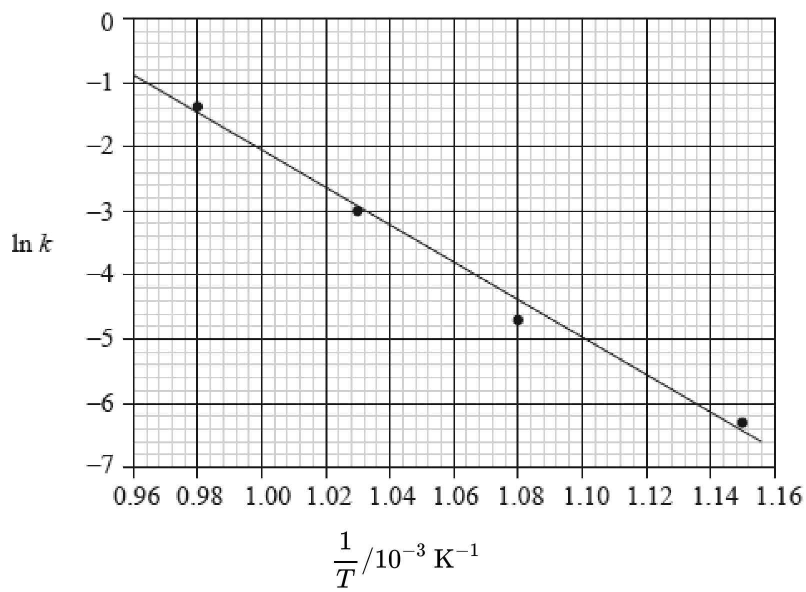
# HL Paper 2

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.

$$N_2O \rightarrow N_2 + O$$




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 $0.244\ \mathrm{dm^3 mol^{-1} s^{-1}}$ at 750 °C. [2]

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

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Consider the following reaction studied at 263 K.

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

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

Consider the following equilibrium reaction.

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

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

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

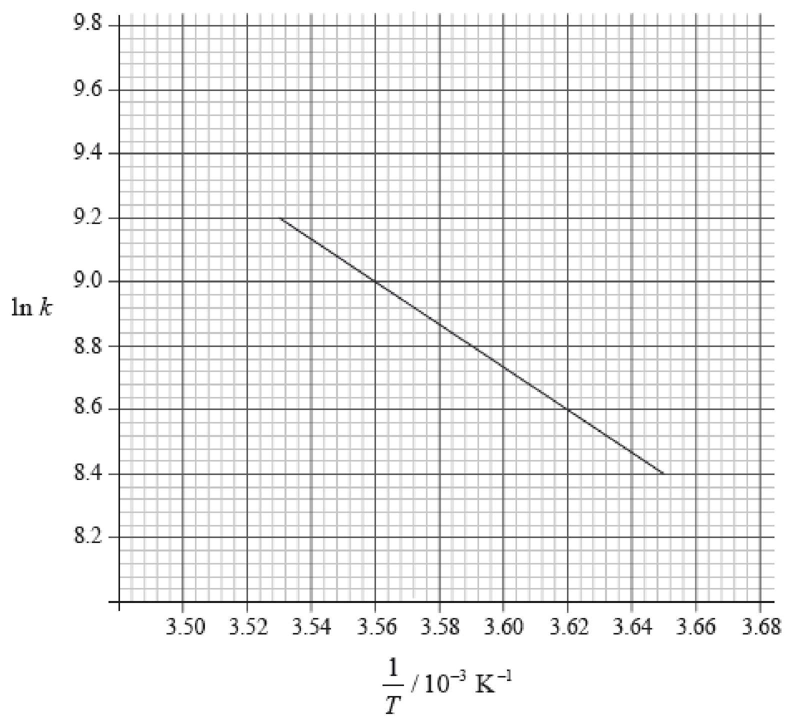
Possible reaction mechanisms are:

| | | |
|---|---|---|
| Above 775 K: | $NO_2 + CO \rightarrow NO + CO_2$ | slow |
| Below 775 K: | $2NO_2 \rightarrow NO + NO_3$ | slow |
| | $NO_3 + CO \rightarrow NO_2 + CO_2$ | fast |

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 $N_2O_4$ into $NO_2$. Determine the activation energy in $kJ\ mol^{-1}$ 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]

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.

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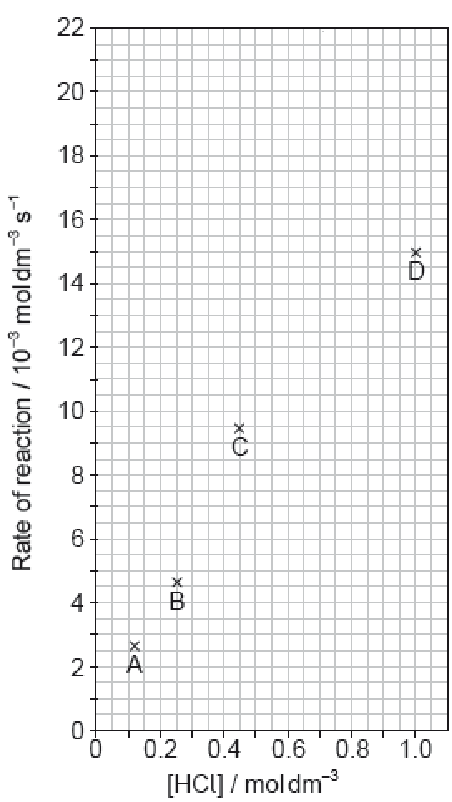
Calcium carbonate reacts with hydrochloric acid.

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

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]

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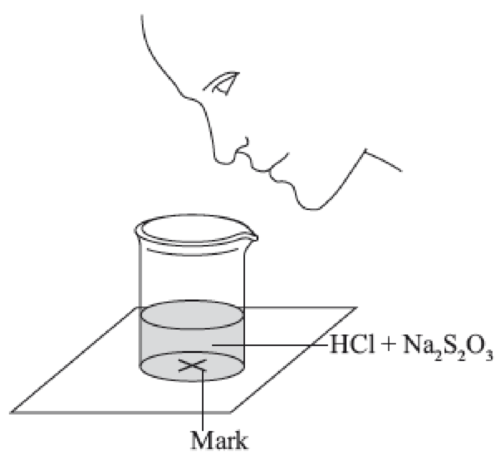
A group of students investigated the rate of the reaction between aqueous sodium thiosulfate and hydrochloric acid according to the equation below.

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

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

One proposed mechanism for this reaction is:

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

$HS_2O_3^-(aq) + H^+(aq) \rightarrow SO_2(g) + S(s) + H_2O(l)$ 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 mol dm$^{-3}$ HCl | 0.0200 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.

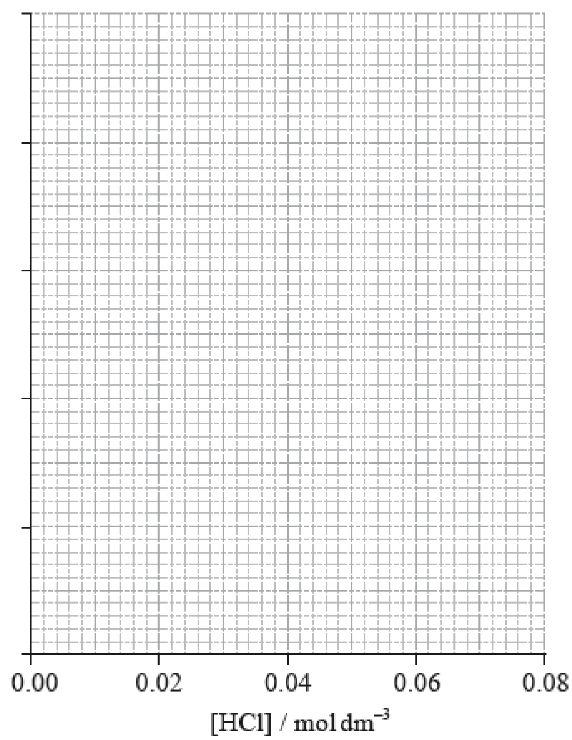
(iii) If the reaction were first order with respect to the thiosulfate ion, predict the time it would take for the mark on the paper to be obscured when the concentration of sodium thiosulfate solution is halved.

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, $T_1$ [6]

and $T2$ $(T_2 > T_1)$, at which the rate of reaction would be significantly different.

(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 $1.00 \times 10^5$ 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 $1.25 \times 10^{-2}$ mol dm$^{-3}$, determine the pH of a $2.00$ mol dm$^{-3}$ solution of sulfur dioxide.

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

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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.

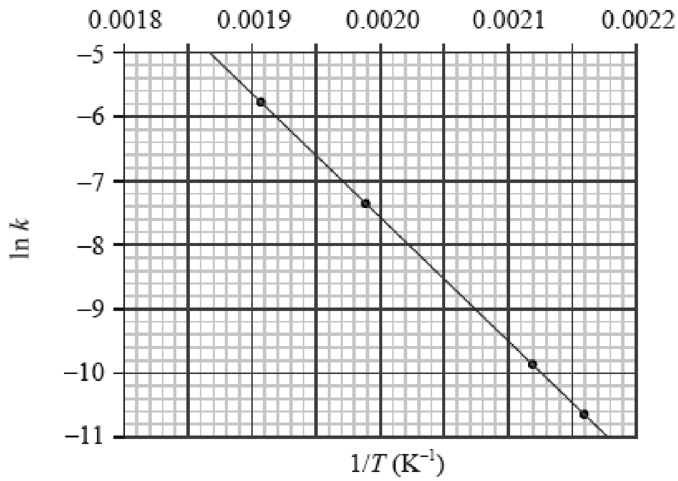
$$\text{Step 1:} \quad N_2O(g) \xrightarrow{k_1} N_2(g) + O(g)$$
$$\text{Step 2:} \quad N_2O(g) + O(g) \xrightarrow{k_2} N_2(g) + O_2(g)$$

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, $\Delta H$, 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]

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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 $C_4H_9Br$ and NaOH, using the data above. [3]

$C_4H_9Br$

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 $S_N1$ and $S_N2$ type mechanisms. Explain why $C_4H_9Br$ reacts via the mechanism described in (d) (i). [1]

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

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

$$BF_3(g) + NH_3(g) \rightarrow F_3BNH_3(g)$$

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

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

e.i. Identify the type of bond present between $BF_3$ and $NH_3$ in $F_3BNH_3(g)$ 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 | $[BF_3(g)]$ / mol dm$^{-3}$ | $[NH_3(g)]$ / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | $1.00 \times 10^{-1}$ | $6.67 \times 10^{-2}$ | $2.27 \times 10^{-2}$ |
| 2 | $1.00 \times 10^{-1}$ | $3.75 \times 10^{-2}$ | $1.28 \times 10^{-2}$ |
| 3 | $2.50 \times 10^{-1}$ | $2.50 \times 10^{-1}$ | $2.13 \times 10^{-1}$ |
| 4 | $3.00 \times 10^{-1}$ | $1.00 \times 10^{-1}$ | $1.02 \times 10^{-1}$ |

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 $\text{rate} = k[NO]^2[H_2]$. 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 $NO_2(g)$ with CO (g), where $k_2 \gg k_1$. [2]

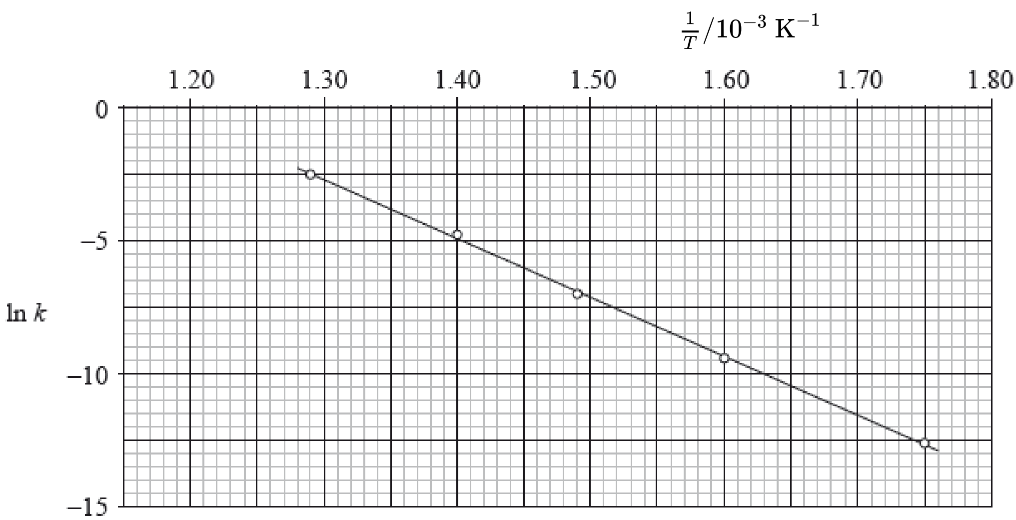
$$\text{Step 1} \quad NO_2(g) + NO_2(g) \xrightarrow{k_1} NO(g) + NO_3(g)$$
$$\text{Step 2:} \quad NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$$
$$\text{Overall:} \quad NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

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.

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]

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

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

Reaction B is much faster than reaction A, so the iodine, $I_2$, formed in reaction A immediately reacts with thiosulfate ions, $S_2O_3^{2-}$, 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 $cm^3$ of 2.00 $mol\,dm^{-3}$ hydrogen peroxide ($H_2O_2$)

5.0 ± 0.1 $cm^3$ of 1% aqueous starch

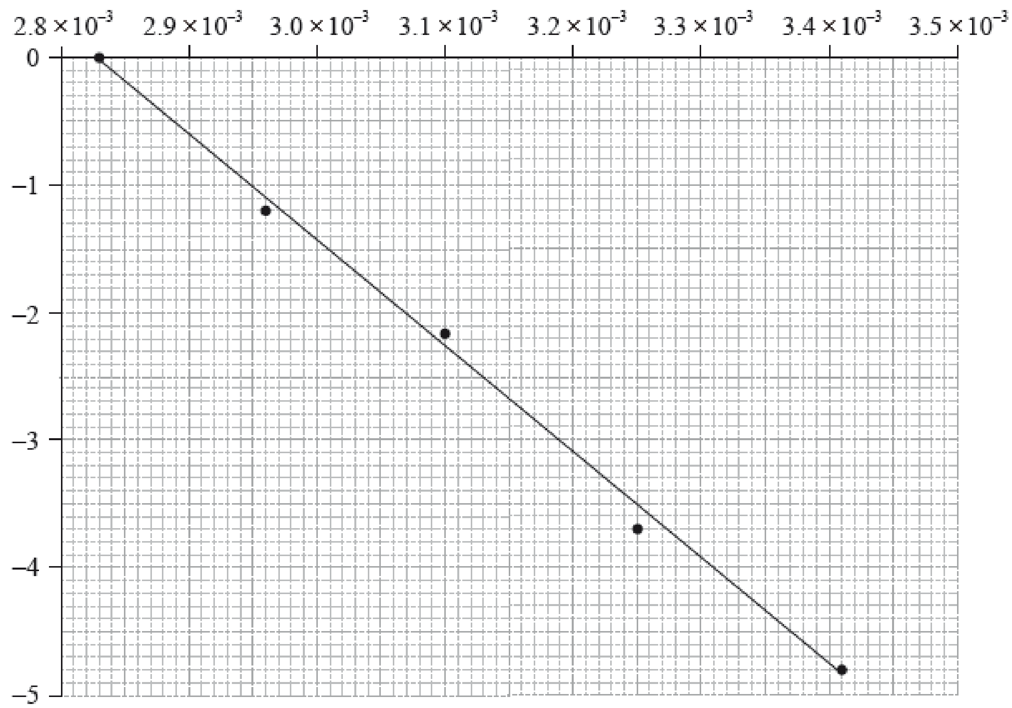
20.0 ± 0.1 $cm^3$ of 1.00 $mol\,dm^{-3}$ sulfuric acid ($H_2SO_4$)

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

50.0 ± 0.1 $cm^3$ 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 $cm^3$, 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 $1.00 \times 10^{-4}$ 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:

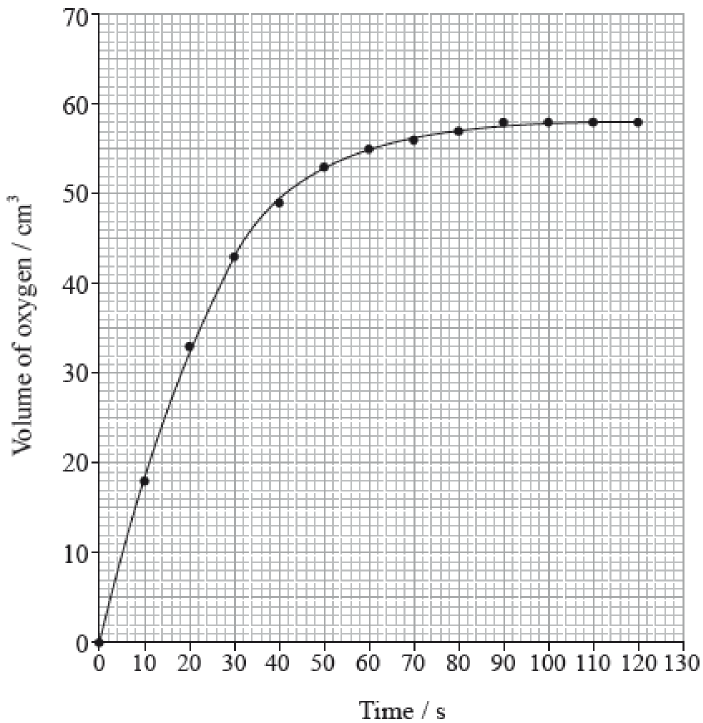
f.ii. Use the graph to determine the activation energy of the reaction, in $kJ\ mol^{-1}$, correct to **three** significant figures. [3]

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]

Hydrogen peroxide decomposes according to the equation below.

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

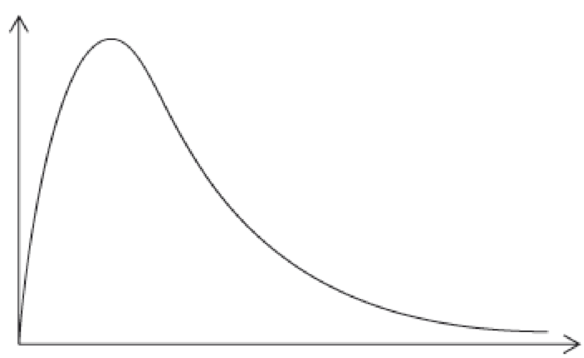
The rate of the decomposition can be monitored by measuring the volume of oxygen gas released. The graph shows the results obtained when a solution of hydrogen peroxide decomposed in the presence of a CuO catalyst.




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]



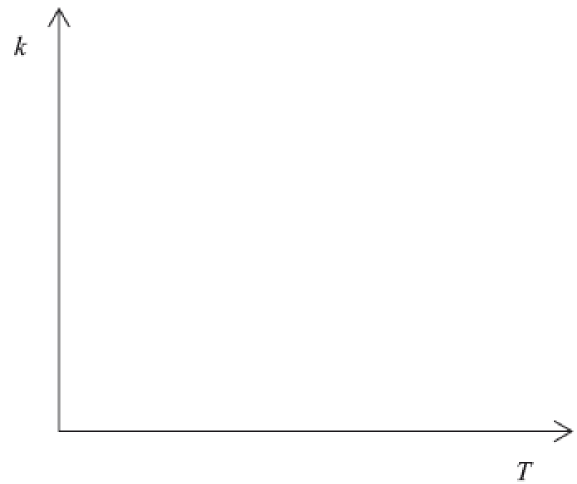
c. (i) In some reactions, increasing the concentration of a reactant does not increase the rate of reaction. Describe how this may occur. [2]

(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.

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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 $mol\ dm^{-3}$ $H^+(aq)$ | $5.00\times10^{-3}$ $mol\ dm^{-3}$ $I_2$ in KI | |
| 1 | 10.0 | 60.0 | 10.0 | 20.0 | $4.96\times10^{-6}$ |
| 2 | 10.0 | 50.0 | 10.0 | 30.0 | $5.04\times10^{-6}$ |
| 3 | 5.0 | 65.0 | 10.0 | 20.0 | $2.47\times10^{-6}$ |
| 4 | 10.0 | 65.0 | 5.0 | 20.0 | $2.51\times10^{-6}$ |

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.

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Consider the following sequence of reactions.

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

$RCH_3$ 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 | $2.0\times10^{-2}$ | $2.0\times10^{-2}$ | $4.0\times10^{-3}$ |
| 2 | $2.0\times10^{-2}$ | $4.0\times10^{-2}$ | $4.0\times10^{-3}$ |
| 3 | $4.0\times10^{-2}$ | $4.0\times10^{-2}$ | $8.0\times10^{-3}$ |

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 $S_N2$. 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 $C_4H_9Br$. 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]

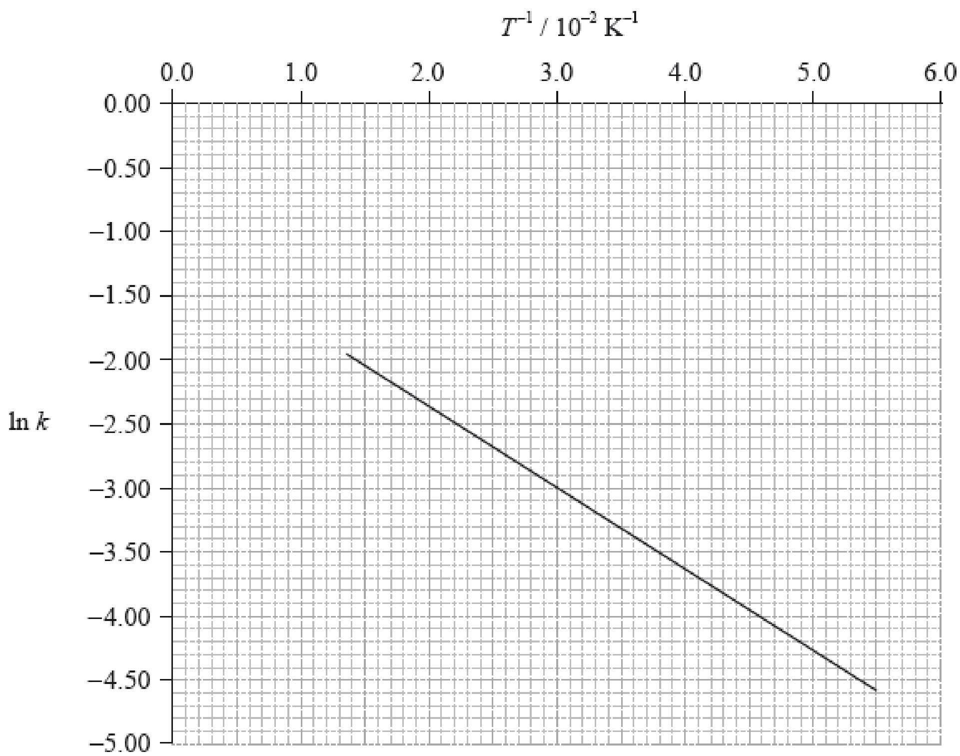
(ii) Determine the value of the rate constant for the reaction and state its units.

(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.

---

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.



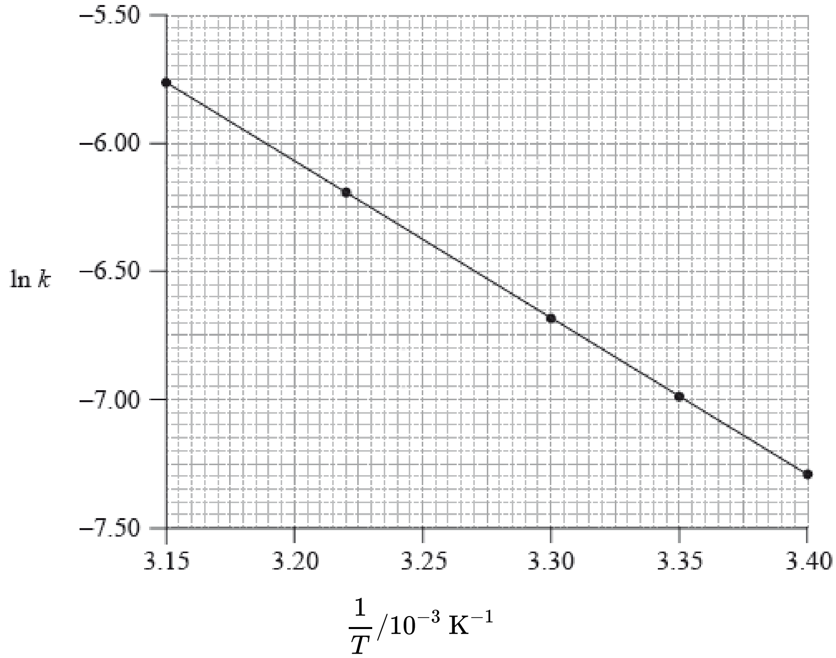

a. Define the term *activation energy*, $E_a$. [1]

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

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

---

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]

---

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

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

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

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

$$\text{rate} = k[H_2(g)][NO(g)]^2$$

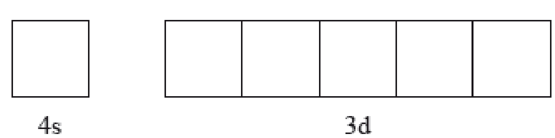
When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:

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

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 $[Cu(H_2O)_6]^{2+}$ ion is coloured and why the $[CuCl_4]^{2-}$ 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.

---

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.

---

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 $\rightarrow$ 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 | $1.00\times10^{-1}$ | $1.00\times10^{-1}$ | $2.30\times10^{-1}$ |
| 2 | $5.00\times10^{-2}$ | $1.00\times10^{-1}$ | $5.75\times10^{-2}$ |
| 3 | $5.00\times10^{-2}$ | $3.00\times10^{-2}$ | $1.73\times10^{-2}$ |

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.

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

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

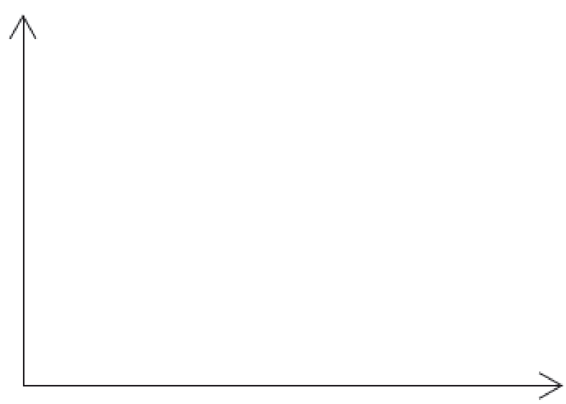
(ii) Temperature and the addition of a catalyst are two factors that can affect the rate of a reaction. State **two** other factors.

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

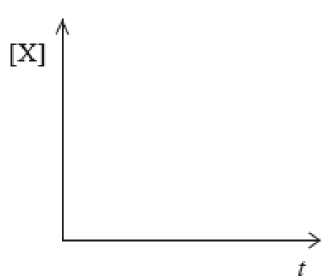
$$ClO_3^-(aq) + 5Cl^-(aq) + 6H^+(aq) \rightarrow 3Cl_2(aq) + 3H_2O(l)$$

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

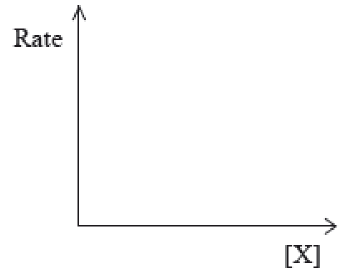
(ii) Sketch the **two** Maxwell–Boltzmann energy distribution curves for a fixed amount of gas at two different temperatures, $T_1$ and $T_2$ $(T_2 > T_1)$. Label **both** axes.



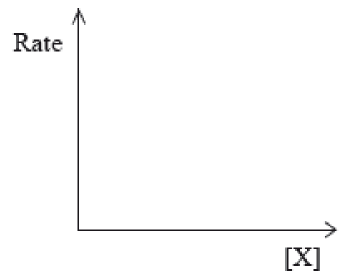
c. (i) Concentration of reactant X against time for a **zero-order** reaction. [3]




(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]

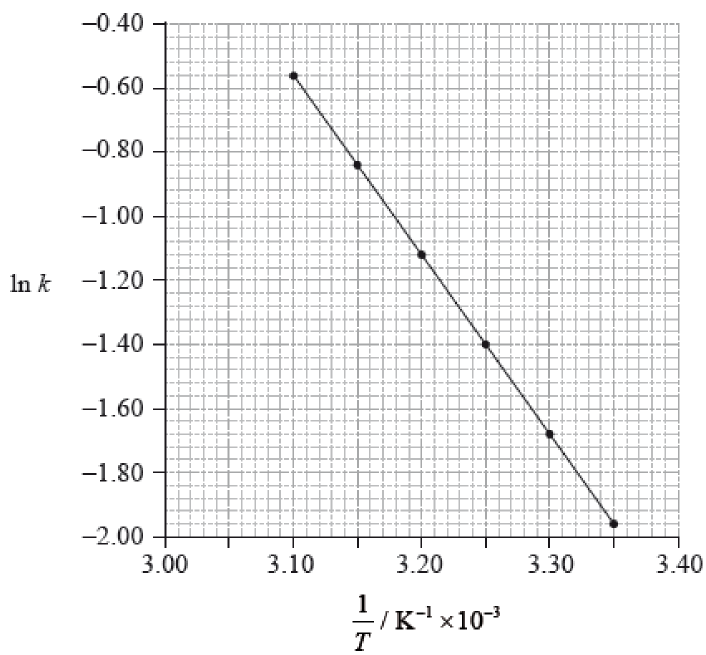
(ii) Determine the rate constant, $k$, and state its units, using the data from Experiment 2.

(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:

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.

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]

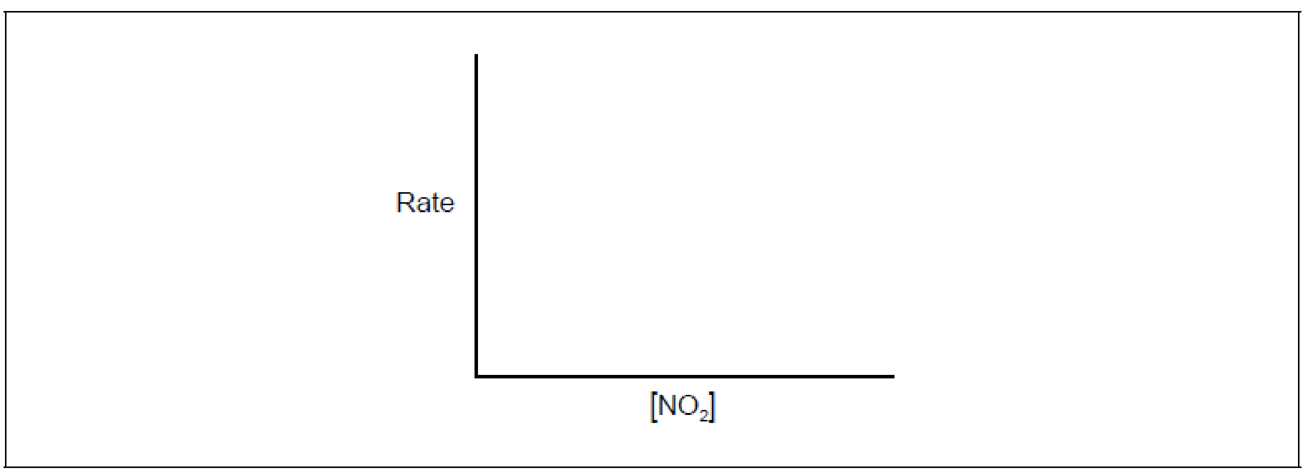
b.ii. The following mechanism is proposed for the reaction. [1]

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

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.

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** | $1.30 \times 10^{-1}$ | $1.30 \times 10^{-1}$ | $3.95 \times 10^{-1}$ |
| **2** | $1.30 \times 10^{-1}$ | $2.60 \times 10^{-1}$ | $7.90 \times 10^{-1}$ |
| **3** | $2.60 \times 10^{-1}$ | $2.60 \times 10^{-1}$ | 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:

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

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

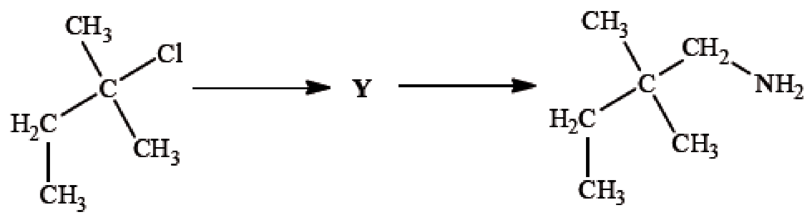
2-methylbutan-2-ol, $(CH_3)_2C(OH)CH_2CH_3$, is a liquid with a smell of camphor that was formerly used as a sedative. One way of producing it starts with 2-methylbut-2-ene.

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**:

---

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 | $1.66 \times 10^{-3}$ |
| 2 | 0.50 | 1.00 | $8.31 \times 10^{-4}$ |
| 3 | 0.25 | 0.25 | $1.02 \times 10^{-4}$ |
| 4 | 1.00 | 0.50 | $8.29 \times 10^{-4}$ |

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 $\sigma$ and $\pi$ bonds in an alkene. [2]

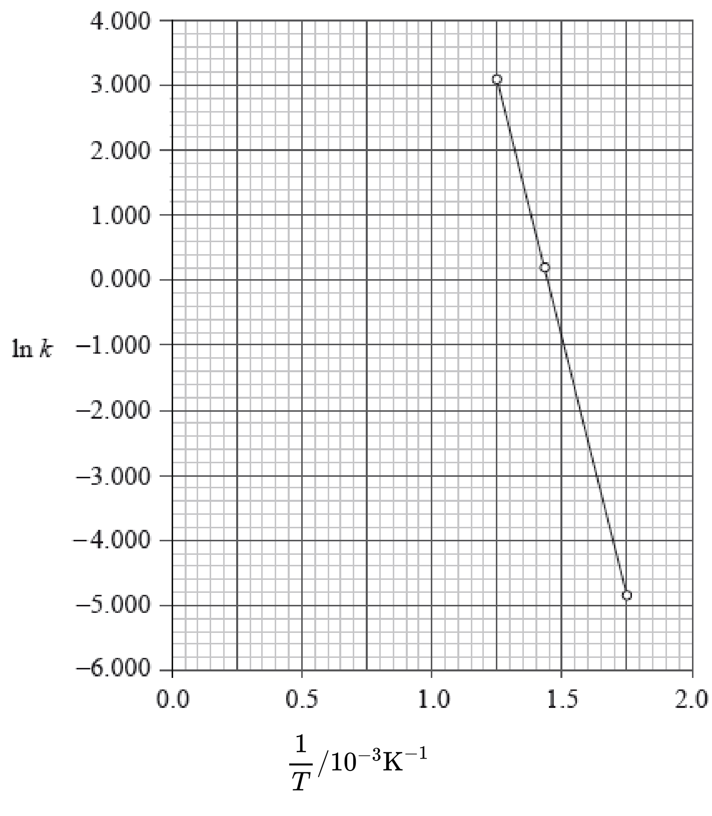
g. The two most abundant isotopes of bromine have the mass numbers 79 and 81. [2]

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

---

The reaction between carbon monoxide, CO(g), and nitrogen dioxide, $NO_2(g)$, 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 $Fe^{3+}$ ions.

(iii) Cyanide ions, $CN^-$, can act as ligands. One complex ion that involves the cyanide ion is $[Fe(CN)_6]^{3-}$. 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, $[Fe(CN)_6]^{3-}$.

(iv) Explain why complexes of $Fe^{3+}$ 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 $NO_2(g)$.

(iii) Calculate the numerical value of A.

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:

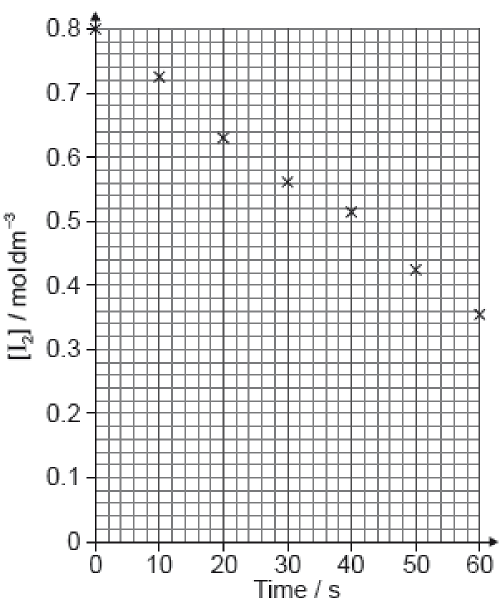
$$\text{Rate} = [H_3CCOCH_3(aq)]^m \times [I_2(aq)]^n \times [H^+(aq)]^p$$

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 $[H^+] = 0.15\ \text{mol dm}^{-3}$. Propanone and acid were in excess and iodine was the limiting reagent. [2]

Determine the relative rate of reaction when $[H^+] = 0.15\ \text{mol dm}^{-3}$.




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:

. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .

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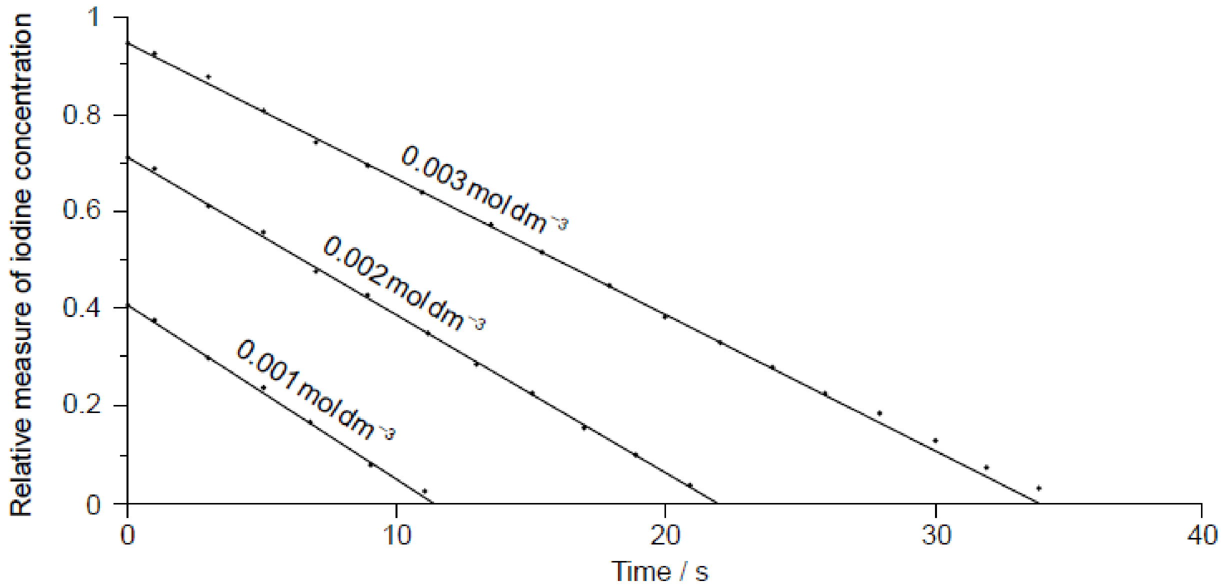
Order of reaction with respect to $[H^+]$:

. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .

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:

. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .

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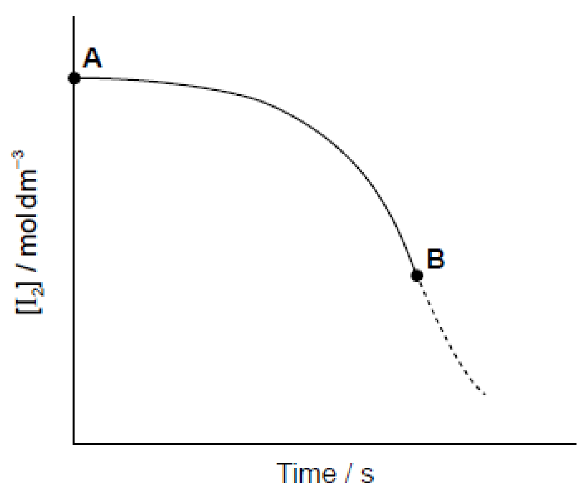
d. When the reaction is carried out in the absence of acid the following graph is obtained. [2]




Discuss the shape of the graph between A and B.

The reaction between hydrogen and nitrogen monoxide is thought to proceed by the mechanism shown below.

| | |
|---|---|
| $2NO(g) \rightleftharpoons N_2O_2(g)$ | fast equilibrium |
| $N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ | slow reaction |
| $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ | fast reaction |

a. (i) State the equation for the overall reaction. [7]

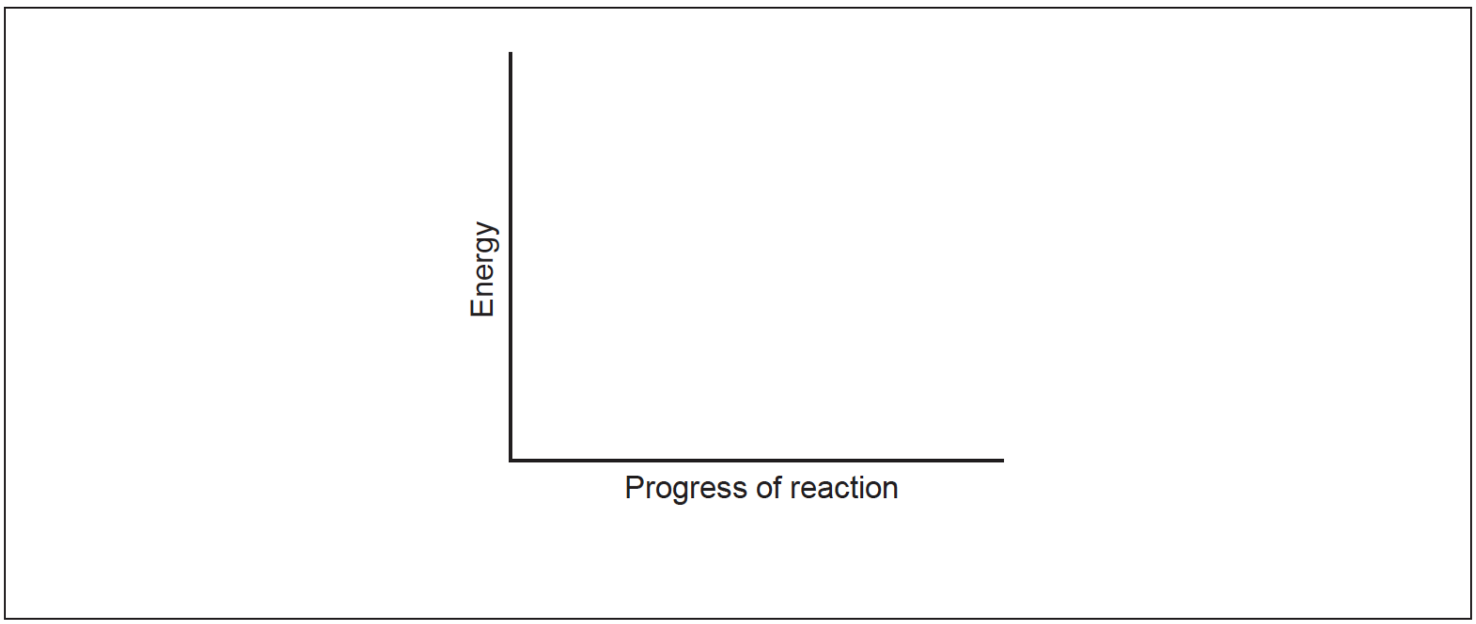
(ii) Deduce the rate expression consistent with this mechanism.

(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.

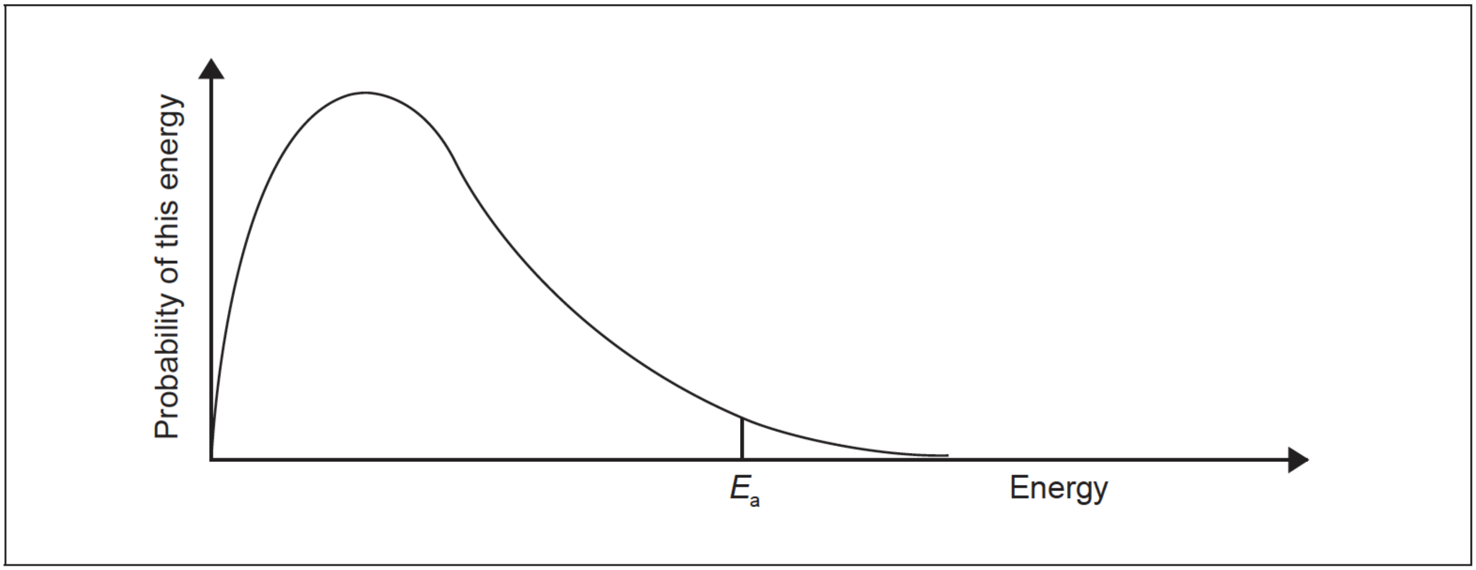
b. The enthalpy change for the reaction between nitrogen monoxide and hydrogen is –664 kJ and its activation energy is 63 kJ. [6]




(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.