CHEMISTRY

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question, or part question.

This document consists a total of **15** printed pages.

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1 **(a)** Explain, with the aid of a Boltzmann distribution curve, the effect of, when the following changes are applied separately:

(i) decreasing the temperature; [3]

(ii) using a catalyst; [2]

on the rate constant of a reaction.

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(b) The Arrhenius equation relates the rate constant of a reaction with respect to the temperature and activation energy. This equation is expressed as

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

where A is the activity constant, a proportionality constant,
R is the molar gas constant,
E_a is the activation energy, and
T is the temperature in Kelvin.

A student wishes to find the activation energy of a redox reaction between IO_x^- and I^- in acidic conditions. I_2 is the only iodine containing product.

(i) Showing your working clearly, construct a balanced chemical equation for the reaction between IO_x^- and I^-. The stoichiometric coefficient of IO_x^- should be 1. [2]

Part **(b)** continues on the next page.

The rate equation of the reaction is given by

$$\text{rate} = k\,[IO_x^-]^a\,[I^-]^b\,[H^+]^c$$

where *a*, *b*, *c* are constants.

At a temperature of *T* K, a solution containing iodide ions was added to an acidified solution of IO_x^- which also contains $S_2O_3^{2-}$ and starch solution.

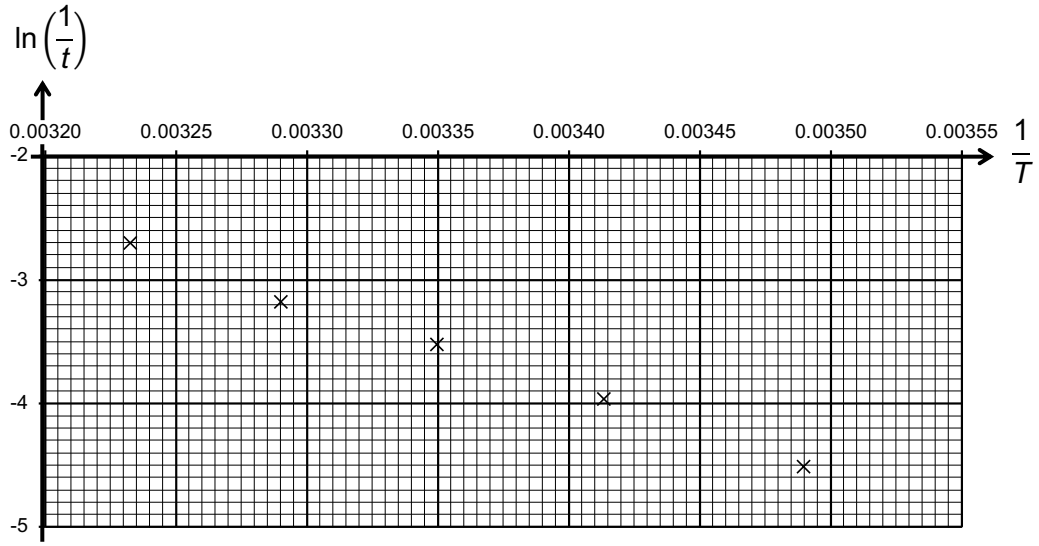
Iodine produced initially will react with $S_2O_3^{2-}$ ions via the equation below.

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

When all $S_2O_3^{2-}$ ions have been depleted, the solution will turn dark blue in colour. The time taken, *t* seconds, for the solution to turn dark blue in colour after mixing is recorded.

The experiment was repeated for different values of *T*, with the other reaction conditions kept the same.

A graph of $\ln\left(\frac{1}{t}\right)$ against $\frac{1}{T}$ was plotted below.



(ii) Define *order of reaction*. [1]

(iii) Explain why the amount of thiosulfate used in this reaction should be small. [1]

(iv) Explain why the reciprocal of *t* is proportional to the rate constant, although the rate constant is not explicitly computed. [1]

(v) Using the information provided in **(iv)**, and by linearising the Arrhenius equation, determine the activation energy of the reaction with an appropriate unit. [4]

(vi) Determine the units of A in the Arrhenius equation in terms of a, b and c. [1]

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[Total: 15]

2 **(a)** Enzymes exhibit substrate-specificity which is achieved by having active sites that have complementary shape, charge and hydrophobic or hydrophilic characteristics to substrates. The kinetics of an enzymatic reaction mechanism typically involves the binding on an enzyme, **E**, to a substrate, **S**, to form the enzyme-substrate complex, **ES**. The **ES** in turn reacts to form the enzyme-product complex via an alternative pathway with lower activation energy, and releases a product, **P**.

The enzyme-catalysed reaction may be represented schematically by:

$$\text{Step 1: } \mathbf{E} + \mathbf{S} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{ES}$$

$$\text{Step 2: } \mathbf{ES} \xrightarrow{k_{cat}} \mathbf{E} + \mathbf{P}$$

where k_f is the rate constant of the forward reaction of Step 1, k_b is the rate constant of the backward reaction of Step 1, and k_{cat} is the rate constant of Step 2.

(i) Explain why the rate of change of [**ES**] is given by

$$\frac{\mathrm{d}\,[\mathbf{ES}]}{\mathrm{d}t} = k_f\,[\mathbf{E}][\mathbf{S}] - k_b\,[\mathbf{ES}] - k_{cat}\,[\mathbf{ES}]$$

and find the rate of formation of **P** in terms of [**ES**]. [2]

(ii) The initial concentration of the enzyme, $[\mathbf{E}]_0$, is the sum of the concentration of the enzyme, [**E**], and the concentration of the enzyme-substrate complex, [**ES**], at any time, *t*. That is, $[\mathbf{E}]_0 = [\mathbf{E}] + [\mathbf{ES}]$.

Explain why $[\mathbf{E}]_0 = [\mathbf{E}] + [\mathbf{ES}]$. [1]

(iii) By assuming that

$$\frac{\mathrm{d}\,[\mathbf{ES}]}{\mathrm{d}t} = 0$$

derive an expression for [**ES**] in terms of $[\mathbf{E}]_0$, [**S**], k_f, k_b, k_{cat}. [2]

(iv) Use your answer to **(iii)** to show that the rate of product formation for the enzyme-catalysed reaction may be given by the Michaelis-Menten equation:

$$\frac{\mathrm{d}\,[\mathbf{P}]}{\mathrm{d}t} = k_{cat}[\mathbf{E}]_0 \frac{[\mathbf{S}]}{\mathrm{K_M} + [\mathbf{S}]} \text{ where } \mathrm{K_M} = \frac{k_b + k_{cat}}{k_f}$$ [2]

(v) Sketch a graph of the rate of reaction (rate of formation of **P**), against substrate concentration, [**S**]. [1]

Part **(a)** continues on the next page.

(vi) Explain the shape of your graph in **(v)**, **without** reference to the Michaelis-Menten equation. [2]

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(b) Concern has been expressed about the presence of a type of bacteria, called listeria, which is present in soft cheese and can be harmful. The danger is most acute due to the growth of listeria when the cheese is brought from a refrigerator to room temperature. At the temperature of the refrigerator (3 °C), the number of listeria cells doubles in 18 hours but, at room temperature (20 °C), the doubling time is reduced to 7 hours. This increase in rate can be attributed to the increase in the rate of enzyme-catalysed reaction.

The relationship between the doubling time *d* and the rate constant *k* of a reaction is given by:

$$kd = \ln 2$$

(i) Suggest and explain the overall order of reaction for the enzyme-catalysed reaction. [1]

(ii) Calculate the rate constants for the enzyme-catalysed reactions in listeria at

- 3 °C
- 20 °C [2]

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(c) State 2 reasons why an enzyme qualifies as a catalyst. [2]

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3 Under mildly acidic conditions, acetone can undergo a halogenation reaction with iodine to form iodopropanone, which is colourless in solution.

(a) One commonly accepted mechanism for this reaction is:

acetone → enol (*slow*)

enol + I_2 → iodopropanone + H^+ + I^-

(i) Deduce the order of reaction with respect to acetone and I_2. [1]

(ii) Hence construct a rate law for this reaction. You do **not** have to take into account the fact that H^+ ions catalyse this reaction. [1]

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(b) An experiment was conducted to determine the rate constant of this reaction.

Acetone was dissolved in a buffered solution (solution that maintains a constant pH). The concentration of acetone is 0.0100 mol dm^{-3}.

50.0 cm^3 of acetone was transferred into a conical flask. Then 50.0 cm^3 of aqueous iodine of the **same** concentration was transferred into the conical flask.

At 3 minutes intervals, 10 cm^3 of the solution was pipetted from the conical flask, and quenched with aqueous sodium hydrogencarbonate, $NaHCO_3$.

The aliquot was titrated against a known concentration of aqueous sodium thiosulfate, $Na_2S_2O_3$, which reacts with unreacted iodine in the aliquot. The volume of thiosulfate needed to reach the endpoint against the time elapsed since the transfer of aqueous iodine was plotted below in **Fig 3.1**.

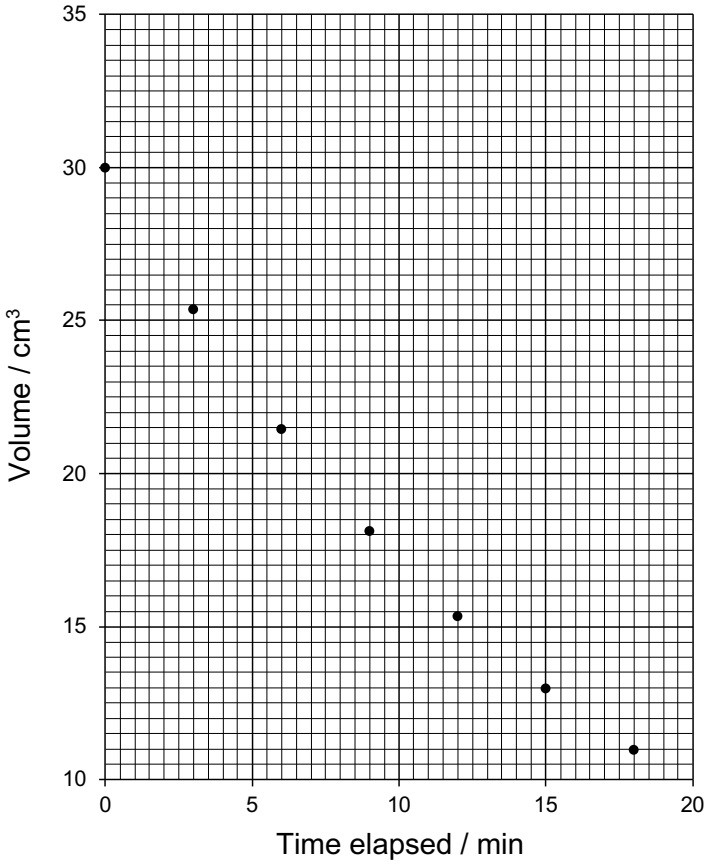

Fig 3.1

(i) Explain why **Fig 3.1** alone **cannot** allow you to conclude the order of reaction with respect to iodine. [1]

(ii) The experiment was repeated again, but the concentration of iodine was **reduced** to 0.00100 mol dm^{-3}. The concentration of $Na_2S_2O_3$ was altered so that the titre values recorded have a lower percentage uncertainty.

Fig 3.2 shows the graph of volume of thiosulfate needed to reach the endpoint against the time elapsed.

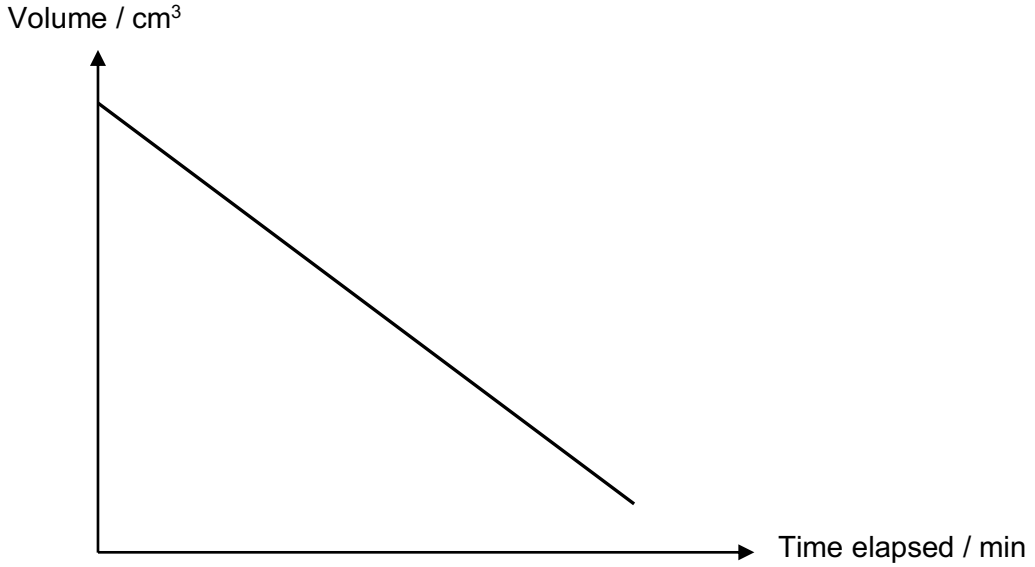

Fig 3.2

Show that **Fig 3.1 <u>and</u> Fig 3.2** supports your answer in **(a)(ii)**. [3]

(iii) Outline a **different** method to show that the order of reaction with respect to acetone is that stated in **(a)(i)**. [2]

(iv) The reaction is catalysed by the production of H^+ ions. Explain why the solution must be buffered. [1]

(v) State another method to monitor the concentration of iodine. [1]

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(c) Refer to information in part **(b)**. Find

(i) the concentration of sodium thiosulfate used for the first experiment; [1]

(ii) the rate constant of this reaction; [1]

(iii) and the gradient and vertical intercept of the straight line in **Fig 3.2**, given that the concentration of sodium thiosulfate used in the second experiment is 10 times dilute of that in the first experiment. [3]

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