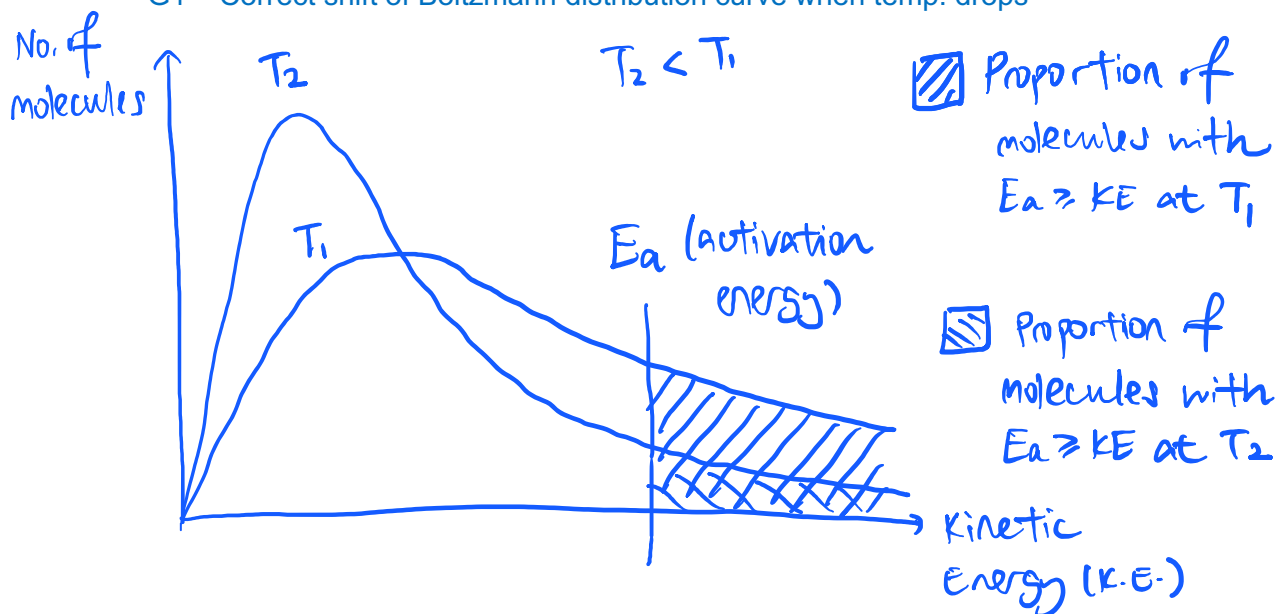**1 (a)** Explain, with the aid of a Boltzmann distribution curve, the effect of, when the following changes are applied separately:

(i) decreasing the temperature; [3]

G1 – Correct shift of Boltzmann distribution curve when temp. drops

No. of molecules

T_2

$T_2 < T_1$

▨ Proportion of molecules with $E_a \geq KE$ at T_1

T_1

E_a (activation energy)

▨ Proportion of molecules with $E_a \geq KE$ at T_2

→ Kinetic Energy (K.E.)

A1 – Correct link
Lower temperature → reactants move at lower speed/velocity → lower kinetic energy → proportion of reactants with kinetic energy greater than or equal to activation energy decreases → lower frequency of effective collisions → lower rate of reaction

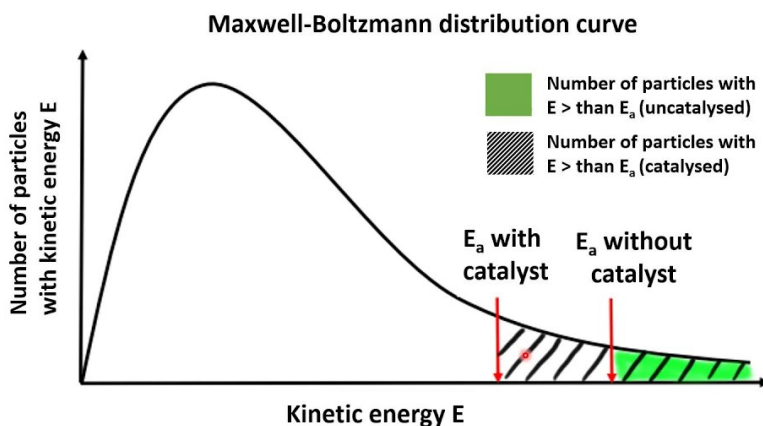**A1 – For declaring that lower rate of reaction → lower rate constant** (with all other variables unchanged) (A1 mark can be awarded if candidate makes the correct link in **(ii)**)

(ii) using a catalyst; [2]

on the rate constant of a reaction.

G1 – Correct shift of E_a when catalyst is used

Maxwell-Boltzmann distribution curve

A1 – Correct link
Catalyst → lowers activation energy →proportion of reactants with kinetic energy greater than or equal to activation energy increases → higher frequency of effective collisions → higher rate of reaction → higher rate constant

(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]

M1 – Correct oxidation half equation and reduction half equation (award 0.5 pts for 1 correct)
Oxidation: $I^- \rightarrow \frac{1}{2} I_2 + e^-$
Reduction: $IO_x^- + (2x - 1) e^- + 2x H^+ \rightarrow \frac{1}{2} I_2 + x H_2O$

Accept approach of using oxidation numbers to balance equation, but oxidation numbers of each iodine-containing species must be clearly shown.

A1 – Correct answer
Combined: $IO_x^- + (2x - 1) I^- + 2x H^+ \rightarrow x I_2 + x H_2O$

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.

$$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$$
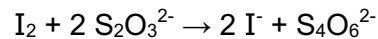
When all $S_2O_3^{2-}$ ions have been depleted, the solution will turn dark blue in colour. The time taken, *t* seconds, for the solution to turn dark blue in colour after mixing is recorded.

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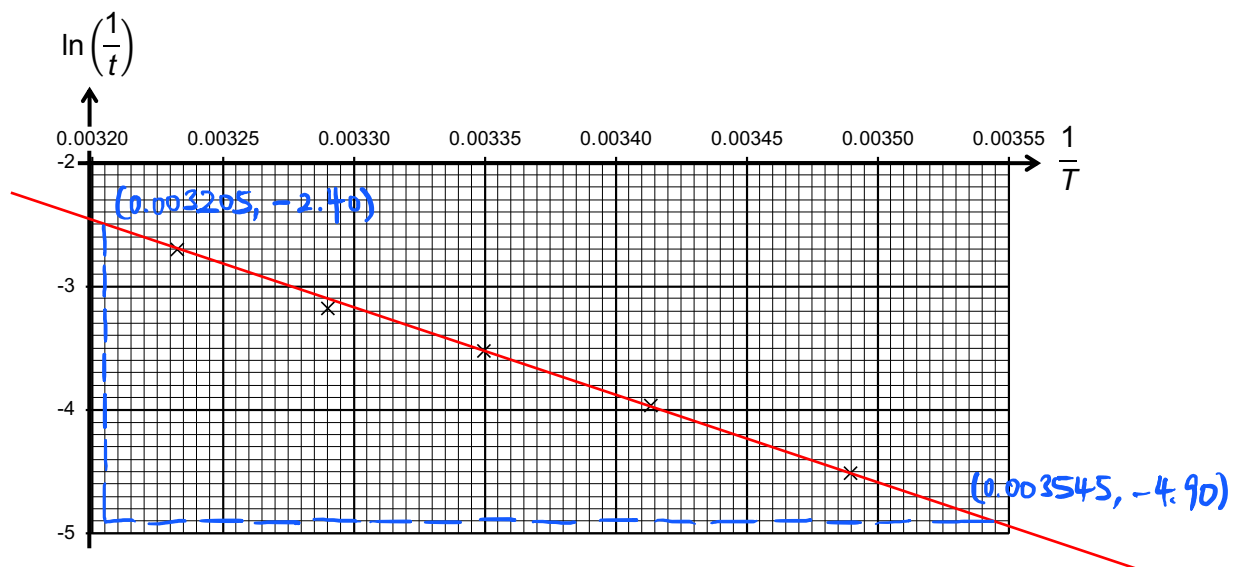
(ii) Define *order of reaction*. [1]

B1 – Order of reaction with respect to a reactant is the <u>power of the concentration term of the reactant in the rate law</u>.

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

B1 – This is to ensure that the reaction only happens to a <u>small extent</u>, so that the <u>average rate computed approximates the initial rate</u>.

(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]

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:

$$\text{Step 1: } \mathbf{E + S} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{ES}$$
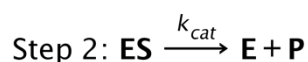
$$\text{Step 2: } \mathbf{ES} \xrightarrow{k_{cat}} \mathbf{E + P}$$

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

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

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

A1 – Convincing explanation
The rate of formation of [**ES**] is $k_f\,[\mathbf{E}][\mathbf{S}]$
The rate of depletion of [**ES**] is $k_b\,[\mathbf{ES}] + k_{cat}\,[\mathbf{ES}]$
Rate of change = rate of formation – rate of depletion (OWTTE)

A1 – rate of formation of P = $k_{\text{cat}}\,[\mathbf{ES}]$

(ii) The initial concentration of the enzyme, [**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, [**E**]$_0$ = [**E**] + [**ES**].

Explain why [**E**]$_0$ = [**E**] + [**ES**]. [1]

A1 – Convincing explanation
The enzyme can either be free by itself as **E**, or bound to a substrate as **ES**. Adding these 2 concentrations gives the initial concentration of enzyme since all forms of how the enzyme can exist are accounted for. (OWTTE)

(iii) By assuming that

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

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

M1 – Makes [**ES**] the subject
$$[ES] = \frac{k_f[E][S]}{k_b + k_{cat}}$$

MA1 – Substitutes [**E**] = [**E**]$_0$ – [**ES**] and makes [**ES**] the subject again
$$[ES] = \frac{k_f[S]([E]_0 - [ES])}{k_b + k_{cat}}$$
$$[ES]\left(1 + \frac{k_f[S]}{k_b + k_{cat}}\right) = \frac{k_f[E]_0[S]}{k_b + k_{cat}}$$
$$[ES] = \frac{k_f[E]_0[S]}{(k_b + k_{cat})\left(1 + \frac{k_f[S]}{k_b + k_{cat}}\right)} = \frac{k_f[E]_0[S]}{k_b + k_{cat} + k_f[S]}$$

(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:

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

[2]

M1 – Correct substitution

MA1 – Divides numerator and denominator by k_f and gets final answer.

$$\frac{d[P]}{dt} = k_{cat}[ES] = k_{cat}[E]_0 \frac{k_f[S]}{k_b + k_{cat} + k_f[S]}$$

$$= k_{cat}[E]_0 \frac{[S]}{\frac{k_b + k_{cat}}{k_f} + [S]} = k_{cat}[E]_0 \frac{[S]}{K_M + [S]}$$

Note: In H2 Chemistry, you are expected to be familiar with the manipulation of linear terms and making a variable the subject.

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

G1 – Correct graph (plateaus at the end, proportional relationship at the start)
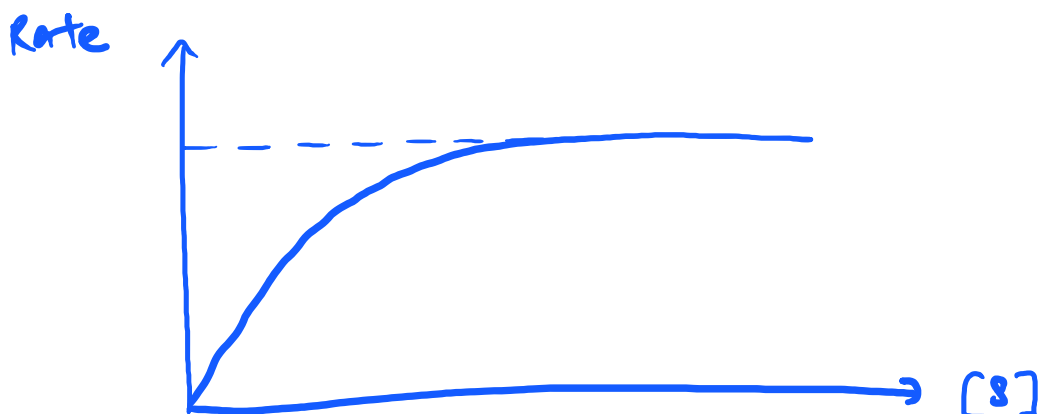
(vi) Explain the shape of your graph in **(v)**, **without** reference to the Michaelis-Menten equation. [2]

B1 – At low concentrations of substrate, not all the active sites of the enzyme are occupied. Hence the rate of reaction is proportional to [S].

B1 – At high concentrations of substrate, all active sites of enzyme are occupied/saturated at any point of time. Increasing the concentration of substrate will not increase the rate of reaction further, hence the rate plateaus at a maximum.

(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]

B1 – First order overall because the dimension of the rate constant is a reciprocal of time (or units of rate constant is s^{-1} or $hours^{-1}$)

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

- 3 °C
- 20 °C [2]

MA1 each

3 degrees Celsius – $1/18 = 0.0556$ $hours^{-1}$
20 degrees Celsius – $1/7 = 0.143$ $hours^{-1}$

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

B1 each
- Enzyme lowers the activation energy through another reaction pathway
- Enzyme remains chemically unaltered after the reaction

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:

$$acetone \rightarrow enol \ (slow)$$
$$enol + I_2 \rightarrow iodopropanone + H^+ + I^-$$
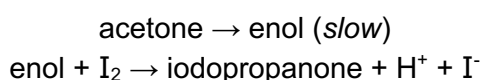
(i) Deduce the order of reaction with respect to acetone and I_2. [1]

B1 – Convincing explanation (0.5 pts for 1 correct)
w.r.t.
acetone $\rightarrow$ 1 because slow step involves 1 molecule of acetone
iodine $\rightarrow$ 0 because iodine is used up after the slow step

(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]

(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$_2$S$_2$O$_3$, 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**.
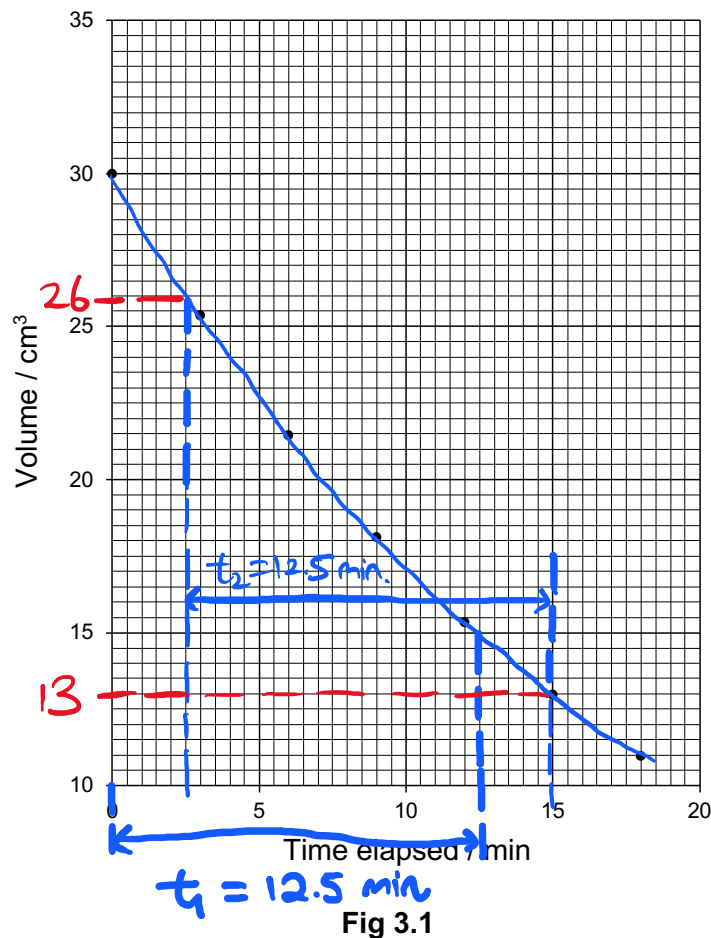
Fig 3.1

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

B1 – Because the concentration of iodine and acetone are the same, we cannot conclude if it's iodine or acetone that has first order characteristics because ==none of iodine and acetone was in great excess.==

(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.

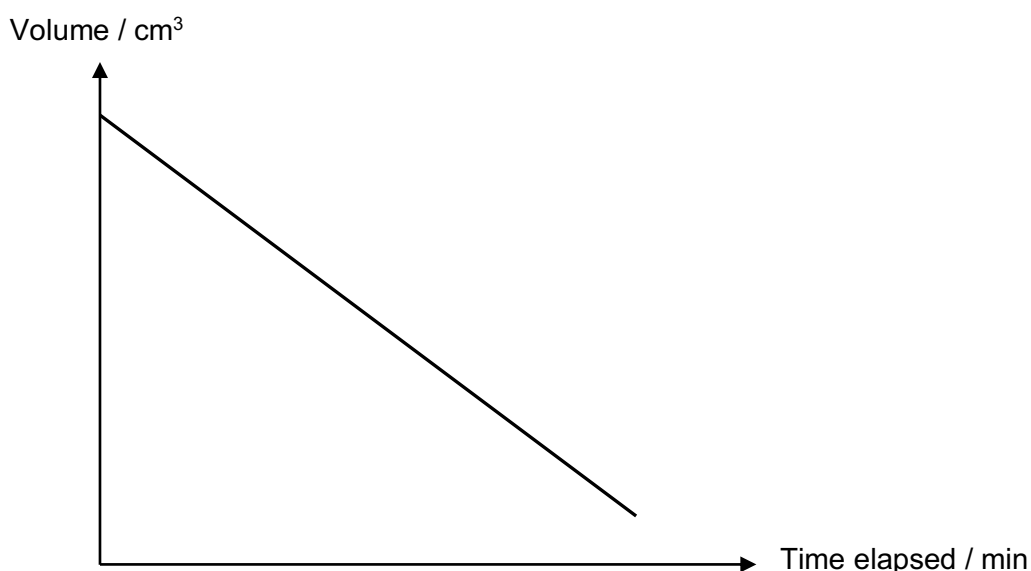**Fig 3.2** shows the graph of volume of thiosulfate needed to reach the endpoint against the time elapsed.

Volume / cm^3

Fig 3.2

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

B1 – Correct conclusion for iodine
When acetone is in excess, from **Fig 3.2**
  • Straight line → constant rate → rate is independent of $[I_2]$ → zeroth order w.r.t. I_2

G1 – Completes **Fig 3.1** to show constant half-life
  • Best-fit curve
  • Labels ==2== half-lives correctly

B1 – Correct conclusion for acetone, with explanation

- Zeroth order w.r.t. iodine, so it has to be first order w.r.t. acetone <u>because of the constant half-life at 12.5 mins</u>

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

B1 – Double concentration of acetone for second experiment to 0.0200 mol dm^{-3} but concentration of I_2 remains at 0.00100 mol dm^{-3}

B1 – Plot same graph as Fig 3.2 for this experiment → gradient of straight line will double → rate proportional to [acetone]

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

B1 – Buffered solution maintains constant pH hence constant [H$^+$] → rate of reaction will not be affected by [H$^+$] since it remains constant.

What a buffered solution does is given in the question, candidates need to draw the inference.

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

B1 – Colorimetry OR measure absorbance of solution

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

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

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

MA1 – Correct answer with working

$$n_{S_2O_3^{2-}} = 2 \times \frac{10}{100} \times \frac{50.0}{1000} \times 0.0100 = 0.000100\ mol$$

$$[S_2O_3^{2-}] = \frac{0.000100}{\frac{30.00}{1000}} = 0.00333\ \text{mol dm}^{-3}$$

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

MA1 – Correct answer with working

$$k = \frac{\ln 2}{12.5} = 0.0555\ \text{min}^{-1}$$

(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]

B1 – Vertical intercept is 30.0 (<mark>no explanation required</mark> – since the concentration is 10 times dilute too, the volume used should be the same as the first time)

M1 – Able to realise that rate is constant, where

$$rate = k[acetone] = \frac{\ln 2}{12.5} \times 0.0100 = 0.0005545 \text{ mol dm}^{-3} \text{ min}^{-1}$$

So the rate of depletion of iodine is also 0.0005545 mol dm^{-3} min^{-1}

MA1 – Deduces horizontal intercept and correct answer

The time taken for [I$_2$] to be zero is $\frac{0.00100}{0.0005545} = 1.803$ min, horizontal intercept is 1.803.

So gradient $= -\frac{30.0}{1.803} = -16.6$ (no units)
- Deduct 0.5 pts for no negative sign

There are other acceptable ways to do this question, but this is a simple solution which uses the horizontal and vertical intercept to find the gradient – a skill which is useful when tasked to do so during your practicals.