# Physical Chemistry Revision – Kinetics

## MCQ

**1** [CJC 2011] Two substances, **A** and **B**, react according to the following equation:

**A + 2 B → C**

To determine the order of reaction with respect to each substance, four experiments were performed and the results are shown below:

| Experiment | [A] / mol dm$^{-3}$ | [B] / mol dm$^{-3}$ | Initial rate of formation of C / mol dm$^{-3}$ min$^{-1}$ |
|---|---|---|---|
| 1 | 0.10 | 0.10 | 0.0010 |
| 2 | 0.40 | 0.10 | 0.0160 |
| 3 | 0.10 | 0.20 | 0.0020 |
| 4 | 0.20 | 0.20 | **?** |

Which is the correct value for the initial rate of formation of **C** for experiment 4?

**A** 0.0040 **B** 0.0080 **C** 0.0160 **D** 0.0320

**2** [VJC 2009] An experiment was carried out to investigate the initial rate of reaction between ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, an oxidising agent, and potassium iodide, KI. The initial concentrations of $(NH_4)_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

| Initial [$(NH_4)_2S_2O_8$] /mol dm$^{-3}$ | Initial [KI] /mol dm$^{-3}$ | Time taken to darken /s |
|---|---|---|
| 0.10 | 0.20 | 35 |
| 0.05 | 0.20 | 70 |
| 0.10 | 0.067 | 105 |
| 0.02 | 0.75 | ? |

What is the expected time taken(in seconds) to darken when the experiment is repeated using initial concentrations of$(NH_4)_2S_2O_8$ and KI to be 0.02 mol dm$^{-3}$ and 0.75 mol dm$^{-3}$ respectively?

**A** 40 **B** 47 **C** 60 **D** 72

**3** [VJC 2009] Which of the following statements best explains why a small increase in temperature leads to a significant increase in the rate of a gaseous reaction?

**A** The frequency of collisions between the molecules is greater at a higher temperature.

**B** The activation energy of the reaction is lower when the gases are at a higher temperature.

**C** The average kinetic energy of the molecules is greater at a higher temperature.

**D** The frequency of effective collisions between molecules with kinetic energy greater than the activation energy is greater at a higher temperature.

4 [HCI 2007]

Two colourless substances, **X** and **Y**, react to give a coloured substance **Z**. The times, *t*, taken for various initial concentrations of **X** and **Y** to produce **Z** are recorded below.

| [**X**]/ mol dm$^{-3}$ | [**Y**]/ mol dm$^{-3}$ | *t*/s |
|---|---|---|
| 0.05 | 0.05 | 44 |
| 0.05 | 0.10 | 22 |
| 0.10 | 0.05 | 44 |

What is the rate equation for the reaction?

**A** rate = $k$[**Y**] **B** rate = $k$[**X**][**Y**]

**C** rate = $k$[**Y**]$^2$ **D** rate = $k$[**X**][**Y**]$^2$

**5** The following data were obtained from the studies of the reaction between NO and $O_2$ in a vessel at constant temperature.

| Experiment | 1 | 2 | 3 |
|---|---|---|---|
| Initial total pressure / atm | 1.00 | 1.60 | 2.00 |
| Initial partial pressure of NO / atm | 0.40 | 0.40 | 0.80 |
| Initial rate of reaction / atm s$^{-1}$ | 1.08 | 2.16 | 8.64 |

Which of the following statements are true regarding the above reaction?

1 The overall order of the reaction is 2.

2 The rate-determining step involves 1 oxygen molecule.

3 The rate constant has units of $atm^{-2}s^{-1}$.

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**6** [PJC 2011] The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known and small amount of $Na_2S_2O_3$ and a little starch.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The time taken for an intense blue colour to be observed is then determined.

| Experiment | Volume used / $cm^3$ | | | Time / s |
|---|---|---|---|---|
| | 1.0 mol $dm^{-3}$ KI | 0.040 mol $dm^{-3}$ $Na_2S_2O_8$ | $H_2O$ | |
| 1 | 10.0 | 5.0 | 25.0 | 170 |
| 2 | 15.0 | 5.0 | 20.0 | 113 |
| 3 | 15.0 | 10.0 | 15.0 | 56.5 |
| 4 | 20.0 | ***X*** | ***y*** | 21.3 |

What are the values of ***x*** and ***y*** in Experiment 4?

| | ***x*** | ***y*** |
|---|---|---|
| **A** | 5.0 | 15.0 |
| **B** | 10.0 | 10.0 |
| **C** | 15.0 | 5.0 |
| **D** | 20.0 | 0.0 |

**7** [RI 2009]

The rate of the reaction between substances A and B is found to follow the rate law

$$\text{rate} = k\,[A]^m\,[B]$$

where $k$ is the rate constant and has units of $mol^{-2}\ dm^6\ s^{-1}$.

Two experiments to study the kinetics of this reaction were carried out and the data obtained are tabulated below.

| Experiment | Initial [A] / mol $dm^{-3}$ | Initial [B] / mol $dm^{-3}$ | Initial rate / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|
| 1 | 0.040 | 0.080 | R |
| 2 | 0.020 | *y* | ½ R |

What is the value of *y* in Experiment 2?

**A** 0.020
**B** 0.040
**C** 0.160
**D** 0.320

**8** [HCI 2009] The bromination of propanone is acid-catalysed.

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^-$$

The rate of disappearance of the colour of bromine was measured for several different concentrations of propanone, bromine and $H^+$ at a certain temperature and the results tabulated below.

| Expt | $[CH_3COCH_3]$/ mol $dm^{-3}$ | $[Br_2]$/ mol $dm^{-3}$ | $[H^+]$ / mol $dm^{-3}$ | Rate of disappearance of $Br_2$ colour / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|---|
| 1 | 0.30 | 0.05 | 0.05 | $5.70 \times 10^{-5}$ |
| 2 | 0.30 | 0.10 | 0.05 | $5.70 \times 10^{-5}$ |
| 3 | 0.30 | 0.05 | 0.10 | $1.14 \times 10^{-4}$ |
| 4 | 0.40 | 0.05 | 0.20 | $3.04 \times 10^{-4}$ |

Which of the following statements about the above reaction is true?

**A** The rate equation for the reaction is rate = $k[CH_3COCH_3][Br_2]$.
**B** The rate constant for the reaction is $3.8 \times 10^{-3}\ mol^{-1}\ dm^3\ s^{-1}$.
**C** The rate constant of the reaction doubles when $[CH_3COCH_3]$ is doubled.
**D** The rate constant of the reaction remains unchanged when temperature is doubled.

**9** [ACJC 2011] An experiment was carried out to investigate the initial rate of reaction between ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The initial concentrations of $(NH_4)_2S_2O_8$ and KI solutions in the mixture, together with the time taken for the mixture to darken for the various experimental runs are given below:

| **Experiment** | **Initial [$(NH_4)_2S_2O_8$] / mol dm$^{-3}$** | **Initial [KI] / mol dm$^{-3}$** | **Time taken to darken / s** |
|---|---|---|---|
| **1** | 0.10 | 0.20 | 35 |
| **2** | 0.05 | 0.20 | 70 |
| **3** | 0.10 | 0.067 | 105 |
| **4** | 0.02 | 0.75 | ? |

Which of the following statements about the reaction is/are true?

**1** The reaction involves the formation of an intermediate.

**2** The time taken for the mixture to darken in Experiment 4 is 47 s.

**3** The slow step involves the reaction between one $S_2O_8^{2-}$ and one $I^-$.

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**10** [NYJC 2011] The kinetics of the reaction between iodide and peroxodisulfate can be investigated by varying the volume of the reactants used. The two reactants are mixed in the presence of a known amount of $Na_2S_2O_3$ and a little starch. The time taken for an intense blue colour to be observed is then determined.

| Experiment | Vol used / cm$^3$ | | | Time |
|---|---|---|---|---|
| | 1.0 mol dm$^{-3}$ KI | 0.040 mol dm$^{-3}$ $Na_2S_2O_3$ | $H_2O(l)$ | t / s |
| 1 | 10.0 | 5.0 | 25.0 | 170 |
| 2 | 15.0 | 5.0 | 20.0 | 113 |
| 3 | 15.0 | 10.0 | 15.0 | 56.5 |
| 4 | 20.0 | 20.0 | 0.0 | **x** |

What is the value of **x** in Experiment 4?

**A** 11 **B** 21 **C** 85 **D** 1360

**11.** [SAJC 2009] The table below gives data gathered from the reactions between **Q** and **R** at constant temperature.

| Experiment | [Q] / mol dm $^{-3}$ | [R] / mol dm $^{-3}$ | initial rate / mol dm $^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.3 | 0.2 | $4.0 \times 10^{-4}$ |
| 2 | 0.6 | 0.4 | $1.6 \times 10^{-3}$ |
| 3 | 0.6 | 0.8 | $6.4 \times 10^{-3}$ |

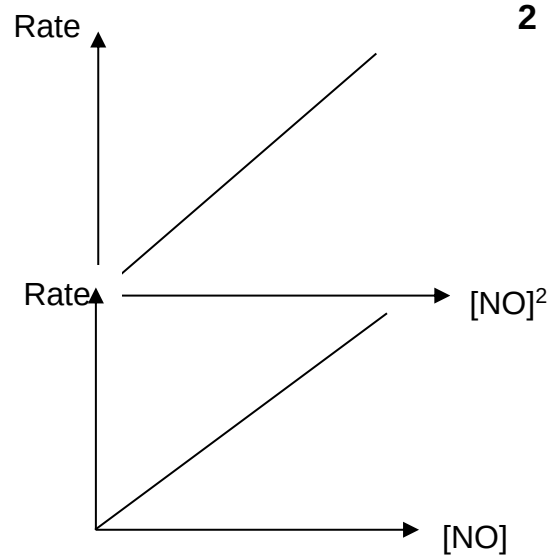
What are the units of the rate constant for the reaction?

**A** $mol^2\ dm^{-6}\ s^{-1}$ **B** $mol^{-2}\ dm^6\ s^{-1}$ **C** $mol\ dm^{-3}\ s^{-1}$ **D** $mol^{-1}\ dm^3\ s^{-1}$

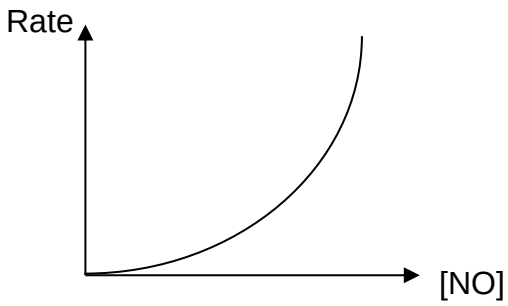
**12** [CJC 2011] A student proposed that the conversion of nitrogen monoxide, NO, to nitrogen dioxide is second-order with respect to nitrogen monoxide.

Which graphs show that the student's proposal may be correct?

**1**




**2**




**3**



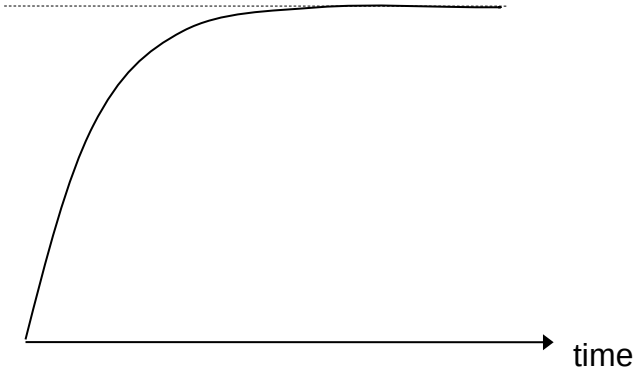

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**13** The reaction between KI(aq) with excess $Na_2S_2O_8$(aq) was studied and the following graph was obtained.




Which of information may be obtained from the graph above?

1 the rate of reaction at any given instant

2 order of reaction with respect to $I^-$

3 order of reaction with respect to $S_2O_8^{2-}$

**A** 1, 2 and 3

**B** 1 and 2 only

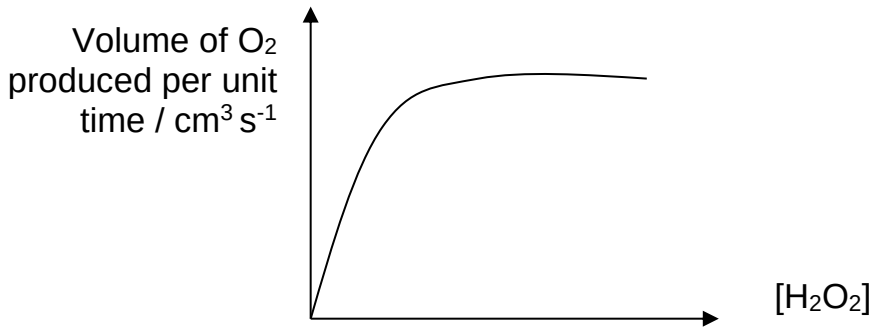
**C** 2 and 3 only

**D** 1 only

**14** [AJC 2011] The rate of decomposition of aqueous $H_2O_2$ increases in the presence of the enzyme, catalase.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The following graph was obtained in a study to investigate the effect of catalase on the rate of decomposition of $H_2O_2$.




The steps predicted for this enzymatic decomposition of $H_2O_2$ are shown below.

catalase + $H_2O_2$ $\rightleftharpoons$ catalase–$H_2O_2$ complex slow step

Catalase–$H_2O_2$ complex $\longrightarrow$ $H_2O + O_2$ + catalase fast step

Which statements about the enzymatic decomposition of $H_2O_2$ are correct?

**1** At low $[H_2O_2]$, the rate of decomposition increases with increasing amount of catalase used.

**2** At low $[H_2O_2]$, catalase lowers the activation energy of the decomposition by forming temporary bonds with $H_2O_2$ molecules.

**3** At high $[H_2O_2]$, all the active sites of the catalase enzyme are saturated with $H_2O_2$ molecules.

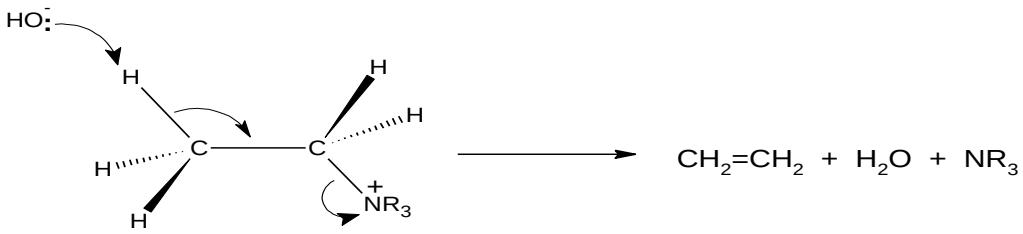
**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**15** [PJC 2011] Quaternary ammonium ions can undergo Hofmann elimination in a single step mechanism as shown.




quaternary ammonium ion

The following concentrations of $OH^-$ and $CH_3CH_2NR_3^+$ were used in *Experiment 1* and the half-life was found to be 10 s.

$[OH^-] = 0.001$ mol dm$^{-3}$ $[CH_3CH_2NR_3^+] = 0.100$ mol dm$^{-3}$

What will be the half–life when the experiment is repeated with the following changes in concentrations?

| | Half-life for *Experiment 2* when only $[OH^-]$ is doubled | Half-life for *Experiment 3* when only $[CH_3CH_2NR_3^+]$ is doubled |
|---|---|---|
| **A** | 10 s | 10 s |
| **B** | 10 s | 5 s |
| **C** | 5 s | 10 s |
| **D** | 5 s | 5 s |

**16** [HCI 2011] Consider the following reaction: **E** + 3**F** → **EF**$_3$

The mechanism involves the following steps:

$$2\mathbf{F} \rightleftharpoons \mathbf{F}_2 \qquad \text{fast}$$

$$\mathbf{E} + \mathbf{F}_2 \rightarrow \mathbf{EF}_2 \qquad \text{slow}$$

$$\mathbf{EF}_2 + \mathbf{F} \rightarrow \mathbf{EF}_3 \qquad \text{fast}$$

Based on the information, what is the rate equation for this reaction?

**A** Rate = $k[\mathbf{F}]^2$ **B** Rate = $k[\mathbf{E}][\mathbf{F}]^2$

**C** Rate = $k[\mathbf{E}][\mathbf{F}]^3$ **D** Rate = $k[\mathbf{E}][\mathbf{F}_2]$

**17** [AJC 2007]

The reaction of nitrogen monoxide with hydrogen

$$2NO\,(g) + 2H_2\,(g) \longrightarrow N_2\,(g) + 2H_2O\,(g)$$

is thought to involve the following steps:

$$2NO\,(g) + H_2\,(g) \longrightarrow N_2O\,(g) + H_2O\,(g) \qquad \text{(slow)}$$
$$N_2O\,(g) + H_2\,(g) \longrightarrow N_2\,(g) + H_2O\,(g) \qquad \text{(fast)}$$

Which of the following statements is correct?

**A** Hydrogen is reduced by nitrogen monoxide.
**B** The reaction is second order with respect to $H_2$.
**C** The rate equation for the reaction is: rate = $k\,[NO]^2\,[H_2]$.
**D** $N_2O$ acts as a catalyst in this reaction.

**18** [HCI 2007]

The mechanism for the production of nitrosyl bromide, NOBr, from nitrogen monoxide and bromine is thought to be as follows.

$$NO + Br_2 \rightleftharpoons NOBr_2 \quad \text{(fast)}$$
$$NOBr_2 + NO \rightarrow 2NOBr \quad \text{(slow)}$$

Which of the following rate equations is consistent with the mechanism?

**A** rate = $k[NOBr_2][NO]$

**B** rate = $k[NO]^2[Br_2]$

**C** rate = $k[NO][Br_2]$

**D** rate = $k[NO][Br_2]^2$

**19** Compounds **Q** and **S** react in the presence of a dilute acid as follows:

$$\mathbf{2Q}(aq) + \mathbf{S}(aq) \rightarrow \mathbf{U}(aq) + \mathbf{V}(aq)$$

It is found that the rate equation for the reaction is rate = $k$ $[\mathbf{Q}]^2[H^+]$.

Which statement is **incorrect**?

**A** The magnitude of $k$ increases with temperature.

**B** $H^+$ provides an alternative pathway of lower activation energy.

**C** Increasing [**Q**] by a factor of 2 and $[H^+]$ by a factor of 2 at constant temperature causes a six-fold increase in the reaction rate.

**D** Increasing [**Q**] by a factor of 2 and $[H^+]$ by a factor of 1 at constant temperature causes a four-fold increase in the reaction rate.

**20** [TJC 2007] The mechanism for a given reaction is shown below.

| | |
|---|---|
| $2\mathbf{A} \rightleftharpoons \mathbf{C}$ | fast |
| $\mathbf{C} + \mathbf{B} \rightarrow \mathbf{D}$ | slow |
| $\mathbf{D} + \mathbf{B} \rightarrow \mathbf{A_2B_2}$ | fast |

What conclusions can be drawn from the information given above?

**1** rate = $k[\mathbf{A}]^2[\mathbf{B}]^2$

**2** The overall equation is $2\mathbf{A} + 2\mathbf{B} \rightarrow \mathbf{A_2B_2}$.

**3** The rate of formation of $\mathbf{A_2B_2}$ is proportional to the initial concentration of **B**.

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

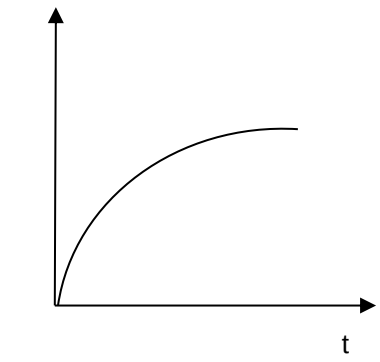
**D** 1 only

**21** The reaction represented by the following equation was carried out.

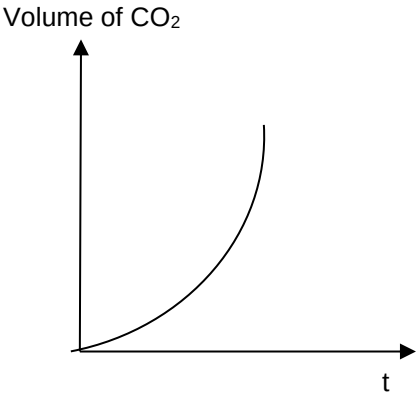
$MnO_4^-(aq) + 5\ C_2O_4^{2-}(aq) + 16\ H^+ \rightarrow Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$

Which graph best shows the relationship between volume of $CO_2$ collected over time from the mixing of the reactants?

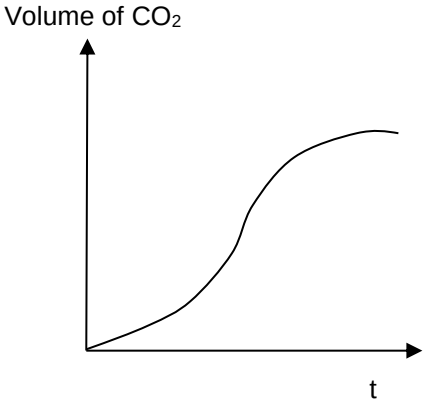
**A**



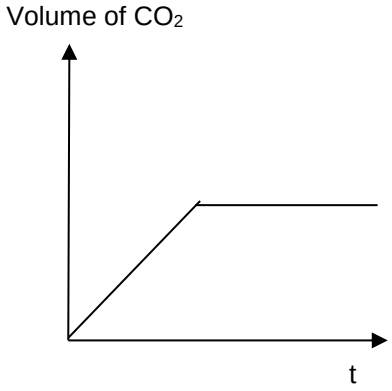

**C**




**B**




**D**




**22** [NYJC 2009] Given that a reaction has the overall equation and proceeds via the following mechanism as shown below:

**2P + Q → R + S**

Step 1: **P** + **Q** → **R** + **T** (fast) $\Delta H = +45\ kJ\ mol^{-1}$

Step 2: **P** + **T** → **S** (slow) $\Delta H = -98\ kJ\ mol^{-1}$

Which of the following statement is true?

**A** The overall order of reaction is 2.

**B** The enthalpy change for the reaction is $-53\ kJ\ mol^{-1}$

**C** The activation energy needed for Step 1 is $+ 45\ kJ\ mol^{-1}$

**D** Compound **T** is acting as a catalyst.

**23** [SAJC 2009] Radioactive decay is a first order reaction.

Carbon-14 is a radioactive element with a half-life of 5600 years. A piece of wood, containing carbon-14 from an ancient ship gives 10 counts per minute, while carbon-14 obtained from a new wood gives 15 counts per minute.

What is the age of the ship (in years)?

**A** 2800 **B** 3276 **C** 3733 **D** 8876

**24.** [SAJC 2009] The reaction between acidified aqueous KI and $H_2O_2$(aq): $2I^-$(aq) + $H_2O_2$(aq) + $2H^+$(aq) → $I_2$(aq) + $2H_2O$(*l*) is thought to involve the following steps:

$H_2O_2 + I^- \rightarrow H_2O + OI^-$ (slow)

$OI^- + H^+ \rightarrow HOI$ (fast)

$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

Which conclusions can be drawn from the above information?

**1** The rate equation for the reaction is: rate = k $[H_2O_2]$ $[I^-]$

**2** Hydrogen peroxide is reduced by the iodide ion.

**3** The acid acts as a catalyst.

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**25** (VJC 13) Benzyl chloride ($C_6H_5CH_2Cl$) was reacted with aqueous sodium hydrosulfide (NaSH) in the presence of aqueous sodium iodide (NaI). The time taken for the reaction to complete and the initial concentrations are given in the following table:

| **Experiment** | **[$C_6H_5CH_2Cl$]** | **[NaSH]** | **[NaI]** | ***t* /s** |
|---|---|---|---|---|
| 1 | 0.1 | 0.05 | 0.05 | 120 |
| 2 | 0.2 | 0.05 | 0.05 | 60 |
| 3 | 0.1 | 0.10 | 0.05 | 120 |
| 4 | 0.05 | 0.10 | 0.10 | 240 |
| 5 | 0.4 | 0.15 | 0.04 | ? |

Which of the following statements are correct?

**1** The value of ***t*** for experiment 5 is 30 s.

**2** For experiment 1, iodomethylbenzene ($C_6H_5CH_2Cl$) is formed in greater amount than phenylmethanethiol ($C_6H_5CH_2SH$).

**3** The reaction proceeds via $S_N1$ mechanism as the positive charge generated on carbocation is stabilized by resonance.

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**26** (HCI 14) 2.0 mol $dm^{-3}$ of 2-bromo-2-methylpropane was reacted with an excess of hot aqueous sodium hydroxide. The following results were obtained.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

| Time/min | 0 | 15 | 40 | 80 | ∞ |
|---|---|---|---|---|---|
| $[(CH_3)_3COH]$/ mol $dm^{-3}$ | 0 | 0.5 | 1.0 | 1.5 | 2.0 |

What is the value of the rate constant?

**A** $8.66 \times 10^{-3}$

**B** $1.73 \times 10^{-2}$

**C** $2.77 \times 10^{-2}$

**D** $4.62 \times 10^{-2}$

**27** (NJC 14) Hydrogen peroxide reacts with acidified iodide ions liberating iodine according to the equation below:

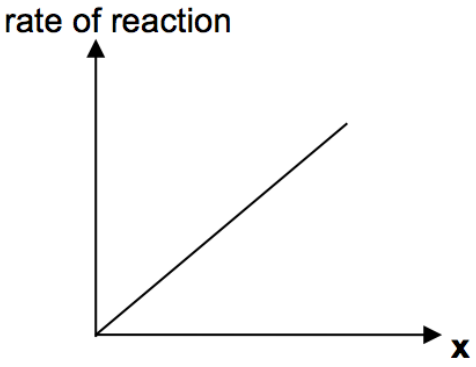
$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The kinetics of this reaction were investigated and it was found to have the following rate equation:

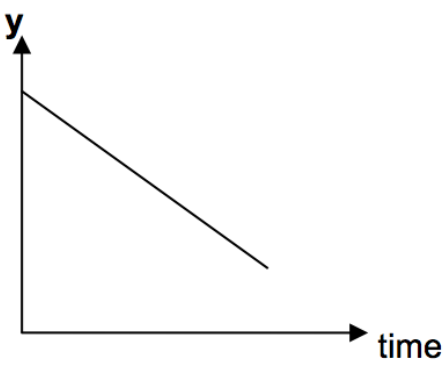
$$\text{rate} = k[H_2O_2][I^-]$$

Two series of experiments were conducted giving rise to **Graph A** and **Graph B**. The concentrations of reagents used for both experiments were as follows: $[H_2O_2] = 0.1$ mol $dm^{-3}$, $[I^-] = 0.1$ mol $dm^{-3}$, $[H^+] = 0.01$ mol $dm^{-3}$

**Graph A**




**Graph B**



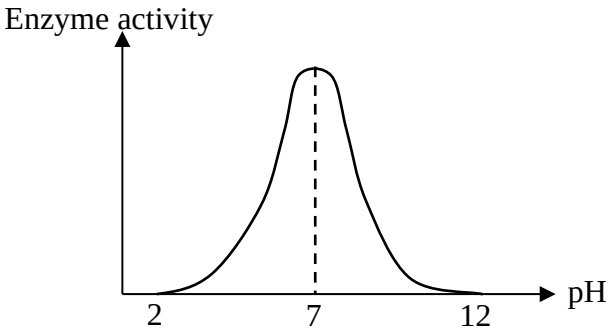

Which combination shows the correct labelling of the x-axis for **Graph A** and y-axis for **Graph B**?

| | **x-axis for Graph A** | **y-axis for Graph B** |
|---|---|---|
| **A** | $[I^-][H^+]$ / mol$^2$ dm$^{-6}$ | $[H_2O_2]$ / mol dm$^{-3}$ |
| **B** | $[H_2O_2][I^-]$ / mol$^2$ dm$^{-6}$ | $[H^+]$ / mol dm$^{-3}$ |
| **C** | $[H_2O_2]$ / mol dm$^{-3}$ | $[H^+]$ / mol dm$^{-3}$ |
| **D** | $[I^-]$ / mol dm$^{-3}$ | $[H_2O_2]$ / mol dm$^{-3}$ |

**28** (NYJC 14) Decomposition of hydrogen peroxide can be catalysed by an enzyme, catalase.

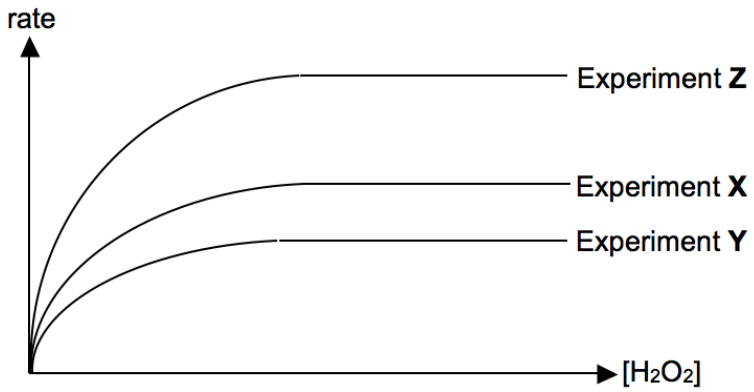
$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$

Enzymes are made of proteins and works most effectively at a particular pH, known as the optimum pH.




The optimum pH for catalase is pH 7. It is completely denatured under extreme low and high pH conditions.

A student performed experiment **X** to investigate the decomposition of $H_2O_2$ using catalase at pH 7. He also performed experiments **Y** and **Z** to further investigate the reaction by changing two other conditions.




Which statements are correct?

**1** Experiment **Y** is carried out at pH 8.
**2** Experiment **Z** is carried out with higher concentration of catalase.
**3** The activation energy of experiment **Y** is the largest.

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**29** (RI 14) Quarter-life, $t_{1/4}$, of a radioactive isotope is defined as the time taken for the sample to decay to ¼ its original amount.
Potassium-argon dating is used to determine the age of a rock. $^{40}K$ is a radioactive isotope of potassium and it decays to $^{40}Ar$ with a constant $t_{1/4}$ of $2.50 \times 10^9$ years.
A sample of moon rock was found to contain 6.25% of the original amount of $^{40}K$.

How old is the rock?

**A** $2.50 \times 10^9$ years
**B** $5.00 \times 10^9$ years
**C** $7.50 \times 10^9$ years
**D** $1.00 \times 10^{10}$ years

**30** (RV 14) A reaction is represented as follows:

$$\mathbf{X} + 2\mathbf{Y} \rightarrow \mathbf{XY_2}$$

The mechanism involved in the formation of $XY_2$ is shown below:
Step I : $\mathbf{X} + \mathbf{Y} \rightarrow \mathbf{XY}$ (fast)
Step II : $\mathbf{XY} + \mathbf{Y} \rightarrow \mathbf{XY_2}$ (slow)

What is the rate equation for this reaction?

**A** Rate = k[**XY**][**Y**]

**B** Rate = k[**X**][**Y**]
**C** Rate = k[**X**][**Y**]$^2$
**D** Rate = k[**XY**][**Y**]$^2$

**31** (RV 14) The table gives data for the reaction between **X** and **Y** at constant temperature.

**X + Y → Z**

| Experiment | [X] / mol dm$^{-3}$ | [Y] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.4 | 0.1 | $2.5 \times 10^{-4}$ |
| 2 | 0.2 | 0.2 | $5.0 \times 10^{-4}$ |
| 3 | 0.2 | 0.4 | $1.0 \times 10^{-3}$ |

Which statements follow from these results?
**1** The half-life of this reaction is 277 s.
**2** The mechanism involves more than 1 step.
**3** The rate equation can be written as: rate = k[**X**][**Y**].

**A** 1, 2 and 3
**B** 1 and 2 only
**C** 2 and 3 only
**D** 1 only

**32** (SAJC 14) Which of the following will decrease the rate constant for a reaction?
**A** Decrease in concentration
**B** Decrease in temperature
**C** Decrease in pressure
**D** Addition of catalyst

**33** (TJC 14) For the reaction 2X(aq) + Y(aq) ⟶ Z(aq) at room temperature, the rate equation is

$$\text{Rate} = k\,[H^+][X]^2$$

Which of the following statements is **not** correct?
**A** $H^+$ is a catalyst in the reaction.
**B** The reaction involves the formation of an intermediate.
**C** When the concentration of X is halved, the rate decreases.
**D** If the concentrations of $H^+$ and X are doubled, the rate increases by six times.

**34** (TJC 14) Which of the following factors would always affect the rate of a reaction?
**1** concentration of reactants
**2** temperature

**3** catalyst

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

**35** (VJC 14) The mechanism below has been proposed for the reaction of $CHCl_3$ with $Cl_2$.

Step 1: $Cl_2(g) \rightleftharpoons 2Cl(g)$ fast
Step 2: $Cl(g) + CHCl_3(g) \rightarrow CCl_3(g) + HCl(g)$ slow
Step 3: $CCl_3(g) + Cl(g) \rightarrow CCl_4(g)$ fast

Which of the following rate equations is consistent with this mechanism?

**A** rate = $k[CHCl_3][Cl]$
**B** rate = $k[CHCl_3][Cl_2]$
**C** rate = $k[CHCl_3][Cl_2]^{1/2}$
**D** rate = $\frac{k[CHCl_3]}{[Cl_2]}$

**36** (VJC 14) The table below shows the results of three experiments conducted for the reaction **P** + **Q** $\rightarrow$ products.

| [**P**] / mol dm$^{-3}$ | [**Q**] / mol dm$^{-3}$ | rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|
| 0.012 | 0.005 | 0.9 x 10$^{-4}$ |
| 0.024 | 0.010 | 2.0 x 10$^{-4}$ |
| 0.048 | 0.010 | 4.0 x 10$^{-4}$ |

If the rate constant doubles for each 10 $^{o}$C rise in temperature, which pairs of experimental conditions will result in the same rate?

| | [**P**] / mol dm$^{-3}$ | [**Q**] / mol dm$^{-3}$ | temperature / $^{o}$C |
|---|---|---|---|
| condition 1 | 0.10 | 0.20 | 40 |
| condition 2 | 0.20 | 0.20 | 30 |
| condition 3 | 0.30 | 0.30 | 20 |

**1** conditions 1 and 2
**2** conditions 1 and 3
**3** conditions 2 and 3

**A** 1, 2 and 3

**B** 1 and 2 only

**C** 2 and 3 only

**D** 1 only

## Structured Questions

**1** [VJC 2007 P3/3] Azomethane, $CH_3–N=N–CH_3$, is a common compound used in cancer research. It decomposes according to the following equation:

$$CH_3–N=N–CH_3(g) \rightarrow CH_3CH_3(g) + N_2(g)$$

**(i)** Suggest a variable that can be monitored experimentally to study the rate of the reaction. Explain your answer.

The concentration of ethane, $[CH_3CH_3]$, was determined at different times in a particular experiment and is shown below:

| **t /s** | **$[CH_3CH_3]$ /mol dm$^{-3}$** |
|---|---|
| 0 | 0.0000 |
| 1000 | 0.0121 |
| 2000 | 0.0176 |
| 3000 | 0.0200 |
| 4000 | 0.0211 |
| 5000 | 0.0216 |
| 6000 | 0.0218 |
| 7000 | 0.0219 |
| 8000 | 0.0220 |
| 9000 | 0.0220 |
| 10000 | 0.0220 |

**(ii)** Using the given data, plot a suitable graph to determine the order of the reaction with respect to azomethane.

**(iii)** Calculate the rate constant for this reaction and state its units.

**(iv)** Using relevant bond energy values from the *Data Booklet*, calculate the enthalpy change for this reaction.

**(v)** With the aid of the Boltzmann distribution, explain why the addition of a catalyst increases the rate of a reaction.

[9]

**2.** [AJC 2007 P2/1]

**(a)** The dehydration reaction of 2-butanol to form butene is catalysed by an acid. Three experiments were carried out to find the relationship between rate of reaction and the initial concentrations of 2-butanol and the acid catalyst.

| Experiment | $[2\text{-butanol}]_{initial}$ / mol $dm^{-3}$ | $[H^+]_{initial}$ / mol $dm^{-3}$ | Initial rate / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|
| 1 | 0.25 | 0.25 | $1.4 \times 10^{-7}$ |
| 2 | 0.50 | 0.25 | $2.8 \times 10^{-7}$ |
| 3 | 0.50 | 0.50 | $2.8 \times 10^{-7}$ |

**(i)** Deduce the order of reaction with respect to:

- 2-butanol,
- $H^+$.

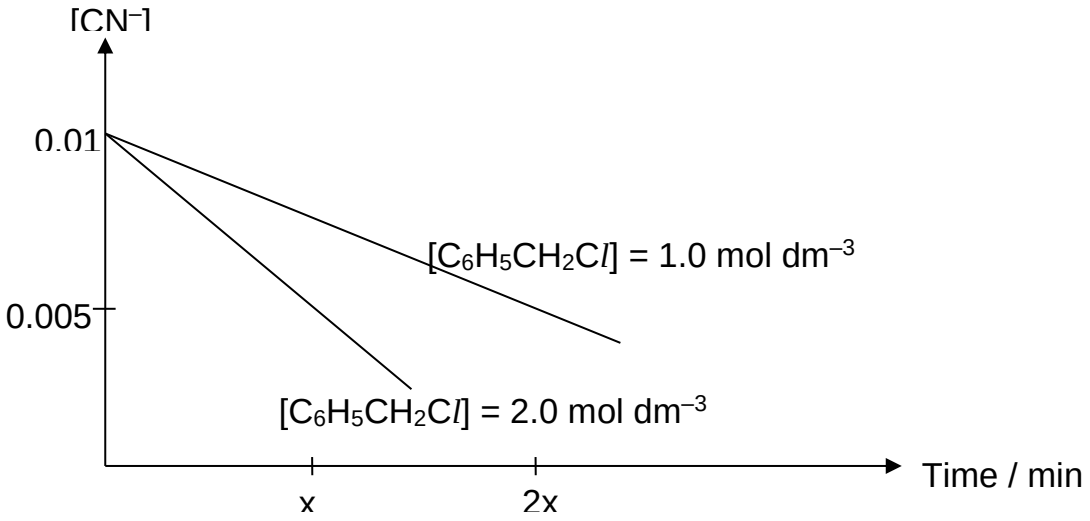
**(ii)** Hence, calculate the rate constant for this reaction, stating its units.

**(b)** Explain how an increase in temperature will affect the rate of this reaction.

**3.** [DHS 2009 P3/3] The reaction below is an example of nucleophilic substitution.

$$C_6H_5CH_2Cl + CN^- \rightarrow C_6H_5CH_2CN + Cl^-$$

The reaction kinetics of this reaction is determined by monitoring the change in the concentration of $CN^-$ with time. The results are shown below:




**(i)** Determine the rate equation for the above reaction.

**(ii)** With the aid of Maxwell-Boltzmann distribution curve, predict and explain the effect on the rate of this reaction when the reaction temperature is decreased.

[7]

**4(a)** [VJC 2009 P3] Reacting compounds **A** and **B** with phosphorus pentachloride, $PCl_5$, yield compounds **D** and **E** respectively. Effervescence of white fume was observed. Both **D** and **E** are then hydrolysed with NaOH(aq) and the data from kinetics studies are collected.

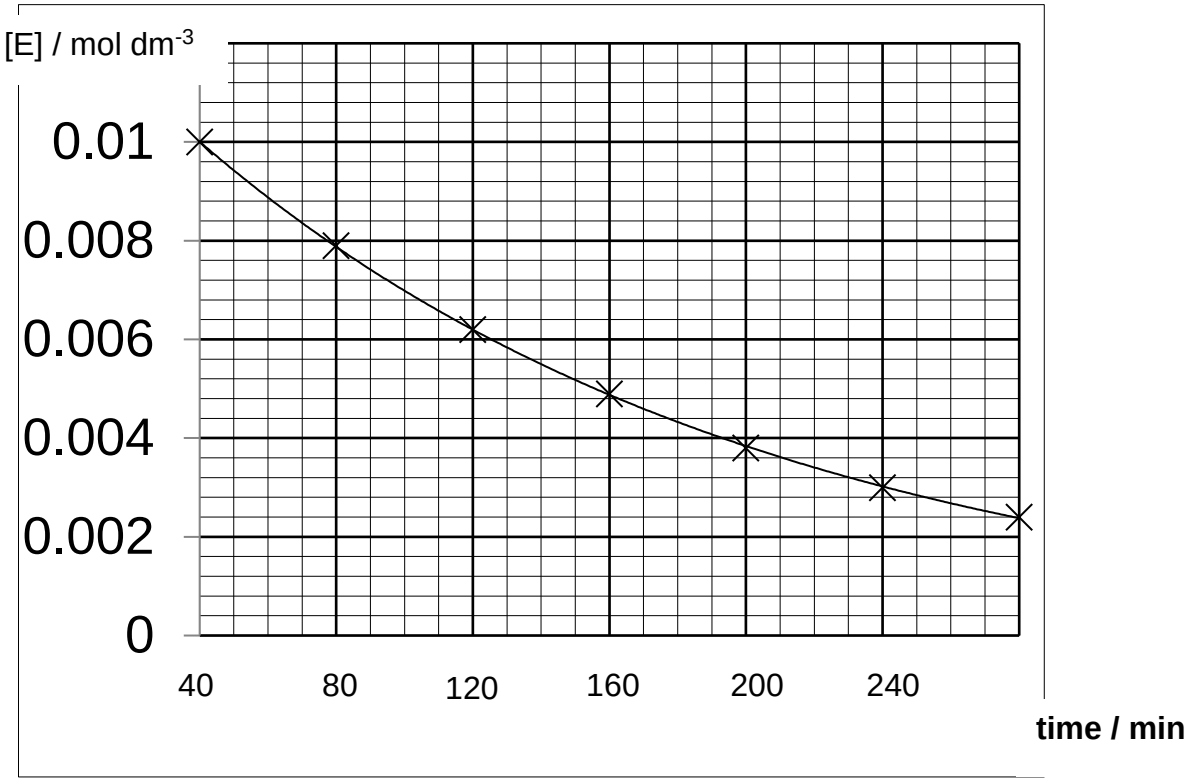
The results for the hydrolysis of compound **D** is as shown.

| Experiment | [**D**] / mol $dm^{-3}$ | [$OH^-$] / mol $dm^{-3}$ | Initial rate/ mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|
| **1** | 0.0100 | 0.120 | $1.8 \times 10^{-4}$ |
| **2** | 0.0050 | 0.240 | $1.8 \times 10^{-4}$ |
| **3** | 0.0050 | 0.480 | $3.6 \times 10^{-4}$ |

**(i)** Using the above data, deduce the orders of reaction with respect to **D** and $OH^-$.

**(ii)** Hence, construct the rate equation and use it to calculate a value of the rate constant, $k_1$, for the hydrolysis of **D**, including its units.

**(b)** The results for the hydrolysis of compound **E** is shown in the form of graphical representation. The overall concentration of aqueous NaOH remained virtually constant at 0.120 mol $dm^{-3}$.




**(i)** Use the graph above to determine the order of reaction with respect to **E**.

**(ii)** Given that the same plot was obtained when the experiment was repeated with 0.240 mol $dm^{-3}$ of NaOH(aq), calculate the value of the rate constant, $k_2$, including its units, for the hydrolysis of **E**.

**(iii)** Using the initial rate data given in **a (i)** and the graph above, calculate the ratio of the initial rates of hydrolyses of **D**: **E**. Hence, suggest the functional group which is likely to be present in **B**. Explain clearly your reasoning.

[7]

**5** [2009 RIJC] Ethene reacts with bromine in tetrachloromethane to form 1,2–dibromoethane as shown by the equation:

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

To find out the orders of reaction with respect to ethene and bromine, ethene and bromine were first dissolved separately in tetrachloromethane. Various volumes of these solutions and tetrachloromethane were mixed and the time taken for the colour of bromine to disappear was recorded. The results are shown in the table below:

| Experiment | Volume of $CH_2{=}CH_2$ in $CCl_4$ / $cm^3$ | Volume of $Br_2(l)$ / $cm^3$ | Volume of $CCl_4$ / $cm^3$ | Time taken for colour of $Br_2$ to disappear/ s |
|---|---|---|---|---|
| **1** | 20 | 20 | 0 | 15 |
| **2** | 12 | 20 | 8 | 25 |
| **3** | 20 | 10 | 10 | 15 |
| **4** | 40 | 20 | 20 | $t_4$ |

Discuss **(i)** to **(iii)** with reference to experiments **1** to **3**.

**(i)** Explain why varying volumes of tetrachloromethane were used.

**(ii)** State the relationship between the rate of reaction and

- time taken for the colour of bromine to disappear
- volume of bromine used

**(iii)** Deduce the order of reaction with respect to ethene and show that the order of reaction with respect to bromine is 1.

**(iv)** Suggest a value for $t_4$, time taken for the colour of bromine to disappear in experiment **4**.

**(v)** When methanol is used as a solvent instead of tetrachloromethane, another product with the formula of $C_3H_7OBr$ is formed. Draw its displayed formula and explain how it is formed. [9]

## Answers 7) Kinetics

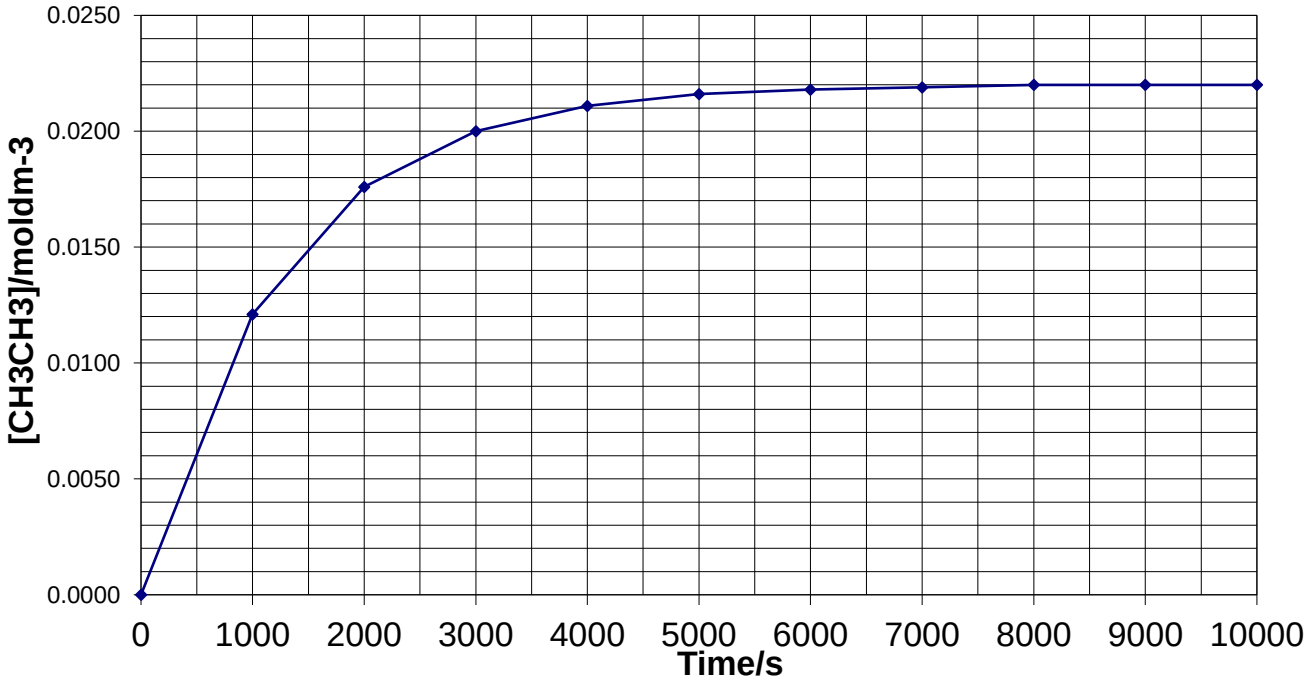
### MCQ

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **B** | 6 | **D** | 11 | **D** | 16 | **B** | 21 | **B** | 26 | **B** | 31 | **B** | 36 | **D** |
| 2 | **B** | 7 | **C** | 12 | **B** | 17 | **C** | 22 | **B** | 27 | **B** | 32 | **B** | | |
| 3 | **D** | 8 | **B** | 13 | **B** | 18 | **B** | 23 | **B** | 28 | **B** | 33 | **D** | | |
| 4 | **A** | 9 | **A** | 14 | **A** | 19 | **C** | 24 | **B** | 29 | **B** | 34 | **C** | | |
| 5 | **C** | 10 | **B** | 15 | **B** | 20 | **C** | 25 | **A** | 30 | **C** | 35 | **C** | | |

### Structured

1(i) Pressure/volume can be monitored as there is a change in the number of moles of gas as the reaction progresses.

(ii)




As reaction proceeds:

Reactant changes from 1 → ½ → ¼ → 1/8 → … → 0

product changes from 0 → ½ → ¾ → 7/8 → … → 1

[$CH_3CH_3$]: 0 → 0.0110 → 0.0165

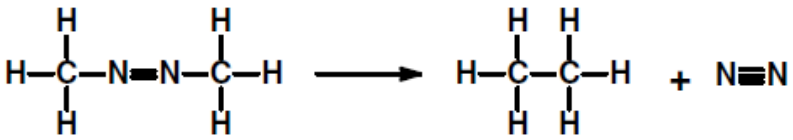
Since half-life is constant at 875 s, the reaction follows first order kinetics.

(iii) $T_{1/2} = \dfrac{\ln 2}{k}$

k = ln2 /875

= 7.92 x $10^{-4}$ $s^{-1}$

**(iv)**

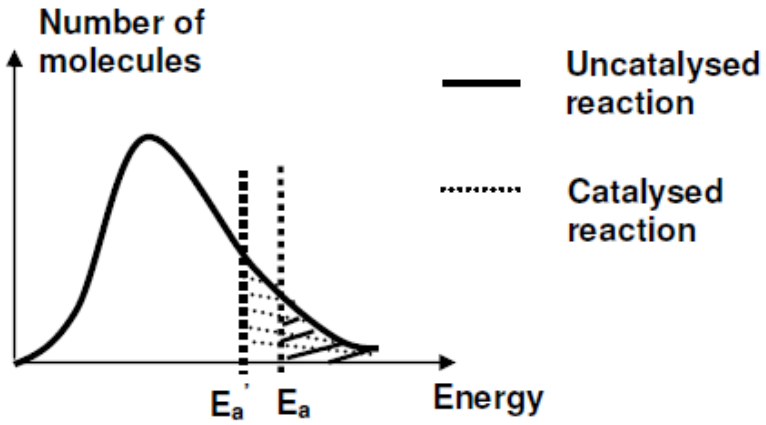


**Bonds broken = 2(C–N) + N=N**
**= 2(305) + 410 = 1020 kJ $mol^{-1}$**
**Bonds formed = (C–C) + N≡N**
**= 350 + 994 = 1344 kJ $mol^{-1}$**
**$\Delta H_{rxn}$ = 1020 – 1344**
**= – 324 kJ $mol^{-1}$**

**(v)** A catalyst provides an alternative reaction pathway with lower activation energy.

More molecules possess energy greater or equal to activation energy, as shown by shaded areas below.

Frequency of effective collisions increases, therefore rate increases.




**2(a)(i)** let rate eqn be:rate = k[2-butanol]$^x$ [$H^+$]$^y$

$$\frac{rate(2)}{rate(1)} = \frac{k(0.5)^x(0.25)^y}{k(0.25)^x(0.25)^y}$$

$2 = (2)^x$

$\therefore x = 1$

Using expt 2 & 3,

$$\frac{rate(3)}{rate(2)} = \frac{k(0.5)^x(0.5)^y}{k(0.5)^x(0.25)^y}$$

$1 = (2)^y$

$\therefore y = 0$

(ii) Using expt 1, rate = k [2-butanol]

$1.4 \times 10^{-7} = k\,[0.25]$

$k = 5.60 \times 10^{-7}\ s^{-1}$

(b) When temperature **<u>increases</u>**,

✓ **kinetic energy** of the reacting molecules **<u>increases</u>**

✓ **fraction of molecules with energy E ≥ $E_a$ <u>increases</u>**

✓ **frequency** of **effective collisions <u>increases</u>**

✓ Since rate of reaction is **proportional** to the **frequency of effective collisions**, **rate of reaction <u>increases.</u>**

***increased in collision frequency also leads to increase in effective collision but it is a secondary factor compared to “more molecules having energy greater than activation energy”

3(i) Since a straight line graph is obtained, rate of reaction is constant regardless of concentration of $CN^-$, $\Rightarrow$ order of reaction wrt $CN^-$ is **0**

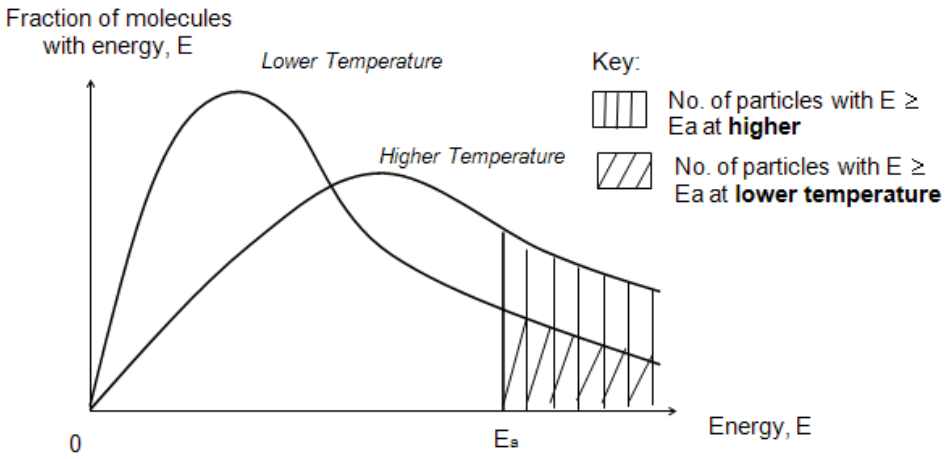
When [$C_6H_5CH_2Cl$] doubles from 1.0 mol $dm^{-3}$ to 2.0 mol $dm^{-3}$, time taken for [$CN^-$] to halve is also halved (fr *2x* min to *x* min).

$\Rightarrow$ order of reaction wrt $C_6H_5CH_2Cl$ = 1

**Rate = k[$C_6H_5CH_2Cl$]**

**** Another method to determine order of reaction w.r.t $C_6H_5CH_2Cl$ is to calculate the initial gradient and compare the gradient. But cannot use this method for this Qn because there is not enough markings on the graph to calculate gradient. ****

(ii)




When temperature of the reaction **<u>decreases</u>**,

✓ **kinetic energy** of the reacting molecules **<u>decreases</u>**

✓ **fraction of molecules with E ≥ $E_a$ decreases** *<u>as can be seen in the above diagram.</u>*

✓ **frequency** of **effective collisions <u>decreases</u>**

✓ Since rate of reaction is **proportional** to the **frequency of effective collisions**, **rate of reaction <u>decreases.</u>**

**4a(i)** From experiments 2 and 3,

**Inspection method:**

When [$OH^-$] doubles and [**D**] remains constant, the initial rate doubles.

Hence, the reaction is first order wrt $OH^-$.

**Mathematical method:**

Let the rate eqn be: Rate = k[$OH^-$][**D**]$^a$

$$\frac{\text{rate } 1}{\text{rate } 2} = \frac{[\text{D}]^a[\text{OH}^-]}{[\text{D}]^a[\text{OH}^-]}$$

$$\frac{1.8 \text{ x } 10^{-4}}{1.8 \text{ x } 10^{-4}} = \frac{[0.0100]^a[0.120]}{[0.0050]^a[0.240]}$$

$$a = 1$$

Hence, the reaction is first order wrt **D**.

*** Students are advised to use the mathematical method to avoid using the wrong expressions in the inspection method.

(ii) Using expt 1, rate = $k_1$[**D**][$OH^-$]

1.8 x $10^{-4}$ = $k_1$(0.0100)(0.120)

$k_1$ = 0.15 $mol^{-1}dm^3 s^{-1}$

**b(i)** From 0.01 $moldm^{-3}$ to 0.005 $moldm^{-3}$, $t_{1/2}$ = 115 min

From 0.005 $moldm^{-3}$ to 0.0025 $moldm^{-3}$, $t_{1/2}$ = 115 min

Since $t_{1/2}$ is(approximately) constant, thus the reaction is first order wrt **E**.

**(ii)** When [$OH^-$] is doubled, the same plot is obtained,

Rate of reaction remains constant, hence order of reaction w.r.t $OH^-$ is zero.

Overall order of reaction is dependent on **E** only.

**Rate = k[E]**

rate constant, $k_2 = \frac{\ln 2}{115} = 6.03 \times 10^{-3}$ $min^{-1}$

**(iii)** Initial rate of hydrolysis of **E** = gradient of tangent at t = 0

$$= \frac{0.010 - 0.0088}{20 \times 60} = 1.0 \times 10^{-6} \text{moldm}^{-3}\text{s}^{-1}$$

From the table in a (i),

the initial rate when [**D**] = 0.010 mol $dm^{-3}$ and [$OH^-$] = 0.012 mol $dm^{-3}$ is 1.8 x $10^{-4}$ mol $dm^{-3}s^{-1}$.

Ratio of initial rate of **D**: E = 180: 1

Since both **A** and **B** reacts with $PCl_5$ to evolve white fume of HCl, both compounds contain either an alcohol or a carboxylic acid functional group.

**D** is ethanoyl chloride formed from the reaction of ethanoic acid and $PCl_5$.

Since the hydrolysis of **D** is much faster than that of **E**, we can deduce that an alcohol functional group is present in compound **B** since a chloroalkane undergoes hydrolysis slower than an acyl chloride.

**5(i)** To **<u>keep the total volume constant</u>** so that the concentration of ethene or bromine in each reaction mixture is directly proportional to the volume used.

**(ii)** Rate of reaction is **<u>inversely proportional to the time taken</u>** for the colour of bromine to disappear and **<u>directly proportional to the volume of bromine</u>** used.

**(iii)** Rate $\propto \frac{V_{Br_2}}{t}$

Let the rate eqn be: rate=k[ethene]$^x$[bromie]$^y$

Comparing experiments **1** and **2**,

$$\frac{rate(2)}{rate(1)} = \frac{k(12)^x(20)^y}{k(20)^x(20)^y}$$

$$\frac{V_{Br_2}(2) \,/\, t\_(2)}{V_{Br_2}(1) \,/\, t\_(1)} = (\frac{3}{5})^x$$

$$\frac{20/25}{15/20} = (\frac{3}{5})^x$$

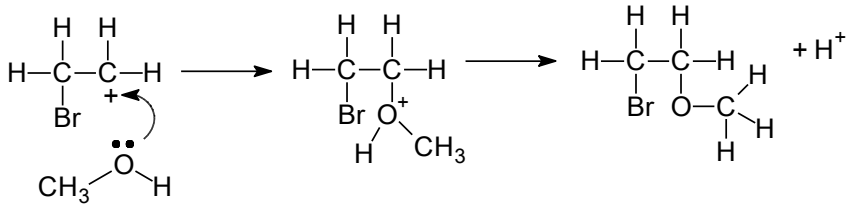
$$(\frac{3}{5}) = (\frac{3}{5})^x$$

$\therefore x = 1$

**(iv)** 15 s

**(v)** The reaction progresses via electrophilic addition mechanism with the formation of carbocation, $CH_2BrCH_2^+$.

Subsequent addition of $CH_3OH$ to the carbocation and loss of $H^+$ results in the formation of product as shown: **[1]**


H
H
H—C—C—H
+
Br
CH3
O
H
H
H
H—C—C—H
Br
O
+
H
CH3
H
H
H—C—C—H
Br
O—C
H
H
H
+ H+