Tutorial 6: Reaction Kinetics – Suggested Answers

9 (a) (I) The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the rate equation.

(II) The rate constant of a rection is the constant of proportionality in the rate equation of the reaction.

(III) The half-life of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

(b) Comparing experiments I and II,
when initial [sucrose] $\times$ (0.15/0.10 =) 1.5, initial rate $\times$ (0.036/0.024 =) 1.5
$\Rightarrow$ rate $\propto$ [sucrose], i.e. reaction is <u>first order with respect to sucrose</u>.

Comparing experiments I and III,
when initial [HC*l*] $\times$ 2, initial rate $\times$ 2
$\Rightarrow$ rate $\propto$ [HC*l*], i.e. reaction is <u>first order with respect to HC*l*</u>.

$\therefore$ rate equation: rate = k[sucrose][HC*l*]

Using data from experiment I, $k = \dfrac{0.024}{0.10 \times 0.10}$ = <u>2.40 mol^{-1} dm^3 s^{-1}</u>

(data from experiment II or III can be used as well)

(c) rate = k[sucrose][HC*l*]
0.048 = 2.40(**y**)(0.25) $\therefore$ **y** = 0.08

(d) rate = k[sucrose][HC*l*]

Since HC*l* is a catalyst in the reaction, its concentration is effectively constant during the reaction. The rate equation can be simplified to:

rate = k'[sucrose], where k' = k[HC*l*].

The reaction becomes a <u>pseudo first-order reaction</u> with <u>constant half-life</u>:

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\text{HC}l]} = \frac{\ln 2}{k(0.10)} = 3.0 \text{ s}$$

For experiment II, [HC*l*] is the same as experiment I.
Hence, $t_{1/2}$ of sucrose in experiment II
= $t_{1/2}$ of sucrose in experiment I
= <u>3.0 s</u>
For experiment III, [HC*l*] is double that of experiment I.
Hence, $t_{1/2}$ of sucrose in experiment III $= t_{1/2} = \dfrac{\ln 2}{k'} = \dfrac{\ln 2}{k(2 \times 0.10)} = \dfrac{3.0}{2} =$ <u>1.5 s</u>

10 Compare experiments 1 and 2:
When $[NO_2]$ x 2, rate x 2
$\Rightarrow$ rate $\propto [NO_2]$, i.e. reaction is <u>first order with respect to NO_2</u>.

Let rate = $k[NO_2][SO_2]^m$ where m is the order of reaction with respect to SO_2.

Compare experiments 2 and 3:
$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{k(0.040)(0.40)^m}{k(0.020)(0.20)^m} = \frac{8}{2}$$
Solving, m = 1

So rate = $k[NO_2][SO_2]$

<u>Alternative presentation</u>
Compare experiments 2 and 3:
When $[NO_2]$ x 2 and $[SO_2]$ x 2, rate x 4
But since reaction is first order with respect to NO_2, it means that
rate x 2 due to $[NO_2]$ x 2 AND
rate x 2 due to $[SO_2]$ x 2
$\Rightarrow$ rate $\propto [SO_2]$, i.e. reaction is <u>first order with respect to SO_2</u>.

Since $[SO_2]$ >> $[NO_2]$ in all 3 experiments, this is a pseudo first-order reaction and rate = $k'[NO_2]$, where $k' = k[SO_2]$.

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[SO_2]}$$

Since the $[SO_2]$ in expt 1 and 2 are the same, the half-life should be the same at 48 s. Since $[SO_2]$ in expt 3 is twice that in expt 1, the half-life would be halved to 24 s.

11 **Ans: B**

As the decomposition is a first order reaction, $t_{1/2} = \frac{\ln 2}{k}$.

$t_{½}$ is independent of $[H_2O_2]$, i.e. doubling $[H_2O_2]$ from 0.1 mol dm^{-3} to 0.2 mol dm^{-3} has no effect on $t_{½}$. Since ln 2 and k are constants, $t_{½}$ is constant and likewise, time taken for H_2O_2 to decompose by 10 % will also be constant at 5 min.

12 **(a)** Since rate of reaction $\propto \frac{\Delta[I_2]}{\Delta t} \propto \frac{\text{volume of } I_2\text{(aq) used}}{\text{time taken for solution to turn colourless}}$, by calculating $\frac{\text{volume of } I_2\text{(aq) used}}{\text{time taken for solution to turn colourless}}$, we will be able to compare the rate of reaction for following experiments.

Expt. No.	vol. of CH_3COCH_3 / cm^3	vol. of I_2 / cm^3	vol. of H_2SO_4(aq) / cm^3	vol. of water / cm^3	time taken for solution to decolourise / min	$\frac{\text{vol of } I_2}{\text{time taken}}$ / cm^3 min^{-1}
1	8.0	4.0	8.0	0.0	1.0	4.0
2	8.0	4.0	4.0	4.0	2.0	2.0
3	4.0	4.0	8.0	4.0	2.0	2.0
4	8.0	2.0	8.0	2.0	0.5	4.0

Comparing experiments 1 and 2,
when volume of H_2SO_4 x 0.5 (corresponding to $[H^+]$ x 0.5), rate x 0.5.
$\Rightarrow$ rate $\propto [H^+]$, i.e. reaction is <u>first order with respect to H^+.</u>

Comparing experiments 1 and 3,
When volume of CH_3COCH_3 x 0.5 (corresponding to $[CH_3COCH_3]$ x 0.5, rate $\times$ 0.5.
$\Rightarrow$ rate $\propto [CH_3COCH_3]$, i.e. reaction is <u>first order with respect to CH_3COCH_3</u>.

Comparing experiments 1 and 4,
When volume of I_2 x 0.5 (corresponding to $[I_2]$ x 0.5, rate remains unchanged.
$\Rightarrow$ rate $\propto [I_2]^0$, i.e. reaction is <u>zero order with respect to I_2</u>.

(b) (I) The rate equation for a reaction is a mathematical expression that relates the rate of reaction to the concentration of each reactant raised to the appropriate power.

(II) The rate-determining step is the slowest step in the reaction mechanism of a multi-step reaction and it determines the overall reaction rate.

(c) rate = $k[CH_3COCH_3][H^+]$; Overall order = 2

(d) In mechanism **A**, the slow step (also the rate-determining step) is a bimolecular elementary reaction involving <u>one molecule of CH_3COCH_3</u> and <u>one H^+ ion</u>. The rate equation is rate = $k'[CH_3COCH_3][H^+]$, which is similar to the rate equation in **(c)**.

$\Rightarrow$ <u>Mechanism **A**</u> fits the observed kinetic data.

In mechanism **B**, the slow step is a bimolecular elementary reaction involving <u>one molecule of CH_3COCH_3</u> and <u>one molecule of I_2</u>. The rate equation is rate = $k''[CH_3COCH_3][I_2]$, which is different from the rate equation in **(c)**.

$\Rightarrow$ Mechanism **B** is inconsistent with the observed kinetic data.

[Note: The reaction is zero order with respect to I_2, so I_2 is only involved in the fast step (which is not rate-determining).]

(e) As the reaction proceeds by a similar mechanism, <u>bromine (like iodine) is not involved in the slow/rate-determining step</u>. The reaction is therefore <u>zero order with respect to bromine</u>. Hence, the rate of reaction is <u>similar</u> to that of the reaction between propanone and iodine under the same experimental conditions.

(Note: Even though the Br−Br bond is stronger than the I−I bond, the rate of reaction will be similar, because slow/rate-determining step does not involve the breaking of the halogen-halogen bond.)

13 **(a)** amount of $S_2O_3^{2-}$ used = 0.050 x 0.0020 = 0.000100 mol

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

amount of I_2 = ½ x 0.000100 = <u>5.00 x 10^{-5} mol</u>

(b) $[I_2] = \frac{\text{amount of iodine}}{\text{volume of mixture}} = \frac{5.00 \times 10^{-5}}{0.100} = 5.00 \times 10^{-4}$ mol dm^{-3}

Initial rate of reaction $\approx \frac{[I_2]}{t}$

Expt No	Time for the appearance of deep blue colour/ s	Initial rate $\approx \frac{[I_2]}{t}$/ mol dm^{-3} s^{-1}
1	33	1.52 x 10^{-5}
2	100	5.00 x 10^{-6}
3	67	7.46 x 10^{-6}
4	50	1.00 x 10^{-5}

Comparing experiments 2 and 4,
when volume of $H_2O_2 \times 2$ (corresponding to $[H_2O_2] \times 2$), initial rate $\times$ 2.
$\Rightarrow$ rate α $[H_2O_2]$
$\Rightarrow$ reaction is <u>first order with respect to H_2O_2</u>.

Comparing experiments 2 and 3,
when volume of KI $\times$ 1.5 (corresponding to [KI] $\times$1.5), initial rate $\times$ 1.5.
$\Rightarrow$ rate α [KI]
$\Rightarrow$ reaction is <u>first order with respect to KI</u>.

Let rate equation be rate = $k[H_2O_2][KI][HCl]^b$ where b is the order of reaction with respect to HC*l*.

Comparing experiments 1 and 2 and using the fact that [X] $\propto V_X$ since total volume is a constant,

$$\frac{Rate_1}{Rate_2} = \frac{k(15)(10)(5)^b}{k(5)(10)(10)^b} = \frac{1.52x10^{-5}}{5.00x10^{-6}} \Rightarrow 3(0.5)^b = 3.04 \Rightarrow b = 0$$

$\Rightarrow$ reaction is <u>zero order with respect to HC*l*</u>.

(c) rate = $k[H_2O_2][KI]$; units of rate constant is $mol^{-1}\ dm^3\ s^{-1}$.

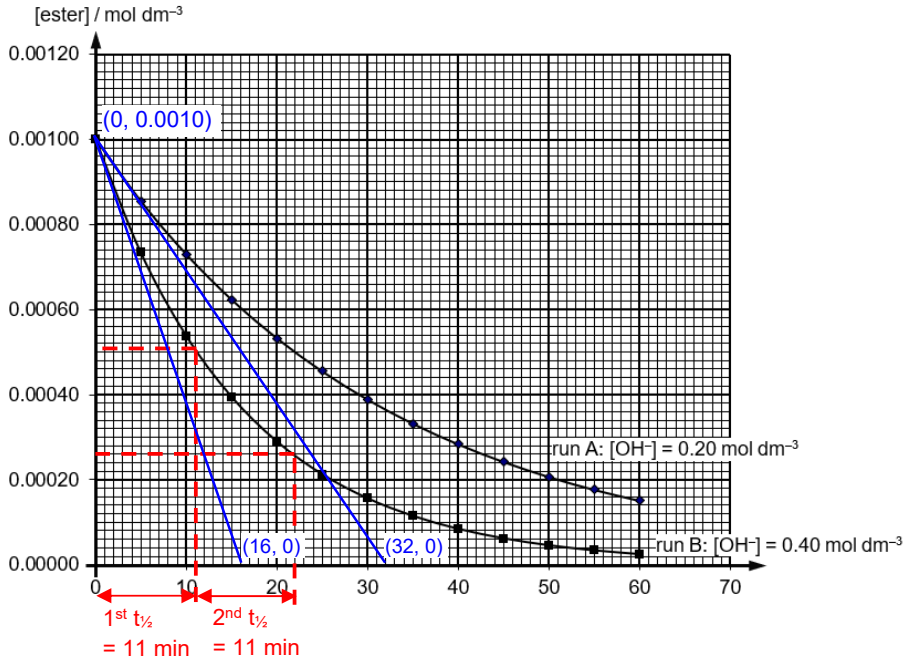
(d) <u>y = 33 s</u>.
Explanation (not required by question):
The total volume is twice that of all the other experiments.
The volume of each reagent used is twice that of Experiment 1
$\Rightarrow$ initial concentrations of all reactants are the same as that of Experiment 1
$\therefore$ time taken is the same as Experiment 1.

14 **(a)** Measuring change in colour intensity with time

The reactants (i.e. ester and hydroxide ion) are colourless while the product, **A**, is yellow. Since colour intensity $\propto$ [**A**], the change in the colour intensity of **A** over time may be used to measure the rate of reaction.

1. The reactants are mixed and the colour intensity of the reaction mixture may be measured using a colorimeter and the readings are taken at regular time intervals.
2. Samples containing **A** of various concentrations, e.g., 0.001, 0.005, 0.100 mol dm^{-3}, are prepared and their colour intensities measured using the colorimeter. A calibration curve is obtained by plotting colour intensity against concentration. The concentration of **A** corresponding to each colour intensity obtained in step 1 is found using the calibration curve. The concentration of **A** is then plotted against time.
3. Instantaneous rate is found by drawing a tangent to the curve and finding its gradient g_1, where rate = g_1.

(b) **(i)** Use the graphs to calculate the initial rates of reaction during the two runs.



For run A, initial rate = $-\frac{0.0010 - 0}{0 - 32} = \underline{3.125 \times 10^{-5}} = \underline{3.13 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}}$

For run B, initial rate $= -\frac{0.0010 - 0}{0 - 16} = \underline{6.25 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}}$

(Note: On the graph, label coordinates used to obtain the initial rates.)

(ii) Comparing run A and run B,
when $[OH^-] \times 2$, initial rate $\times 2$
$\Rightarrow$ rate α $[OH^-]$
$\Rightarrow$ reaction is <u>first order with respect to OH^-</u>

(iii) From the graph of run B,
First $t_{1/2}$ = Second $t_{1/2}$ = 11 min $\Rightarrow$ <u>$t_{1/2}$ is constant</u>
$\therefore$ reaction is <u>first order with respect to ester</u>.

[Note: Show all construction lines and label at least two $t_{½}$ on the graph (refer to the above graph in **(b)(i)**)]

[For run B, $[OH^-]$ is $\frac{0.40}{0.0010} = 400$ times that of [ester] and $[OH^-]$ remains effectively constant during the reaction. Hence the reaction follows pseudo first-order kinetics.]

(iv) rate = k[ester][OH^-]

(v) From run B, $6.25 \times 10^{-5} = k(0.0010)(0.40)$
$\therefore k =$ 0.156 mol^{-1} dm^3 min^{-1}

OR

From run A, $3.125 \times 10^{-5} = k(0.0010)(0.20)$
$\therefore k =$ 0.156 mol^{-1} dm^3 min^{-1}

(vi) Since the reaction follows pseudo first-order kinetics.

rate = k'[ester], where $k' = k[OH^-]$ and $t_{½}$= 11 min (from **(iii)**)

$$t_{1/2} = \frac{\ln 2}{k'} \Rightarrow k' = \frac{\ln 2}{t_{1/2}} \Rightarrow k[OH^-] = \frac{\ln 2}{t_{1/2}}$$

$$\therefore k = \frac{\ln 2}{t_{1/2}[OH^-]} = \frac{\ln 2}{(11)(0.40)} =$$ 0.158 mol^{-1} dm^3 min^{-1}

15 (a) (i) [B] remains approximately constant as the reaction proceeds. The rate of reaction is only dependent on [A] and the order of reaction with respect to A can thus be found.

Comments:

- Many students realised that A was the limiting reagent when B was added in excess. However, the emphasis in this question is on "*large* excess". Examiners are looking for an answer that is related to how we study the kinetics of the reaction.
- Examiners accepted answers that described a pseudo first-order reaction. However, in actual fact, when B is added in excess, we do not yet know if the reaction is a pseudo first-order or a pseudo second-order reaction. It would be more accurate to simply describe the reaction as a pseudo order reaction.

(ii) If the reaction were to go to completion, final [C] = initial [A]
= 0.12 mol dm^{-3}

First $t_{½}$ is time taken for [C] to increase from 0 to 0.06 mol dm^{-3} while second $t_{½}$ is time taken for [C] to increase from 0.06 to 0.09 mol dm^{-3}.

From the graph, 1st $t_{½}$ = 3.7 min and 2nd $t_{½}$ = 3.7 min
Since 1st $t_{½}$ = 2nd $t_{½}$, the reaction is first order with respect to A.

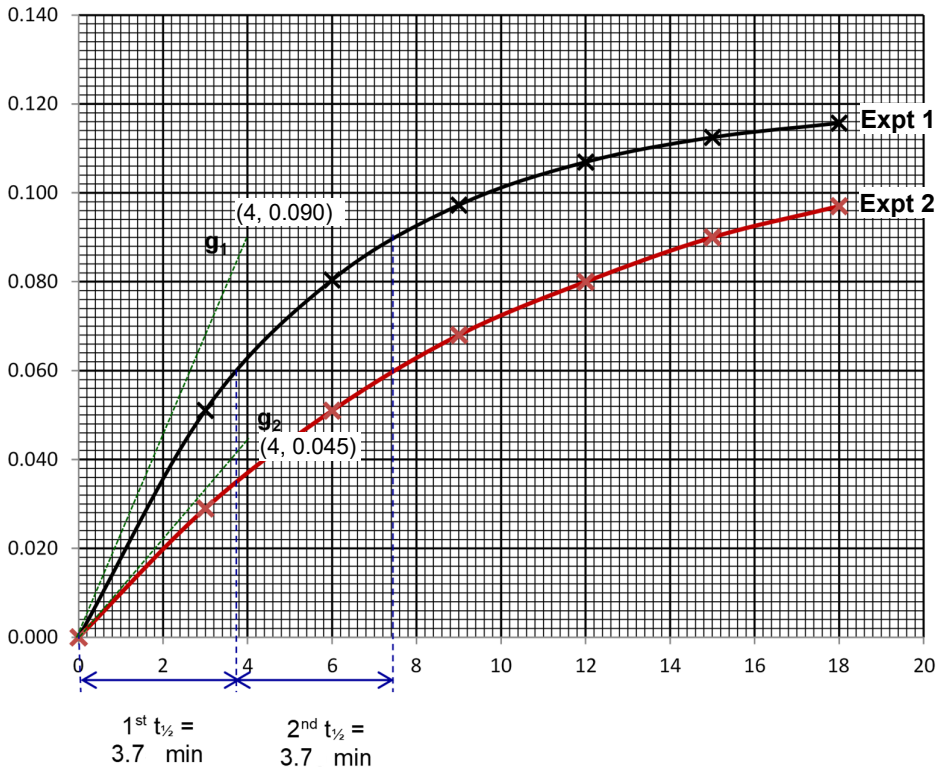
Note:

- The final [C] should be used to determine $t_{½}$.
- Show all construction lines and label at least two $t_{½}$ on the graph (refer to graph in solutions to **(b)(i)** on the next page)

Comments:

- The final [C] should be calculated using the stoichiometric ratios of the equation given and the calculation should take into account the fact that A is the limiting reagent. In this case, the final [C] cannot be obtained from the graph.
- Students should learn how to find the half-life of a reaction using a [product] vs time graph. The half-lives should also be clearly marked out on the graph, and the values written in the space provided for the answer. Quite a number of students stated the 2nd half-life is 7.4 min, which is wrong. 7.4 min is the sum of the first two half-lives.

(b) **(i)**



Comments:

- Generally well done, but a few students forgot to include the point at the origin.
- Use a sharp pencil to plot the points accurately.

(ii) **Method 1**: Compare initial rates of experiments 1 and 2.

$$\text{initial rate of experiment 1} = g_1 = \frac{0.090 - 0}{4.0 - 0} = 0.0225 \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$\text{initial rate of experiment 2} = g_2 = \frac{0.045 - 0}{4.0 - 0} = 0.01125 \text{ mol dm}^{-3} \text{ min}^{-1}$$

Since initial rate is halved when [B] is halved, the reaction is first-order with respect to B.

(Note: On the graph, label coordinates used to obtain g_1 and g_2)

Method 2: Compare half-lives of experiments 1 and 2.

Let order of reaction with respect to B be y.

Rate = k[A][B]^y = k'[A] where k' = k[B]^y

Since B is used in large excess, [B]^y is approximately constant such that the reaction is a pseudo first-order reaction.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[B]^y} \Rightarrow t_{\frac{1}{2}} \propto \frac{1}{[B]^y} \Rightarrow t_{\frac{1}{2}} \times [B]^y \text{ is a constant}$$

For experiment 1, $t_{\frac{1}{2}}$ = 3.7 min and [B] = 2.00 mol dm^{-3}

For experiment 2, $t_{\frac{1}{2}}$ = 7.4 min and [B] = 1.00 mol dm^{-3}

$3.7(2.00)^y = 7.4(1.00)^y$

$$\frac{3.7}{7.4} = \left(\frac{1.00}{2.00}\right)^y \Rightarrow y = 1 \Rightarrow \text{reaction is } \underline{\text{first order with respect to B}}.$$

Comments:

- The initial rate is obtained by drawing a tangent to a curve at t = 0 and finding the gradient of that tangent. Some students chose to draw a tangent at some value of t for which t > 0 and found the instantaneous rate instead. Students who used instantaneous rate were unable to arrive at the correct answer as the calculations were more difficult.
- Students should show, on the graph, the construction lines for the tangent. Students also need to show the examiners how the value of the gradient was calculated. Note that the unit for time is in minutes (min).
- Students should be mindful of how they use words such as "increased by 2 times". When 3 increases by 2 times, it becomes 3 + 2(3) = 9, not 6. When 3 is doubled, the result is 6.
- Students who used **Method 2** often did not show clearly how the half-life is related to [B].
- Obtaining a constant half-life for the reaction in experiment 2 meant that the reaction was first-order with respect to A, not first-order with respect to B.

(iii) rate = k[A][B]

Comments:

- Some students gave wrong answers such as "rate equation= k[A][B]" and "k = [A][B]".

(iv) **Method 1**: Use initial rate

Using results from experiment 1 in **(b)(ii)**,

initial rate of expt 1= 0.0225 mol dm^{-3}

Since rate = k[A][B], at t = 0 min, 0.0225 = k(0.12)(2.00)

$$\Rightarrow k = \frac{0.0225}{(0.12)(2.00)} = \underline{0.0938 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}}$$

Method 2: half-life

Using results from experiment 1 in **(b)(ii)**,

$$t_{½} = \frac{\ln 2}{k'} = \frac{\ln 2}{k(2.00)} = 3.7$$

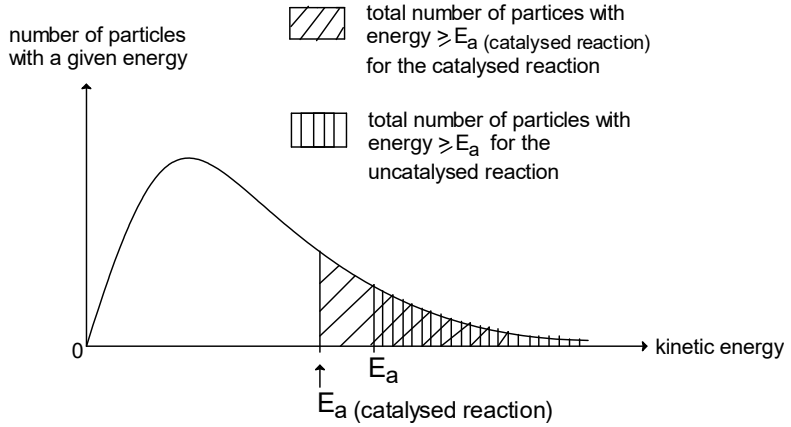
$$k = \frac{\ln 2}{(3.7)(2.00)} = \underline{0.0937 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}}$$

Comments:

- Many students did not realise that time was in minutes rather than seconds.
- Students who prefer using the half-life method should bear in mind that that $k' = k[B]$, as the reaction given is a pseudo first-order reaction. The required rate constant is k, not k'.

(c) (i) A catalyst increases the rate of a reaction by providing an alternative reaction pathway of lower activation energy.

In the catalysed reaction, since the activation energy ($E_{a\ (catalysed\ reaction)}$) is lower than that of the uncatalysed reaction (E_a), more reactant particles have energy greater than or equal to the activation energy than in the uncatalysed reaction. This is shown by the larger shaded area for the catalysed reaction in the diagram below.



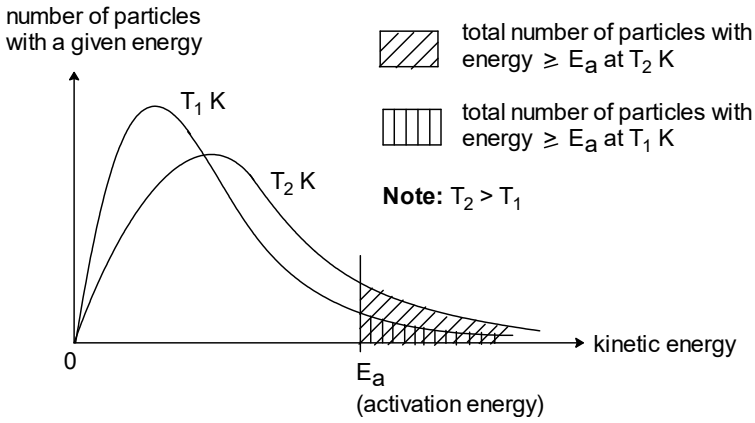
The frequency of effective collision increases accordingly, and hence the reaction rate increases.

A lower activation energy also results in the reaction having a larger rate constant, and hence an increase in the reaction rate.

Comments:

- This is a simple "recall question". Students must learn how to sketch the Maxwell-Boltzmann distribution curves properly and use them to explain how the rate of a reaction is affected by either a change in temperature or the use of a catalyst.
- In this case, there is only one curve. The asymmetric curve must start from the origin and the asymptotic behaviour must be shown. Indicate the legend clearly.

(ii) As temperature increases from T_1 to T_2 K, the average kinetic energy of the reactant particles increases. As such, significantly more reactant particles have energy greater than or equal to the activation energy of the reaction. This is shown by the significantly larger shaded area at a higher temperature in the diagram below.



Consequently, the frequency of effective collisions increases accordingly, and hence the reaction rate increases.
An increase in temperature also results in a larger rate constant, and hence an increase in the reaction rate.

16 An enzyme catalyses a reaction by providing active sites for reaction to take place.

At low $[H_2O_2]$, not all of the active sites on catalase are occupied.

In this case, rate $\propto [H_2O_2]$ and reaction is first-order with respect to H_2O_2.

At high $[H_2O_2]$, all the active sites on catalase become saturated / are fully occupied by molecules of H_2O_2.
In this case, any increase in $[H_2O_2]$ will not have any effect on the reaction rate / reaction is zero order with respect to H_2O_2 / rate is independent of $[H_2O_2]$.

Comments:

- Students were required to account (i.e. explain) for the shape of the graph. Hence, it is important to explain WHY the rate of reaction increases with increasing $[H_2O_2]$ initially, but becomes constant at high $[H_2O_2]$. It is insufficient to simply state that the rate increases because the enzyme catalyses the reaction.
- A number of students discussed how the limiting reagent (i.e. limiting H_2O_2 initially and limiting catalase at high $[H_2O_2]$) affects the reaction rate, without showing clear understanding of the concepts of a substrate binding to an enzyme active site and the saturation of active sites at high [substrate].
- The increase in rate of reaction is NOT due to an increase in frequency of effective collisions between the enzyme and its substrate. Rather, it is due to the enzymes providing an alternative reaction pathway with lower activation energy. To bring about this, the enzyme forms an enzyme-substrate complex with the substrate.
- At low $[H_2O_2]$, the reaction is first-order (NOT second-order) w.r.t. H_2O_2. Hence, rate increases linearly (NOT exponentially) with $[H_2O_2]$.
- The active sites are on the enzyme (catalase) and the substrate (H_2O_2) binds to the active sites, not the other way round!
- Do not confuse *enzyme* with *heterogeneous catalyst*. A substrate binds to the active site of enzymes whereas a reactant adsorbs onto the surface of a heterogeneous catalyst.
- Note the use of terminologies, e.g. active site (NOT binding site, activation sites, etc.) and the proper phrasing of answer in a concise manner.

17 The reaction is an autocatalytic reaction with the H^+ ions, produced from the dissociation of CH_3CO_2H, acting as the autocatalyst.

Initially, the reaction is slow as it has a high activation energy.

The reaction rate then increases as the H^+ ions produced act as the autocatalyst, providing an alternative pathway with lower activation energy.

Towards the end of the reaction, the concentrations of the reactants are very low, so the reaction rate decreases even though there is an adequate supply of catalyst.