REACTION KINETICS MCQ PART 1

1 The reaction between NO and Br_2 is proposed to proceed via the following mechanism:

$$\text{step 1: } NO + Br_2 \rightleftharpoons NOBr_2 \quad \text{(fast)}$$

$$\text{step 2: } NOBR_2 + NO \longrightarrow 2NOBR \quad \text{(slow)}$$

Which statements are correct?

1 $NOBr_2$ is a radical.
2 The rate equation for this reaction is rate = $k[Br_2][NO]^2$.
3 $NOBr_2$ is a transition state.

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

2 Sucrose undergoes an acid–catalysed hydrolysis according to the following equation.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The following results were obtained using hydrochloric acid as the catalyst.

experiment	initial [HC*l*] / mol dm^{-3}	initial [sucrose] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
I	0.10	0.10	0.024
II	0.10	0.15	0.036
III	0.30	0.10	0.072

The half–life of sucrose in experiment I was 3.0 s.

What is the half–life of sucrose in experiment II and in experiment III?

	experiment II	experiment III
A	3.0	3.0
B	3.0	1.0
C	2.0	1.0
D	2.0	3.0

3 Which suggested mechanism is consistent with the experimentally obtained rate equation?

	rate equation	suggested mechanism
1	rate = $k_1 [H_2O_2] [I^-]$	$H_2O_2 + I^- \xrightarrow{\text{slow}} H_2O + OI^-$ $OI^- + H^+ \xrightarrow{\text{fast}} HOI$ $HOI + H^+ + I^- \xrightarrow{\text{fast}} I_2 + H_2O$
2	rate = $k_2 [H_2] [I_2]$	$H_2 \xrightarrow{\text{slow}} 2H$ $2H + I_2 \xrightarrow{\text{fast}} 2HI$
3	rate = $k_3 [HBr]^2 [O_2]^{½}$	$2HBr + O_2 \xrightarrow{\text{fast}} 2HBrO$ $HBrO + HBr \xrightarrow{\text{slow}} H_2O + Br_2$

A 1 and 2 only

B 1 only

C 1 and 3 only

D 2 and 3 only

4 In the presence of gold wire as a catalyst, 25.0 kPa of dinitrogen oxide, N_2O, decomposes in a closed container according to the equation below.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The units of the rate constant was found to be s^{-1}.

Which of the following remains constant during the experiment?

A The rate of the reaction.

B The total pressure of the reaction mixture.

C The value of rate constant in the absence of gold.

D The time taken for the pressure of N_2O to drop by half.

5 The rate equation for a reaction between **A** and **B** is given by: rate = k[**A**].

Which of the following statements about the reaction is true?

1 **A** is involved in the rate−determining step in the reaction mechanism.
2 The rate constant, k, increases with increasing concentration of **A**.
3 A graph of rate against [**A**] gives a straight line that passes through the origin.

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

6 The reaction between carbon dioxide and potassium hydroxide is exothermic. The proposed two–step mechanism of the reaction is shown below:

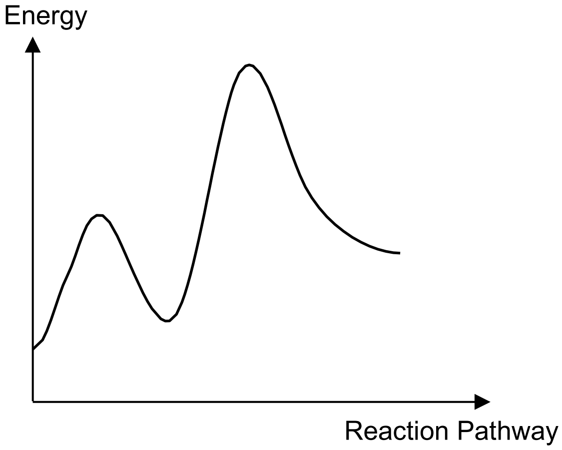
Step 1: $CO_2(aq) + KOH(aq) \rightarrow KHCO_3(aq)$
Step 2: $KHCO_3(aq) + KOH(aq) \rightarrow K_2CO_3(aq) + H_2O(l)$

Experiments were carried out to study the rate of the reaction above.

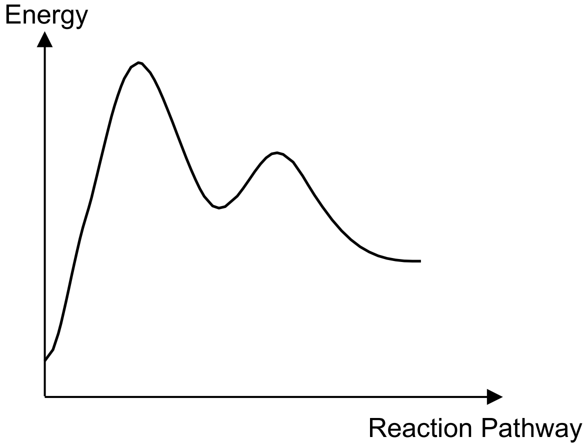
Experiment Number	Initial concentration of CO_2 / mol dm^{-3}	Initial concentration of KOH / mol dm^{-3}	Initial reaction rate / mol dm^{-3} s^{-1}
1	0.2	0.2	0.0034
2	0.4	0.2	0.0068
3	0.2	0.1	0.0017

Which of the following graphs most likely describes the energy profile of the reaction above?

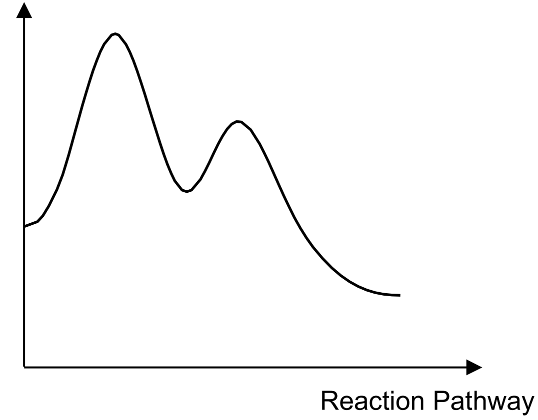
A



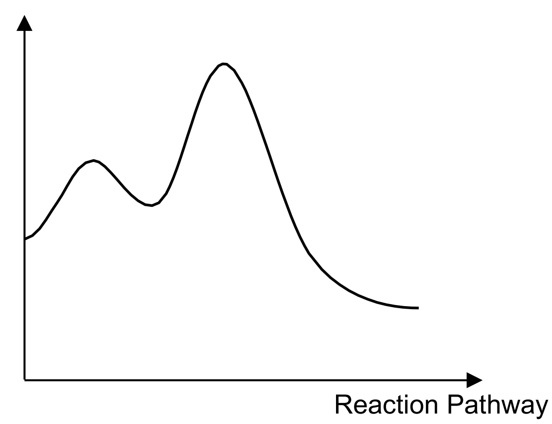
B



C



D



7 A few drops of 1–chlorobutane, 1–bromobutane, 1–iodobutane were placed separately into three test–tubes each, containing 1.0 cm^3 of aqueous silver nitrate at 60 °C.

A hydrolysis reaction occurred. (X is the halogen atom)

$H_2O + CH_3CH_2CH_2CH_2X + Ag^+ \longrightarrow CH_3CH_2CH_2CH_2OH + AgX + H^+$

Which of the following would be the best explanation for the rate of the reaction?

A The bond energy of C–X bond decreases from C–C*l* to C–I.
B The bond polarity of C–X bond decreases from C–C*l* to C–I.
C The electron deficiency of the carbon atom bonded to X decreases from C–C*l* to C–I.
D The solubility of AgX decreases from AgC*l* to AgI.

8 Nitric oxide, NO, reacts with hydrogen gas to give nitrogen and water only.

Given that rate = $k[NO]^2[H_2]$, which reaction mechanism best agrees with the experimentally determined rate law?

A $NO + NO \rightleftharpoons N_2O_2$ (slow)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (fast)

B $NO + H_2 \rightarrow HNO + H\bullet$ (slow)
$HNO + H\bullet \rightarrow \frac{1}{2}N_2 + H_2O$ (fast)

C $2NO + H_2 \rightarrow N_2O + H_2O$ (slow)
$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

D $2NO + H_2 \rightarrow 2HNO$ (slow)
$2HNO \rightarrow N_2 + H_2O_2$ (fast)

9 The initial rate method was used to investigate the reaction between compounds **K** and **L** which is catalysed by reagent **M**.

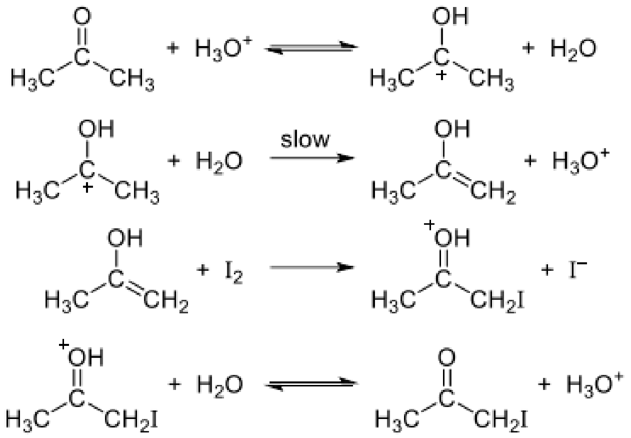
The results obtained are shown below.

experiment	initial [**K**] / mol dm^{-3}	initial [**L**] / mol dm^{-3}	initial [**M**] / mol dm^{-3}	relative rate / s^{-1}
1	0.0025	0.08	0.80	0.50
2	0.0010	0.08	0.80	0.20
3	0.0050	0.08	0.40	0.25
4	0.0050	0.04	0.80	0.50

What is the rate equation for this reaction?

A rate = k[**K**][**L**][**M**]
B rate = k[**K**][**L**]^2[**M**]
C rate = k[**K**][**L**][**M**]^2
D rate = k[**K**][**L**]^2[**M**]^2

10 The mechanism for the acid-catalysed reaction between CH_3COCH_3 and I_2 is given.



Which statements are correct for the reaction?

1 At low pH, the reaction is observed to be pseudo-first order.

2 The rate constant increases as pH decreases.

3 The rate of reaction is independent of $[I_2]$.

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

11 The equation for the bromination of propanone is shown below.

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

The rate of disappearance of the bromine colour was measured for several different concentrations of CH_3COCH_3, Br_2 and H^+ at a certain temperature.

$[CH_3COCH_3]$/ mol dm^{-3}	$[Br_2]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	rate of disappearance of Br_2 colour/ mol dm^{-3} s^{-1}
0.30	0.05	0.05	5.70×10^{-5}
0.30	0.10	0.05	5.70×10^{-5}
0.30	0.05	0.10	1.14×10^{-4}
0.40	0.05	0.20	3.04×10^{-4}

Which statement about the above reaction is correct?

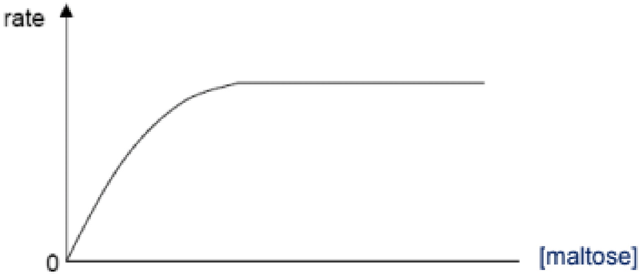
A The rate equation for the reaction is rate = $k[CH_3COCH_3][Br_2]$.

B The rate constant for the reaction is 3.80×10^{-3} mol^{-1} dm^3 s^{-1}.

C The rate constant of the reaction doubles when $[CH_3COCH_3]$ is doubled.

D The time taken for the concentration of CH_3COCH_3 to decrease to half its initial value is the same for all experiments.

12 The graph shows the result of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied, but that of amylase was kept constant.



Which conclusions can be deduced from these results?

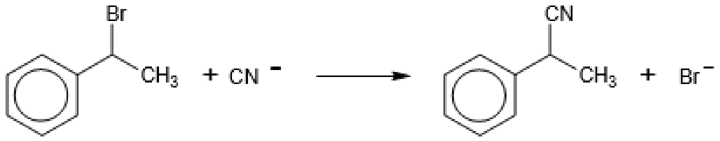
1 When [maltose] is low, the rate is first order with respect to [maltose].

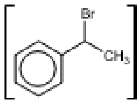
2 When [maltose] is high, the rate is independent of [maltose].

3 When [maltose] is high, the rate is independent of [amylase].

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

13 The reaction of (1-bromoethyl)benzene with sodium cyanide, NaCN, is investigated in a series of experiments.

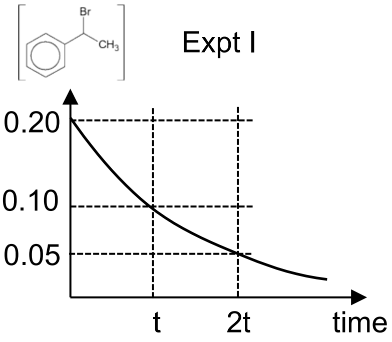


Experiment	 / mol dm^{-3}	[CN$^-$] / mol dm^{-3}
I	0.20	2.00
II	2.00	0.20
III	2.00	2.00

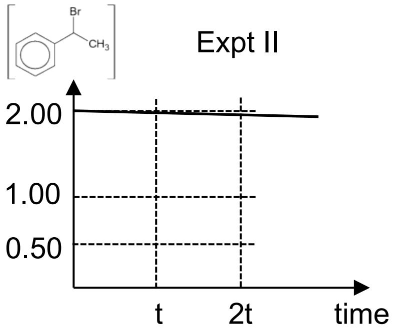
It was known that the reaction is first order with respect to (1-bromoethyl)benzene.

Which graph shows a correct experimental result and proves the reaction is zero order with respect to sodium cyanide?

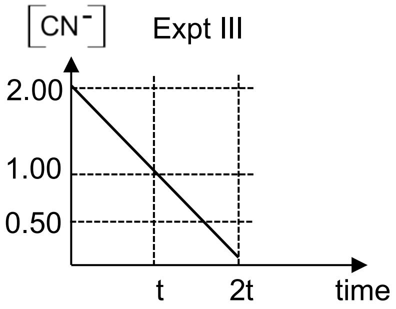
A



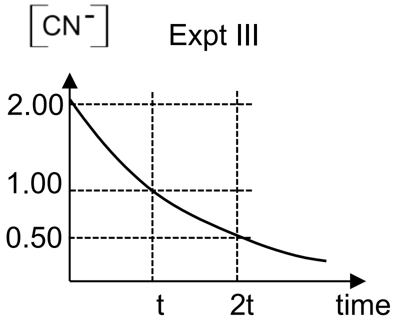
B



C



D



14 The kinetics of the following reaction is investigated, and the experimental data is given in the table below.

$$2R + 2S \rightarrow T + U$$

[R] / mol dm^{-3}	[S] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
0.015	0.010	5.10×10^{-4}
0.030	0.020	4.08×10^{-3}
0.045	0.010	1.53×10^{-3}

What is the numerical value of the rate constant for this reaction?

A 0.00294 **B** 3.40 **C** 227 **D** 340

REACTION KINETICS STRUCTURED QUESTIONS PART 1

1 **(a)** The kinetics of the chlorination of methane is studied.

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

The first two steps of the mechanism of the reaction are shown below.

step 1 $Cl_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2Cl\bullet$ fast

step 2 $Cl\bullet + CH_4 \xrightarrow{k_2} HCl + \bullet CH_3$ slow

(i) The rate equation for the reverse of step 1 is rate = $k_r [Cl\bullet]^2$.

At equilibrium, the rates of the forward and reverse reactions in step 1 are equal.

Write the rate equation for the forward reaction of step 1 and hence write an expression for the concentration of the intermediate $Cl\bullet$ radicals.

…………………………………………………………………………………………………

…………………………………………………………………………………………………[2]

(ii) Write the rate equation for the forward reaction of step 2.

…………………………………………………………………………………………………[1]

(iii) Use your answer to **(a)(i)** and the rate equation for step 2 to write the overall rate equation for the chlorination of methane.

Hence, deduce the orders of reaction with respect to the concentration of the species in the overall rate equation and the overall order of the reaction.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………[2]

(b) When chlorine and bromine react with methane, light of different energy and wavelength is required for stage 1 of the reaction.

stage 1 $X_2 \rightarrow 2X\bullet$ (X = C*l*, Br)

Light of longer wavelength is lower in energy than light of shorter wavelength.

This relationship between the energy and wavelength of light is shown in the equation below.

$$E = \frac{hc}{\lambda}$$

Where: E is the energy of the light of certain wavelength in Joule (J)
h is Planck constant = 6.63×10^{-34} J s
c is the speed of light = 3.00×10^{8} m s^{-1}
λ is the wavelength of light in metre (m)

(i) Bond energy is the energy required to break **one mole** of a covalent bond in the gaseous state.

Using the *Data Booklet* and the equation $E = \frac{hc}{\lambda}$, determine the wavelength of light required to break **one** C*l*–C*l* bond.

Leave your answer in nanometres (nm). One nm is equivalent to 10^{-9} m.

[2]

(ii) Using Table 5.1, identify the colour of light that provides the minimum energy for the reaction between chlorine and methane.

Table 5.1

Colour	Wavelength / nm
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

……………………………………………………………………………………………….[1]

(iii) Hence, explain why the bromination of methane can be carried out with yellow light. (Calculation is not required)

……………………………………………………………………………………………………

……………………………………………………………………………………………………[1]

(c) Fig. 5.1 shows four possible monohalogenoalkanes that can be formed from the reaction of 2-methylbutane with chlorine or bromine. (X = C*l* or Br)

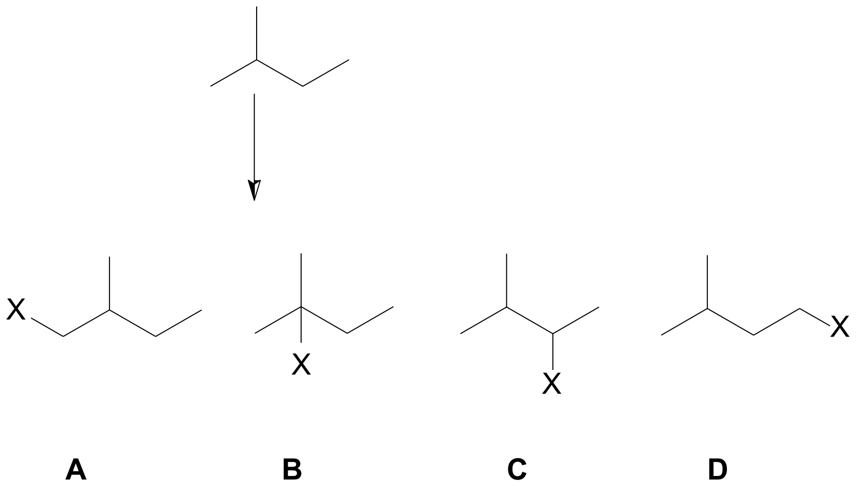


Fig. 5.1

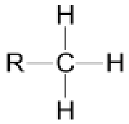
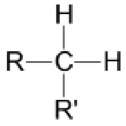
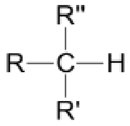
(i) State the expected ratio of products **A, B, C** and **D** in the mixture, assuming equal rate of substitution of all the H atoms.

……………………………………………………………………………………………………[1]

(ii) The ratio of the isomeric products is more accurately determined if the relative rates of substitution of different H atoms by different halogen atoms are taken into account.

The types of hydrogen atoms in alkanes, together with their relative rates of substitution by C*l* and Br atom, are shown in Table 5.2.

Table 5.2

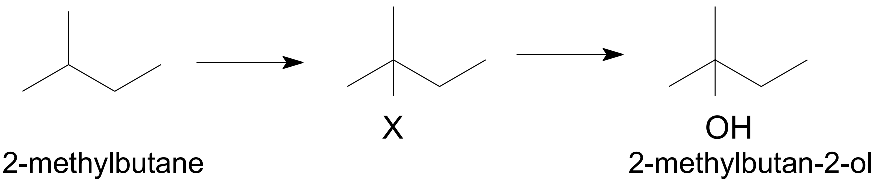
Types of H atoms	**Structure**	**Relative rate of substitution by C*l* atom**	**Relative rate of substitution by Br atom**
Primary	 $\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}H}$	1	1
Secondary	 $\mathrm{R{-}\overset{H}{\underset{R'}{C}}{-}H}$	3	80
Tertiary	 $\mathrm{R{-}\overset{R''}{\underset{R'}{C}}{-}H}$	5	1600

By taking into account the relative rates of substitution of H atoms given above, show that:

- the monochlorinated forms of products **A, B, C** and **D** are formed in the ratio of 6:5:6:3.
- the monobrominated forms of products **A, B, C** and **D** are formed in the ratio of 6:1600:160:3.

[2]

(iii) 2-methylbutan-2-ol may be synthesised from 2-methylbutane by using the reaction scheme as shown.



Using the ratios given in **(c)(ii)**, explain if chlorine or bromine is a better choice of reagent in this synthesis.

....

....[1]

(d) One of the possible termination steps in the free radical substitution reaction is the reaction between two alkyl radicals to form an alkane.

The equation shows the collision of two propyl radicals in the termination step of a reaction between propane and chlorine.

$$2{\bullet}C_3H_7(g) \rightarrow C_6H_{14}(g)\ \Delta S^{\ominus} = -190\ J\ K^{-1}\ mol^{-1}$$

(i) Use the data in Table 5.3 to calculate the enthalpy change for this termination step at 298 K.

Table 5.3

species	$\Delta H^{\ominus}_f$ / kJ mol^{-1}
$\bullet\,C_3H_7(g)$	+103
$C_6H_{14}(g)$	-167

[1]

(ii) Explain how the values of ΔH^{o} and ΔS^{o} relate to the changes that occur at the molecular level for this termination step.

....

....

....

....[2]

(iii) Calculate ΔG^o for this termination step at 298 K and explain the effect on the spontaneity of this reaction of increasing the temperature above 298 K.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

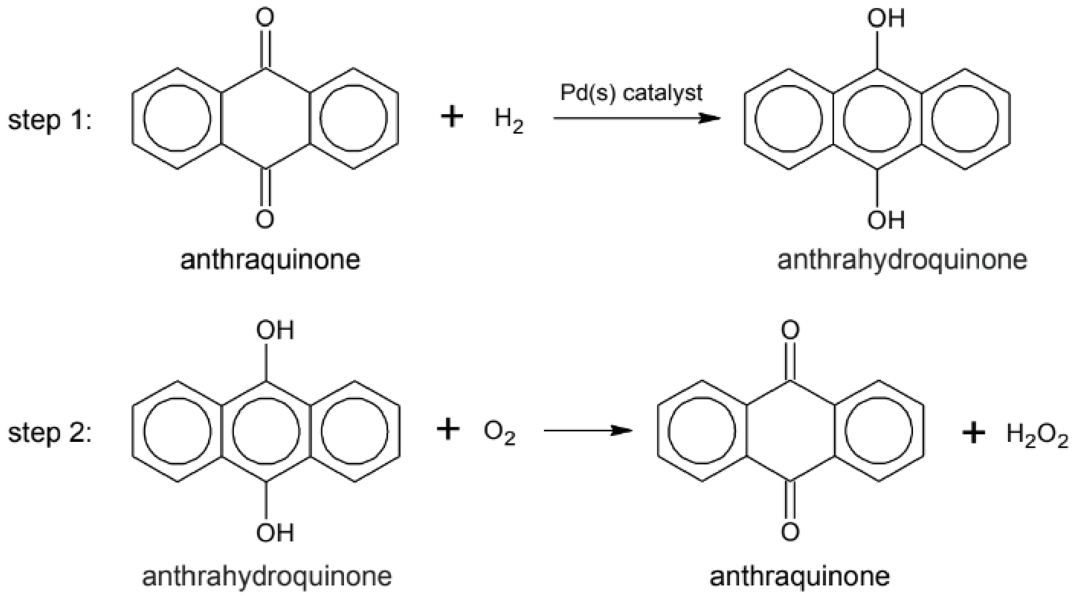
…………………………………………………………………………………………………

………………………………………………………………………………………………[2]

[Total: 18]

2 Hydrogen peroxide, H_2O_2, finds its applications in a diversity of fields. Amongst many uses, it is an important precursor for the synthesis of organic peroxides and polymers. As such the manufacture of hydrogen peroxide has been an important industrial process since the 20th century.

Today, most of the world's hydrogen peroxide is manufactured by the anthraquinone process. This process involves the two steps shown below.



(a) Step 1 involves the adsorption of H_2 gas onto the surface of the palladium metal catalyst.

(i) State the property that palladium possesses that allows it to act as a catalyst in step 1, and explain how the adsorption of H_2 gas onto palladium increases the rate of reaction.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(ii) A study of the kinetics of step 1 revealed that at low pressures, the rate of reaction increases with increasing pressure of H_2. However, at high pressures, increasing the pressure of H_2 has no effect on the rate of reaction.

Explain these observations.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………........ [2]

Although palladium and nickel belong to Group 10 of the Periodic Table, both elements have different ways of filling up their d orbitals. For palladium, it has a fully filled 4d subshell.

(iii) Draw, on the Cartesian axes provided in Fig. 4.1, the orbital from which the first electron of palladium is removed. Label the axes and orbitals clearly.

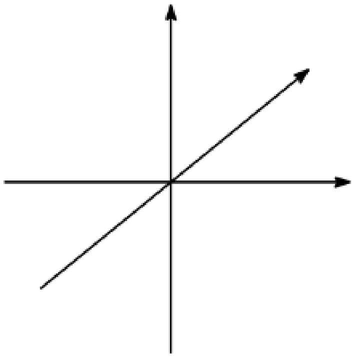


Fig. 4.1

[1]

(iv) It is observed that the first ionisation energies of the Period 4 transition elements remain relatively invariant. Explain this observation.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………........ [2]

(b) At the end of step 1, anthrahydroquinone is extracted from the reaction mixture before reacting it with O_2 in step 2.

It is observed that step 2 follows the rate equation below.

$$\text{rate} = k[\text{anthrahydroquinone}][O_2]$$

In this step, a large excess of O_2 is required to ensure that anthrahydroquinone is completely oxidised back to anthraquinone, producing hydrogen peroxide.

(i) Explain why the rate equation for step 2 can be rewritten as

rate = k'[anthrahydroquinone].

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………….................. [1]

(ii) Hence sketch, on Fig 4.2, a labelled graph to show how the concentration of H_2O_2 in step 2 will vary over time.

Fig 4.2

[2]

(iii) Step 2 was repeated with different initial pressures of O_2 and different initial concentrations of anthrahydroquinone.

Table 4.1 shows the initial quantities of reactants used for each experiment and the time required for the initial concentration of anthrahydroquinone to be halved for experiment 1.

Table 4.1

experiment	initial pressure of O_2(g) / Pa	initial [anthrahydroquinone] / mol dm^{-3}	time required for initial [anthrahydroquinone] to be halved / min
1	4×10^5	1.00	12.0
2	4×10^5	0.50	
3	8×10^5	1.00	

Complete Table 4.1 and explain your answer.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………….............. [2]

(c) At the end of step 2, the reaction mixture contains only anthraquinone and H_2O_2. H_2O_2 can be separated out from the reaction mixture by adding water to the reaction mixture.

With reference to the bonding between relevant molecules, explain how the addition of water allows this to happen.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

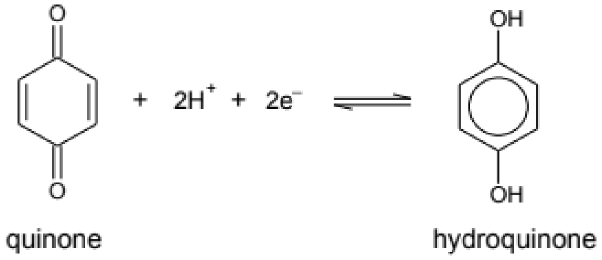
……………………………………………………………………………………………………

……………………………………………………………………………………………………

………………………………………………………………………………………………... [2]

(d) Quinone and hydroquinone have similar structures to anthraquinone and anthrahydroquinone respectively.

The standard reduction potential of the quinone–hydroquinone system is +0.70 V.



$E^{\theta} = +0.70$ V

An electrolytic cell was set up under standard conditions with a mixture of aqueous quinone and dilute sulfuric acid as the electrolyte and platinum rods as electrodes.

State the products formed at the anode and the cathode.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………….. [2]

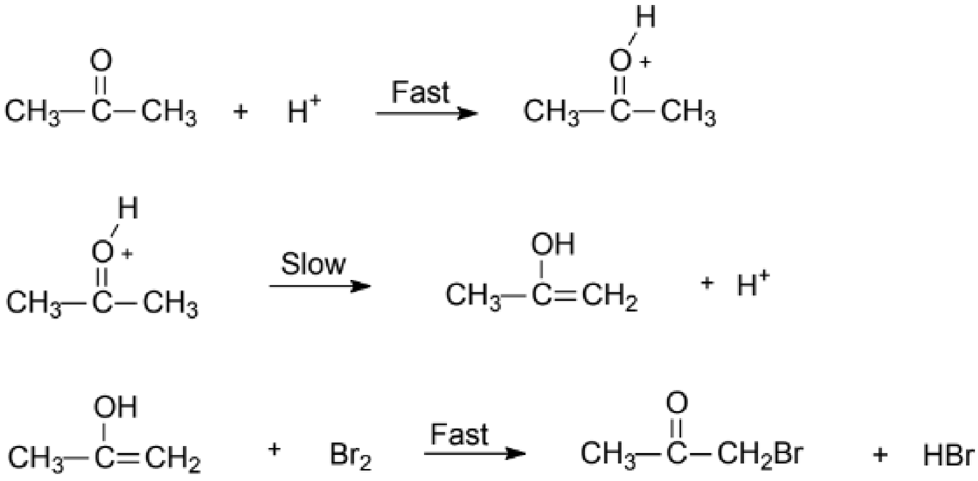
[Total: 16]

3 Carbonyl compounds can react with halogens in acidic or alkaline medium to form different products. Kinetic studies are conducted to investigate the orders of reaction and the mechanisms of these reactions.

In acidic medium, propanone reacts with bromine to form bromopropanone as shown in the equation below:

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + HBr$$

The kinetic studies of the above reaction have shown that the reaction is second order overall, and a three-step mechanism is involved in this reaction.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H^+ \xrightarrow{\text{Fast}} CH_3-\overset{\overset{H-O^+}{\|}}{C}-CH_3$$

$$CH_3-\overset{\overset{H-O^+}{\|}}{C}-CH_3 \xrightarrow{\text{Slow}} CH_3-\overset{\overset{OH}{|}}{C}=CH_2 + H^+$$

$$CH_3-\overset{\overset{OH}{|}}{C}=CH_2 + Br_2 \xrightarrow{\text{Fast}} CH_3-\overset{\overset{O}{\|}}{C}-CH_2Br + HBr$$

(a) From the mechanism above, construct the rate equation for the above reaction.

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

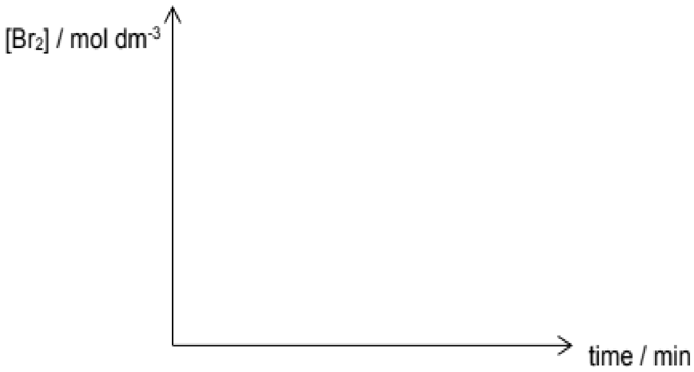
(b) From the mechanism above, how can you deduce that H^+ is acting as a catalyst?

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(c) Sketch, in the space below, the graph of $[Br_2]$ against time in minutes, given that the initial concentration of Br_2 is 0.008 mol dm^{-3} and initial concentration of propanone, CH_3COCH_3, is 0.80 mol dm^{-3}.



[1]

(d) Explain what will happen to the rate of reaction if chlorine is used in place of bromine, assuming that the mechanism remains unchanged?

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(e) The kinetics data for the experiment may be collected using a continuous sampling method, which requires a sample of the chemical reaction to be extracted at various time intervals from a reaction mixture followed by titration.

Briefly describe a physical property that allows you to determine the $[Br_2]$ at various times.

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]

(f) The reaction between CH_3COCH_3 and Br_2 was carried out in experiments **1** and **2**, and the following results were obtained:

Experiment	Initial [CH_3COCH_3]/ mol dm^{-3}	Initial [H^+] / mol dm^{-3}	Initial [Br_2] / mol dm^{-3}	Half-life / min
1	0.40	0.30	0.20	22.5
2	0.60	0.10	0.20	s

The half-life of CH_3COCH_3 in experiment **1** was found to be constant at 22.5 minutes. Predict the value of half-life of CH_3COCH_3 in experiment **2**, **s**, giving your reasoning.

………

………

………

………

……… [2]

(g) With the aid of a labelled Boltzmann distribution diagram, explain how the presence of a catalyst affects the rate of a chemical reaction.

[3]

[Total: 10]

4 Nitrogen dioxide, NO_2, is a highly reactive gas due to the presence of an unpaired electron on the nitrogen atom.

(a) (i) State three basic assumptions of the kinetic theory as applied to an ideal gas.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

(ii) Fig. 2.1 shows how $\frac{pV}{T}$ varies with pressure for 1 mol of ideal gas and 1 mol of NO_2 at T1 K.

On Fig. 2.1, sketch a graph to show how $\frac{pV}{T}$ varies with pressure for 1 mol of NO_2 at a higher temperature of T_2 K. Label your graph as **(a)(ii)** and explain your answer.

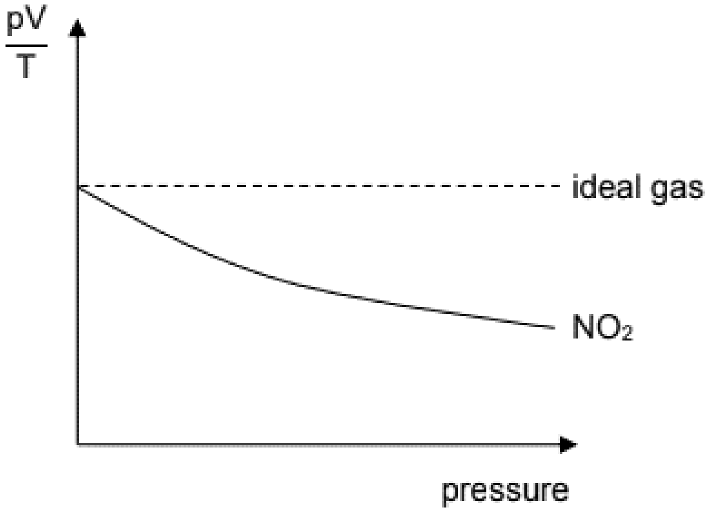


Fig. 2.1

....

....

....

....

(b) Nitrogen dioxide undergoes the following gas phase reaction with hydrogen chloride, as shown in equation 2.1.

equation 2.1 $2NO_2(g) + HCl(g) \rightarrow NOCl(g) + HNO_3(g)$

To study the kinetics for this reaction, three separate experiments were carried out in a vessel of fixed volume at a constant temperature of 500 K. The initial concentrations of NO_2 and HC*l* are shown in Table 2.1.

Table 2.1

experiment	initial [NO_2] / mol dm^{-3}	initial [HC*l*] / mol dm^{-3}
1	1.00	0.05
2	0.50	0.05
3	0.50	0.01

To monitor the progress of the reaction for each experiment, the total pressure in the vessel was measured at regular time intervals and the corresponding concentrations of NOC*l* were calculated.

Fig. 2.2 shows how the concentration of NOC*l* varies with time for experiments 1 and 2.

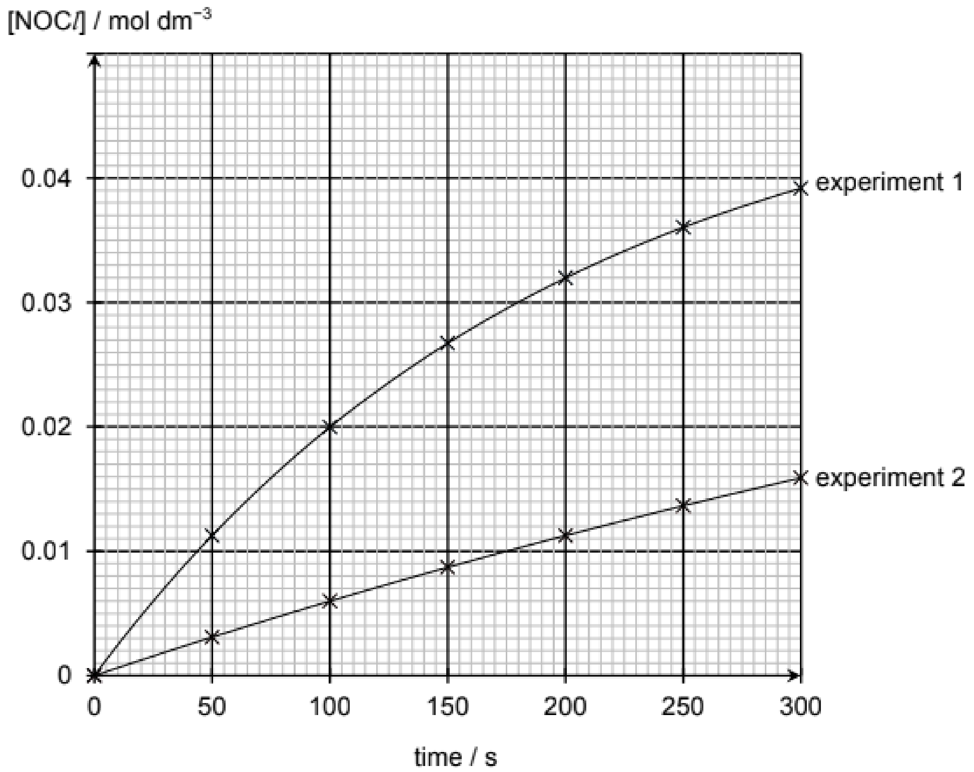


Fig. 2.2

(i) With reference to Fig. 2.2, calculate the mole fraction of NOC*l* present in the vessel for experiment 1 at *t* = 200 s.

[2]

(ii) Calculate the total pressure, in Pa, in the vessel for experiment 1 at *t* = 200 s.

You may assume that all the gases behave ideally.

[2]

(iii) Using Fig. 2.2, determine the initial rate or reaction for experiments 1 and 2.

Hence, deduce the order of reaction with respect to NO_2.

[2]

(iv) State the final concentration of NOC*l* in the vessel for experiment 1 if the reaction were to proceed to completion.

……………………………………………………………………………………….... [1]

(v) Hence, determine the order of reaction with respect to HC*l*.

Show your working, including construction lines on Fig. 2.2.

[2]

(vi) The half-life of the reaction in experiment 2 was found to be 540 s.

With reference to Table 2.1, suggest how the half-life of the reaction in experiment 3 will compare to that of experiment 2. Explain your answer.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [2]

(c) N_2O_4 can undergo dissociation to form NO_2, which then reacts with ethene to form 1,2-dinitroethane. The reaction mechanism consists of three steps as shown in Fig. 2.3.

step 1 $N_2O_4(g) \rightleftharpoons 2\dot{N}O_2$ fast

step 2 $CH_2CH_2(g) + \dot{N}O_2)(g) \xrightarrow{k_2} \dot{C}H_2CH_2NO_2\ (g)$ slow

step 3 $\dot{C}H_2CH_2NO_2(g) + \dot{N}O_2(g) \xrightarrow{k_3} O_2NCH_2CH_2NO_2(g)$ fast

Fig. 2.3`

(i) Write an overall equation for the reaction.

………………………………………………………………………………………………… [1]

(ii) Name the type of reaction occurring in **(c)(i)**.

………………………………………………………………………………………………… [1]

(iii) The dissociation of N_2O_4 in step 1 of the mechanism rapidly reaches equilibrium due to the use of solid platinum which acts as a heterogeneous catalyst.

Outline the mode of action of the platinum catalyst in the dissociation of N_2O_4.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [2]

(iv) The equilibrium constant for step 1 of the mechanism is K_c.

Write an expression for $[NO_2]$ in terms of K_c.

[1]

(v) Using your answer in **(c)(iv)** and the mechanism in Fig. 2.3**,** write the overall rate equation for the reaction.

[1]

[Total: 20]

ANSWERS FOR REACTION KINETICS MCQ PART 1

1 The reaction between NO and Br_2 is proposed to proceed via the following mechanism:

step 1: $NO + Br_2 \rightleftharpoons NOBr_2$ (fast)

step 2: $NOBR_2 + NO \longrightarrow 2NOBR$ (slow)

Which statements are correct?

1 $NOBr_2$ is a radical.
2 The rate equation for this reaction is rate = $k[Br_2][NO]^2$.
3 $NOBr_2$ is a transition state.

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

Statement 1: Correct. There is one unpaired electron on the N atom in the molecule.
Statement 2: Correct.
From the slow step,

$$\text{Rate} = k[NOBr_2][NO] \text{ --- (1)}$$

$$\text{From step 1, } K_c = \frac{[NOBr_2]}{[NO][Br_2]}$$

$$[NOBr] = K_c[NO][Br_2] \text{ --- (2)}$$

$$\text{Sub. (2) into (1), Rate} = k(K_c[NO][Br_2])[NO]$$

$$= k'[NO]^2[Br_2]$$

Statement 3: Incorrect. $NOBr_2$ is an intermediate as it appears in the reaction mechanism but does not appear in the overall equation.

2 Sucrose undergoes an acid–catalysed hydrolysis according to the following equation.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The following results were obtained using hydrochloric acid as the catalyst.

experiment	initial [HC*l*] / mol dm^{-3}	initial [sucrose] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
I	0.10	0.10	0.024
II	0.10	0.15	0.036
III	0.30	0.10	0.072

The half–life of sucrose in experiment I was 3.0 s.

What is the half–life of sucrose in experiment II and in experiment III?

	experiment II	experiment III
A	3.0	3.0
B	3.0	1.0
C	2.0	1.0
D	2.0	3.0

comparing expt I and II, when [sucrose] increased 1.5times, the initial rate increased by 1.5times. Since rate of reaction is directly proportional to [sucrose], order of reaction wrt sucrose is 1.

Comparing expt I and III, when [HC*l*] is tripled, the initial rate tripled. Since the rate of reaction is directly proportional to [HC*l*], order of reaction wrt HC*l* is 1.

Rate = *k* [HC*l*]
[sucrose] rate = *k*'
[sucrose]
where *k*' = *k* [HC*l*] ∵ HC*l* is a catalyst and its concentration remains constant

Since the half–life of expt I is 3.0 s and

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k\,[HCl]_I} = 3.0\text{s for 1}^{st}\text{ order reaction wrt sucrose,}$$

expt II Since [HC*l*] is constant, half–life for expt II will remain as 3.0 s.
expt III As [HC*l*] is tripled, half–life for expt III will be 1.0 s

$$(t_{1/2}\text{ for expt III} = \frac{\ln 2}{k\,[HCl]_{III}} = \frac{\ln 2}{k(3[HCl]_I)} = \frac{1}{3}\frac{(\ln 2)}{k\,[HCl]_I} = \frac{1}{3}(3.0) = \underline{1.0\text{ s}})$$

3 Which suggested mechanism is consistent with the experimentally obtained rate equation?

	rate equation	suggested mechanism
1	rate = $k_1 [H_2O_2] [I^-]$	$H_2O_2 + I^- \xrightarrow{\text{slow}} H_2O + OI^-$ $OI^- + H^+ \xrightarrow{\text{fast}} HOI$ $HOI + H^+ + I^- \xrightarrow{\text{fast}} I_2 + H_2O$
2	rate = $k_2 [H_2] [I_2]$	$H_2 \xrightarrow{\text{slow}} 2H$ $2H + I_2 \xrightarrow{\text{fast}} 2HI$
3	rate = $k_3 [HBr]^2 [O_2]^{1/2}$	$2HBr + O_2 \xrightarrow{\text{fast}} 2HBrO$ $HBrO + HBr \xrightarrow{\text{slow}} H_2O + Br_2$

A 1 and 2 only

B 1 only

C 1 and 3 only

D 2 and 3 only

The rate equation / order of reaction of a reaction can be derived from the stoichiometric coefficients of the species involved in the slow step, including preceding fast step(s).

1 is consistent. 1 mol of H_2O_2 reacts with 1 mol of I^- in the slow step (r.d.s.), which is also the first step. Hence the rate equation is as shown.

2 is inconsistent. Correct rate equation should be rate = $k_2[H_2]$ since only 1 mol of H_2 is involved in the slow step.

3 is consistent. As the slow step is not the first step, you need to consider the preceding fast step. Based on the elementary step, rate = $k_3[HbrO][HBr]$

However, HbrO is an intermediate and its concentration is dependent on the reaction between HBr and O_2 so you need to include this in the rate equation.

Shortcut for consideration: If the intermediate is the ONLY product formed in the preceding fast step, you can just change its stoichiometric coefficient to be the same as that in the slow step. Similarly, multiply by the same factor for the reactants in the fast step. In this case, the mechanism can be rewritten as

$$HBr + \frac{1}{2}O_2 \xrightarrow{\text{fast}} HbrO$$

$$HbrO + HBr \xrightarrow{\text{slow}} H_2O + Br_2$$

Hence the rate equation is rate $= k_3[HBr][HbrO]$

$= k_3'[HBr][HBr][O_2]^{\frac{1}{2}}$

$= k_3'[HBr]^2[O_2]^{\frac{1}{2}}$

4 In the presence of gold wire as a catalyst, 25.0 kPa of dinitrogen oxide, N_2O, decomposes in a closed container according to the equation below.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The units of the rate constant was found to be s^{-1}.

Which of the following remains constant during the experiment?

A The rate of the reaction.

B The total pressure of the reaction mixture.

C The value of rate constant in the absence of gold.

D The time taken for the pressure of N_2O to drop by half.

Since this is a first order reaction based on the rate constant units, only the half-life remains constant.
Option A: Rate should decrease as the pressure of reactant decreases.
Option B: The total pressure should increase as the volume remains constant but more gas products are formed.
Option C: The rate constant is different without the use of gold as reaction rate will decrease.

5 The rate equation for a reaction between **A** and **B** is given by: rate = *k*[**A**].

Which of the following statements about the reaction is true?

1 **A** is involved in the rate−determining step in the reaction mechanism.
2 The rate constant, *k*, increases with increasing concentration of **A**.
3 A graph of rate against [**A**] gives a straight line that passes through the origin.

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

Concept: Reaction mechanism

1. **True statement. From the rate equation, 1 molecule of A is involved in the rate determining step of the reaction.**
2. **False. Rate constant, *k*, is only affected by temperature and catalyst.**
3. **True statement. From the rate equation, rate is directly proportional to [A] hence is reflected as a straight line passing through the origin.**

Answer: B

6 The reaction between carbon dioxide and potassium hydroxide is exothermic. The proposed two–step mechanism of the reaction is shown below:

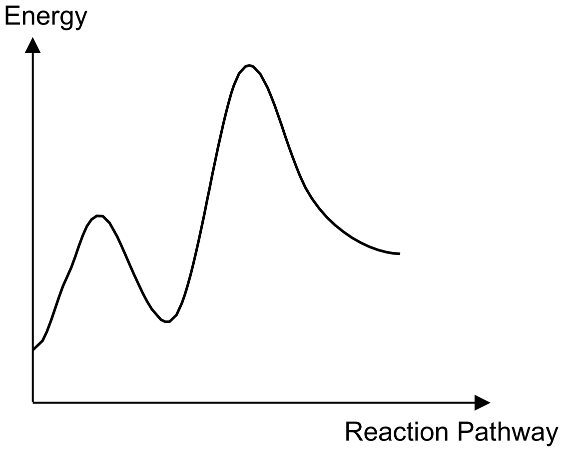
Step 1: $CO_2(aq) + KOH(aq) \rightarrow KHCO_3(aq)$
Step 2: $KHCO_3(aq) + KOH(aq) \rightarrow K_2CO_3(aq) + H_2O(l)$

Experiments were carried out to study the rate of the reaction above.

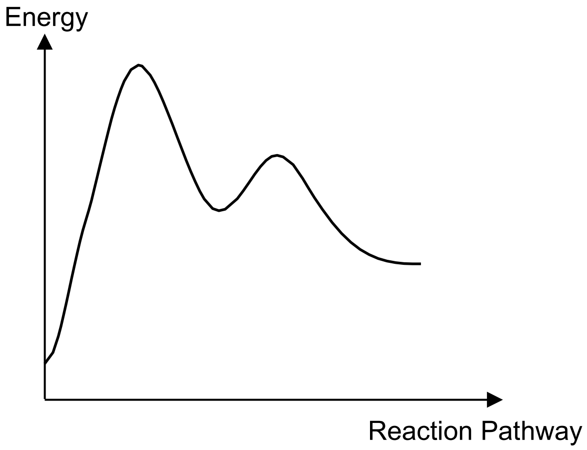
Experiment Number	Initial concentration of CO_2 / mol dm^{-3}	Initial concentration of KOH / mol dm^{-3}	Initial reaction rate / mol dm^{-3} s^{-1}
1	0.2	0.2	0.0034
2	0.4	0.2	0.0068
3	0.2	0.1	0.0017

Which of the following graphs most likely describes the energy profile of the reaction above?

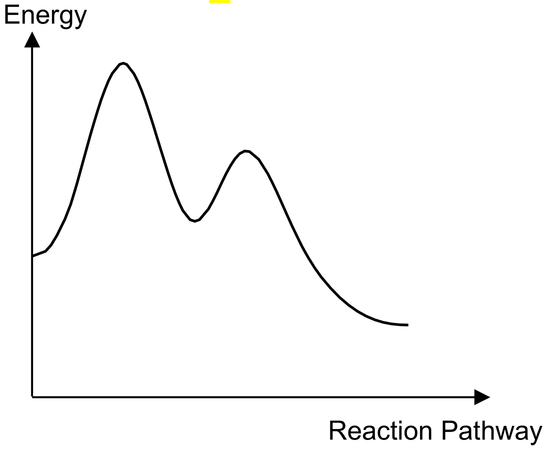
A



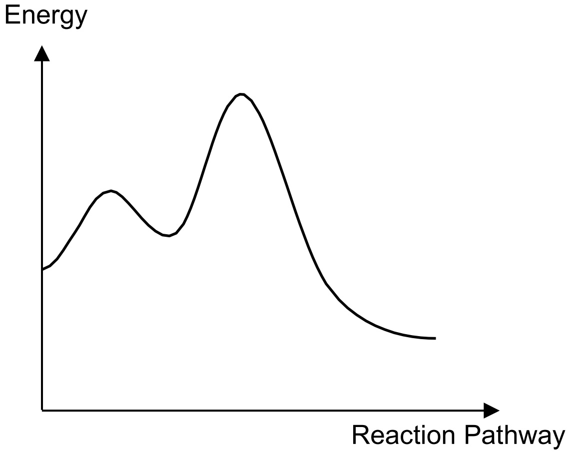
B



C



D



Concept: Kinetics (Reaction mechanism and order of reactions)

Answer: C

Comparing Expts 1 and 2, using the inspection method, by keeping concentrations of KOH constant, while doubling the concentration of CO_2, the rate doubles. Hence, the rate of reaction is directly proportional to $[CO_2]$.
Therefore the reaction is first order wrt CO_2.

Comparing Expts 1 and 3, using the inspection method, by keeping concentrations of CO_2 constant, while halving the concentration of KOH, the rate is halved. Hence, the rate of reaction is directly proportional to [KOH].
Therefore the reaction is first order wrt KOH.

Rate = $k[CO_2][KOH]$

Based on the rate equation, it can be inferred that 1 molecule of CO_2 reacts with 1 molecule of KOH in the rate determining step, i.e. slow step which corresponds to step 1 of the reaction mechanism proposed.
Since the slow step has a high activation energy and is an overall exothermic reaction, therefore the graph reflected corresponds to option C.

7 A few drops of 1–chlorobutane, 1–bromobutane, 1–iodobutane were placed separately into three test–tubes each, containing 1.0 cm^3 of aqueous silver nitrate at 60 °C.

A hydrolysis reaction occurred. (X is the halogen atom)

$$H_2O + CH_3CH_2CH_2CH_2X + Ag^+ \longrightarrow CH_3CH_2CH_2CH_2OH + AgX + H^+$$

Which of the following would be the best explanation for the rate of the reaction?

A The bond energy of C–X bond decreases from C–C*l* to C–I.
B The bond polarity of C–X bond decreases from C–C*l* to C–I.
C The electron deficiency of the carbon atom bonded to X decreases from C–C*l* to C–I.
D The solubility of AgX decreases from AgC*l* to AgI.

Topic: Halogen Derivatives Concept: Hydrolysis in RX

Answer: A
Bond energy of C–X (kJ mol^{-1}) : C–C*l* (340) > C–Br (280) > C–I (240).
The rate of hydrolysis increases from $CH_3CH_2CH_2CH_2Cl$ to $CH_3CH_2CH_2CH_2I$. The rate of hydrolysis is determined by the bond energy of C–X bond.
The bond energy of C–X bond decreases from C–C*l* to C–I. Ease to break the C–X bond increases from C–C*l* to C–I.

8 Nitric oxide, NO, reacts with hydrogen gas to give nitrogen and water only.

Given that rate = $k[NO]^2[H_2]$, which reaction mechanism best agrees with the experimentally determined rate law?

A $NO + NO \rightleftharpoons N_2O_2$ (slow)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (fast)

B $NO + H_2 \rightarrow HNO + H\bullet$ (slow)
$HNO + H\bullet \rightarrow \frac{1}{2}N_2 + H_2O$ (fast)

C $2NO + H_2 \rightarrow N_2O + H_2O$ (slow)
$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

D $2NO + H_2 \rightarrow 2HNO$ (slow)
$2HNO \rightarrow N_2 + H_2O_2$ (fast)

The proposed reaction mechanism must fulfill two criteria: 1. Given that rate = k$[NO]^2$[H2], the slow step should involve two NO molecules and one H2 molecule. 2. The overall equation should contain the products N2 and H2O only, as given in the question.		
✗	**A**	Does not fulfil both criteria: • Only two NO molecules involved in the slow step, missing one H2 molecule. • Final products are N2O and H2O, not N2 and H2O.
✗	**B**	Does not fulfil criterion (1): • Only one NO molecule and one H2 molecule involved in slow step, missing one NO molecule.
✓	**C**	Fulfils both criteria.
✗	**D**	Does not fulfil (2): • Products of the reaction are N2 and H2O2, not N2 and H2O.

9 The initial rate method was used to investigate the reaction between compounds **K** and **L** which is catalysed by reagent **M**.

The results obtained are shown below.

experiment	initial [**K**] / mol dm^{-3}	initial [**L**] / mol dm^{-3}	initial [**M**] / mol dm^{-3}	relative rate / s^{-1}
1	0.0025	0.08	0.80	0.50
2	0.0010	0.08	0.80	0.20
3	0.0050	0.08	0.40	0.25
4	0.0050	0.04	0.80	0.50

What is the rate equation for this reaction?

A rate = k[**K**][**L**][**M**]

B rate = k[**K**][**L**]^2[**M**]

C rate = k[**K**][**L**][**M**]^2

D rate = k[**K**][**L**]^2[**M**]^2

Let the orders of reaction with respect to **K**, **L** and **M** be x, y and z respectively. rate = $k[\mathbf{K}]^x[\mathbf{L}]^y[\mathbf{M}]^z$
Comparing experiments 1 and 2, keeping [**L**] and [**M**] constant, when [**K**] is decreased by a factor of 2.5, relative rate decreases by a factor of 2.5. Hence, reaction is 1st order with respect to **K** i.e. $x = 1$.

Comparing experiments 2 and 3, keeping [**L**] constant, when [**K**] is increased by a factor of 5 while [**M**] is halved, relative rate increased by a net factor of 1.25. Since the reaction is first order with respect to **K**, relative rate should have increased by a factor of 5. Hence, halving [**M**] have resulted the relative rate to decrease by a factor of 4 (i.e. 5 ÷ 1.25 = 4). Reaction is second order with respect to **M**, i.e. $z = 2$.

Mathematically,

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{k\,[\text{K}]^x_{\text{expt2}}}{k\,[\text{K}]^x_{\text{expt3}}}\,\frac{[\text{L}]^y_{\text{expt2}}}{[\text{L}]^y_{\text{expt3}}}\,\frac{[\text{M}]^z_{\text{expt2}}}{[\text{M}]^z_{\text{expt3}}}$$

$$\frac{0.20}{0.25} - \frac{k\,(0.0010)^x}{k\,(0.0050)^x}\,\frac{(0.08)^y}{(0.08)^y}\,\frac{(0.80)^z}{(0.40)^z}$$

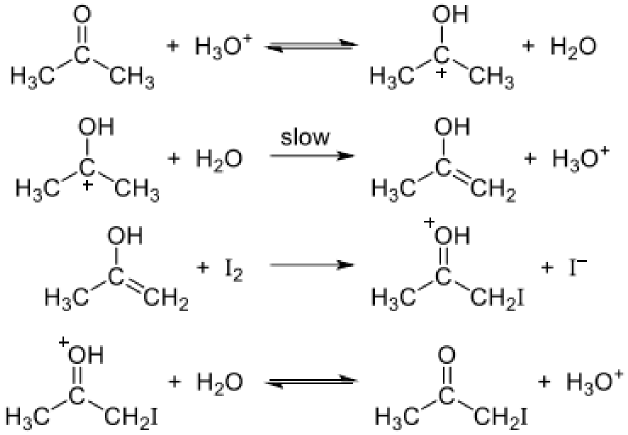
$\frac{4}{5} = \frac{1}{5}\left(\frac{0.8}{0.4}\right)^{z}$

$4 = (2)^{z}$

$Z = 2$

Comparing experiments 3 and 4, keeping [**K**] constant, when [**L**] is halved while [**M**] is doubled, relative rate increased by a net factor of 2. Since reaction is second order with respect to **M**, rate should have increased by a factor of 4. Hence, halving [**L**] have resulted the relative rate to decrease by a factor of 2 (i.e. 4 ÷ 2 = 2). Reaction is first order with respect to **L**, i.e. *y* = 1.

10 The mechanism for the acid-catalysed reaction between CH_3COCH_3 and I_2 is given.



Which statements are correct for the reaction?

1 At low pH, the reaction is observed to be pseudo-first order.

2 The rate constant increases as pH decreases.

3 The rate of reaction is independent of $[I_2]$.

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

1 √: From the slow step,
rate = $k[(CH_3)_2C^+(OH)][H_2O]$
= $k'[(CH_3)_2C(=O)][H_3O^+]$, $k' = kK_c$
At low pH, $[H_3O^+]$ is high and is essentially a constant.
rate = $k''[(CH_3)_2C(=O)]$

2 *x*: rate constant, $k = Ae^{\frac{E_a}{RT}}$
only on the E_a and T.

3 √: I_2 is only involved in a fast step after the slow (rate determining) step.
Hence rate or reaction independent of $[I_2]$.

11 The equation for the bromination of propanone is shown below.

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

The rate of disappearance of the bromine colour was measured for several different concentrations of CH_3COCH_3, Br_2 and H^+ at a certain temperature.

$[CH_3COCH_3]$/ mol dm^{-3}	$[Br_2]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	rate of disappearance of Br_2 colour/ mol dm^{-3} s^{-1}
0.30	0.05	0.05	5.70×10^{-5}
0.30	0.10	0.05	5.70×10^{-5}
0.30	0.05	0.10	1.14×10^{-4}
0.40	0.05	0.20	3.04×10^{-4}

Which statement about the above reaction is correct?

A The rate equation for the reaction is rate = $k[CH_3COCH_3][Br_2]$.

B The rate constant for the reaction is 3.80×10^{-3} mol^{-1} dm^{3} s^{-1}.

C The rate constant of the reaction doubles when $[CH_3COCH_3]$ is doubled.

D The time taken for the concentration of CH_3COCH_3 to decrease to half its initial value is the same for all experiments.

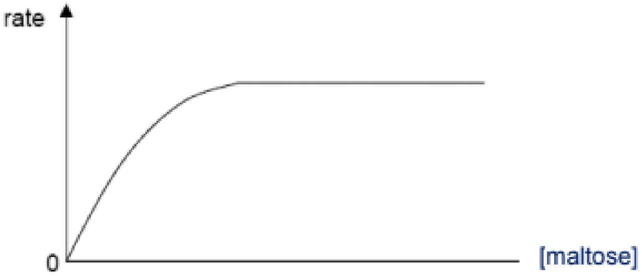
Comparing the first two sets of experiments, when concentration of bromine doubles while the concentrations of other reactants remain unchanged, the rate of reaction remains the same. Hence, it should be zero order with respect to Br_2.

Comparing the first and third sets of experiments, when concentration of H^+ doubles while the concentrations of other reactants remain unchanged, rate doubles. Hence it is first order with respect to H^+.

Comparing the third and fourth sets of experiments, when the concentration of H^+ doubles and the concentration of propanone increases 4/3 times, the rate of reaction increases by (2 × 4/3) times. Hence it is first order with respect to propanone.

Option	Explanation
A	Rate equation should be rate = $k[CH_3COCH_3][H^+]$.
B	The rate constant value may be obtained by substituting the rate and concentrations from any set of experiments.
C	Rate constant is only affected by temperature or addition of catalyst.
D	Overall order is not 1. Hence half lives may not be the same across different experiments.

12 The graph shows the result of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied, but that of amylase was kept constant.



Which conclusions can be deduced from these results?

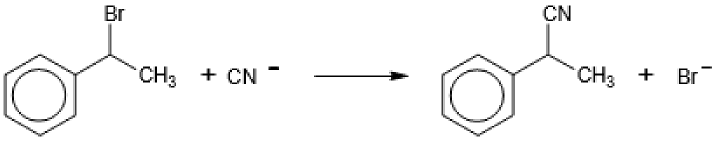
1 When [maltose] is low, the rate is first order with respect to [maltose].

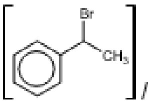
2 When [maltose] is high, the rate is independent of [maltose].

3 When [maltose] is high, the rate is independent of [amylase].

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

13 The reaction of (1-bromoethyl)benzene with sodium cyanide, NaCN, is investigated in a series of experiments.

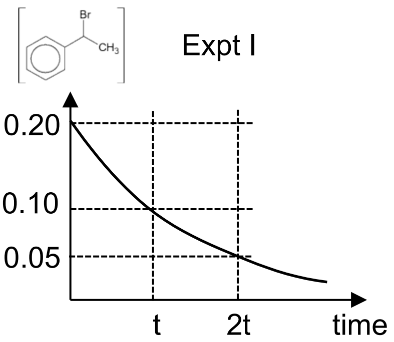


Experiment	 / mol dm^{-3}	[CN$^-$] / mol dm^{-3}
I	0.20	2.00
II	2.00	0.20
III	2.00	2.00

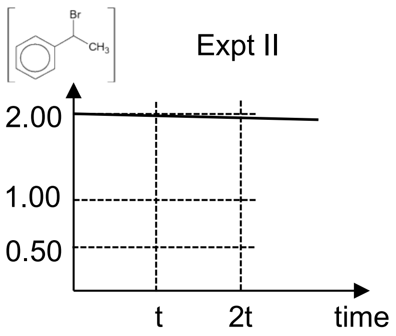
It was known that the reaction is first order with respect to (1-bromoethyl)benzene.

Which graph shows a correct experimental result and proves the reaction is zero order with respect to sodium cyanide?

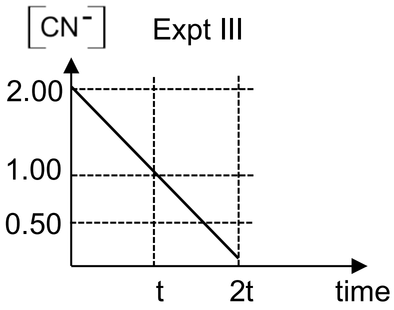
A



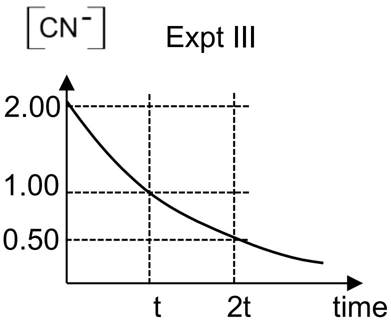
B



C



D



A cannot prove order wrt CN -. As rxn proceeds, [CN"] remains relatively constant as it is in huge excess. To reduce order wrt to CN^{-}. we look at how rate changes as [CN^{-}] changes. Since [CN-] does not change, any change in rate is not due to CN^{-}

.

B is the opposite of A. It would allow us to determine order wrt CN^{-}. However, the graph of [(1-bromoethyl)benzene] is plotted instead. We cannot determine order wrt CN^{-} when the rate appears to be zero.

C is wrong. When the same concentrations of [CN-] and [(1-bromoethyl)benzene] are used, the decrease in concentrations must follow the same shape i.e. since we know the graph of [(1-bromoethyl)benzene] against time follows 1st order kinetics with constant half-lives, the graph of [CN^{-}] against time must follow the same overall first order kinetics with constant half-lives.

D is therefore the correct answer. Another way to understand why the shape of the graph of [CN^{-}] against time will show constant half-lives is to recognise the mechanism as SN1. In the slow step, [(1- bromoethyl)benzene] decreases following first order kinetics. Any carbocation formed immediately reacts with CN" in the fast step. Hence the decrease in [CN-] will mirror the decrease in [(1-bromoethyl)benzene].

14 The kinetics of the following reaction is investigated, and the experimental data is given in the table below.

$$2R + 2S \rightarrow T + U$$

[R] / mol dm^{-3}	[S] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
0.015	0.010	5.10×10^{-4}
0.030	0.020	4.08×10^{-3}
0.045	0.010	1.53×10^{-3}

What is the numerical value of the rate constant for this reaction?

A 0.00294 **B** 3.40 **C** 227 **D** 340

Comparing the first and third experiments,

When [R] × 3 while keeping [S] constant, initial rate × 3 ⇒ rate α [R].

Hence, order of reaction with respect to R is 1.

Comparing the first and second experiments,

When [R] × 2 and [S] × 2, initial rate × 8.

Since the order of reaction with respect to R is 1, rate α $[S]^2$.

Hence, order of reaction with respect to S is 2.

The rate equation is: rate = $k[R][S]^2$

Using data from the first experiment,

$k = 5.10 \times 10^{-4} \div (0.015 \times 0.010^2) = \underline{340}$ mol^{-2} dm^{6} s^{-1}

ANSWERS FOR REACTION KINETICS STRUCTURED QUESTIONS PART 1

1 **(a)** The kinetics of the chlorination of methane is studied.

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

The first two steps of the mechanism of the reaction are shown below.

step 1 $Cl_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2Cl\bullet$ fast

step 2 $Cl\bullet + CH_4 \xrightarrow{k_2} HCl + \bullet CH_3$ slow

(i) The rate equation for the reverse of step 1 is rate = $k_r[Cl\bullet]^2$.

At equilibrium, the rates of the forward and reverse reactions in step 1 are equal.

Write the rate equation for the forward reaction of step 1 and hence write an expression for the concentration of the intermediate $Cl\bullet$ radicals.

rate = $k_f[Cl_2]$ [1]

$k_f[Cl_2] = k_r[Cl\bullet]^2$

$[Cl\bullet] = \sqrt{(k_f[Cl_2]/k_r)}$ [1]

Comments:
Most students were able to obtain the correct rate equation. However, some did not use the information that "rates of the forward and reverse reactions in step 1 are equal" to equate the forward and reverse rate equations and write an expression for $Cl\bullet$ radicals.

[2]

(ii) Write the rate equation for the forward reaction of step 2.

rate = $k_2[Cl\bullet][CH_4]$ [1] [1]

Comments: Most students got this correct. Careless ones did not use the correct rate constant as stated on the equation for step 2 in the question.

(iii) Use your answer to **(a)(i)** and the rate equation for step 2 to write the overall rate equation for the chlorination of methane.

Hence, deduce the orders of reaction with respect to the concentration of the species in the overall rate equation and the overall order of the reaction.

rate = $k_2[Cl\bullet][CH_4]$
rate = $k_2\sqrt{(k_f[Cl_2]/k_r)}[CH_4]$
= $k[Cl_2]^{1/2}[CH_4]$[1]

Order of reaction with respect to $[Cl_2]$ is ½.

Order of reaction with respect to $[CH_4]$ is 1.

The overall order of reaction is 1.5. [1]…[2]

Comments:
Several students were clearly confused when they saw that the order of reaction with respect to [Cl_2] is ½. They either changed their working and gave a different rate equation or concluded that the order with respect to [Cl_2] is 1 or 2 instead. Please note that ½ order is common for reactions involving radicals.

(b) When chlorine and bromine react with methane, light of different energy and wavelength is required for stage 1 of the reaction.

stage 1 $X_2 \rightarrow 2X\bullet$ (X = Cl, Br)

Light of longer wavelength is lower in energy than light of shorter wavelength.

This relationship between the energy and wavelength of light is shown in the equation below.

$$E = \frac{hc}{\lambda}$$

Where: *E* is the energy of the light of certain wavelength in Joule (J)
h is Planck constant = 6.63×10^{-34} J s
c is the speed of light = 3.00×10^{8} m s^{-1}
λ is the wavelength of light in metre (m)

(i) Bond energy is the energy required to break **one mole** of a covalent bond in the gaseous state.

Using the *Data Booklet* and the equation $E = \frac{hc}{\lambda}$, determine the wavelength of light required to break **one** Cl–Cl bond.

Leave your answer in nanometres (nm). One nm is equivalent to 10^{-9} m.

Bond energy of Cl–Cl bond = 244 kJ mol^{-1}

Amount of energy to break one Cl–Cl bond = $\frac{244 \times 1000}{6.02 \times 10^{23}} = 4.053 \times 10^{-19}$ [1]

Using $E = \frac{hc}{\lambda}$,

$\lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{4.053 \times 10^{-19}} = 4.907 \times 10^{-7}$ m $= 490.7 \times 10^{-9}$ m = **491 nm** [1]

[2]

Comments:
*Many students did not understand the instructions in the question to find wavelength of light to break **one** bond and did not divide the bond energy by Avogadro's number. As such, many substituted the value of E as 244000 J instead and were penalized 1 mark. It also affected their ability to solve (ii) as the answer did not fall into the range of wavelengths provided.*

(ii) Using Table 5.1, identify the colour of light that provides the minimum energy for the reaction between chlorine and methane.

Table 5.1

Colour	Wavelength / nm
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

Blue/Violet [1]

*Comments: Despite being unable to solve for the correct wavelength in **(i)**, some students were able to identify that blue/violet light were required for the reaction, possibly because they remember the FRS conditions is uv light. It is good to see students drawing links to relevant prior knowledge for solving questions!*

(iii) Hence, explain why the bromination of methane can be carried out with yellow light. (Calculation is not required)

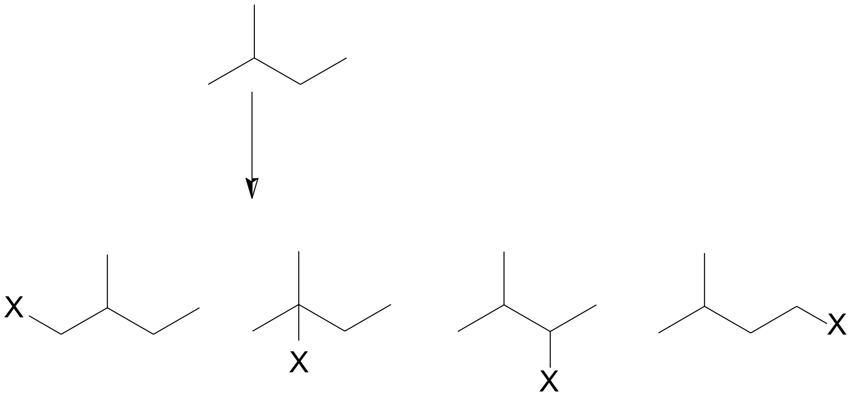
Br–Br bond is weaker than C*l*–C*l* bond.

Less energy is required to **break the Br–Br bond in the initiation step**.

Hence yellow light with a longer wavelength and lower energy, is adequate. …[1]

Comments:
As this question has a "hence", its intention is to relate to the answer in (ii).
*Since blue light is required to break the Cl-Cl bond while yellow light can be used for bromination, the difference in colour required is due to the **difference in strength of bonds** and hence **different energy** and **wavelength of light** required to break the bonds. All 3 points must be present for complete explanation.*

(c) Fig. 5.1 shows four possible monohalogenoalkanes that can be formed from the reaction of 2-methylbutane with chlorine or bromine. (X = C*l* or Br)



A **B** **C** **D**

Fig. 5.1

(i) State the expected ratio of products **A, B, C** and **D** in the mixture, assuming equal rate of substitution of all the H atoms.

6:1:2:3 [1]

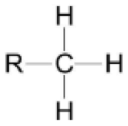
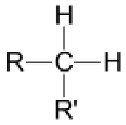
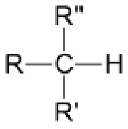
Comments:

Majority were able to state the ratio of products successfully. However, some students were still unable to recognise skeletal structures, particularly for structure A. The most common error is to state the proportion of A as 3 instead of 6. These students probably did not realise that monosubstitution of either one of the **TWO** $-CH_3$ groups attached to the same carbon will give product A.

(ii) The ratio of the isomeric products is more accurately determined if the relative rates of substitution of different H atoms by different halogen atoms are taken into account.

The types of hydrogen atoms in alkanes, together with their relative rates of substitution by C*l* and Br atom, are shown in Table 5.2.

Table 5.2

Types of H atoms	Structure	Relative rate of substitution by C*l* atom	Relative rate of substitution by Br atom
Primary	 $R-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-H$	1	1
Secondary	 $R-\overset{\overset{H}{\vert}}{\underset{\underset{R'}{\vert}}{C}}-H$	3	80
Tertiary	 $R-\overset{\overset{R''}{\vert}}{\underset{\underset{R'}{\vert}}{C}}-H$	5	1600

By taking into account the relative rates of substitution of H atoms given above, show that:

- the monochlorinated forms of products **A, B, C** and **D** are formed in the ratio of 6:5:6:3.
- the monobrominated forms of products **A, B, C** and **D** are formed in the ratio of 6:1600:160:3.

Ratio of monochlorinated products	**A**	**:**	**B**	**:**	**C**	**:**	**D**	
Based on number of H	6	:	1	:	2	:	3	
	×		×		×		×	
Based on relative rate	1	:	5	:	3	:	1	
Combined ratio	6	:	5	:	6	:	3	[1]

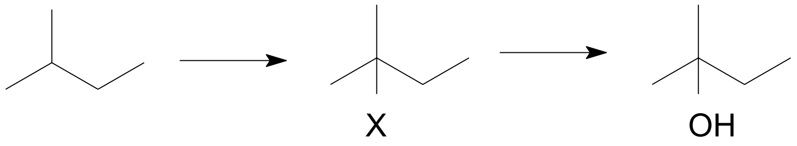
Ratio of monobrominated products	**A**	**:**	**B**	**:**	**C**	**:**	**D**	
Based on number of H	6	:	1	:	2	:	3	
	×		×		×		×	
Based on relative rate	1	:	1600	:	80	:	1	
Combined ratio	6	:	1600	:	160	:	3	[1]

Comments:
Most students who were able to answer (i) correctly had no problem in (ii). These students were able to deduce that A, B, C and D are obtained by substitution of a primary H, tertiary H, secondary H and primary H respectively.

As the ratio of products were already stated in the question, it was rather obvious that the ratio can be obtained by taking into account the probability of substitution (from ratio in (i)) and the relative rate of substituting each type of hydrogen by each halogen.

[2]

(iii) 2-methylbutan-2-ol may be synthesised from 2-methylbutane by using the reaction scheme as shown.



2-methylbutane 2-methylbutan-2-ol

Using the ratios given in **(c)(ii)**, explain if chlorine or bromine is a better choice of reagent in this synthesis.

Bromine is a better choice as it forms larger proportion of the required mono- brominated intermediate (2-bromo-2-methylbutane) and hence gives a better yield of the product. /

OR

The ratios show larger proportion of the tertiary halogenoalkane (or product B) will be formed when bromine is used instead of chlorine, resulting in a better yield of the tertiary alcohol. [1]

Answer must include:

larger proportion/fraction/ratio of the required mono-brominated intermediate AND higher yield of desired product / lower proportion of unwanted side products formed due to substitution at other H atoms.

[1]

(d) One of the possible termination steps in the free radical substitution reaction is the reaction between two alkyl radicals to form an alkane.

The equation shows the collision of two propyl radicals in the termination step of a reaction between propane and chlorine.

$$2{\bullet}C_3H_7(g) \rightarrow C_6H_{14}(g)\ \Delta S^{\ominus} = -190\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(i) Use the data in Table 5.3 to calculate the enthalpy change for this termination step at 298 K.

Table 5.3

species	$\Delta H^{\ominus}_f$ / kJ mol^{-1}
$\bullet\, C_3H_7(g)$	+103
$C_6H_{14}(g)$	-167

$\Delta H^{\ominus} = \Delta H_f^{\ominus}(\text{product}) - 2\Delta H_f^{\ominus}(\text{reactant})$
$= -167 - 2(103)$
$= -373$ kJ mol^{-1} [1]

Comments:
Most students successfully calculated the enthalpy change by using an energy cycle or the formula as shown.
However, some students incorrectly took $\Delta H \frac{O}{T}$ (reactant) to subtract $\Delta H \frac{O}{T}$ (product), while some carelessly omitted the coefficient "2" for $\Delta H \frac{O}{T}$(reactant) to account for the 2 mol of $\bullet C_3H_7(g)$ radicals

[1]

(ii) Explain how the values of ΔH^{o} and ΔS^{o} relate to the changes that occur at the molecular level for this termination step.

$\Delta H^{\theta} < 0$ as propyl free radical reacts to form a C–C bond, releasing heat energy and thus it is an exothermic reaction. [1]

$\Delta S^{\theta} < 0$ as there is one less gaseous product than reactant ($\Delta n = -1$), there are less ways to distribute particles and energies. There is decrease in disorderliness/the system gets more ordered and thus entropy change is negative. [1] [2]

Comments:
This question was quite badly done despite it being similar to a tutorial question. Students did not seem to understand the question. Students should note that "molecular level" usually refers to the specific changes observed in a chemical equation.
Some answers attempted to explain what a negative ΔH^{θ} and a negative ΔS^{θ} means rather than explaining why the termination reaction cause these changes to be negative, which includes a discussion of the C-C bond formation (for negative ΔH^{θ}) and the decrease in number of gaseous molecules (for negative ΔS^{θ}). A common omission in the explanation of the negative ΔS^{θ} is the concept of 'less ways to distribute particles and energies.' This is needed for a complete explanation.

(iii) Calculate ΔG^{o} for this termination step at 298 K and explain the effect on the spontaneity of this reaction of increasing the temperature above 298 K.

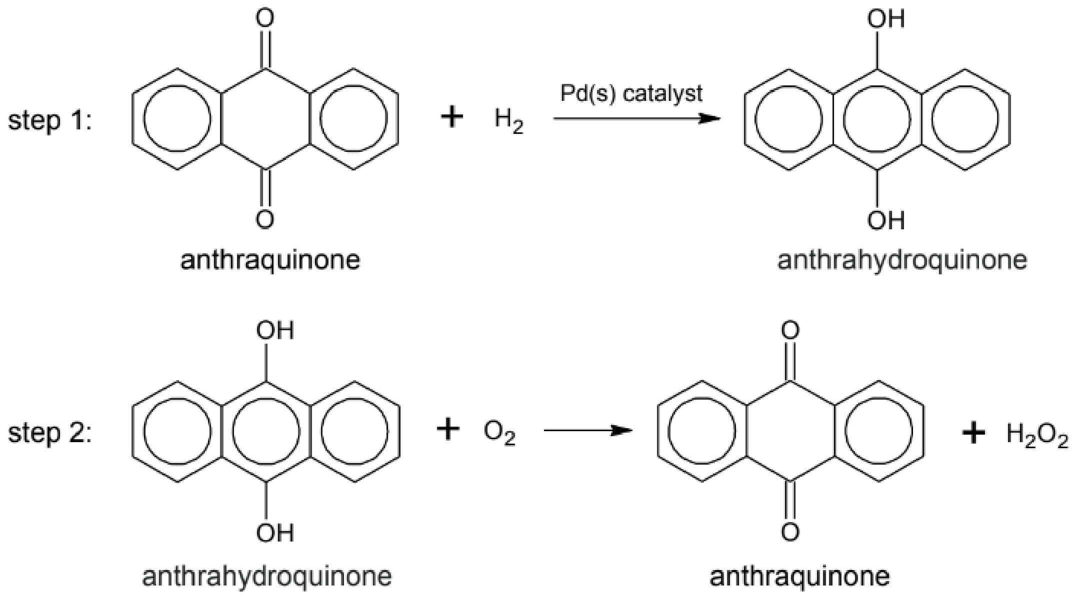
$\Delta G^{o} = \Delta H^{\ominus} - T\Delta S^{o}$
$= -373 - 298(-0.190)$
$= -316$ kJ mol^{-1} [1] [2]

Comments:
- *Though majority of the students recalled the formula for this calculation, many carelessly forgot to change both $\Delta H^{\ominus}$ and ΔS^{o} to the same units.*
- *In explaining the effect of increasing temperature on the spontaneity, many answers still vaguely refer to increase **ΔG** rather than a positive change. It has to be emphasized again that when referring to changes of **ΔG**, $\Delta H^{\ominus}$ and ΔS^{o} it is only clear to use 'negative/positive' changes and not 'increase/decrease' as these quantities has a sign.*
- *Some answers omitted the impact on the **$-T\Delta S$** term in the explanation, and mark is not given for incomplete explanation.*

[Total: 18]

2 Hydrogen peroxide, H_2O_2, finds its applications in a diversity of fields. Amongst many uses, it is an important precursor for the synthesis of organic peroxides and polymers. As such the manufacture of hydrogen peroxide has been an important industrial process since the 20th century.

Today, most of the world's hydrogen peroxide is manufactured by the anthraquinone process. This process involves the two steps shown below.



(a) Step 1 involves the adsorption of H_2 gas onto the surface of the palladium metal catalyst.

(i) State the property that palladium possesses that allows it to act as a catalyst in step 1, and explain how the adsorption of H_2 gas onto palladium increases the rate of reaction.

Palladium has low-lying vacant / partially filled d orbitals.

The adsorption of H_2 weakens the H–H bond, and allows it to break more readily, lowering the activation energy. Hence, rate of reaction increases [2]

(ii) A study of the kinetics of step 1 revealed that at low pressures, the rate of reaction increases with increasing pressure of H_2. However, at high pressures, increasing the pressure of H_2 has no effect on the rate of reaction.

Explain these observations.

At low pressures, the surface of palladium has available active sites for H_2 to adsorb as it is not saturated. Hence, the rate of reaction increases when the pressure of H_2 is increased.

In contrast, at high pressures, the surface of palladium is saturated with H_2 and there are no active sites for adsorption to occur / active sites are fully occupied with H_2. Hence, the rate of reaction is no longer affected by the increase in H_2 pressure. [2]

Although palladium and nickel belong to Group 10 of the Periodic Table, both elements have different ways of filling up their d orbitals. For palladium, it has a fully filled 4d subshell.

(iii) Draw, on the Cartesian axes provided in Fig. 4.1, the orbital from which the first electron of palladium is removed. Label the axes and orbitals clearly.

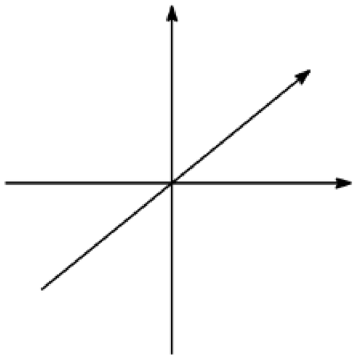
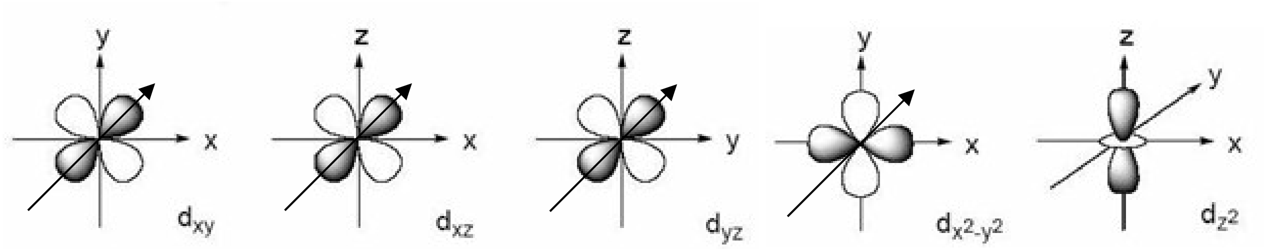


Fig. 4.1

Any one the following with correctly labelled axes and orbitals:



[1]

(iv) It is observed that the first ionisation energies of the Period 4 transition elements remain relatively invariant. Explain this observation.

- The first ionisation energy of Period 4 transition elements involves the removal of an electron from the 4s orbital.
- Across the transition elements, electrons are added to the penultimate 3d orbitals.
- As such, the increase in nuclear charge is cancelled out by the increase in shielding effect.
- Effective nuclear charge remains relatively constant. Hence, the energy required to remove the 4s electron remains relatively invariant. [2]

(b) At the end of step 1, anthrahydroquinone is extracted from the reaction mixture before reacting it with O_2 in step 2.

It is observed that step 2 follows the rate equation below.

$$\text{rate} = k[\text{anthrahydroquinone}][O_2]$$

In this step, a large excess of O_2 is required to ensure that anthrahydroquinone is completely oxidised back to anthraquinone, producing hydrogen peroxide.

(i) Explain why the rate equation for step 2 can be rewritten as

$$\text{rate} = k'[\text{anthrahydroquinone}].$$

This is because O_2 is in large excess and hence the concentration / pressure of O_2 remains relatively constant throughout the reaction. As such, the rate equation can be rewritten as rate = k'[anthrahydroquinone] where $k' = k[O_2]$ is a constant [1]

(ii) Hence sketch, on Fig 4.2, a labelled graph to show how the concentration of H_2O_2 in step 2 will vary over time.

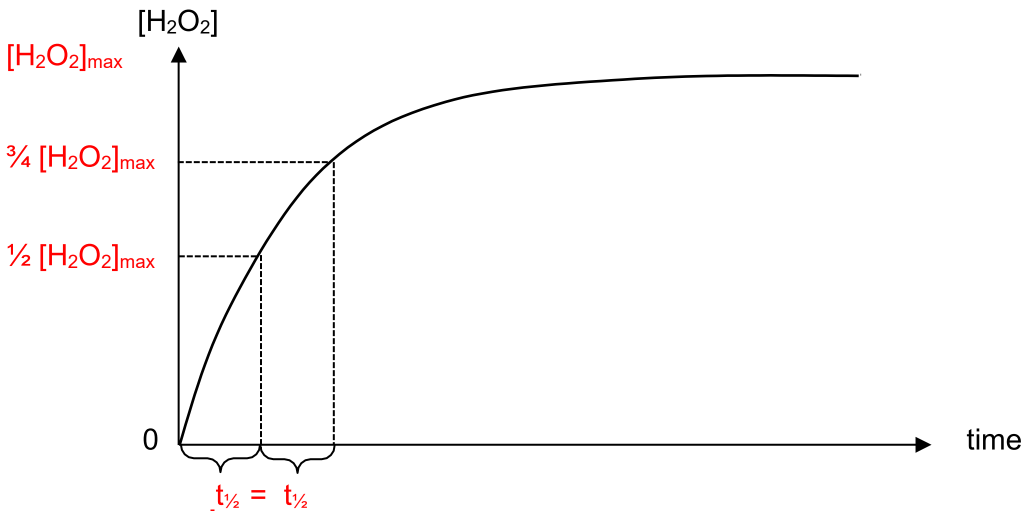


Fig 4.2

[2]

(iii) Step 2 was repeated with different initial pressures of O_2 and different initial concentrations of anthrahydroquinone.

Table 4.1 shows the initial quantities of reactants used for each experiment and the time required for the initial concentration of anthrahydroquinone to be halved for experiment 1.

Table 4.1

experiment	initial pressure of $O_2(g)$ / Pa	initial [anthrahydroquinone] / mol dm^{-3}	time required for initial [anthrahydroquinone] to be halved / min
1	4×10^5	1.00	12.0
2	4×10^5	0.50	12.0
3	8×10^5	1.00	6.0

Complete Table 4.1 and explain your answer.

Since $t_{1/2} = \frac{\ln 2}{k'}$, where $k' = k[O_2]$,

changes in the concentration of anthrahydroquinone has no effect on the half- life of the reaction. Instead, doubling the initial pressure of O_2 would halve the half-life of the reaction. [2]

(c) At the end of step 2, the reaction mixture contains only anthraquinone and H_2O_2. H_2O_2 can be separated out from the reaction mixture by adding water to the reaction mixture.

With reference to the bonding between relevant molecules, explain how the addition of water allows this to happen.

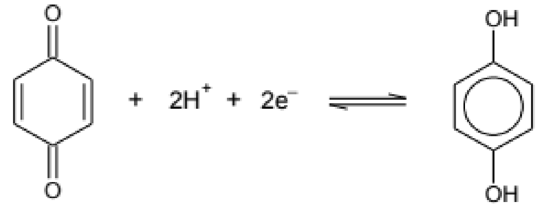
H_2O_2 can form hydrogen bonding with the water molecules. Hence, H_2O_2 will dissolve in water.

In contrast, anthraquinone has large non-polar benzene rings which will interfere with the hydrogen bonding it forms with water. Hence, anthraquinone will not dissolve in water but remain in the reaction mixture.

[2]

(d) Quinone and hydroquinone have similar structures to anthraquinone and anthrahydroquinone respectively.

The standard reduction potential of the quinone–hydroquinone system is +0.70 V.



$E^\theta = +0.70$ V

quinone hydroquinone

An electrolytic cell was set up under standard conditions with a mixture of aqueous quinone and dilute sulfuric acid as the electrolyte and platinum rods as electrodes.

State the products formed at the anode and the cathode.

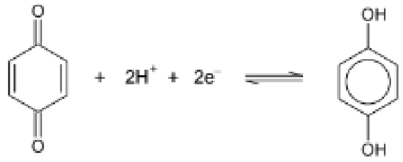
Possible oxidations at the anode:

$O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O$ $E^\ominus = +1.23$ V

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01$ V

Since $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(S_2O\ ^{2-}/SO_8\ ^{2-})$, H_2O will be preferentially oxidised to oxygen gas at the anode.

Possible reductions at the cathode:



$E^\circ = +0.70$ V

$2H^+ + 2e^- \rightleftharpoons H_2$ $E^\ominus = 0.00$ V

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V

Since $E^\ominus_{\text{quinone/hydroquinonw}}$ is most positive, quinone will be preferentially reduced to hydroquinone at the cathode.

[2]

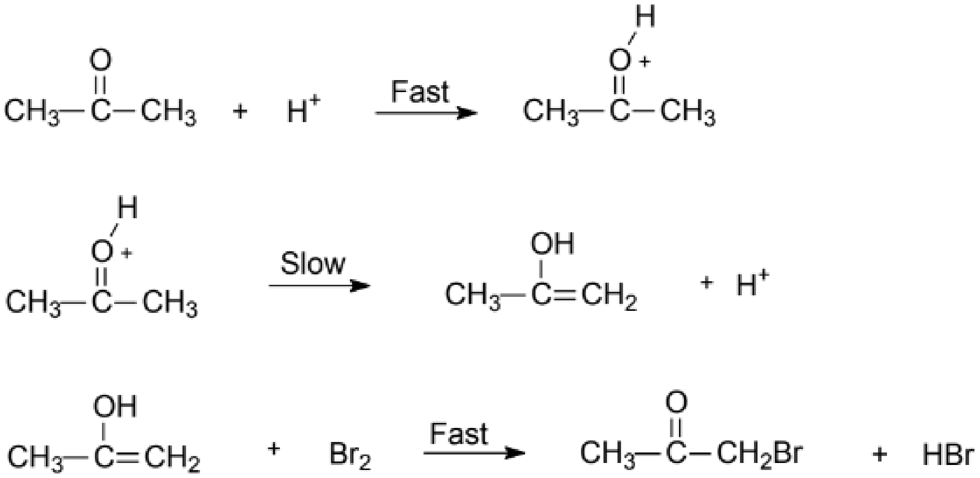
[Total: 16]

3 Carbonyl compounds can react with halogens in acidic or alkaline medium to form different products. Kinetic studies are conducted to investigate the orders of reaction and the mechanisms of these reactions.

In acidic medium, propanone reacts with bromine to form bromopropanone as shown in the equation below:

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + HBr$$

The kinetic studies of the above reaction have shown that the reaction is second order overall, and a three-step mechanism is involved in this reaction.



(a) From the mechanism above, construct the rate equation for the above reaction.

Rate = $k\,[CH_3COCH_3]\,[H^+]$

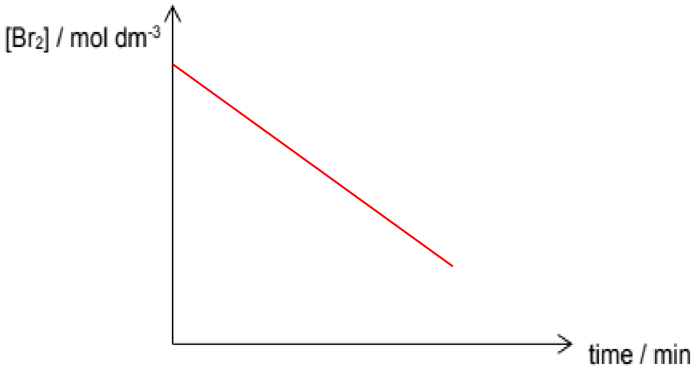
[1]

(b) From the mechanism above, how can you deduce that H^+ is acting as a catalyst?

H^+ is consumed/reacted in step 1 but is regenerated in step 2.

[1]

(c) Sketch, in the space below, the graph of $[Br_2]$ against time in minutes, given that the initial concentration of Br_2 is 0.008 mol dm^{-3} and initial concentration of propanone, CH_3COCH_3, is 0.80 mol dm^{-3}.



[1]

Rate = k [CH_3COCH_3] [H^+] [Br_2]^0

Given: [Br_2] = 0.008 mol dm^{-3} and [CH_3COCH_3] = 0.80 mol dm^{-3}

Since CH_3COCH_3 is used in large excess, its conc. remains effectively constant as only a small fraction of CH_3COCH_3 reacted during the reaction.

Since H^+ is a catalyst, its conc. remains constant throughout the reaction.

∴ the rate equation can be simplified as

rate = k' [Br_2]^0, where k' = k [CH_3COCH_3][H^+] = constant

Hence the reaction is an overall zero order. Any change in [Br_2] has no effect on the reaction rate. So the graph of [Br_2] vs time graph is a straight line with a constant negative gradient.

(d) Explain what will happen to the rate of reaction if chlorine is used in place of bromine, assuming that the mechanism remains unchanged?

There will be no change to the rate of reaction as halogen is not involved in the rate determining/slow step (or [X_2] is not in the rate equation) (or the reaction is zero order with respect to [X_2])

[1]

(e) The kinetics data for the experiment may be collected using a continuous sampling method, which requires a sample of the chemical reaction to be extracted at various time intervals from a reaction mixture followed by titration.

Briefly describe a physical property that allows you to determine the [Br_2] at various times.

The colour intensity of the reaction solution can be measured at various time using a **colorimeter/spectrometer.

As the [Br_2] decreases, the orange-brown colour intensity of the reaction solution decreases.

Hence, the absorbance measured a various time t is directly proportional to the [Br_2] left at t.

[1]

(f) The reaction between CH_3COCH_3 and Br_2 was carried out in experiments **1** and **2**, and the following results were obtained:

Experiment	Initial [CH_3COCH_3]/ mol dm^{-3}	Initial [H^+] / mol dm^{-3}	Initial [Br_2] / mol dm^{-3}	Half-life / min
1	0.40	0.30	0.20	22.5
2	0.60	0.10	0.20	s

The half-life of CH_3COCH_3 in experiment **1** was found to be constant at 22.5 minutes. Predict the value of half-life of CH_3COCH_3 in experiment **2**, **s**, giving your reasoning.

rate = k [H^+] [propanone], an overall second order reaction.

Since H^+ is a catalyst, [H^+] remains constant throughout the reaction.

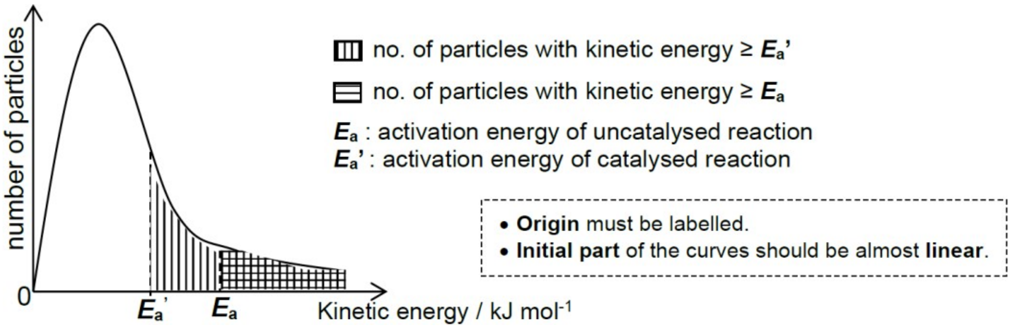
∴ rate = k' [propanone] where k' = k [H^+] = constant. It is an overall pseudo first order reaction

and $t_{1/2} = \frac{In\ 2}{k`} = \frac{In\ 2}{k\ [H^+]}$ or $t_{1/2} \propto \frac{1}{[H^+]}$

Since $[H^+]$ decreases by a factor of 1/3 from expt 1 to expt 2, $t_{1/2}$ would increase by a factor of 3, from 22.5 min in expt 1 to 67.5 min in expt 2.

[2]

(g) With the aid of a labelled Boltzmann distribution diagram, explain how the presence of a catalyst affects the rate of a chemical reaction.



- **Origin** must be labelled.
- **Initial part** of the curves should be almost **linear**.

[3]

- A catalyst provides an alternative reaction pathway/mechanism of lower activation energy (E_a') than that of the uncatalysed reaction.
- There is a greater proportion/number of particles of reactant molecules with kinetic energy ≥ E_a' (as indicated by the larger shaded area). Hence the frequency of effective collision between reactant particles increases and the rate of reaction increases.

[Total: 10]

4 Nitrogen dioxide, NO_2, is a highly reactive gas due to the presence of an unpaired electron on the nitrogen atom.

(a) **(i)** State three basic assumptions of the kinetic theory as applied to an ideal gas.

Any three of the following:

- An ideal gas consists of particles of negligible volume.
- The gas particles exert negligible attractive forces on one another.
- The gas particles are in constant random motion.
- Collisions between the gas particles are perfectly elastic.
- The average kinetic energy of particles in a gas is constant at constant temperature. OR The average kinetic energy is proportional to the absolute temperature [2]

(ii) Fig. 2.1 shows how $\frac{pV}{T}$ varies with pressure for 1 mol of ideal gas and 1 mol of NO_2 at T1 K.

On Fig. 2.1, sketch a graph to show how $\frac{pV}{T}$ varies with pressure for 1 mol of NO_2 at a higher temperature of T_2 K. Label your graph as **(a)(ii)** and explain your answer.

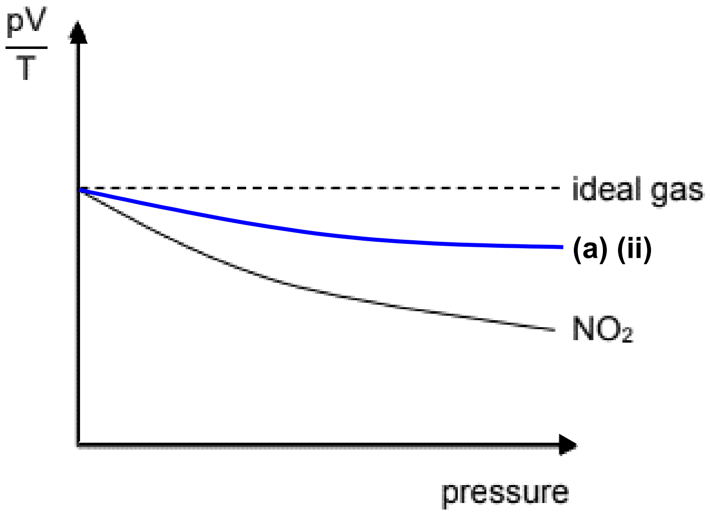


Fig. 2.1

At higher temperature of T_2 K, the NO_2 gas molecules have higher kinetic energy and are better able to overcome the intermolecular attractive forces. Hence it would exhibit less deviation from an ideal gas as compared to at a lower temperature of T_1 K.

(b) Nitrogen dioxide undergoes the following gas phase reaction with hydrogen chloride, as shown in equation 2.1.

equation 2.1 $2NO_2(g) + HCl(g) \rightarrow NOCl(g) + HNO_3(g)$

To study the kinetics for this reaction, three separate experiments were carried out in a vessel of fixed volume at a constant temperature of 500 K. The initial concentrations of NO_2 and HC*l* are shown in Table 2.1.

Table 2.1

experiment	initial [NO_2] / mol dm^{-3}	initial [HC*l*] / mol dm^{-3}
1	1.00	0.05
2	0.50	0.05
3	0.50	0.01

To monitor the progress of the reaction for each experiment, the total pressure in the vessel was measured at regular time intervals and the corresponding concentrations of NOC*l* were calculated.

Fig. 2.2 shows how the concentration of NOC*l* varies with time for experiments 1 and 2.

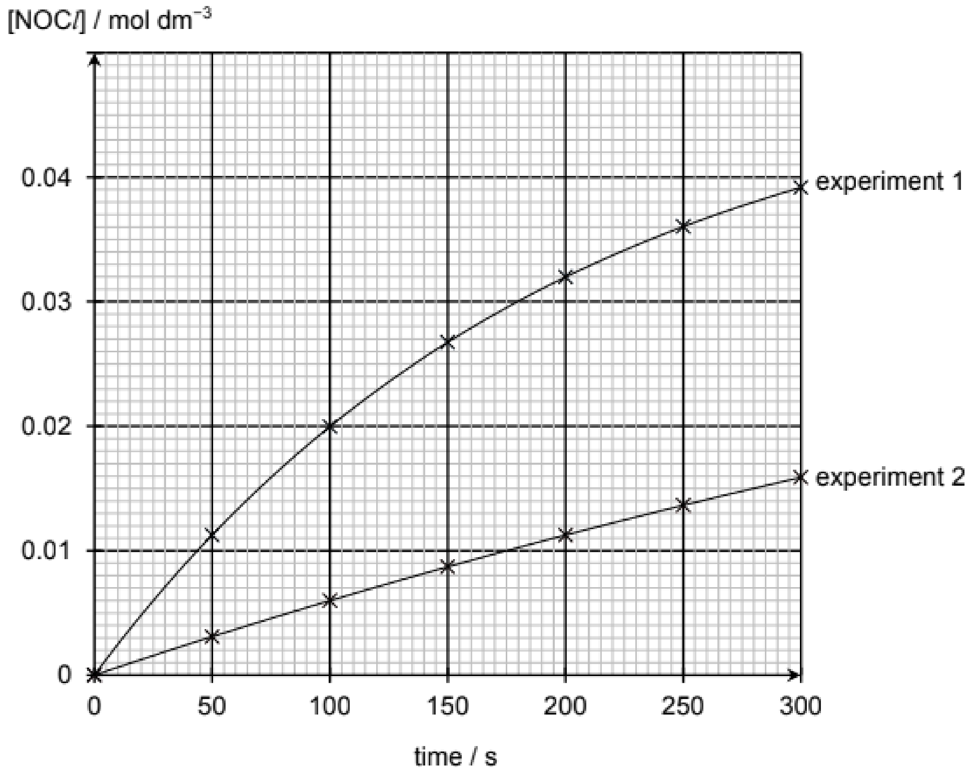


Fig. 2.2

(i) With reference to Fig. 2.2, calculate the mole fraction of NOC*l* present in the vessel for experiment 1 at *t* = 200 s.

At *t* = 200 s, [NOC*l*] = 0.032 mol dm^{-3}

	$2NO_2(g)$	+	$HCl(g)$	→	$NOCl(g)$	+	$HNO_3(g)$
initial conc / mol dm^{-3}	1.00		0.05		0		0
change in conc / mol dm^{-3}	−0.064		−0.032		+0.032		+0.032
conc at 200 s / mol dm^{-3}	0.936		0.018		0.032		0.032

$$\text{mole fraction of NOC}l = \frac{0.032}{0.936 + 0.018 + 0.032 + 0.032} = \underline{0.0314}$$

[2]

(ii) Calculate the total pressure, in Pa, in the vessel for experiment 1 at *t* = 200 s.

You may assume that all the gases behave ideally.

$pV = nRT$

$p_{NOCl}V = n_{NOCl}RT$

$p_{NOCl} = \frac{n_{NOCl}}{V} RT$

$= \frac{0.032}{10^{-3}} (8.31)(500)$

$= 1.3296 \times 10^5$ Pa

$p_{NOCl} = X_{NOCl} \times P_{total}$

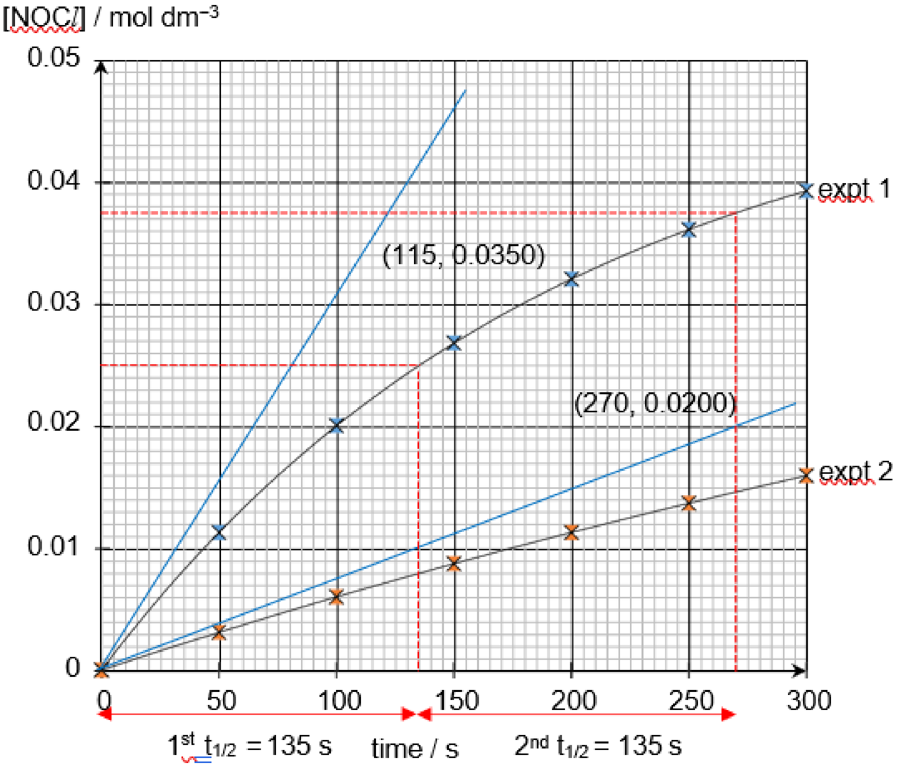
$P_{total} = \frac{1.3296 \times 10^5}{0.0314}$

$\underline{= 4.23 \times 10^6 \text{ PA}}$

[2]

(iii) Using Fig. 2.2, determine the initial rate or reaction for experiments 1 and 2.

Hence, deduce the order of reaction with respect to NO_2.



[2]

Initial rate of reaction for experiment 1 = $\frac{0.0350-0}{115-0}$ = 3.04×10^{-4} mol dm^{-3} s^{-1}

Initial rate of reaction for experiment 2 = $\frac{0.0200-0}{270-0}$ = 7.41×10^{-5} mol dm^{-3} s^{-1}

$$\frac{\text{initial rate of expt 1}}{\text{initial rate of expt 2}} = \frac{3.04 \times 10^{-4}}{7.41 \times 10^{-5}} = 4.10 \approx \underline{4} \text{ (to nearest integer)}$$

Comparing experiments 1 and 2, when $[NO_2] \times 2$, rate × 4.
$\Rightarrow$ rate $\propto [NO_2]^2$,
$\Rightarrow$ reaction is second order with respect to NO_2.

(iv) State the final concentration of NOC*l* in the vessel for experiment 1 if the reaction were to proceed to completion.

Final [NOC*l*] = 0.0500 mol dm^{-3} [1]

(v) Hence, determine the order of reaction with respect to HC*l*.

Show your working, including construction lines on Fig. 2.2.

For experiment 1, final [NOC*l*] = 0.05 mol dm^{-3}.

1st $t_{½} \Rightarrow$ time taken for [HC*l*] to decrease from 0.05 mol dm^{-3} to 0.025 mol dm^{-3}
$\Rightarrow$ time taken for [NOC*l*] to increase from 0 mol dm^{-3} to 0.025 mol dm^{-3}
$\Rightarrow$ 135 s

2nd $t_{½} \Rightarrow$ time taken for [HC*l*] to decrease from 0.025 mol dm^{-3} to 0.0125 mol dm^{-3}
$\Rightarrow$ time taken for [NOC*l*] to increase from 0.025 mol dm^{-3} to 0.0375 mol dm^{-3}
$\Rightarrow$ 135 s

Since $t_{½}$ is constant, reaction is first order with respect to HC*l*.

[2]

(vi) The half-life of the reaction in experiment 2 was found to be 540 s.

With reference to Table 2.1, suggest how the half-life of the reaction in experiment 3 will compare to that of experiment 2. Explain your answer.

Since NO_2 is in large excess, rate = k'[HC*l*] where $k' = k[NO_2]^2$.

Hence $t_{½} = \frac{In\ 2}{K`} = \frac{In\ 2}{k[NO_2^2}$

OR

Since NO_2 is in large excess, the overall reaction is pseudo first-order with respect to HC*l*.
Hence $t_{½}$ is independent of [HC*l*].

As initial $[NO_2]$ of experiment 3 is the same as that of experiment 2, $t_{½}$ would remain the same at 540 s even though [HC*l*] is different. [2]

(c) N_2O_4 can undergo dissociation to form NO_2, which then reacts with ethene to form 1,2-dinitroethane. The reaction mechanism consists of three steps as shown in Fig. 2.3.

step 1 $N_2O_4(g) \rightleftharpoons 2\dot{N}O_2$ fast

step 2 $CH_2CH_2(g) + \dot{N}O_2)(g) \xrightarrow{k_2} \dot{C}H_2CH_2NO_2\ (g)$ slow

step 3 $\dot{C}H_2CH_2NO_2(g) + \dot{N}O_2(g) \xrightarrow{k_3} O_2NCH_2CH_2NO_2(g)$ fast

Fig. 2.3`

(i) Write an overall equation for the reaction.

$N_2O_4 + CH_2CH_2 \rightarrow O_2NCH_2CH_2NO_2$ [1]

(ii) Name the type of reaction occurring in **(c)(i)**.

Addition reaction [1]

(iii) The dissociation of N_2O_4 in step 1 of the mechanism rapidly reaches equilibrium due to the use of solid platinum which acts as a heterogeneous catalyst.

Outline the mode of action of the platinum catalyst in the dissociation of N_2O_4.

The N_2O_4 molecules diffuse to the surface of the Pt catalyst and they become adsorbed onto the active sites of the Pt surface.

The adsorption weakens the covalent bonds in the N_2O_4 molecules and lowers the activation energy.

Once the NO_2 molecules are formed, they desorb from the surface and diffuse away from the Pt catalyst, freeing up the active sites for adsorbing other N_2O_4 molecules. [2]

(iv) The equilibrium constant for step 1 of the mechanism is K_c.

Write an expression for $[NO_2]$ in terms of K_c.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$[NO_2] = \sqrt{K_c\,[N_2O_4]}$ OR $K_c^{1/2}\,[N_2O_4]^{1/2}$ [1]

(v) Using your answer in **(c)(iv)** and the mechanism in Fig. 2.3**,** write the overall rate equation for the reaction.

rate = $k_2[NO_2][CH_2CH_2]$
rate = $k'[N_2O_4]^{\frac{1}{2}}\,[CH_2CH_2]$ where $k' = k_2\,K_c^{\frac{1}{2}}$

[1]

[Total: 20]