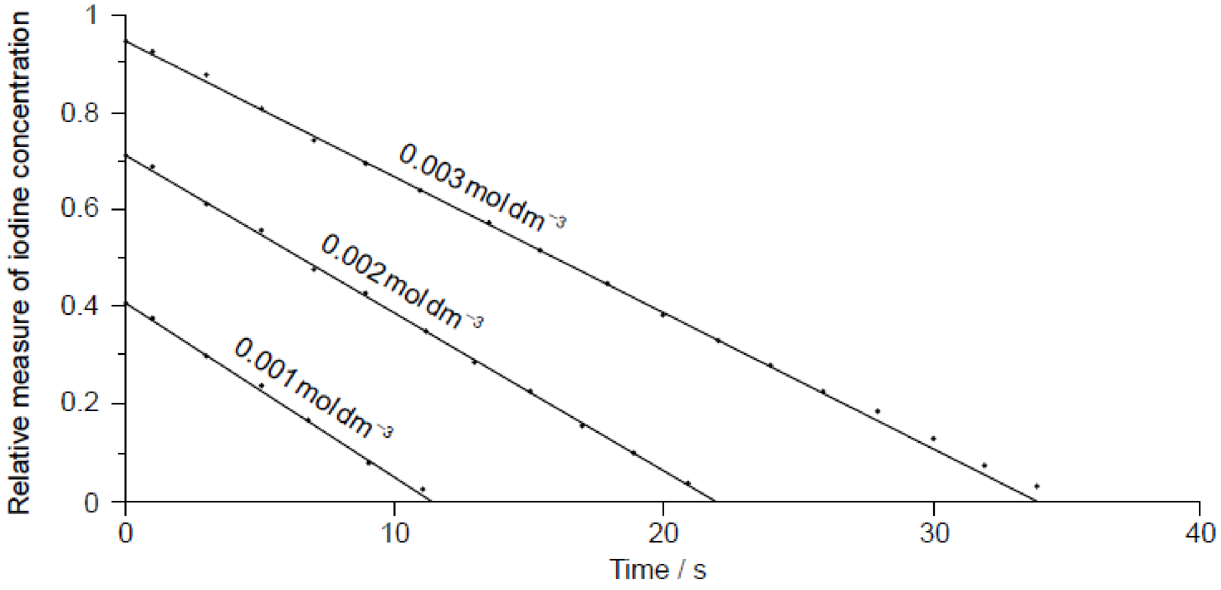
$[H^+]$ / mol dm^{-3}	Relative rate of reaction
0.05	0.0025
0.10	0.0051
0.20	0.0100

Determine the relationship between the rate of reaction and the concentration of acid and the order of reaction with respect to hydrogen ions.

Relationship:

Order of reaction with respect to $[H^+]$:

c. When the concentration of iodine is varied, while keeping the concentrations of acid and propanone constant, the following graphs are obtained. [2]



Deduce, giving your reason, the order of reaction with respect to iodine.

Order with respect to iodine:

. . . .

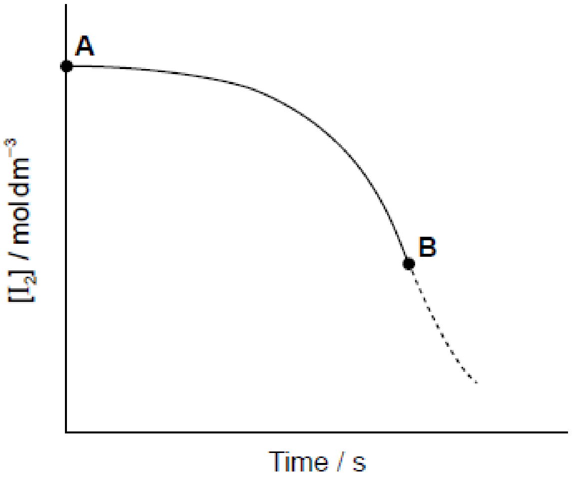
Reason:

. . . .

. . . .

. . . .

d. When the reaction is carried out in the absence of acid the following graph is obtained. [2]



Discuss the shape of the graph between A and B.

Markscheme

a.i. use a colorimeter/monitor the change in colour

OR

take samples ***AND*** quench ***AND*** titrate «with thiosulfate»

Accept change in pH.

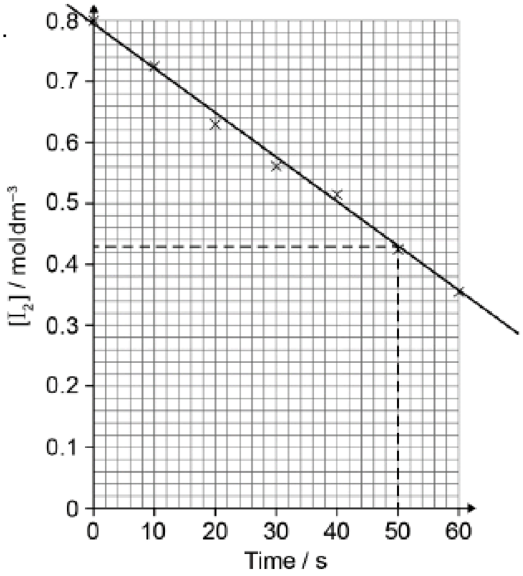
Accept change in conductivity.

Accept other suitable methods.

Method must imply "change".

[1 mark]

a.ii.



best fit line

relative rate of reaction $= \ll \frac{-\Delta y}{\Delta x} = \frac{-(0.43-0.80)}{50} = \gg \ 0.0074/7.4 \times 10^{-3}$

Best fit line required for M1.

M2 is independent of M1.

Accept range from 0.0070 to 0.0080.

[2 marks]

b. *Relationship:*

rate of reaction is «directly» proportional to [H$^+$]

OR

rate of reaction α [H$^+$]

Order of reaction with respect to [H$^+$]:
first

Accept "doubling the concentration doubles the rate".

*Do **not** accept "rate increases as concentration increases".*

[2 marks]

c. zero order

rate of reaction is the same for all concentrations of iodine

Accept "all graphs have same/similar gradient".

[2 marks]

d. slow rate of reaction which gradually increases

as H^+ ions are produced «to catalyse the reaction»
OR
reaction is autocatalytic

M1 should mention "rate of reaction".

[2 marks]

Examiners report

a.i. [N/A]
a.ii. [N/A]
b. [N/A]
c. [N/A]
d. [N/A]

The reaction between hydrogen and nitrogen monoxide is thought to proceed by the mechanism shown below.

$$2NO(g) \rightleftharpoons N_2O_2(g) \qquad \text{fast equilibrium}$$

$$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g) \qquad \text{slow reaction}$$

$$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g) \qquad \text{fast reaction}$$

a. (i) State the equation for the overall reaction. [7]

(ii) Deduce the rate expression consistent with this mechanism.

(iii) Explain how you would attempt to confirm this rate expression, giving the results you would expect.

(iv) State, giving your reason, whether confirmation of the rate expression would prove that the mechanism given is correct.

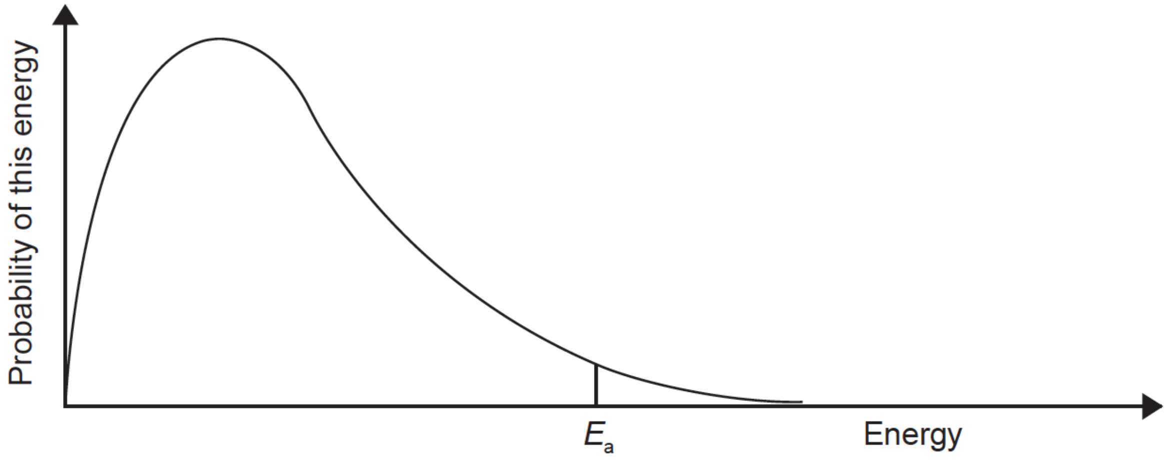
(v) Suggest how the rate of this reaction could be measured experimentally.

b. The enthalpy change for the reaction between nitrogen monoxide and hydrogen is –664 kJ and its activation energy is 63 kJ. [6]

(i) Sketch the potential energy profile for the overall reaction, using the axes given, indicating both the enthalpy of reaction and activation energy.

(ii) This reaction is normally carried out using a catalyst. Draw a dotted line labelled “Catalysed” on the diagram above to indicate the effect of the catalyst.

(iii) Sketch and label a second Maxwell–Boltzmann energy distribution curve representing the same system but at a higher temperature, T_{higher}.



(iv) Explain why an increase in temperature increases the rate of this reaction.

c. One of the intermediates in the reaction between nitrogen monoxide and hydrogen is dinitrogen monoxide, N_2O. This can be represented by the resonance structures below: [4]

(i) Analyse the bonding in dinitrogen monoxide in terms of σ-bonds and Δ-bonds.

(ii) State what is meant by resonance.

Markscheme

a. (i)

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

(ii)
rate = k $[NO]^2[H_2]$

(iii)
test the effect «on the reaction rate» of varying each concentration «independently»
OR
test the effect of varying [NO] «on rate», whilst keeping $[H_2]$ constant ***AND*** test effect of varying $[H_2]$ «on rate», whilst keeping [NO] constant

rate proportional to $[NO]^2$
OR
doubling [NO] quadruples rate

rate proportional to $[H_2]$
OR
doubling $[H_2]$ doubles rate

*Remember to refer back to a (ii) for **ECF**.*

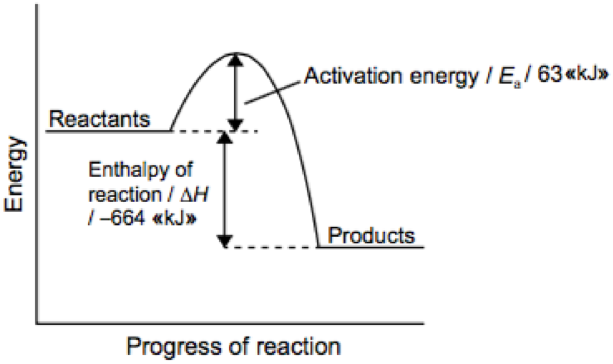
If only one species in rate expression, third mark can be awarded for zero order discussion.

(iv)
no ***AND*** different mechanisms could give the same rate expression
OR
no ***AND*** mechanisms can only be disproved
OR
no ***AND*** just suggest it is consistent with the mechanism given
OR
no ***AND*** does not give information about what occurs after RDS

(v)
change of pressure «at constant volume and temperature» with time
OR
change of volume «at constant pressure and temperature» with time

Accept other methods where rate can be monitored with time

b. (i)

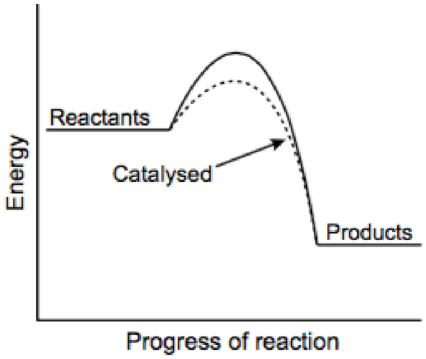


products lower than reactants ***AND*** enthalpy of reaction correctly marked and labelled with name or value

activation energy correctly marked and labelled with name or value

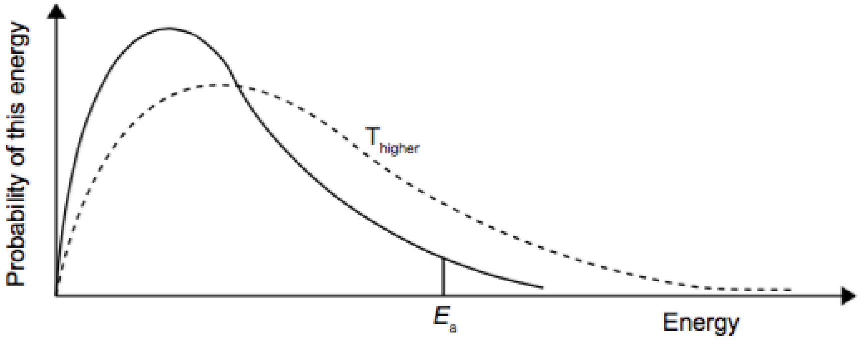
Accept other clear ways of indicating energy/ enthalpy changes.

(ii)



lower dotted curve, between same reactants and products levels, labelled “Catalysed”

(iii)



second curve at a higher temperature is correctly drawn (maximum lower and to right of original)

(iv)

greater proportion of molecules have E ≥ E_a or E > E_a

OR

greater area under curve to the right of the E_a

greater frequency of collisions «between molecules»
OR
more collisions per unit time/second

*Do **not** accept just particles have greater kinetic energy.*

*Do **not** accept just “more collisions”.*

c. (i)

ALTERNATIVE 1:

σ-bond from N to N ***AND*** from N to O

π-bond from N to N

<u>delocalized</u> π-bond/π-electrons «extending over the oxygen and both nitrogens»

ALTERNATIVE 2:
both have 2 σ-bonds «from N to N and from N to O» ***AND*** π-bond from N to N
one structure has second π-bond from N to N and the other has π-bond from N to O
delocalized π-bond/π-electrons

*Award **[1 max]** if candidate has identified both/either structure having 2 σ-bonds and 2 π-bonds*

(ii)
more than one possible position for a multiple/π-/pi- bond

Accept "more than one possible Lewis structure".

Accept reference to delocalisation if M3 not awarded in c (i).

Accept reference to fractional bond orders.

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]