

SECTION 13 Industrial Chemistry

Chemical Kinetics

AL96(II)_01b

- (i) Draw the Maxwell-Boltzmann curves for the distribution of molecular speeds at two different temperatures for an ideal gas. (2 marks)
- (ii) Use your curves in (i) to explain why, for a fixed mass of an ideal gas at constant volume, the pressure increases as the temperature is raised. (2 marks)

AL97(II)_03

The reaction of iodine with propanone in acidic solutions can be represented by the following equation:



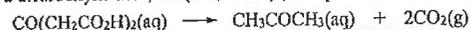
- (a) (i) The progress of the reaction can be monitored by a titrimetric method. Outline the experimental procedure. [For reference] (3 marks)
- (ii) State how the initial rate of the reaction can be determined from the titrimetric results. (2 marks)
- (iii) Suggest another method to monitor the progress of the reaction. (1 mark)
- (b) Following initial rates and initial concentrations were obtained in an experiment at 298 K:

Initial rate / mol dm ⁻³ s ⁻¹	Initial concentration / mol dm ⁻³		
	[I ₂ (aq)]	[CH ₃ COCH ₃ (aq)]	[H ⁺ (aq)]
3.5 × 10 ⁻⁵	2.5 × 10 ⁻⁴	2.0 × 10 ⁻¹	5.0 × 10 ⁻³
3.5 × 10 ⁻⁵	1.5 × 10 ⁻⁴	2.0 × 10 ⁻¹	5.0 × 10 ⁻³
1.4 × 10 ⁻⁴	2.5 × 10 ⁻⁴	4.0 × 10 ⁻¹	1.0 × 10 ⁻²
7.0 × 10 ⁻⁵	2.5 × 10 ⁻⁴	4.0 × 10 ⁻¹	5.0 × 10 ⁻³

- (i) Deduce the rate equation for the reaction. (3 marks)
- (ii) Calculate the rate constant for the reaction at 298 K. (2 marks)
- (c) For a given set of initial concentrations, the initial rate doubles when temperature is increased from 298 K to 308 K. calculate the activation energy of the reaction. (2 marks)

AL98(II)_03a

The table below lists the rate constants, k , at different temperatures, T , for the first order decomposition of a dicarboxylic acid, $\text{CO}(\text{CH}_2\text{CO}_2\text{H})_2$, in aqueous solution:

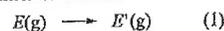


T/K	273	393	313	333	353
k / s^{-1}	2.46×10^{-5}	4.75×10^{-4}	5.76×10^{-3}	5.48×10^{-2}	?

- (i) Determine the activation energy for the reaction by plotting an appropriate graph. (5 marks)
- (ii) Estimate the rate constant of the reaction at 353 K and hence calculate the half-life of the reaction at the same temperature. [OUT] (3 marks)
- (iii) Suggest a method to monitor the progress of the reaction. (1 mark)

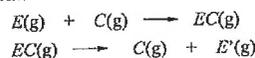
AL98(II)_03b

The exothermic reaction



is a single stage reaction.

- (i) Sketch curves to show the distribution of molecular kinetic energy of the reaction, $E(\text{g})$, at two different temperatures. (2.5 marks)
- (ii) With reference to your answer in (i), explain why the rate of reaction (1) increases with temperature. (1.5 marks)
- (iii) In the presence of a catalyst, C, reaction (1) will proceed at a faster rate via the following mechanism:



(EC is the reaction intermediate.)

Sketch labelled energy profiles for the conversion of $E(\text{g})$ to $E'(\text{g})$, with and without catalyst. Explain why reaction (1) proceeds faster in the presence of the catalyst. (4 marks)

AL99(II)_03a

Consider the following data for the reaction:



Initial concentration / mol dm^{-3}		Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
[A]	[B]	
4.0×10^{-2}	4.0×10^{-2}	6.4×10^{-5}
8.0×10^{-2}	4.0×10^{-2}	12.8×10^{-5}
4.0×10^{-2}	8.0×10^{-2}	6.4×10^{-5}

For this reaction

- (i) deduce its rate equation, (2 marks)

- (ii) calculate the rate constant, and (1 mark)
- (iii) sketch a possible energy profile. (3 marks)

AL00(I)_07b

Without giving any experimental detail, outline what measurements have to be taken in order to determine the activation energy of a reaction. (4 marks)

AL00 (II)_03b

At 333K, the initial rate of the hydrolysis of CH_3Br , a $\text{S}_{\text{N}}2$ reaction, was found to be $8.23 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentrations of CH_3Br and OH^- ions were 0.05 mol dm^{-3} and 0.20 mol dm^{-3} respectively.

- (i) Calculate the rate constant, k , for the hydrolysis at 333 K. (2 marks)

- (ii) The table below lists the rate constants for the hydrolysis at three other temperatures, T .

T / K	293	308	323
$k / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	1.05×10^{-4}	6.15×10^{-4}	3.07×10^{-3}

Determine the activation energy, E_a , for the hydrolysis by plotting an appropriate graph. (5 marks)

AL01(II)_03

At an elevated temperature and in the presence of argon, iodine atoms combine to form iodine molecules:



The table below lists some data about the reaction:

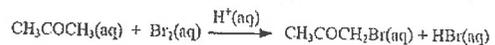
Initial concentration / mol dm^{-3}		Initial rate $\frac{d[\text{I}_2(\text{g})]}{dt} / \text{mol dm}^{-3} \text{ s}^{-1}$
$[\text{I}(\text{g})] / \text{mol dm}^{-3}$	$[\text{Ar}(\text{g})] / \text{mol dm}^{-3}$	
1.0×10^{-5}	1.0×10^{-3}	8.70×10^{-4}
2.0×10^{-5}	1.0×10^{-3}	3.48×10^{-3}
1.0×10^{-5}	5.0×10^{-4}	4.35×10^{-4}

For this reaction,

- (a) Deduce the rate equation. (3 marks)
- (b) Calculate the rate constant. (1 mark)
- (c) Suggest a possible reaction mechanism consistent with the rate equation, state the role of argon, and sketch the energy profile. (4 marks)

ASL02(I)_02

An experiment was carried out to study the acid-catalyzed bromination of propanone at 298 K.



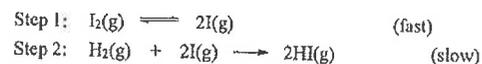
The table below lists the results of the experiment.

Initial concentration / mol dm ⁻³			Initial rate / mol dm ⁻³ s ⁻¹
[CH ₃ COCH ₃ (aq)]	[Br ₂ (aq)]	[H ⁺ (aq)]	
0.30	0.050	0.050	5.7 × 10 ⁻⁵
0.30	0.100	0.050	5.7 × 10 ⁻⁵
0.30	0.050	0.100	1.2 × 10 ⁻⁴
0.40	0.050	0.200	3.1 × 10 ⁻⁴
0.40	0.050	0.050	7.6 × 10 ⁻⁵

- (a) Deduce the rate equation for the reaction. (3 marks)
- (b) Calculate the rate constant for the reaction at 298 K. (2 marks)

AL03(I)_02b

The following mechanism was proposed for the reaction of H₂(g) with I₂(g) to give HI(g).



- (i) Write an expression for the equilibrium constant, K_c, for Step 1. (1 mark)
- (ii) Based on this mechanism, show that the reaction of H₂(g) with I₂(g) is first order with respect to H₂(g) and to I₂(g). (3 marks)

ASL03(I)_04

Chlorofluorocarbons (CFCs) were once widely used as aerosol propellants and refrigerants. It is now known that the release of CFCs into the atmosphere will lead to the depletion of ozone in the stratosphere. In the stratosphere, molecules of CFCs and O₃ absorb ultra-violet radiation and undergo decomposition to give Cl• and O atoms respectively. The following two reactions then occur:

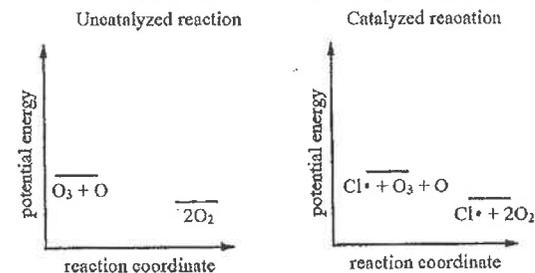


Combination of the above equations gives the overall equation for the depletion of ozone:



- (a) Cl• can be considered as a catalyst in the depleting of ozone. (1 mark)
- (i) Is Cl• a homogeneous catalyst or a heterogeneous catalyst? Explain.

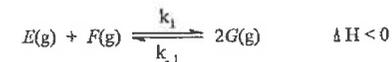
- (ii) Sketch the energy profiles for the uncatalyzed and catalyzed reactions.



- (b) Explain why a CFC molecule can lead to the depletion of a large number of ozone molecules in the stratosphere. (2 marks)

AL04(I)_03a

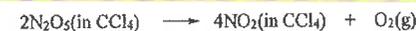
Consider the following system which comprises two single step reactions.



- (k₁ and k₋₁ are the rate constants)
- (i) Write the respective rate equations for the forward and backward reactions. (1 mark)
- (ii) Sketch a labelled energy profile for the forward reaction. (2 marks)
- (iii) Predict, with explanation, whether k₁ or k₋₁ will increase to a greater extent when temperature of the system is increased. (1 mark)

AL04(II)_03a

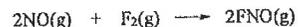
The decomposition of dinitrogen pentoxide in tetrachloromethane can be represented by the following equation:



- (i) Suggest an experimental method that can be used to follow the progress of the decomposition, and state the underlying principle of the method. (2 marks)
- (ii) The rate constant for the decomposition at 332 K was found to be 5 times that at 318 K. Calculate the activation energy for the decomposition. (2 marks)

AL05(I)_02a

Nitrogen monoxide reacts with fluorine to form nitrosyl fluoride, FNO, according to the following equation:



(i) Draw the electronic structure of nitrosyl fluoride. (1 mark)

(ii) What is the oxidation state of nitrogen in the following compounds?
 NO FNO
 (1 marks)

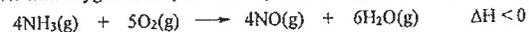
(iii) The rate equation for the above reaction is:
 $\text{rate} = k[\text{NO}(\text{g})][\text{F}_2(\text{g})]$

The commonly accepted mechanism for this reaction involves two steps, one of these steps produces FNO and the free radical F• in equimolar amounts.

Write balanced equations for the two mechanistic step, indicating which is the rate determining step. (2 marks)

ASL06(II)_10a

Ammonia reacts with oxygen in the presence of platinum to give nitrogen monoxide.



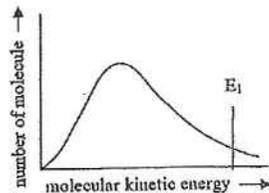
(i) $\text{NH}_3(\text{g})$ and $\text{O}_2(\text{g})$ are allowed to react in a vessel of constant volume. Find the rate of consumption of $\text{O}_2(\text{g})$ if the rate of formation of $\text{NO}(\text{g})$ is $1.24 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. (2 marks)

(ii) Platinum is a catalyst in the above reaction. What is meant by the term 'catalyst'? (1 mark)

(iii) State an important industrial product that can be obtained from $\text{NO}(\text{g})$ (1 mark)

ASL06(II)_10b

The graph below shows the distribution of the molecular kinetic energies of a gas at a certain temperature. E_1 is the activation energy for a reaction of the gas without a catalyst.



(i) Copy the graph, including the position of E_1 and mark on it the expected activation energy, E_2 , of the reaction in the presence of a catalyst at the same temperature. Explain your answer. (2 marks)

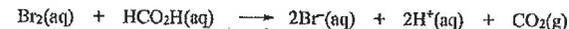
(ii) Explain why the rate of a catalyzed reaction would be different from that of an uncatalyzed

one at the same temperature.

(2 marks)

ASL07(II)_02

Consider the reaction below:



(a) Suggest an experimental method to follow the change in concentration of $\text{Br}_2(\text{aq})$ in the reaction mixture. Give a reason for your suggestion. (2 marks)

The table below lists the experimental data obtained at a certain temperature:

Run	Volume used / cm^3			Initial rate for the disappearance of $\text{Br}_2(\text{aq})$ / $\text{mol dm}^{-3} \text{ s}^{-1}$
	0.010 M $\text{Br}_2(\text{aq})$	0.20 M $\text{HCO}_2\text{H}(\text{aq})$	$\text{H}_2\text{O}(\text{l})$	
1	2.0	10.0	8.0	1.2×10^{-5}
2	4.0	10.0	6.0	2.4×10^{-5}
3	8.0	10.0	2.0	4.8×10^{-5}

(b) Suggest how the initial rate for the disappearance of $\text{Br}_2(\text{aq})$ can be found. (2 marks)

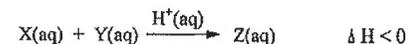
(c) Why is it necessary to keep the concentration of $\text{HCO}_2\text{H}(\text{aq})$ much higher than that of $\text{Br}_2(\text{aq})$? (2 marks)

(d) Deduce the order of the reaction with respect to $\text{Br}_2(\text{aq})$. (2 marks)

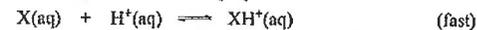
(e) Suggest how the order of the reaction with respect to $\text{HCO}_2\text{H}(\text{aq})$ can be determined. (1 mark)

ASL07(II)_03

Consider the acid-catalyzed reaction:



The following mechanism was proposed:



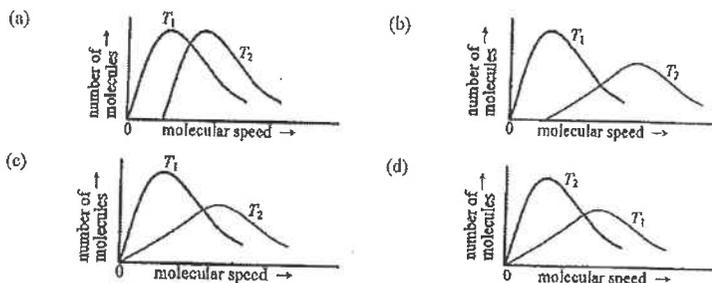
Based on this mechanism,

(a) Sketch a labelled energy profile, and (2 marks)

(b) Deduce the rate equation. (2 marks)

AL08(I)_03a

Which one of the following graphs represents the distribution of molecular speeds of one mole of a gas at two different temperature T_1 and T_2 , where $T_2 > T_1$?



ASL08(II)_03

The gaseous reaction below takes place at 750 °C in a closed container with a fixed volume.



(a) Suggest an experimental method that can be used to follow the concentration of $\text{N}_2(\text{g})$ in the reaction mixture. Briefly explain the principle of your suggested method.

(2 marks)

(b) The table below lists three sets of experimental data of the reaction at 750 °C:

Experiment	Initial concentration / mol dm ⁻³		Initial rate for the formation of $\text{N}_2(\text{g})$ / mol dm ⁻³ s ⁻¹
	$\text{H}_2(\text{g})$	$\text{NO}(\text{g})$	
1	0.010	0.0250	0.500
2	0.005	0.0250	0.250
3	0.010	0.0125	0.125

Deduce the rate equation for the reaction, and calculate its rate constant at 750 °C.

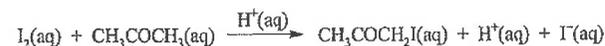
(3 marks)

(c) Is the reaction an elementary reaction? Explain.

(1 mark)

ASL09(II)_05

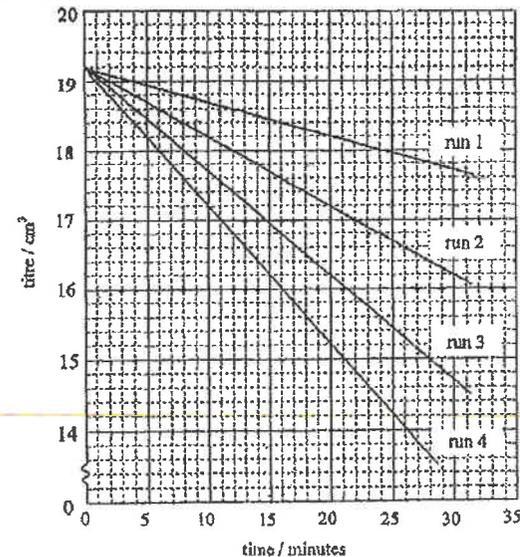
An experiment was devised to study the kinetics of the following acid-catalyzed reaction:



Four runs of the experiment were conducted at the same temperature, and the reaction mixtures used were prepared according to the table below:

Run	Volume used / cm ³			
	0.02 M $\text{I}_2(\text{aq})$	1.0 M $\text{CH}_3\text{COCH}_3(\text{aq})$	$\text{H}_2\text{O}(\text{l})$	1.0 M $\text{H}_2\text{SO}_4(\text{aq})$
1	50.0	5.0	20.0	25.0
2	50.0	10.0	15.0	25.0
3	50.0	15.0	10.0	25.0
4	50.0	20.0	5.0	25.0

In each run, 10.0 cm³ of the reaction mixture was withdrawn at regular time intervals and added to excess $\text{NaHCO}_3(\text{aq})$. When effervescence subsided, the resulting mixture was titrated against standard $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ using starch solution as indicator. The graph below shows the plot of the titre against time for each run.



(a) What is the purpose of adding the reaction mixture to excess $\text{NaHCO}_3(\text{aq})$ before each titration?

(1 mark)

(b) Deduce the reaction order with respect to iodine.

(3 marks)

- (c) Using the above information, plot a graph to deduce the reaction order with respect to propanone. (3 marks)
- (d) Suggest how the reaction order with respect to $\text{H}^+(\text{aq})$ can be determined. (3 marks)

AL10(I)_01

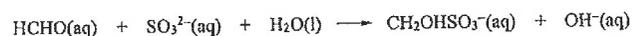
- (b) A student made the following remark:

'The rate of an elementary gaseous reaction increases with temperature because the average kinetic energy of the reactant molecules increases with temperature.'

Is the explanation provided by the student regarding the increase in reaction rate appropriate? Elaborate your answer. (3 marks)

ASL10(II)_08

'Methanal clock experiment' is based on the following reaction:



In a methanal clock experiment, five 20.0 cm³ methanal solutions were prepared by mixing different volume of 0.30 mol dm⁻³ HCHO(aq) and H₂O(l). A small but fixed amount of a solution containing 0.20 mol dm⁻³ NaHSO₃(aq), 0.05 mol dm⁻³ Na₂SO₃(aq) and a few drops of phenolphthalein indicator was added to each of the five methanal solutions. The time for the first appearance of a pink color in each run was recorded.

The table below lists the experimental data obtained:

Run	1	2	3	4	5
Volume of 0.30 mol dm ⁻³ HCHO(aq) used / cm ³	5.0	7.5	10.0	12.5	15.0
Volume of H ₂ O(l) used / cm ³	15.0	12.5	10.0	7.5	5.0
Time for the first appearance of the pink color / s	35.7	23.3	17.9	14.1	12.0

- (a) Given that NaHSO₃(aq) and Na₂SO₃(aq) constitute a buffer system, account for the appearance of the pink color in the reaction mixtures. (2 marks)
- (b) Explain why a small but fixed amount of the buffer solution is used in the experiment. (1 mark)
- (c) Using the above information, plot a graph to deduce the reaction order with respect to methanal. (4 marks)

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- (d) With reference to the above experimental data, identify ONE major error in this experiment. (1 mark)
- (e) Can methyl orange be used instead of phenolphthalein to perform methanal clock experiments? Explain. (1 mark)

ASL11(I)_03

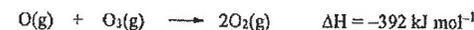
The reaction between A(g) and B(g) has a rate constant of $9 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Which one of the following is a possible rate equation for this reaction?

- A. $\text{rate} = k [\text{A}(\text{g})]^2 [\text{B}(\text{g})]^2$
 B. $\text{rate} = k [\text{A}(\text{g})][\text{B}(\text{g})]^2$
 C. $\text{rate} = k [\text{A}(\text{g})]^2$
 D. $\text{rate} = k [\text{B}(\text{g})]^{-1}$

(1 mark)

ASL11(II)_01

In the upper atmosphere, ozone is converted to diatomic oxygen according to the equation shown below. This reaction is an elementary reaction with a rate constant of $2.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 210 K.



- (a) Write the rate equation for this reaction. (1 mark)
- (b) The relationship between reaction rate constant k and absolute temperature T can be represented by the Arrhenius equation:

$$k = A e^{-E_a/RT} \quad \text{where } R \text{ is the gas constant, } A \text{ is the Arrhenius constants, and } E_a \text{ is the activation energy.}$$

Given that A for this reaction is $4.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, calculate its E_a . (2 marks)

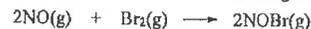
- (c) If chlorine free radicals ($\bullet\text{Cl}$) are present in the upper atmosphere, they will catalyze the conversion of ozone to diatomic oxygen leading to ozone depletion.
- (i) Given that the rate equation for the $\bullet\text{Cl}$ catalyzed ozone depletion is:
 $\text{rate} = k[\text{O}_3(\text{g})][\bullet\text{Cl}(\text{g})]$
 propose a mechanism that is consistent with the rate equation. Briefly explain your answer.
- (ii) The activation energy for the $\bullet\text{Cl}$ catalyzed ozone depletion is 0.44 kJ mol^{-1} . On the same diagram, sketch labelled energy profile for the conversion of ozone to diatomic oxygen in the absence and in the presence of $\bullet\text{Cl}$ respectively. (You are NOT required to draw the energy profiles to scale.) (4 marks)

(4 marks)

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ASL12(II)_04

An experiment was conducted to study the kinetics of the following reaction at a certain temperature.



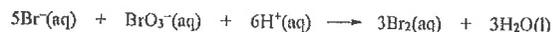
The table below lists the results obtained:

Trial	Initial concentration		Initial rate of appearance of NOBr(g) / $10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
	NO(g) / mol dm^{-3}	Br ₂ (g) / mol dm^{-3}	
1	0.0160	0.0120	3.24
2	0.0160	0.0240	6.38
3	0.0320	0.0060	6.42

- (a) Find the initial rate of disappearance of Br₂(g) in Trial 1. (1 mark)
- (b) For this reaction, deduce its rate equation, and calculate its rate constant at this temperature. (4 marks)
- (c) From the above information, student D proposed that this reaction is an elementary reaction while student E consider it not.
- (i) Suggest ONE reason to support students D's view. (1 mark)
- (ii) Suggest ONE reason to support students E's view. (1 mark)

ASL13(II)_04 (modified)

Consider the following experiment for studying the kinetic of reaction (β):



A solution containing Br⁻(aq) ions, BrO₃⁻(aq) ions, a small fixed amount of phenol and a few drops of methyl red indicator is mixed with H⁺(aq). The Br₂(aq) formed then reacts rapidly with the phenol present to give a colorless product. Once all the phenol is consumed, any further Br₂(aq) will bleach the methyl red indicator. Thus the time taken for the red color of the mixture to disappear represents the time for the reaction (β) to reach a certain point.

The table below lists the results obtained in four trials of such an experiment at 25 °C.

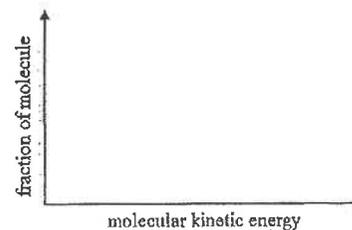
Trial	Initial concentration / mol dm^{-3}			Time taken for the red color to disappear / s
	Br ⁻ (aq)	BrO ₃ ⁻ (aq)	H ⁺ (aq)	
1	0.034	0.007	0.100	1026
2	0.017	0.007	0.100	2052
3	0.034	0.021	0.100	342
4	0.017	0.007	0.400	128

- (a) Explain why a small fixed amount of phenol is used. (1 mark)
- (b) From the experimental results, deduce the order of reaction with respect to each of the reactants. (4 marks)

- (c) The experiment was repeated at 50 °C with all reactants at the same initial concentrations as in Trial 1. The time taken for the red color to disappear was found to be 145 s. Calculate the activation energy of reaction (β). (3 marks)
- (d) Would such an experiment give reliable results if it was conducted at temperature above 80 °C? Explain. (1 mark)

ASL13(II)_05

- (a) Using the axes given below, sketch two curves to show the distribution of molecular kinetic energies of a gas at two temperature T_1 and T_2 , where $T_1 < T_2$.



- (b) Explain why the rate of gas-phase elementary reaction increases with temperature. (2 marks)

DSE11SP_01a

In acid solution, chlorate ions (ClO₃⁻) slowly oxidize chloride ions to chlorine. The following kinetic data are obtained at 25 °C:

[ClO ₃ ⁻ (aq)] / mol dm^{-3}	[Cl ⁻ (aq)] / mol dm^{-3}	[H ⁺ (aq)] / mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
0.08	0.15	0.20	1.0×10^{-5}
0.08	0.15	0.40	4.0×10^{-5}
0.16	0.15	0.40	8.0×10^{-5}
0.08	0.30	0.20	2.0×10^{-5}

- (i) Write the balanced equation for this reaction. (1 mark)
- (ii) Determine the order of the reaction with respect to each reactant. (3 marks)
- (iii) Determine the rate constant at this temperature. (3 marks)
- (iv) If the rate of the reaction is found to be doubled when the temperature is raised by 10°C, deduce the activation energy of the reaction. (Gas constant R = 8.31 J K⁻¹ mol⁻¹) (2 marks)

DSE12PP_01b

The atmospheric oxidation of L-ascorbic acid is a first order reaction.

- (i) What do you understand by the term 'first order reaction'? (1 mark)
- (ii) The table below lists the rate constants k for this reaction at four different temperatures T :

T / K	313	323	333	343
$k / 10^{-3} \text{ h}^{-1}$	27.0	35.4	50.4	65.4

By plotting a suitable graph, determine the activation energy E_a of this reaction.

(Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

(5 marks)

DSE12_01c

Three trials of an experiment were performed at the same temperature for the study of the kinetics of the following reaction.



The table below shows the data obtained:

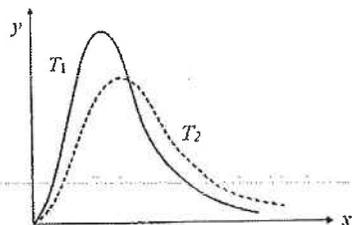
Trial	Initial concentration of NO(g) / mol dm^{-3}	Initial concentration of H ₂ (g) / mol dm^{-3}	Initial rate with respect to N ₂ (g) / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	2.50×10^{-2}	5.00×10^{-3}	1.20×10^{-6}
2	2.50×10^{-2}	1.00×10^{-2}	2.40×10^{-6}
3	1.25×10^{-2}	1.00×10^{-2}	6.00×10^{-7}

- (i) Explain why 'initial rate' is commonly used in the study of the kinetics of a reaction. (1 mark)
- (ii) Deduce the order of reaction with respect to NO(g) and that to H₂(g). (2 marks)
- (iii) State the rate equation for the reaction, and calculate its rate constant at the temperature of the experiment. (2 marks)

DSE13_01a

For gaseous reactions, an increase in temperature leads to an increase in reaction rate.

- (i) The graph below shows the Maxwell-Boltzmann distribution curves of molecular kinetic energies of a gas at two temperatures, T_1 and T_2 .

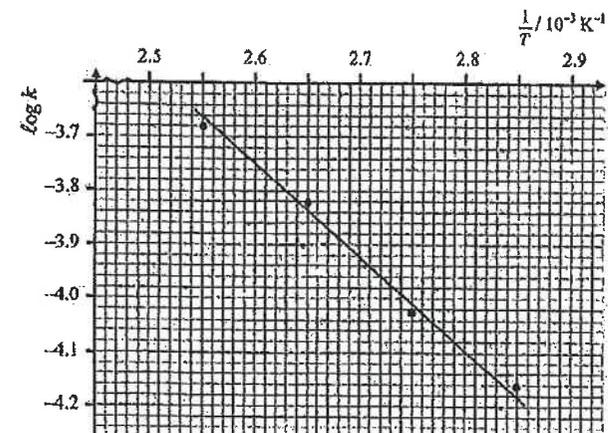


16

- (1) What do the axes, x and y , in the above graph respectively represent? (2 marks)

- (2) With reference to the above graph, suggest why an increase in temperature can lead to an increase in the reaction rate of a gaseous reaction. (2 marks)

- (ii) In a chemical kinetics experiment, the rate constants (k) of a reaction at various temperatures (T) were determined. The graph below shows the plot of $\log k$ against $\frac{1}{T}$. Calculate the activation energy of this reaction. (Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)



(3 marks)

DSE14_01a

Answer the following short questions:

- (i) What is meant by the term 'activation energy'? (1 mark)
- (ii) At room temperature, ethanol can be produced by fermentation of sugars in the presence of yeast. State the function of yeast, and explain why this function fails at high temperatures. (2 marks)

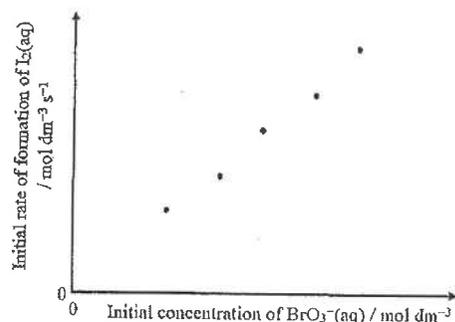
17

DSE14_01b

The kinetics of the following reaction at a certain temperature were studied:



Several trials of an experiment were attempted under the same experimental conditions except varying the initial concentration of $\text{BrO}_3^-(\text{aq})$ to measure the initial rate of formation of $\text{I}_2(\text{aq})$. The following graph shows the experimental results obtained from these trials:



- (i) What is the meant by the term 'initial rate'? (1 mark)
- (ii) Suggest a method, with justification, to follow the progress of the formation of $\text{I}_2(\text{aq})$. (2 marks)
- (iii) With reference to the graph above, deduce the order of reaction with respect to $\text{BrO}_3^-(\text{aq})$. (2 marks)
- (iv) The table below lists the information for two trials of an experiment on the same reaction performed at the same temperature:

	Initial concentration / mol dm ⁻³			Initial rate of formation of $\text{I}_2(\text{aq})$ / mol dm ⁻³ s ⁻¹
	$\text{BrO}_3^-(\text{aq})$	$\text{I}^-(\text{aq})$	$\text{H}^+(\text{aq})$	
Trial 1	0.17	0.15	0.10	2.30×10^{-3}
Trial 2	0.17	0.30	0.20	1.84×10^{-2}

- (1) Given that the order of reaction with respect to $\text{I}^-(\text{aq})$ is 1, deduce the order of reaction with respect to $\text{H}^+(\text{aq})$. (2 marks)
- (2) Based on Trial 1, deduce the initial rate of reaction with respect to $\text{BrO}_3^-(\text{aq})$ under the experimental conditions. (1 mark)

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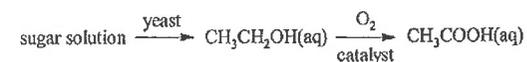
DSE15_01a

- (i) A certain reaction is zeroth order with respect to $\text{I}_2(\text{aq})$ and first order with respect to both $\text{CH}_3\text{COCH}_3(\text{aq})$ and $\text{H}^+(\text{aq})$.
- (1) State the effect, if any, of a change in the concentration of $\text{I}_2(\text{aq})$ in the reaction mixture on the rate of the reaction. (1 mark)
- (2) Write the rate equation for the reaction. (1 mark)
- (iii) The rate constant of a certain reaction doubles when the temperature is increased from 298 K to 308 K. Calculate the activation energy of the reaction. (2 marks)
- (Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$; Arrhenius equation: $\log k = \text{constant} - \frac{E_a}{2.3RT}$)

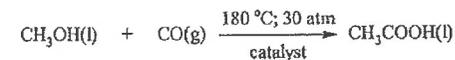
DSE15_01b

Ethanoic acid can be produced by two routes as listed below:

Route (1)



Route (2)



- (i) The reactions in both Routes (1) and (2) require the use of catalysts.
- (1) Draw, the same sketch, TWO labelled energy profiles for a reaction, one with a catalyst and the other one without catalyst. (3 marks)
- (2) Theoretically, catalysts are not consumed in reactions. Suggest why it is still necessary to replace the used catalyst from time to time in industrial processes. (1 mark)

DSE16_01a

- (ii) What does the area under a Maxwell-Boltzmann distribution curve represent? (1 mark)

19

DSE19_01a iii

- (iii) Three trials of an experiment were performed under the same experimental conditions to study the kinetics of the following reaction :



The table below shows the data obtained :

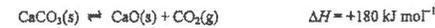
Trial	Initial concentration of A(aq) / mol dm ⁻³	Initial concentration of B(aq) / mol dm ⁻³	Initial rate of formation of D(aq) / mol dm ⁻³ s ⁻¹
1	0.0836	0.202	0.26×10^{-4}
2	0.0836	0.404	1.04×10^{-4}
3	0.0418	0.404	0.52×10^{-4}

Deduce the order of reaction with respect to A(aq) and that with respect to B(aq).

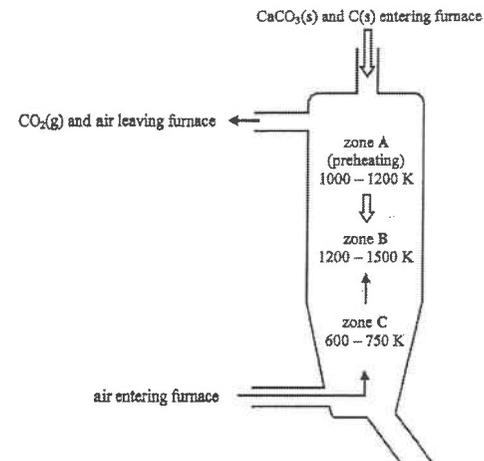
(2 marks)

DSE19_1c

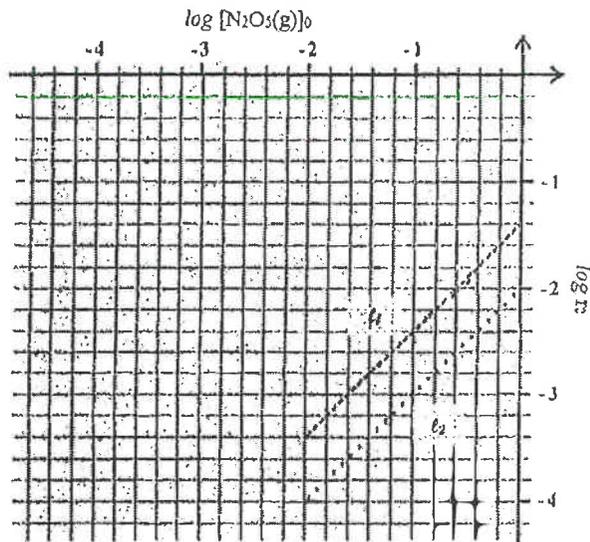
1. (c) In industry, CaO(s) is produced from the decomposition of CaCO₃(s) :



The diagram below shows an operating furnace for producing CaO(s) in an industrial plant. CaCO₃(s) and C(s) enter the furnace from the top while air enters the furnace near the bottom.



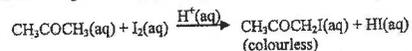
- (i) State one feedstock for CaCO₃(s). (1 mark)
- (ii) Explain why the injection of C(s) and air can result in a higher average temperature in zone B than in zone A. (1 mark)
- (iii) The operation pressure is set at about 1 atm. Give TWO reasons why a higher operation pressure is not preferred. (2 marks)
- (iv) The activation energy of the above decomposition of CaCO₃(s) is 160 kJ mol⁻¹. Calculate the ratio of the rate constant at 1500 K to the rate constant at 1200 K for the decomposition of CaCO₃(s). (Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) (3 marks)
- (v) According to chemical equilibrium, suggest why the decomposition of CaCO₃(s) mainly occurs in zone B. (1 mark)



It is given that $\log t_{1/2} = \log k + n \log [N_2O_5(g)]_0$, where k is the rate constant and n is the order of reaction with respect to N₂O₅(g).

- (i) Given that ℓ_1 and ℓ_2 have the same slope, what can you deduce in terms of chemical kinetics? (1 mark)
- (ii) From ℓ_1 , deduce the order of reaction with respect to N₂O₅(g). (2 marks)
- (iii) From ℓ_2 , deduce the rate constant for the reaction at 345 K. (2 marks)
- (iv) According to the relevant information of the graph, calculate the activation energy of the reaction. (Gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) (3 marks)

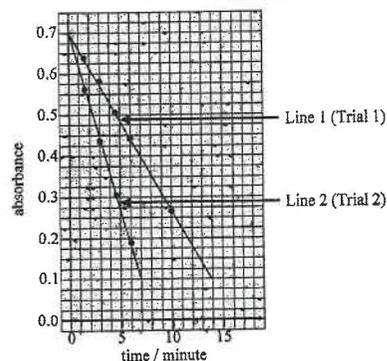
1. (c) Consider the following reaction ($\text{H}_2\text{SO}_4(\text{aq})$ as catalyst) and its rate equation :



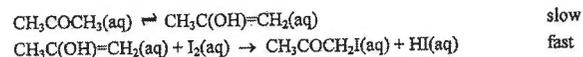
$$\text{Rate} = k_1[\text{I}_2(\text{aq})]^w[\text{CH}_3\text{COCH}_3(\text{aq})]^x[\text{H}^+(\text{aq})]^y \quad (\text{w, x and y are integers})$$

Two trials of an experiment were performed under the same experimental conditions to study its chemical kinetics. The table below shows, in the reaction mixture, the initial concentrations of the reagents used; while the graph shows the variation of the absorbance of the reaction mixtures with time :

Trial	Initial concentration of $\text{CH}_3\text{COCH}_3(\text{aq}) / \text{mol dm}^{-3}$	Initial concentration of $\text{H}_2\text{SO}_4(\text{aq}) / \text{mol dm}^{-3}$	Initial concentration of $\text{I}_2(\text{aq}) / \text{mol dm}^{-3}$
1	1.0	0.10	0.0050
2	2.0	0.10	0.0050



- (i) Explain why the rate of change of the absorbance can represent the rate of reaction. (1 mark)
- (ii) Under these experimental conditions, the rate equation can be simplified as $\text{Rate} = k_2[\text{I}_2(\text{aq})]^w$. With reference to Line 1, deduce w. (2 marks)
- (iii) With reference to Line 1 and Line 2, deduce x of the rate equation. (2 marks)
- (iv) Given that $y = 1$ and the unit of the rate of reaction is $\text{mol dm}^{-3} \text{s}^{-1}$, what is the unit of the rate constant k_1 ? (1 mark)
- (v) It is proposed that the reaction proceeds consecutively in two steps and is exothermic :

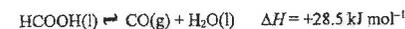


Draw an energy profile for the reaction. Label the axes.

(2 marks)

DSE21_01(a)

- (i) At certain conditions, the activation energy for the decomposition of $\text{HCOOH}(\text{l})$ to $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ shown below is $+77.7 \text{ kJ mol}^{-1}$.



What is the activation energy for the formation of $\text{HCOOH}(\text{l})$ from $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at the same conditions, in kJ mol^{-1} ?

(1 mark)

- (ii) The activation energy for a certain reaction is $+65.0 \text{ kJ mol}^{-1}$. The rate constant of the reaction at 27°C is k_1 . Calculate the rate constant of the reaction at 37°C in terms of k_1 .

$$\left(\text{Gas constant } R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}; \text{ Arrhenius equation : } \log k = \text{constant} - \frac{E_a}{2.3RT}\right)$$

(2 marks)

- (iii) The rate equation for the reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow \text{C}(\text{g})$ at certain conditions is given below, with k_2 being the rate constant :

$$\text{Rate} = k_2[\text{A}(\text{g})][\text{B}(\text{g})]^2$$

- (1) What is the order of reaction with respect to $\text{B}(\text{g})$?

- (2) The unit of the rate is $\text{mol dm}^{-3} \text{s}^{-1}$. State the unit of k_2 .

(2 marks)

DSE21_01(b)(iv)

- (iv) Catalyst is used in the reaction of Haber process.

- (1) Suggest a catalyst that can be used.

- (2) With the aid of a Maxwell-Boltzmann distribution curve, explain why the reaction becomes faster when a catalyst is used.

Answer ALL parts of the question.

1. (a) Answer the following short questions :

(i) Under certain conditions, ethanoic acid can be manufactured by the following reaction :



(1) Suggest one reason why this reaction is considered to be green.

(2) Suggest one reason why this reaction is NOT considered to be green.

(2 marks)

(ii) A factory manufactures catalytic converters with a catalyst coating on a porous structure.

(1) Suggest one advantage of using a porous structure in the catalytic converters.

(2) Explain why the effectiveness of the catalyst may decrease after prolonged use.

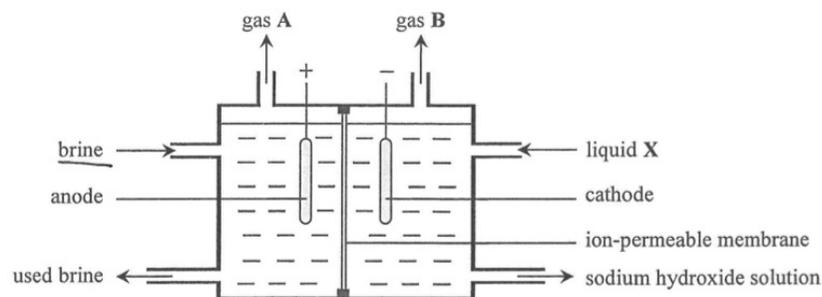
(2 marks)

(iii) Which one of the following items is NOT manufactured from petrochemicals ?

nylon rope, glass bottle, soapless detergent

(1 mark)

(b) The diagram below shows a membrane electrolytic cell used in the chloroalkali industry. Brine and liquid X are continuously added into the membrane electrolytic cell to produce gas A, gas B and sodium hydroxide solution.



(i) What is X ?

(1 mark)

(ii) Gas A is formed at the anode of the membrane electrolytic cell.

(1) What is A ?

(2) Explain why A is formed.

(2 marks)

(iii) Gas B and sodium hydroxide solution are formed at the cathode of the membrane electrolytic cell.

(1) Write a half equation for the formation of B.

(2) Explain why sodium hydroxide solution is formed and why it does not contain sodium chloride.

(3 marks)

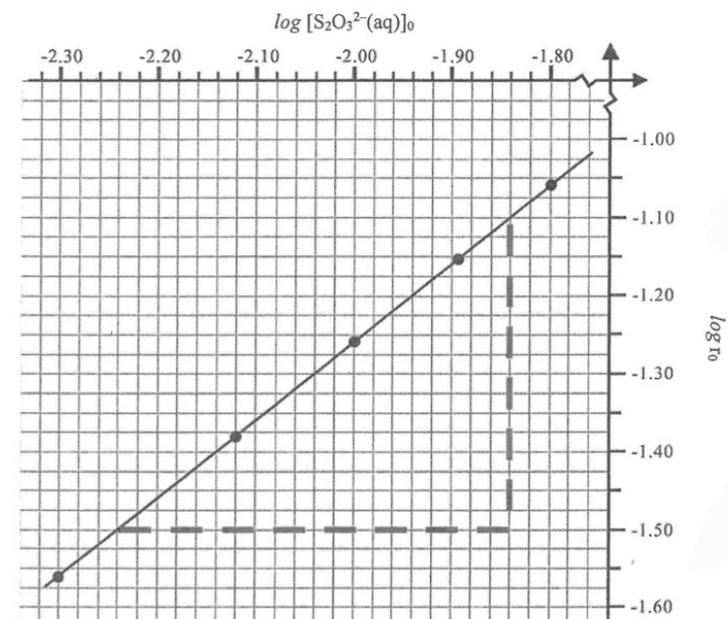
(iv) Suggest a chemical that can be manufactured from the reaction between A and sodium hydroxide solution.

(1 mark)

1. (c) The chemical kinetics of the following reaction at a certain temperature was studied :



Several trials of an experiment were performed under the same experimental conditions, except varying the initial concentration of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ (represented by $[\text{S}_2\text{O}_3^{2-}(\text{aq})]_0$), to measure the initial rate of formation of S(s) (represented by r_0). The following graph shows the experimental results obtained from these trials :



(i) What is meant by the term 'initial rate' ?

(1 mark)

(ii) The rate equation for the reaction is shown below :

$$\text{Rate} = k [\text{S}_2\text{O}_3^{2-}(\text{aq})]^a [\text{H}^+(\text{aq})]^b$$

where k is the rate constant,
 a is the order of reaction with respect to $\text{S}_2\text{O}_3^{2-}(\text{aq})$
and b is the order of reaction with respect to $\text{H}^+(\text{aq})$.

Given that the concentration of $\text{H}^+(\text{aq})$ used was much higher than that of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ in each trial, explain why the above rate equation can be modified as shown below :

$$\text{Rate} = k' [\text{S}_2\text{O}_3^{2-}(\text{aq})]^a$$

where k' is regarded as a constant.

(2 marks)

(iii) By using the dotted lines in the graph above, deduce the order of reaction with respect to $\text{S}_2\text{O}_3^{2-}(\text{aq})$.

(3 marks)

(iv) The experiment was repeated at 25 °C and 35 °C separately, while other experimental conditions were the same. The rate constant of the reaction at 25 °C is k_1 and the rate constant of the reaction at 35 °C is k_2 . The ratio of k_2 to k_1 is 1.9 : 1.0. Calculate the activation energy of the reaction, in kJ mol^{-1} .

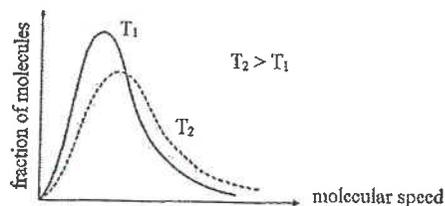
$$\left(\text{Gas constant } R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}; \text{ Arrhenius equation : } \log k = \text{constant} - \frac{E_a}{2.3RT}\right)$$

(2 marks)

END OF SECTION A

Marking Scheme
AL96(II)_01b

(i)



[2]

(ii) As temperature increases, fraction of molecules with high average speed / kinetic energy increases. [1]

Hence, force exerted by the collision of molecules on the container wall / the change in momentum of molecules upon collision / frequency of collision increases. [1]

AL97(II)_03

(a) (i) At regular time intervals, withdraw a known volume of the reaction mixture. Add it to excess NaHCO_3 to quench the reaction. [1]

Titrate against standard $\text{S}_2\text{O}_3^{2-}(\text{aq})$ using starch solution as indicator. [1]

(ii) Plot a graph of the titre against time. [1]

Determine the slope of the curve at $t = 0$. [1]

(iii) Colorimetry / use a colorimeter to monitor the concentration of I_2 . [1]

(b) (i) Initial rate is independent of $[\text{I}_2]$. [1]

\therefore order w.r.t. $[\text{I}_2] = 0$ [1]

Initial rate doubles when $[\text{CH}_3\text{COCH}_3]$ is increased by a factor of 2. [1]

\therefore order w.r.t. $[\text{CH}_3\text{COCH}_3] = 1$ [½]

Initial rate doubles when $[\text{H}^+]$ is increased by a factor of 2. [1]

\therefore order w.r.t. $[\text{H}^+] = 1$ [½]

\therefore Initial rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$ [1]

(ii) $3.5 \times 10^{-5} = k(2.0 \times 10^{-1})(5.0 \times 10^{-3})$ [1]

$k = 3.5 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [1]

(d) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [1]

$\ln 2 = -\frac{E_a}{8.314} \left(\frac{1}{308} - \frac{1}{298} \right)$ [1]

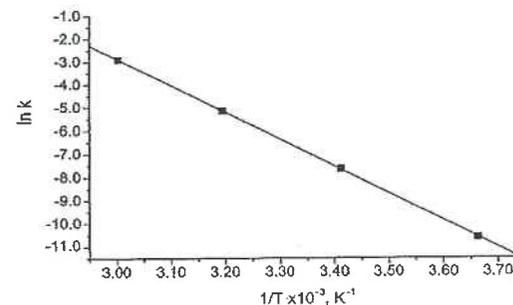
$E_a = +52.9 \text{ kJ mol}^{-1}$ (Range: 52.8 – 53.3) [1]

AL98(II)_03a

k / s^{-1}	$\ln(k)$	T/K	$\frac{1}{T} / \text{K}^{-1}$
2.46×10^{-5}	-10.61	273	3.66×10^{-3}
4.75×10^{-4}	-7.65	293	3.41×10^{-3}
5.76×10^{-3}	-5.16	313	3.19×10^{-3}
5.48×10^{-2}	-2.90	333	3.00×10^{-3}

[1]

graph of $\ln k$ against $\frac{1}{T}$



[2]

(1 mark for the curve and ½ marks for each axis)

Slope = $-E_a / R$ [1]

$E_a = -R(\text{slope}) = -(8.31 \text{ JK}^{-1} \text{ mol}^{-1})(-11646 \text{ K}) = +96.8 \text{ kJ mol}^{-1}$ [1]

(Accept answers from 87.0 to 106.0 kJ mol^{-1} ; error in sign is not acceptable and the answer must be accompanied with the graph.)

(1 mark for numerical answer, ½ marks for the unit)

(ii) From the graph

At 353K, $\ln k = -0.92$

$k = 0.40 \text{ s}^{-1}$

[1½]

(Accept answers from 0.35 to 0.44 s^{-1} ; rate constant obtained by numerical calculation is also acceptable.)

(1 mark for numerical answer, ½ marks for the unit)

For the first order reaction

$k = \frac{\ln 2}{t_{1/2}}, t_{1/2} = \frac{\ln 2}{k} = 1.73 \text{ s}$

[1½]

(Accept answers from 1.56 to 1.90 s)

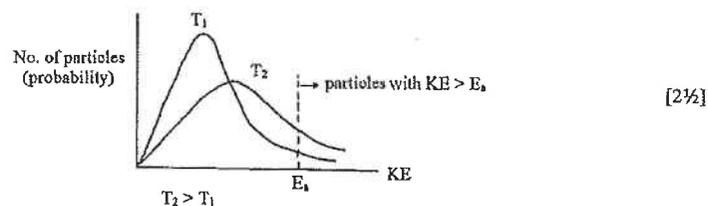
(1 mark for numerical answer, ½ marks for the unit)

(iii) Titrate the concentration of the dicarboxylic acid using a standard solution of an alkali. [1]

OR Measure the volume of CO_2 liberate / the gas pressure at a fixed volume.

AL98(II)_03b

(i)

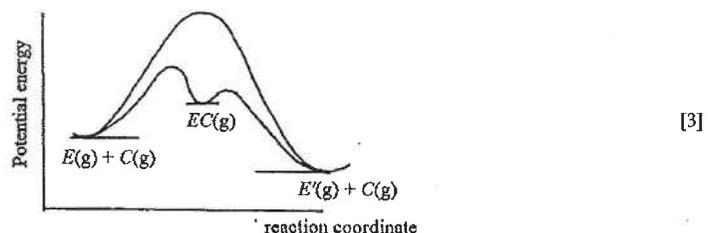


[2½]

(ii) At a higher temperature (T_2), the portion towards high kinetic energy is much larger [½]
 (refer to the curves in (i)). More particles would have sufficient energy to overcome E_a and to react. [½]

Increasing the number of effective collision increases the rate of reaction. [½]

(iii)



[3]

(½ marks for each axis; ½ marks for each curve, the curve for the catalyzed reaction should have a hump; ½ marks for labelling the reactants, products and intermediate; ½ marks for showing a lower energy state for the product (i.e., indication of an exothermic reaction.)

The presence of a catalyst causes the reaction to take place via an alternative reaction pathway with a lower activation energy. [½]

Lowering the kinetic barrier increases the rate of reaction. [½]

AL99(II)_03a

(i) Under the same initial concentration of A, initial rate remains the same when concentration of B is doubled. ∴ order w.r.t [B] = 0 [1]

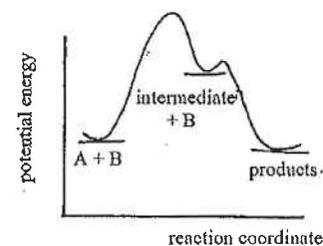
Under the same initial concentration of B, initial rate doubles when concentration of A is doubled. ∴ order w.r.t [A] = 1 [1]

Rate equation: rate = $k[A]$ [½]

(ii) $k = \frac{6.4 \times 10^{-5}}{4.0 \times 10^{-2}} = 1.6 \times 10^{-3} \text{ s}^{-1}$ [1]

(iii) Possible energy profile:

[3]



1 mark for labelling the axes;

1 mark for showing a correct curve, rate determining step involves only one molecule of A;

½ marks for labelling the reactants, products and intermediate.

AL00(I)_07b

Keeping the initial concentrations of the reactants unchanged, carry out the experiment [1]

at different temperatures and determine the corresponding rate constant (k). [2]

Plot a graph $\ln k$ against $1/T$, slope of the graph = $-E_a/R$ [1]

AL00 (II)_03b

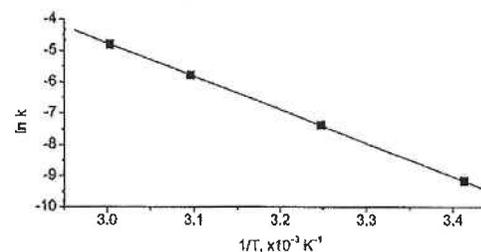
(i) Rate = $k[\text{CH}_3\text{Br}][\text{OH}^-]$ [1]

$$8.23 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} = k \times 0.05 \text{ mol dm}^{-3} \times 0.20 \text{ mol dm}^{-3}$$

$$k = 8.23 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$
 [1]

T / K	293	308	323	333
$\frac{1}{T} / \text{K}^{-1}$	3.413×10^{-3}	3.247×10^{-3}	3.096×10^{-3}	3.003×10^{-3}
$\ln k$	-9.162	-7.394	-5.786	-4.800

graph of $\ln k$ against $\frac{1}{T}$ [1]



[2]

(1 mark for a correct graph; 1 mark for labeling the axes. Deduce 1 mark if only 3 points are used.)

$$\text{slope} = -\frac{E_a}{R} = -10648$$

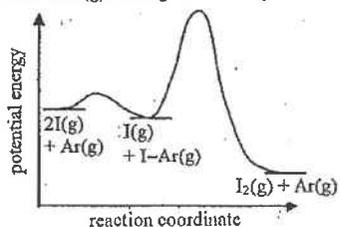
$$E_a = +88.5 \text{ kJ mol}^{-1} \quad (\text{Range: } 86 - 95)$$

AL01(I)_03

- (a) For the same initial conc of Ar(g), initial rate increases by 4 times when the initial conc of I(g) is doubled \therefore order w.r.t. [I(g)] = 2 [1]
 For the same initial conc of I(g), initial rate doubles when the initial conc of Ar(g) is doubled \therefore order w.r.t. [Ar(g)] = 1 [1]
 Rate equation = $k[I(g)]^2[Ar(g)]$ [1]

(b) rate constant = $\frac{8.70 \times 10^{-4}}{(1.0 \times 10^{-5})^2(1.0 \times 10^{-3})} = 8.7 \times 10^9 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ [1]

- (c) Mechanism: two stage mechanism [1]
 $I(g) + Ar(g) \rightarrow I-Ar(g)$ fast [1]
 $I(g) + I-Ar(g) \rightarrow I_2(g) + Ar(g)$ slow [1]
 Role of Ar(g): homogeneous catalyst [1]



ASL02(I)_02

- (a) Rate = $k [CH_3COCH_3(aq)]^x [Br_2(aq)]^y [H^+(aq)]^z$ [1]
 Keeping the initial concentrations of $CH_3COCH_3(aq)$ and $H^+(aq)$ unchanged, doubling $Br_2(aq)$ has no effect on the initial rate. $\therefore y = 0$ [1]
 The reaction is zeroth order w.r.t. $[Br_2(aq)]$ [1]
 Keeping the initial concentrations of $CH_3COCH_3(aq)$ unchanged, doubling $H^+(aq)$ causes the initial rate to increase by 2 times $\therefore z = 1$ [1]
 Keeping the initial concentrations of $H^+(aq)$ unchanged, increasing the initial concentration of $CH_3COCH_3(aq)$ by 1.3 times causes the initial rate to increase by 1.3 times. $\therefore x = 1$ [1]

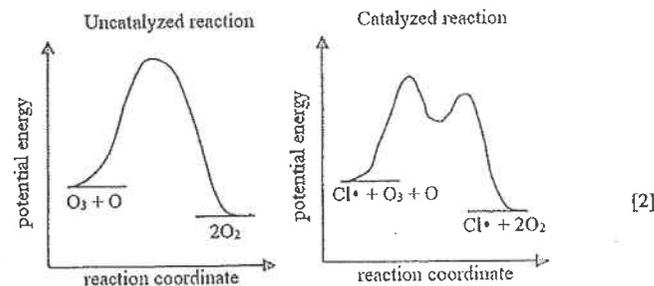
(b) $k = \frac{\text{rate}}{[CH_3COCH_3(aq)][H^+]}$ [1]
 Substitute a set of data (e.g. the first set)
 $k = \frac{5.7 \times 10^{-5}}{0.30 \times 0.050} = 3.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [2]
 (Also accept 3.875×10^{-3} and 4.00×10^{-3})
 (1 mark for method; 1 mark for answer + correct units)

AL03(I)_02b

- (i) $K_c = \frac{[I(g)]^2}{[I_2(g)]}$ [1]
 (ii) From (i), $[I(g)]^2 = K_c[I_2(g)]$ [1]
 Since Step 2 is the rate determining step, [1]
 Rate of overall reaction = $k [H_2(g)][I(g)]^2 = k K_c [I_2(g)][H_2(g)]$ [1]
 The reaction is first order w.r.t. $H_2(g)$ and to $I_2(g)$.

ASL03(I)_04

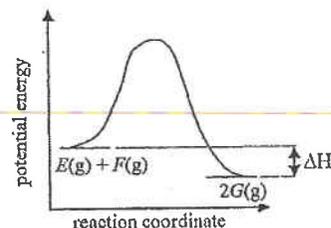
- (a) (i) Homogeneous catalyst because O_3 , O and $Cl\cdot$ are in the gaseous phase. [1]
 (ii)



- (b) The depletion of ozone is a chain reaction. [1]
 As the $Cl\cdot$ radical is regenerated, one $Cl\cdot$ radical can cause the two reactions, which lead to ozone depletion, to repeat thousands of times. [1]

AL04(I)_03a

- (i) forward rate = $k_1[E(g)][F(g)]$ [½]
 backward rate = $k_{-1}[G(g)]^2$ [½]
 (ii) Energy profile



1 mark for an energy profile for an exothermic reaction
 1 mark for labeling the axes

(iii) k_{-1} will increase to a great extent. [½]

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = C - \frac{E_a}{RT}$$

E_a for the backward reaction is greater than E_a for the forward reaction,
 $\therefore k_{-1}$ will increase to a greater extent when T increases. [½]

AL04(II)_03a

(i) Monitor the pressure of the system because both N_2O_5 and NO_2 are soluble in CCl_4 while O_2 is insoluble. [1]

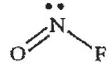
OR, Measure the volume of gas evolved because N_2O_5 and NO_2 are soluble in CCl_4 while O_2 is insoluble. [1]

(ii) $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [1]

$$\ln \frac{5}{1} = -\frac{E_a}{8.314} \left(\frac{1}{332} - \frac{1}{318} \right)$$

$$E_a = +100.9 \text{ kJ mol}^{-1} \quad [1]$$

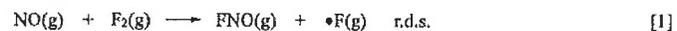
AL05(I)_02a

(i)  [1]

(ii) NO: +2 [½]

FNO: +3 [½]

(iii) Mechanism:



ASL06(II)_10a

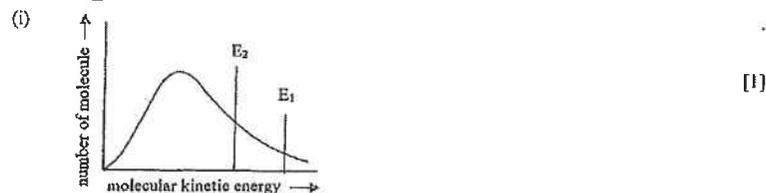
(i) rate of consumption of $O_2 = \frac{5}{4} \times 1.24 \times 10^{-4}$ [1]

$$= 1.55 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1} \quad [1]$$

(ii) Catalyst is a substance which can change the rate of reaction but itself remains chemically unchanged after the reaction. [1]

(iii) Nitric acid / nitrogenous fertilizers [1]

ASL06(II)_10b



In the presence of a (positive) catalyst, the reaction proceeds through another path with a lower activation energy E_2 . [1]

(ii) Number of molecules with energy not less than the activation energy is greater than that without catalyst at the same temperature. [1]

There is an increase in effective collision frequency. [1]

ASL07(II)_02

(a) Colorimetry [1]

$Br_2(aq)$ has a brown color. When the reaction proceeds, the brown color of the reaction mixture becomes less intense. [1]

Concentration of $Br_2(aq) \propto$ absorbance of reaction mixture.

(b) Plot a graph of absorbance against time. [1]

Slope of curve at $t = 0$ represents the initial rate. [1]

(c) Rate = $k[HCO_2H(aq)]^x [Br_2(aq)]^y$ [1]

When $[HCO_2H(aq)] \gg [Br_2(aq)]$, the rate equation becomes

Rate = $k'[Br_2(aq)]^y$, where $k' = k[HCO_2H(aq)]^x$ [1]

$[Br_2(aq)]^y$ is the only factor which affects the reaction rate.

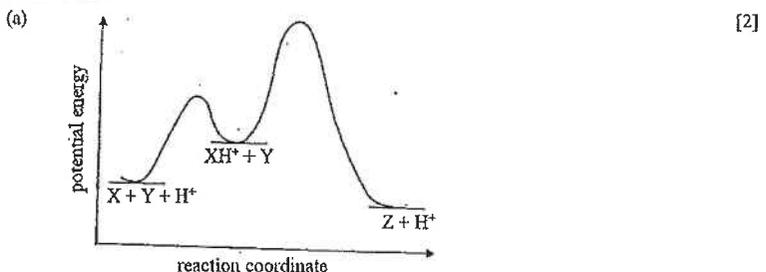
(d) The initial rate doubles when $[Br_2(aq)]$ is doubled. [1]

\therefore order w.r.t. $Br_2(aq)$ is 1. [1]

(e) Repeat the experiment using the same reagents, keeping the volume of $Br_2(aq)$ used constant, and vary the volume of $HCO_2H(aq)$ used. Measure the initial rate in each case. [1]

Compare the initial rates to obtain the order w.r.t. $HCO_2H(aq)$. [1]

ASL07(II)_03



- (b) For the first step, the equilibrium

$$K = \frac{[XH^+]}{[X][H^+]}$$

For the second step,

$$\text{Rate} = k[XH^+][Y]$$

$$= kK[X][Y][H^+]$$

AL08(I)_03a

- (iii) C

ASL08(II)_03

- (a) Monitor the pressure of the reaction system.

Explanation: 4 moles of gases react to give 3 moles of gases.

$\therefore (P_0 - P_t) \propto$ no. of moles of N_2 formed.

- (b) Keeping $[NO]$ constant and doubling $[H_2]$, the initial rate increases 2 times.

\therefore order with respect to $H_2(g) = 1$

Keeping $[H_2]$ constant and doubling $[NO]$, the initial rate increases 4 times.

\therefore order with respect to $NO(g) = 2$

Rate equation:

$$\text{Rate} = k[NO(g)]^2[H_2(g)]$$

$$0.5 = k(0.025)^2(0.01)$$

$$k = 8 \times 10^4 \text{ (mol dm}^{-3}\text{)}^{-2} \text{ s}^{-1}$$

- (c) The reaction is not an elementary reaction.

Explanation (any ONE of the following):

- The order of reaction is different from its molecularity
- The chance for four molecules to collide and react is very low.

ASL09(II)_05

- (a) As the reaction is catalyzed by $H^+(aq)$, treating the reaction mixture with $NaHCO_3(aq)$ can help remove the acid so as to quench the reaction.

- (b) The rate equation should be in the form of

$$\text{Rate} = k[I_2(aq)]^x[CH_3COCH_3(aq)]^y[H^+(aq)]^z$$

The reaction is catalyzed by $H^+(aq)$. $H^+(aq)$ is in large excess and is not consumed.

$\therefore [H^+(aq)]$ is constant.

In each run, $[CH_3COCH_3(aq)] \gg [I_2(aq)]$, $[CH_3COCH_3(aq)]$ can be considered as constant.

Therefore, the rate equation can be simplified as $\text{rate} = k'[I_2(aq)]^x$

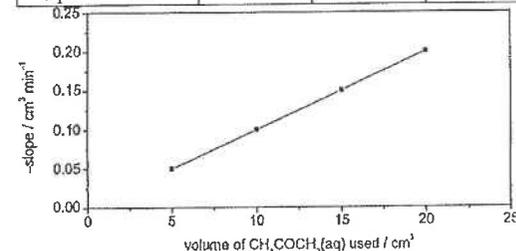
The titre decreases with time linearly, the rate of reaction is independent of $[I_2(aq)]$.

Thus, the rate reactions order w.r.t. to I_2 is 0.

- (c) For each run, the slope of the line represents the rate of reaction.

Plotting a graph of (-slope) against volume of $CH_3COCH_3(aq)$ used can help determine y in the rate equation.

Run	1	2	3	4
-slope / $cm^3 \text{ min}^{-1}$	0.05	0.10	0.15	0.20



A straight line pass through the origin is obtained.

The reaction is first order w.r.t. CH_3COCH_3

- (d) Repeat the experiment by using different volume of $H_2SO_4(aq)$ and $H_2O(l)$ while keeping all other variables constant.

Plot a graph of $\log(\text{rate of reaction})$ against $\log(\text{volume of } H_2SO_4(aq) \text{ used})$.

The slope of the graph obtained is the reaction order w.r.t. $H^+(aq)$.

AL10(I)_01

- (b) Accept both 'yes' and 'no' answer. Marks will be awarded only to the elaboration.

The rate of reaction depends on the collision frequency of the reactant molecules.

Only those colliding molecules with KE greater than activation energy, E_a , of the reaction can react.

When temperature increases, average KE of molecules increases.

Chance of collision between molecules increase and, more importantly, a greater percentage of colliding molecules has $KE > E_a$.

ASL10(II)_08

- (a) The $SO_3^{2-}(aq) / HSO_3^-(aq)$ buffer system maintains the reaction mixture at acidic pH, at which phenolphthalein is colorless, (at the beginning) via the equilibrium



When $SO_3^{2-}(aq)$ is consumed in the reaction, the equilibrium position shifts to the right to counteract the change.

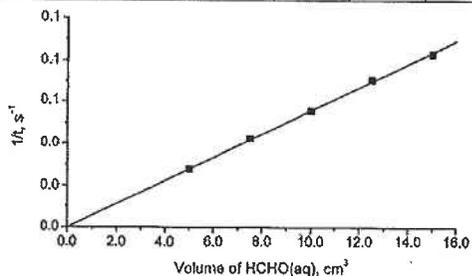
When nearly all of the $HSO_3^-(aq)$ and $SO_3^{2-}(aq)$ ions are reacted, there is excess $OH^-(aq)$ ions, the pH of the solution rises rapidly and phenolphthalein will turn pink.

- (b) This is to ensure that $HCHO(aq)$ is in large excess and the initial rate $1/t$ measured in each run of the experiment refers to the consumption of the same amount of $HCHO$.

(c) Reciprocal of (time for the first appearance of pink color) is close to the initial rate

Volume of HCHO(aq) used / cm ³	5.0	7.5	10.0	12.5	15.0
$\frac{1}{t} / \text{s}^{-1}$	0.0280	0.0429	0.0559	0.0709	0.0833

[1]



[2]

The rate of reaction varies as the concentration of HCHO(aq).

∴ It is first order w.r.t. HCHO.

[1]

(d) Measuring the time for the appearance of the pink color / detecting the color change by eyes.

[1]

(e) No, methyl orange changes color at low pH. The pH of the HSO₃⁻(aq) / SO₃²⁻(aq) system is higher than the pH at which of methyl orange changes color. ∴ methyl orange will remain yellow throughout the experiment.

ASL11(I)_03

B

[1]

ASL11(II)_01

(a) rate = $k[\text{O}(\text{g})][\text{O}_3(\text{g})]$ k can be replaced by $2.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

[1]

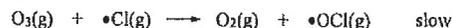
(b) $\ln k = \ln A - \frac{E_a}{RT}$

$$E_a = RT \ln \frac{A}{k} = 8.31(210) \ln \frac{4.8 \times 10^9}{2.6 \times 10^5}$$

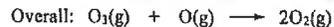
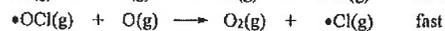
$$= +17.1(4) \text{ kJ mol}^{-1} \quad \text{unit must be present before award mark for the answer}$$

[1]

(c) (i) Mechanism



[2]



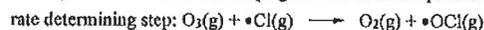
1 mark for having the mechanism agreeing with the rate equation

1 mark for adding all the equations to get the overall equation.

Explanation:

[1]

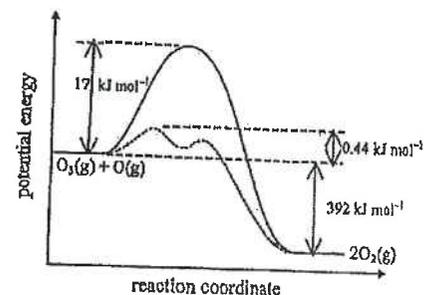
Adding the two mechanistic steps gives the overall equation. The proposed



suggests the rate equation is rate = $k[\text{O}_3(\text{g})][\bullet\text{Cl}(\text{g})]$.

Mechanism agrees with rate equation.

(ii) Energy profiles



[3]

(2 marks for the two curves: 1 mark for the labels)

1 mark for showing the two curves

1 mark for showing P.E. (with unit or unit indicated by energy values) / Energy / H AND reaction coordinate / reaction path AND all chemical species in reactants and products [may include $\bullet\text{Cl}(\text{g})$] and to be balanced

1 mark for labelling 392 (kJ mol^{-1}) / -392 [BUT NOT $\Delta H = +392$] AND either 0.44 or labeling catalyzed and uncatalyzed reactions.

ASL12(II)_04

(a) $\frac{1}{2} \times 3.24 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1} = 1.62 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

[1]

(b) From results of trial 1 & 2, doubling $[\text{Br}_2]_0$ while keeping $[\text{NO}(\text{g})]_0$ constant causes the initial rate to increase by 2 times. ∴ order of reaction w.r.t. $[\text{Br}_2]$ is 1.

[1]

From results of trial 1 & 3, doubling $[\text{NO}(\text{g})]_0$ while decreasing $[\text{Br}_2(\text{g})]_0$ by one-half

[1]

causes the initial rate to increase by 2 times. ∴ order of reaction w.r.t. $[\text{NO}(\text{g})]$ is 2.

Rate equation: rate = $k[\text{NO}(\text{g})]^2[\text{Br}_2(\text{g})]$

[1]

$$\text{Trial 1, } k = \frac{3.24 \times 10^{-4}}{(0.016)^2(0.012)} = 105.5 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1} \quad (\text{Range: } 103 \text{ to } 106)$$

[1]

(if candidates used $1.62 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ as the initial rate, the acceptable range will be from 51.5 to 53 $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$)

(c) (i) For the rate equation: rate = $k[\text{NO}(\text{g})]^2[\text{Br}_2(\text{g})]$, the order w.r.t. each reactant

[1]

matches with the coefficient of the corresponding species in the chemical equation of the elementary reaction.

(ii) The chance for three molecules (two NO and one Br₂) to collide at the same time is very small.

[1]

ASL13(II)_05 (modified)

(a) The time taken for the red color to disappear will be close to the initial rate of reaction. [1]

(b)
$$\text{initial rate} = \frac{1}{\text{time for the red color to disappear}}$$
 [1]

From trials 1 & 2, when $[\text{Br}^-(\text{aq})]$ is doubled, the rate of reaction increases by 2 times.

\therefore Order of reaction w.r.t. $\text{Br}^-(\text{aq})$ ions = 1

From trials 1 & 3, when $[\text{BrO}_3^-(\text{aq})]$ is tripled, the rate of reaction increases by 3 times. \therefore Order of reaction w.r.t. $\text{Br}^-(\text{aq})$ ions = 1 [1]

From trials 2 & 4, when $[\text{H}^+(\text{aq})]$ is increased by 4 times, the rate of reaction increases by 16 times. \therefore Order of reaction w.r.t. $\text{H}^+(\text{aq})$ ions = 2 [1]

(Accept other correct method) [1]

(c) $k = Ae^{-\frac{E_a}{RT}}$ OR $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ [1]

$\ln \frac{1026}{145} = -\frac{E_a}{R} \left(\frac{1}{323} - \frac{1}{298} \right)$ [1]

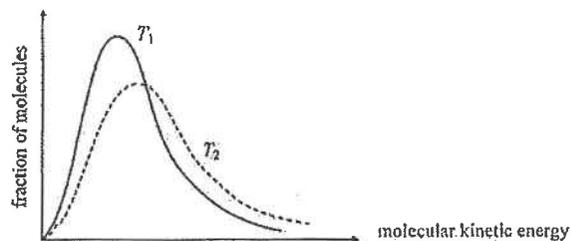
$E_a = +62.6 \text{ kJ mol}^{-1}$ [1]

(d) No. [1]

- Br_2 is volatile. The Br_2 formed will vaporize and will not react with phenol. [1]
- Phenol is volatile. The amount of phenol in the reaction mixture will decrease.
- The rate of reaction is too fast to be determined using this method.

ASL13(II)_05

(a) [2]



(b) In order for a gas-phase elementary reaction to occur, the colliding molecules should have kinetic energy greater than the activation energy E_a of the reaction. [1]

From the graph, the area under the curve for K.E. greater a certain amount increases with temperature. [1]

\therefore rate of reaction increases with temperature.

(i) $\text{ClO}_3^-(\text{aq}) + 5\text{Cl}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Cl}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ [1]

(ii) $\text{Rate} = k [\text{ClO}_3^-(\text{aq})]^x [\text{Cl}^-(\text{aq})]^y [\text{H}^+(\text{aq})]^z$ [1]

$$\frac{1.0 \times 10^{-5}}{4.0 \times 10^{-5}} = \frac{(0.08)^x (0.15)^y (0.2)^z}{(0.08)^x (0.15)^y (0.4)^z}$$

$$z = 2$$

similarly, $x = 1$ and $y = 1$ [2]

(iii) $\text{Rate} = k [\text{ClO}_3^-(\text{aq})][\text{Cl}^-(\text{aq})][\text{H}^+(\text{aq})]^2$ [1]

$$k = \frac{1.0 \times 10^{-5}}{(0.08)(0.15)(0.2)^2}$$

$$= 2.08 \times 10^{-2} \text{ mol}^{-3} \text{ dm}^3 \text{ s}^{-1}$$
 [2]

(iv) Arrhenius equation:

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln 2 = -\frac{E_a}{R} \left(\frac{1}{298 + 10} - \frac{1}{298} \right)$$
 [1]

$$E_a = +52894 \text{ J mol}^{-1} = +52.9 \text{ kJ mol}^{-1}$$
 [1]

DSE12PP_01b

(i) Any ONE of the following: [1]

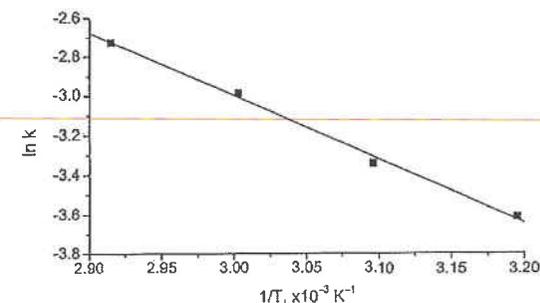
- The rate of reaction is proportional to the concentration of the reactant.
- The half-life of the reaction is constant.

(ii) $\ln k = \text{constant} - \frac{E_a}{RT}$

T / K	313	323	333	343
$k / 10^{-3} \text{ h}^{-1}$	27.0	35.4	50.4	65.4
$1/T$	3.195×10^{-3}	3.096×10^{-3}	3.003×10^{-3}	2.915×10^{-3}
$\ln k$	-3.612	-3.341	-2.988	-2.727

[1]

Graph of $\ln k$ against $\frac{1}{T}$



[2]

(1 mark for the graph; 1 mark for the labels)

$$\text{Slope} = -3227 = -\frac{E_a}{R}$$

DSE11SP_01a

$$E_a = 3227 \times 8.31 = +26.8 \text{ kJ mol}^{-1} \quad (\text{Range: } 24.5 - 29.0) \quad [1]$$

[1]

DSE12_01c

(i) Initial rate is used because the initial concentrations of reactants are known. [1]

(ii) Compare experiments 2 & 3, $[\text{H}_2]$ remains the same but $[\text{NO}]$ is halved, rate is decreased by a factor of 4. Therefore reaction order with respect to $[\text{NO}]$ is two. [1]

Compare experiments 1 & 2, $[\text{NO}]$ remains the same but $[\text{H}_2]$ is doubled, rate is also doubled. Therefore reaction order with respect to $[\text{H}_2]$ is one. [1]

(Deduction must be shown. Accept other means to solve the problem, e.g. mathematical approach)

(iii) $\text{rate} = k[\text{NO}]^2[\text{H}_2]$ [1]

With data from experiment 1,

$$1.20 \times 10^{-6} = k [2.50 \times 10^{-2}]^2 [5.00 \times 10^{-2}]$$

$$\therefore k = 0.384 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad [1]$$

DSE13_01a

(i) (1) x – (molecular kinetic) energy / KE [1]

y – fraction / percentage / number / amount of molecules / particles [1]

(2) (From the sketch), an increase in temperature (from T_1 to T_2) will increase the (average kinetic) energy of the molecules. [1]

This will increase the amount of collisions / increase the collision frequency [1]

/ result in greater effective collisions.

(From the sketch), there is a larger portion of molecules will have kinetic energy greater than E_a . [1]

(ii) $\log k = \text{constant} - \frac{E_a}{2.3RT}$ OR $\ln k = \text{constant} - \frac{E_a}{RT}$ [1]

Slope of the curve = $-\frac{E_a}{2.3RT} = -1.73 \times 10^3$ (Range: -1.67 to -2.05) [1]

$E_a = 1.73 \times 10^3 \times 8.31 \times 2.3 = +33.1 \text{ kJ mol}^{-1}$ (Range: 32 to 39 kJ mol^{-1}) [1]

DSE14_01a

(i) 'Activation energy' refers to the minimum energy possessed by the colliding reactant particles in order that a reaction can occur. [1]

(ii) Yeast provides enzyme / catalyst. [1]

At high temperature, the enzyme (yeast) is denatured / destroyed so that it cannot function as a catalyst. [1]

DSE14_01b

(i) Initial rate is the instantaneous rate at the start of the reaction. [1]

OR, rate at $t = 0$

(ii) Follow the color intensity of the solution / by colorimetry [1]

The solution change from colorless to brown/yellow. [1]

OR Titrate with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Quenching. Add starch indicator. End point: blue to colorless.

(iii) The initial rate is directly proportional to $[\text{BrO}_3^-(\text{aq})]$. / The graph is linear / a straight line / rate $\propto [\text{BrO}_3^-(\text{aq})]$ [1]

Therefore, the order of reaction with respect to $\text{BrO}_3^-(\text{aq}) = 1$ [1]

(iv) (1) $\text{Rate} = k[\text{BrO}_3^-(\text{aq})][\text{I}^-(\text{aq})][\text{H}^+(\text{aq})]^y$

$$\frac{\text{initial rate 1}}{\text{initial rate 2}} = \frac{(0.17)(0.15)(0.10)^y}{(0.17)(0.30)(0.20)^y} = \frac{2.30 \times 10^{-3}}{1.84 \times 10^{-2}}$$

$y = 2$ [1]

Reaction is second order with respect to $\text{H}^+(\text{aq})$. [1]

(Accept other explanation.)

When initial $[\text{I}^-(\text{aq})]$ increases by a factor of $0.30/0.15 = 2$ / doubles and initial $[\text{H}^+(\text{aq})]$ increases by a factor of $0.20/0.10 = 2$ / double while keeping initial $[\text{BrO}_3^-(\text{aq})]$ constant, the initial rate increases by a factor of $1.84 \times 10^{-2}/2.30 \times 10^{-3} = 8$. Since the rate of reaction is first order with respect to I^- , the initial rate increased by four times when the initial $[\text{H}^+(\text{aq})]$ is doubled.

(2) Rate of consumption of $\text{BrO}_3^-(\text{aq}) = 1/3 \times$ rate of formation of I_2

The initial rate with respect to $\text{BrO}_3^-(\text{aq})$ in Trial 1

$$= -2.30 \times 10^{-3} \times \frac{1}{3}$$

$$= -7.67 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1} \quad [1]$$

Remark: negative sign is needed as the initial rate of formation is defined as positive value.

DSE15_01a

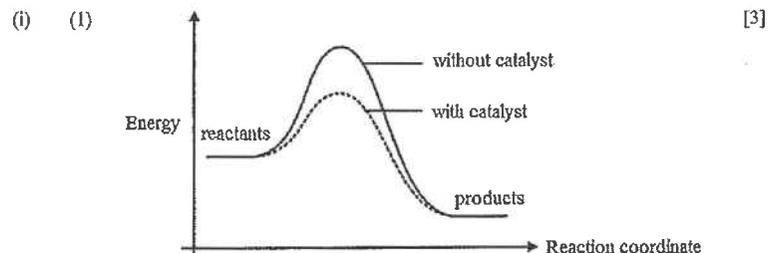
(i) (1) No effect / the reaction rate is independent of the change in $[\text{I}_2(\text{aq})]$. [1]

(2) $\text{Rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]$ [1]

(ii) $\log \frac{k_2}{k_1} = -\frac{E_a}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \log 2 = -\frac{E_a}{2.3R} \left(\frac{1}{308} - \frac{1}{298} \right)$ [1]

$E_a = +52.8 \text{ kJ mol}^{-1}$ (Range: 52.3 – 53.3) [1]

DSE15_01b



(1 mark for each of the energy profiles – total 2 marks: Accept exothermic / endothermic; one peak or multiple peaks)

1 mark for the labels: Accept potential energy / enthalpy but NOT kinetic energy / energy level)

- (2) Catalyst can be poisoned. / Their active sites can be occupied by other chemicals making them inactive. [1]

DSE16_01a

- (ii) Total number of particles / total number of molecules [1]

DSE16_01c

- (i) (1) Compare experiments 1 & 3, ([sucrose] remains the same) but [HCl] is three times, rate is also three times. Therefore reaction order with respect to HCl is one. [1]

Compare experiments 1 & 2, [sucrose] and [HCl] are doubled, the rate is quadrupled. Therefore reaction order with respect to sucrose is one. [1]

OR rate = $k [C_{12}H_{22}O_{11}(aq)]^m [HCl(aq)]^n$

From Trial 1 $6.0 \times 10^{-7} = k (0.010)^m (0.10)^n$ (1)

From Trial 2 $2.4 \times 10^{-6} = k (0.020)^m (0.20)^n$ (2)

From Trial 3 $1.8 \times 10^{-6} = k (0.010)^m (0.30)^n$ (3)

(3)÷(1) $n = 1$ and (2)÷(1) $m = 1$

- (2) (initial) rate = $k [C_{12}H_{22}O_{11}(aq)] [HCl(aq)]$ [1]

OR (initial) rate = $k [sucrose][H^+(aq)][H_2O(l)]^0$

- (3) With data from Trial 1,
 $6.0 \times 10^{-7} = k (0.010) (0.10)$
 $k = 6.0 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} / 6 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} / 0.0006 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [1]

- (ii) Acts as a catalyst. / Increase the rate of hydrolysis / provide another reaction path of lower E_a . [1]

- (iii) Any 2 reasons of the above, with comparative sense 1 mark each [2]
- Need not to separate fructose from the mixture after hydrolysis of starch but the one with sucrose requires.

- Higher atom economy as glucose is the only product from the enzymatic

hydrolysis of starch. / atom economy of hydrolysis of starch is 100% while that of sucrose is 50% / less than 100%

- Harmful / corrosive / irritating HCl(aq) is used in hydrolysis of sucrose while hydrolysis of starch involves enzyme which is biodegradable and less harmful

DSE17_01a

- (ii) The order of reaction with respect to A is zero, $0 / \text{rate} = k[A]^0$. [1]

From the graph, rate of change of [A] is independent to [A] / a constant. [1]

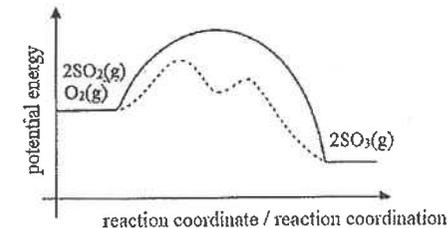
[Accept: A straight line is obtained. / [A] and time has a linear relationship /

The slope of the line is a constant.

NOT accept: [A] is directly proportional to time.

DSE17_01b

- (i) [3]



1 mark for exothermic; i.e. energy of product is lower than that of reactants & E_a of the catalyzed reaction is lower.

1 mark for two steps for the one with catalyst (i.e. two peaks) & one/multiple steps for the energy profile without catalyst

1 mark for the labels of SO_2 & O_2 and SO_3 [Not accept: reactants & products]

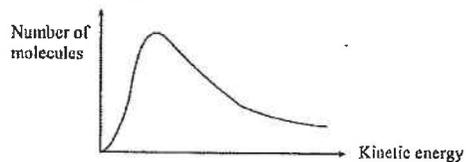
- (ii) (1) Impurities in the reaction mixture may poison the catalyst. [1]
- [Accept: Adsorb / The active sites of the catalyst are occupied by impurities.
- NOT accept: the catalyst is poisoned by the reactants]

DSE17_01c

- (iii) Let rate = $k [CO]^m [Cl_2]^n$
- From doubling [CO] while keeping [Cl₂] unchanged,
 $2.83 = 2^m$ [1]
- $m = 1.5$ [accept 1.5, 1.501] [1]

DSE18_01a

- (ii) x-axis: (molecular) kinetic energy / KE / velocity of molecules
y-axis: fraction / percentage / number of molecules



DSE18_01c

- (i) Order of reaction is not affected by temperature change.

OR, The order reaction is the same.

- (ii) From line ℓ_1 on the graph,

$$\text{slope} = \frac{(-1.4) - (-2)}{0 - (-0.6)} = 1$$

It is the first order with respect to $\text{N}_2\text{O}_5(\text{g})$.

- (iii) $\log k = -2$

$$k = 0.01 \text{ s}^{-1}$$

- (iv) The y-intercepts of ℓ_1 and ℓ_2 are -1.4 and -2 respectively.

Since the y-intercept = $\log k$

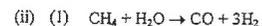
$$\log k_2 - \log k_1 = -\frac{E_a}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$(-2) - (-1.4) = -\frac{E_a}{2.3 \times 8.31} \left(\frac{1}{345} - \frac{1}{360} \right)$$

$$E_a = +94.95 \text{ kJ mol}^{-1} \quad [\text{Range: } 92 - 98]$$

DSE19_1a

1. (a) (i) The Haber process produces ammonia / NH_3 which can make fertilisers to increase crop yield.



- (2) It is because biomass is a renewable energy resource.

- (iii) • Comparing Trial 3 with Trial 2 (both same in $[\text{B}(\text{aq})]$), doubling the $[\text{A}(\text{aq})]$ leads to a double of the initial rate. Hence, the order of reaction with respect to $\text{A}(\text{aq}) = 1$.

- Comparing Trial 1 with Trial 2 (both same in $[\text{A}(\text{aq})]$), doubling the $[\text{B}(\text{aq})]$ leads to four times of the initial rate. Hence, the order of reaction with respect to $\text{B}(\text{aq}) = 2$.

DSE19_1c

- (c) (i) limestone / marble

- (ii) Carbon burns in air to produce heat.

- (iii) • High operation pressure needs high construction cost.
• High operation pressure shifts the equilibrium position to the left, decreasing the yield.

(iv) $\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\log \left(\frac{k_2}{k_1} \right) = \frac{160 \times 10^3}{2.3 \times 8.31} \left(\frac{1}{1200} - \frac{1}{1500} \right)$$

$$\frac{k_2}{k_1} = 24.8$$

- (v) Higher temperature shifts the equilibrium position to the right, increasing the yield.

- (c) (i) The absorbance is directly proportional to the concentration of $\text{I}_2(\text{aq})$ as $\text{I}_2(\text{aq})$ is purple / brown / coloured while the other species are colourless.

- (ii) • The absorbance decreases with time linearly / is directly proportional to the time, so the rate is independent of $[\text{I}_2(\text{aq})]$.

- The order of reaction with respect to $\text{I}_2(\text{aq}) = w = 0$.

- (iii) Trial 2 : slope of the plot = $-0.7 \div 8 = -0.0875$

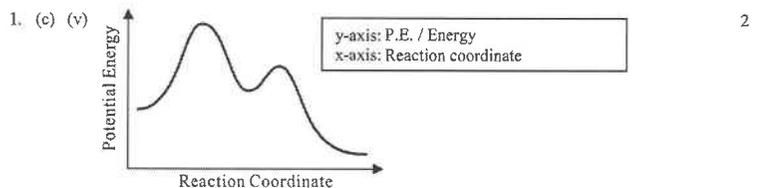
Trial 1 : slope of the plot = $-0.7 \div 16 = -0.04375$

$$(-0.0875) \div (-0.04375) = (2.0 / 1.0)^x$$

Order of reaction with respect to propanone = $x = 1$

- (iv) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

- (c) (i) The absorbance is directly proportional to the concentration of $I_2(aq)$ as $I_2(aq)$ is purple / brown / coloured while the other species are colourless. 1
- (ii) • The absorbance decreases with time linearly / is directly proportional to the time, so the rate is independent of $[I_2(aq)]$. 1
 • The order of reaction with respect to $I_2(aq)$ = $w = 0$. 1
- (iii) Trial 2 : slope of the plot = $-0.7 \div 8 = -0.0875$
 Trial 1 : slope of the plot = $-0.7 \div 16 = -0.04375$
 $(-0.0875) \div (-0.04375) = (2.0 / 1.0)^x$ 1
 Order of reaction with respect to propanone = $x = 1$ 1
- (iv) $dm^3 mol^{-1} s^{-1}$ 1



(1 mark for labels of axes and
 1 mark for 2 peaks + 1st one higher than the 2nd one + exothermic)

Industrial Process

AL96(I)_02a

State the method by which sodium hydroxide is produced industrially. Give TWO other products obtained by this industrial process.

(2 marks)

AL97(II)_08b

The synthesis of ammonia using the Haber Process involves the following:



- (i) State the effect of a change in temperature on the reaction at equilibrium. (2 marks)
- (ii) Name a catalyst for the process and state the effect of the catalyst on the reaction. (3 marks)
- (iii) State how ammonia is isolated from unreacted nitrogen and hydrogen in the process. (1 mark)
- (iv) Give TWO major uses of ammonia in industry. (1 mark)

AL00(II)_02e

- (i) Outline the synthesis of nitric(V) acid from ammonia. Illustrate your answer with balanced equations. (4 marks)
- (ii) A sample of nitric(V) acid contains 68.0% of HNO_3 by mass and has a density of 1.42 g cm^{-3} . Calculate the concentration, in $mol \text{ dm}^{-3}$, of HNO_3 in the sample. (2 marks)
- (iii) An aqueous solution of ammonium nitrate(V) was prepared by neutralization of aqueous ammonia with nitric(V) acid. Suggest how you would obtain crystalline ammonium nitrate(V) from the solution. (2 marks)
- (iv) Dinitrogen oxide (N_2O), an anaesthetic can be prepared by heating a mixture of ammonium chloride and potassium nitrate(V). Write a balanced equation for the reaction involved. (1 mark)

AL03(II)_02d

With the help of equations, outline the manufacture of sodium hydroxide.

(3 marks)

AL04(II)_03d

Chile saltpetre is a mineral with a high sodium nitrate(V) content.

- (i) Chile saltpetre was widely used as a nitrogenous fertilizer in early 1900s prior to the invention of the Haber process.

Suggest two reasons why the use of Chile saltpetre as fertilizer has been phased out after the invention of the Haber process.

(2 marks)

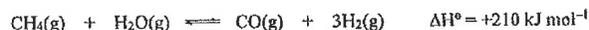
AL06(I)_09

In 1918, Fritz Haber was awarded the Nobel Prize in Chemistry for his work on the synthesis of ammonia from its elements. Write an article on the Haber process and its importance to society.

(20 marks)

AL06(II)_04c (modified)

Hydrogen is manufactured by steam reforming of natural gas, which involves the following reaction:



- (i) Suggest one way to increase the yield of $\text{H}_2(\text{g})$. (1 mark)
- (ii) Additional $\text{H}_2(\text{g})$ can be obtained by the action of steam on the $\text{CO}(\text{g})$ produced. Write the chemical equation for this reaction. (1 mark)
- (iii) Give two advantages of using $\text{H}_2(\text{g})$ as a source of energy. (2 marks)

AL10(II)_03a

Ammonia is manufactured by Haber process;



Suggest TWO ways to increase the yield of ammonia when the process is put into industrial practice.

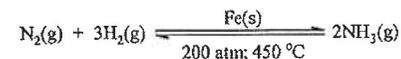
(2 marks)

AL12(I)_06

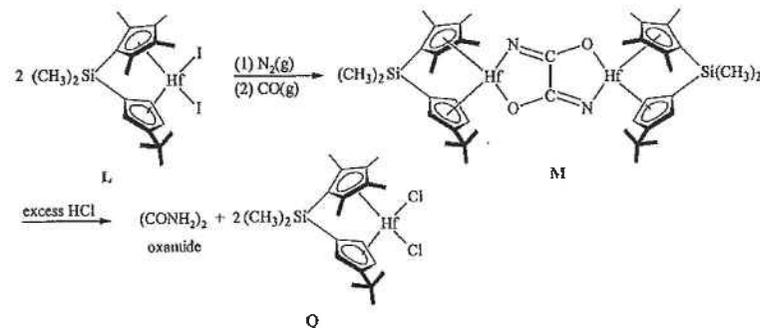
Read the passage below and answer the questions that follow.

Converting Nitrogen to Nitrogen Compounds

Nitrogen (N_2) constitutes 78% of the atmosphere and is very unreactive. The conversion of nitrogen to nitrogen compounds has posed a challenge to chemists. Traditionally, the Haber process provides a successful means for large scale conversion of nitrogen to ammonia for manufacturing nitrogenous fertilizers such as ammonium sulphate(VI).



In recent years, chemists have discovered a means to combine $\text{N}_2(\text{g})$ and $\text{CO}(\text{g})$ to give organic nitrogen compounds such as oxamide (CONH_2)₂. Oxamide is a slow-release nitrogenous fertilizer. The discovered reaction process involves treating a hafnium (Hf) complex L firstly with $\text{N}_2(\text{g})$ and then with $\text{CO}(\text{g})$, at ambient temperature and pressure, to give an intermediate M. M, when treated with excess HCl, gives oxamide and another hafnium complex Q.



Despite the shortcoming of the above reaction process being stoichiometric rather than catalytic, chemists still consider the discovery to be of great research value as it is a 'dream reaction'.

- (a) Explain why nitrogen is very unreactive. (1 mark)
- (b) The manufacture of ammonia by the Haber process is considered as an example of green chemistry. Suggest TWO reasons why. (2 marks)
- (c) Both hafnium and barium are metals in Period 6 of the Periodic Table. Suggest why hafnium forms more complexes than barium does. (2 marks)
- (d) Suggest TWO reasons why oxamide is considered as a better nitrogenous fertilizer than ammonium sulphate(VI). (2 marks)

(2 marks)

(iii) You are given that for the formation of $\text{NH}_3(\text{g})$ from $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ at $300\text{ }^\circ\text{C}$ and 1000 atm , the yield of $\text{NH}_3(\text{g})$ at equilibrium is about 98%. However, the operation conditions of the Haber process in industry are set at about $500\text{ }^\circ\text{C}$ and 200 atm with the yield of $\text{NH}_3(\text{g})$ at equilibrium of about 20%. With reference to the given information, explain why such operation conditions are chosen in industry.

(2 marks)

(iv) In the Haber process, the product mixture is removed from the reaction chamber before reaching the yield of about 20%. Explain why this is so.

(2 marks)

DSE12_01b

Methanol is an important compound in the chemical industry. Methanol can be produced from syngas made from methane.

(i) Why is methanol an important compound in the chemical industry?

(1 mark)

(ii) Write the chemical equation for the reaction in the production of methanol from syngas, and state the conditions required.

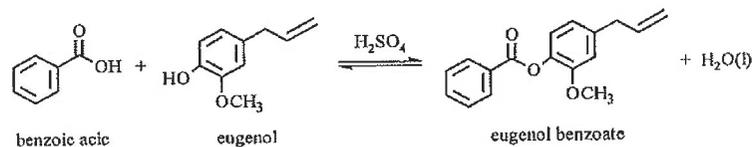
(3 marks)

(iii) State an advancement of the methanol production technology. Explain why it is considered as an advancement.

(2 marks)

DSE13_01b

Eugenol benzoate is a commonly used food flavoring agent. Eugenol benzoate can be synthesized from the reaction of eugenol with benzoic acid in the presence of sulphuric acid as a homogenous catalyst.



(i) Suggest why a catalyst can speed up a reaction.

(1 mark)

(ii) For the above reaction, would the use of concentrated sulphuric acid or that of dilute sulphuric acid give a better yield of eugenol benzoate? Explain your answer.

(1 mark)

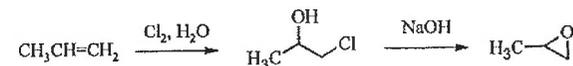
(iii) Eugenol benzoate can also be synthesized from the reaction of eugenol with benzoic acid in the presence of solid acid as a heterogeneous catalyst. With reference to the synthesis of eugenol benzoate, state ONE advantage of using a homogenous catalyst and ONE advantage of using heterogeneous catalyst.

(2 marks)

DSE13_01c

Propylene oxide ($\text{H}_3\text{C}-\text{C}_2\text{H}_4\text{O}$) is a chemical commonly used in the plastic industry. Two methods for producing propylene oxide are shown below:

Method 1



Method 2



(i) The Cl_2 and NaOH used in Method 1 are products of the chloroalkali industry. Briefly describe how these two chemicals are produced.

(3 marks)

DSE14_01a

(iii) Vitamin C can be obtained from fruits. Explain why it is still necessary to synthesize vitamin C industrially.

(1 mark)

(iv) Give TWO important chemicals manufactured in chloroalkali industry.

(1 mark)

DSE14_01c

Read the following passage regarding the Haber process and answer the questions that follow.

Haber process is an important industrial process. It needs natural gas and air as raw materials. In order to speed up the reaction involved in Haber process, iron catalyst in highly porous form is used for increasing the efficiency of the catalyst. Haber process also needs suitable reaction temperature and pressure. Moreover, two factors related to chemistry have been considered before setting the optimal reaction conditions at about $500\text{ }^\circ\text{C}$ and 200 atm . Under these conditions, the reaction yield at equilibrium is about 20%. Through some designs, without changing the optimal reaction conditions, the overall conversion percentage of nitrogen in the process can be increased significantly.

(i) Explain why the Haber process is an important industrial process.

(1 mark)

(ii) Why does the Haber process need natural gas as a raw material?

(1 mark)

(iii) Explain why making the catalyst in highly porous form can increase the efficiency of the catalyst.

(1 mark)

(iv) State TWO factors related to chemistry that have been considered before setting the optimal reaction temperature and pressure.

(2 marks)

- (v) Suggest one design so that the overall conversion percentage of nitrogen in the process can be increased significantly without changing the optimal reaction conditions.

(1 mark)

- (vi) The South American country Chile has a lot of natural nitrate mines. History tells us that the success of the Haber process had led to some impacts on the society of Chile. Suggest one of these impacts.

(1 mark)

DSE15_01a

- (ii) Write a chemical equation for the reaction in forming ammonia in the Haber process.

(1 mark)

DSE15_01c

Chlorine is one of the products manufactured in the chloroalkali industry. The electrolysis involved in the chloroalkali industry can be performed in a mercury electrolytic cell, a diaphragm electrolytic cell OUT or a membrane electrolytic cell.

- (i) State the raw material used in the chloroalkali industry.

(1 mark)

- (ii) Suggest a criterion in choosing a site for building the chemical plant for a chloroalkali industry.

OUT

(1 mark)

- (iii) Write an overall equation for the electrolysis involved in the chloroalkali industry.

(1 mark)

- (iv) Explain why a mercury electrolytic cell is NOT considered to be environmentally friendly.

(1 mark)

- (v) What is the advantage of a membrane electrolytic cell over a diaphragm electrolytic cell? OUT

(1 mark)

- (vi) The chloroalkali industry can also manufacture chlorine bleach and hydrochloric acid. Explain, with the aid of a chemical equation, why chlorine bleach should not be stored together with hydrochloric acid.

(2 marks)

DSE16_01a

- (i) Consider the following reaction for the production of ethanol by using a certain catalyst in industry:



Justify, under a pressure of 65 atm, why the operation temperature is set at 300 °C with reference to equilibrium position and reaction rate.

(2 marks)

- (iii) Syngas is an important starting material in many industrial processes.

- (1) State the TWO major constituent gases in syngas.

(1 mark)

- (2) Suggest one important chemical that can be made directly from syngas through catalytic process.

(1 mark)

DSE16_01b

Consider the manufacture of ammonia by the Haber process in a chemical plant.

- (i) Suggest how nitrogen gas can be obtained in industry.

(1 mark)

- (ii) Explain why there is a need to install a heat exchanger in the chemical plant.

(2 marks)

- (iii) If 420 kg of nitrogen and 96 kg of hydrogen are introduced into the reaction chamber, and with the yield of ammonia of 15%, calculate the mass of ammonia produced.

(3 marks)

- (iv) Nitric acid can also be produced in the chemical plant. Firstly, ammonia is oxidized to give nitrogen monoxide, and nitrogen monoxide is further oxidized to nitrogen dioxide. Finally, oxidation of nitrogen dioxide gives nitric acid. Write the chemical equation for each of the following reactions:

- (1) Oxidizing ammonia to give nitrogen monoxide.

(1 mark)

- (2) Oxidizing nitrogen dioxide to give nitric acid.

(1 mark)

DSE17_01a

- (i) Consider the Haber process:

- (1) Write a chemical equation for the reaction.

(1 mark)

- (2) Suggest how ammonia can be separated from the reaction mixture obtained.

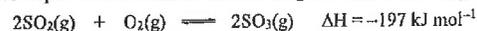
(1 mark)

- (iii) Suggest a potential hazard for the storing methanol in a chemical plant.

(1 mark)

DSE17_01b

The manufacture of sulphuric acid involves the following conversion of $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$:



- (i) Nitrogen oxides (NO and NO_2) were once used as catalysts for the conversion, and the catalytic process is considered to consist of the following two steps:



Draw, in the same sketch, TWO labelled energy profiles (x-axis: reaction coordinate; y-axis: potential energy) for the above conversion: one with nitrogen oxides as the catalysts (using dotted line '- - -'); the other one without catalyst (using solid line '-').

(3 marks)

- (ii) Nowadays in industry, a solid catalyst vanadium(V) oxide is used for the conversion of $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$.

(1) The reactants need to be purified before passing into the reaction chamber containing the catalyst. Why?

(1 mark)

(2) The operation conditions are set at 450°C and 1 atm to achieve a 96% conversion. Suggest why it is NOT preferable to further increase the conversion percentage by each of the following methods:

(I) Lowering the temperature of the reaction system

(1 mark)

(II) Increasing the pressure of the reaction system

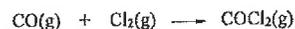
(1 mark)

(3) In order to increase the conversion percentage, one of the reactants used is in slight excess. From the perspective of feedstock, which of $\text{SO}_2(\text{g})$ or $\text{O}_2(\text{g})$ would be in slight excess? Explain your answer.

(1 mark)

DSE17_01c

Phosgene (COCl_2) is an important chemical. It can be produced from the reaction of $\text{CO}(\text{g})$ with $\text{Cl}_2(\text{g})$:



- (i) Write a chemical equation to show how $\text{CO}(\text{g})$ can be obtained from natural gas.

(1 mark)

(ii) Chlorine can be produced by the flowing mercury cell process.

(1) Write the half equation for the change occurring at the anode.

(1 mark)

(2) Write the half equation for the change occurring at the cathode.

(1 mark)

(3) Explain why the following mercury cell process has been gradually phased out.

(1 mark)

- (iii) At a certain temperature, if the concentration of $\text{CO}(\text{g})$ is doubled while the concentration of $\text{Cl}_2(\text{g})$ is kept unchanged, the new rate of reaction will become 2.83 times the original rate. Deduce the order of reaction with respect to $\text{CO}(\text{g})$.

(Note: The order of a reaction may NOT be an integer.)

(2 marks)

DSE18_01a

- (i) Write TWO half equations for the electrolysis of brine using membrane electrolytic cell in chloroalkali industry.

(2 marks)

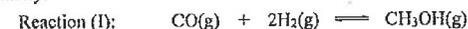
- (iii) Which one of the following species can be a raw material for manufacturing vitamin C in industry?

Acetic acid, acetone, formaldehyde, glucose

(1 mark)

DSE18_01b

Reaction (I) below shows a process of producing methanol using catalyst at 100 atm and 250°C in industry:



- (i) (1) Suggest a suitable catalyst for the reaction.

(1 mark)

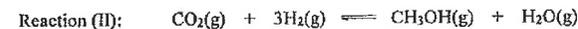
(2) Suggest why the reaction would proceed slowly in the absence of a catalyst.

(1 mark)

(3) Explain why the operation pressure in industry for the reaction is set at 100 atm but not at atmospheric pressure.

(2 marks)

- (ii) Methanol can also be produced from carbon dioxide, a side product of some industrial processes, using another catalyst as shown in Reaction (II) below:



Based on the given information:

(1) Suggest one reason why Reaction (II) can be considered as greener than Reaction (I).

(1 mark)

(2) Suggest a potential benefit of Reaction (II) to the environment.

(1 mark)

- (iii) One of the industrial applications of methanol is to produce ethanoic acid. Write a chemical equation for the reaction involved.

(1 mark)

DSE19_01ai ii

1. (a) Answer the following short questions :

- (i) Explain why the Haber process significantly contributes to crop yield increase. (1 mark)
- (ii) (1) Write the chemical equation for the formation of syngas from methane.
(2) Syngas can be obtained from the conversion of biomass. Suggest why it is considered as an advancement of the methanol production technology. (2 marks)

DSE19_01bi ii

- (b) A chloroalkaline chemical plant uses membrane electrolytic cells to produce hydrogen, chlorine and sodium hydroxide.
 - (i) With the help of chemical equations, briefly describe how hydrogen, chlorine and sodium hydroxide are produced in a membrane electrolytic cell. (4 marks)
 - (ii) Sodium hypochlorite (NaOCl) can be made from the products obtained in the membrane electrolytic cell. Write a chemical equation for its formation. (1 mark)

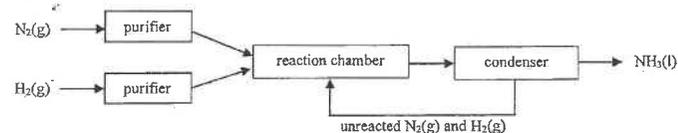
DSE20_01a

1. (a) Answer the following short questions :

- (i) Give TWO advantages of a membrane electrolytic cell over a flowing mercury cell in chloroalkali industry. (2 marks)
- (ii) State the catalyst used in the Haber process. (1 mark)
- (iii) Sketch TWO Maxwell-Boltzmann distribution curves for a gaseous sample, one at temperature T_1 , and the other at a lower temperature T_2 (y-axis : number of molecules; x-axis : kinetic energy). (2 marks)

DSE21_01b(i)-(iii)

(b) The diagram below shows how liquid ammonia is produced by the Haber process.

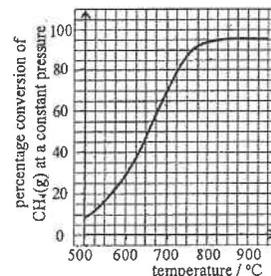


- (i) Explain why $N_2(g)$ and $H_2(g)$ need to be purified before going into the reaction chamber. (1 mark)
- (ii) Explain why the unreacted $N_2(g)$ and $H_2(g)$ are passed again to the reaction chamber. (1 mark)
- (iii) Why does ammonia, but not the other gases, become a liquid in the condenser ? (1 mark)

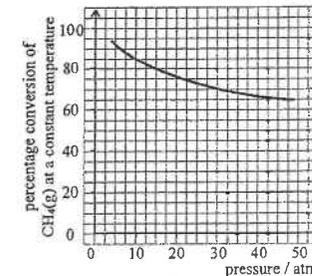
DSE21_01(C)

1. (c) Methanol is an important chemical in industry and can be produced from methane. The production can be considered as separated into two stages.

- (i) State one potential hazard of methanol. (1 mark)
- (ii) Other than natural gas, suggest one source of methane. (1 mark)
- (iii) In the first stage, $CH_4(g)$ reacts with $H_2O(g)$ to form $CO(g)$ and $H_2(g)$, and equilibrium would be attained. The graphs below show the percentage conversion of $CH_4(g)$ at equilibrium under different conditions.



Graph 1



Graph 2

- (1) With reference to Graph 1, explain whether the forward reaction is endothermic or exothermic.
- (2) With reference to Graph 2, explain, with the aid of a chemical equation, the effect of pressure on the percentage conversion of $CH_4(g)$. (4 marks)
- (iv) In the second stage, $CO(g)$ reacts with $H_2(g)$ to form methanol. Write a chemical equation for the reaction. (1 mark)

Marking Scheme

AL96(I)_02a

NaOH(aq) is produced by electrolysis of brine / concentration NaCl(aq). [1]

Other product: H₂ / Cl₂ / NaOCl solution (bleach solution) (any TWO) [1]

AL97(II)_08b

(i) Increase in temperature causes the equilibrium position to shift to the left, lowering the yield of ammonia. [½]
[½]

Increase in temperature increase the rate of formation of ammonia. [1]

(ii) Iron / iron(III) oxide [1]

It can increase the rate of the reaction but has no effect on the yield of the reaction. [1]
[1]

(iii) Condense NH₃ to give a liquid / liquify NH₃ [1]

(iv) Any TWO of the following: [1]

Manufacture of N-fertilizers, e.g. urea, ammonium sulphate(VI), ammonium nitrate(V), ammonium phosphate(V) etc.

Manufacture of nitric(V) acid

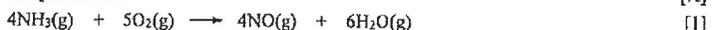
Manufacture of polymers, e.g. nylon, melamine, acrilan etc.

(Accept other correct uses of ammonia, e.g. as refrigerant, as coolant etc.)

AL00(II)_02e

(i) Step 1:

Pass a mixture of NH₃ and air over Pt/Rh/Cu catalyst at about 600 °C / high temperature. [½]
[½]



Step 2:

NO is allowed to undergo oxidation at a low temperature (about 50 °C) [½]



Step 3:

NO₂ produced is absorbed by water [½]



Unreacted NO is allowed to go through steps 2 and 3 again.

(ii) Mass of HNO₃ in 1 dm³ = 1.42 × 1000 × 68% = 965.6

$$\text{Concentration of the acid} = \frac{965.6}{1 + 14 + 16 \times 3} = 15.3 \text{ mol dm}^{-3} \quad [2]$$

Accept answer from 15.0 to 15.6 mol dm⁻³

1 mark for method; 1 mark for answer

(iii) Evaporate / heat / warm the solution to obtain a saturated / concentration solution of NH₄NO₃. [1]

Allow the solution to cool / use an ice bath to obtain NH₄NO₃(s). [½]

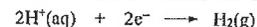
Separate crystal by filtration. [½]

(iv) NH₄Cl(s) + KNO₃(s) → N₂O(g) + KCl(s) + 2H₂O(l) [1]

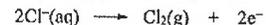
AL03(II)_02d

Electrolysis of brine using steel as cathode and carbon as anode. (Membrane cell) [1]

At cathode: H⁺(aq) is discharged to give hydrogen gas [1]



At anode: Cl⁻(aq) is discharged to give chlorine gas [1]



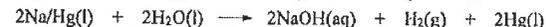
The Na⁺(aq) and OH⁻(aq) ions remaining in the solution constitute a NaOH(aq).

OR Electrolysis of brine using mercury as cathode and carbon as anode. [1]

At cathode: Na⁺(aq) is discharged to give sodium (amalgam). [1]



Treating the sodium amalgam with water gives sodium hydroxide. [1]



(For each method, award 1 mark for the electrolysis involved; 1 mark for the equation(s) of the electrolytic processes involved; 1 mark for the formation of NaOH(aq).)

AL04(II)_03d

(i) Any TWO of the following: [2]

- There is a limited reserve of Chile saltpetre and the supply of the mineral is not inexhaustible / the supply of N₂ and H₂ (from water) is unlimited.
- The cost of transportation of Chile saltpetre is high
- The rapid growth in world population leads to huge demand of fertilizers / lots of Chile saltpetre were used to make explosives.

AL06(I)_09

A. Introduction [2]

- With rapid increase in world population, the demand for food increases. Plants utilize N to build up proteins. The demand for N-fertilizers increased rapidly in late 1800s.
- Prior to the invention of Haber process, minerals which contain nitrates (like Chile saltpetre) were main sources of N-fertilizers.
- The uneven distribution of Chile saltpetre, the transportation cost and other political reasons made the price of N-fertilizers to fluctuate.
- N is highly abundant in the atmosphere, but it is very unreactive. The success to convert N₂ to N-fertilizers can help provide more food.

B. The Process [5]

- The conversion of N₂ to NH₃ involves the reaction:
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}$$
- Reaction conditions:
Pressure: 25 to 150 atm
Temperature: 650 – 720 K
Catalyst: Fe containing KOH as promoter
- The yield of ammonia can be increased by increasing the pressure + elaboration.

- The cost is expensive if the process is operated under very high pressure.
- Operating the process at high temperature can increase the rate of reaction. However, the yield of ammonia decreases with increase in temperature + elaboration. Thus the process is operated at moderate temperature.
 - The reaction has a very high activation energy due to the strength of the $\text{N}\equiv\text{N}$ bond. The use of a catalyst can provide a reaction pathway with lower activation energy. Fe catalyst is therefore used.
 - NH_3 formed is condensed by refrigeration. Unreacted $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ are recycled into the reaction chamber for further reaction.
- C. Raw materials for the process [2]
- Raw materials for H_2 : natural gas, coal or naphtha
- Steam reforming
Pass $\text{CH}_4(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ over a suitable catalyst (NiO) at about 1000 K and 30 atm
$$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$$
After steam reforming, a gaseous mixture containing $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{CO}_2(\text{g})$ is obtained.
 - Shift reaction: to convert $\text{CO}(\text{g})$ in the gas mixture to $\text{CO}_2(\text{g})$
Pass the gas with $\text{H}_2\text{O}(\text{g})$ over a catalyst (iron oxide) at about 600 K.
$$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$$
 $\text{CO}_2(\text{g})$ formed is removed by scrubbing. The synthesis gas contains about 74% $\text{H}_2(\text{g})$, 25% $\text{N}_2(\text{g})$ and 1% $\text{CH}_4(\text{g})$.
 - H_2 can also be obtained from cracking of heavy oil / naphtha
- D. Importance of the Process [5]
- Conversion to nitric(V) acid
 - The reactions:
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
Conditions: 0–13 atm, excess air, Pd/Pt as catalyst, about 1175 K, % conversion is about 96%
$$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$
$$3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{HNO}_3(\text{g}) + \text{NO}(\text{g})$$
Unreacted $\text{NO}(\text{g})$ is recycled.
 - Most HNO_3 formed (>80%) is used to produce $\text{NH}_4\text{NO}_3(\text{s})$ which is used as a fertilizer.
$$\text{NH}_3(\text{aq}) + \text{HNO}_3(\text{aq}) \longrightarrow \text{NH}_4\text{NO}_3(\text{aq})$$
 - Ammonia can be used to produce urea which is used as a fertilizer. The fertilizers produced can be used for plant growth and help solve the starvation problem.
 - HNO_3 can be used to make explosives, e.g. TNT, trinitroglyceride etc.
 - Other uses of ammonia: refrigerant, window cleaner, making smelling salt, etc.

AL06(II)_04c (modified)

- (i) Any ONE of the following: [1]
- Increase the temperature
 - Decrease the pressure
- (ii) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ [1]
- (iii) The combustion of $\text{H}_2(\text{g})$ gives only water which will not cause pollution to our environment. [1]
- Hydrogen has a small molar mass. The ratio of energy output per unit mass of $\text{H}_2(\text{g})$ is higher than that of other fuels. [1]

AL10(II)_03a

- Increase the pressure of the system to about 200 atm (or, to a value which can be withstood by the reaction chamber). [1]
- Remove ammonia by liquefaction and pass the unreacted $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ back into the reaction chamber. [1]

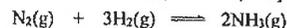
AL12(I)_06

- (a) $\text{N}\equiv\text{N}$ triple bond is strong (946 kJ mol^{-1}). [1]
- (b) Any TWO of the following: [2]
- The reaction in Haber process has very high atom economy (100%)
 - The reactants (N_2 and H_2) are non-toxic and will pose no harm to the environment.
 - The reaction takes place in gas phase. No solvent is required.
 - The raw material (N_2) is available in larger amount in the atmosphere. Depletion is not a problem.
 - The reaction does not require the use of any derivatives.
 - A catalyst (Fe) is used.
- (c) Hf is a transition metal / d-block element, while Ba is a Group II element. [½]
- Hf atom has low lying vacant electron shells for dative bond formation, while this is not the case in Ba. [1]
- (d) Any TWO of the following: [2]
- $(\text{CONH}_2)_2$ has higher percentage by mass of nitrogen than $(\text{NH}_4)_2\text{SO}_4$.
 - Being less soluble than $(\text{NH}_4)_2\text{SO}_4$ in water, $(\text{CONH}_2)_2$ fertilizer is less readily leached into lakes and ponds leading to eutrophication.
 - $(\text{CONH}_2)_2$ is a slow-release fertilizer. A much smaller amount of $(\text{CONH}_2)_2$ will be washed away by rain water.
 - $(\text{NH}_4)_2\text{SO}_4$ can make the soil acidic while $(\text{CONH}_2)_2$ will not.
- (e) The conversion of CO and N_2 to $(\text{CONH}_2)_2$ take place at ambient temperature / ambient pressure. There is less demand for fossil fuel. / It is not necessary to build reaction chamber which can withstand high pressures. [1]
- The discovered means gives organic nitrogen compounds, i.e. compounds with organic functional groups. They can be used as starting materials for the synthesis of useful products such as pharmaceuticals. [1]
- (Accept other reasonable answers.)

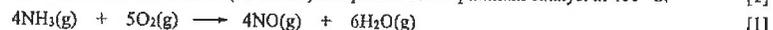
- (f) 2 moles of the HF complex are required for each mole of oxamide formed. The conversion can be very costly. [1]
 OR, The HF complex L cannot be regenerated in the reaction process.

DSE11SP_01b

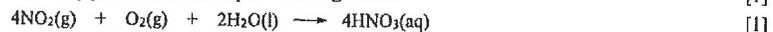
Purified N₂ and H₂ (ratio 1 : 3) are passed over iron catalyst at 450 °C and 200 atm pressure: [1]



Ammonia is mixed with O₂ (excess air) and passed over a platinum catalyst at 400 °C. [1]



Resulting gaseous mixture is passed through water: [1]



DSE12PP_01a

- (i) Any ONE of the following: [1]

- Reichstein process is used for synthesizing vitamin C, which is in great demand as it cannot be synthesized in human body.
- Reichstein process provides a synthetic route to convert *D*-Glucose, a sugar which is highly abundant and cheap, to *L*-ascorbic acid.
- The enzymatic reaction in Reichstein process inverts the sugars from *D*- to *L*-isomer.

- (ii) Reduction / catalytic hydrogenation [1]

- (iii) (I) Commonly used oxidizing agents will also oxidize the other hydroxyl groups in *D*-sorbitol / are not selective as compared with the enzyme. [1]

OR, The enzyme can selectively oxidize the second –OH group in *D*-sorbitol to give *L*-sorbose.

- (II) At pH < 4 or pH > 6, the enzyme will undergo denaturation / the (tertiary/secondary) structure of the enzyme will change leading to loss of catalytic activity. [1]

- (iv) This method uses a catalyst (the enzyme) instead of stoichiometric reagents. [1]
 It uses less hazardous chemicals (e.g. MeOH / acid).

DSE12PP_01c

- (i) At the cathode, H⁺(aq) is preferentially discharged because H⁺ occupies a lower position than Na⁺ in the electrochemical series. [1]



At the anode, Cl⁻(aq) is preferentially discharged because its concentration is high. [1]



The membrane only allows cations to pass through it. [1]

As there is a higher concentration of cations in the anode compartment (because anions are removed), there will be a net flow of Na⁺(aq) ions from the anode compartment to the cathode compartment, and concentrated NaOH(aq) is formed. [1]

- (ii) Cl₂(g) + 2NaOH(aq) → NaCl(aq) + NaOCl(aq) + H₂O(l) [1]



- (iii) Accept both 'Yes' and 'No' answers. [2]

For 'No' answers,

- The production of H₂ in chloroalkali industry requires the use of electricity, which is commonly generated by burning fossil fuel (a major source of air pollutants).
- Cl₂(g) is the main product of the chloroalkali industry. Large scale production of H₂(g) will yield surplus Cl₂(g). The disposal of the unused Cl₂(g) is costly and will cause air pollution problems.

For 'Yes' answers,

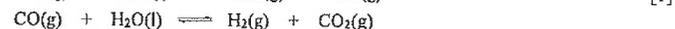
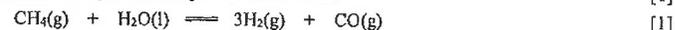
- Burning of H₂(g) gives water only.
- If there is a cheap source of electricity (e.g. photovoltaic cell), production of H₂(g) by electrolysis of brine can be a means of reducing air pollution problems. (Accept other reasonable answers.)

DSE12_01a

- (i) (1) Finely divided iron / iron oxide / FeO, Fe₂O₃, Fe₃O₄ [1]

- (2) It can increase / decrease / alter / change the rate of a reaction by providing an alternative pathway that requires lower / higher / different activation energy. [1]

- (ii) Steam reforming of natural gas / methane / CH₄ [1]



- (iii) The higher temperature is used to speed up the reaction. [1]

The lower pressure is dictated by limits of mechanical design / safety concerns. (Lowering construction / maintenance costs of the plant / lower risk) [1]

- (iv) It takes a long time for the equilibrium (that the NH₃(g) is of highest yield) to be attained. [1]

It can increase the total amount of NH₃(g) produced per unit time. [1]

DSE12_01b

- (i) Methanol is important because it is a 1-carbon compound and acts as a starting material to make organic compounds with larger carbon numbers / methanal / [1]

formaldehyde / ethanoic acid / acetic acid / ether (dimethyl ether, MTBE) / as a solvent.

(Do not accept methanol as fuel, to produce "vinegar", or it is used to produce hydrogen / ethene)

- (ii) CO(g) + 2H₂(g) → CH₃OH(g) (accept irreversible sign) [1]

Any TWO of the following: [2]

Catalyst: Cu / ZnO / Al₂O₃

Temperature: 200 – 300 °C

Pressure: 50 – 100 atm

- (iii) Direct conversion of methane to methanol with the use of a metal oxide catalyst at high temperature and atmospheric pressure. The conversion uses a catalytic reagent / high atom economy. [1]

OR, Oxidation of methane to methanol by microbial reactions. The oxidation has higher energy efficiency. [1]

OR, Conversion of biomass to syngas/biogas for methanol production. The conversion uses renewable feed stocks. [1]

OR, Carbon dioxide in flue gas can be converted to form methanol. The conversion helps to reduce the release of carbon dioxide to the atmosphere. [1]

OR, Unconsumed hydrogen from chemical industries is allowed to react with carbon monoxide to form methanol. The conversion uses up the unconsumed raw materials (hydrogen) [1]

DSE13_01b

- (i) A catalyst provides an alternative pathway with lower activation energy. [1]

(ii) Concentrated H₂SO₄ [1]
Dilute H₂SO₄ contains a lot of H₂O. Water can shift the equilibrium position to the left / reactant side / cause hydrolysis of ester, and thus lowers the yield of the product. [1]
Also accept: conc. H₂SO₄ is a dehydrating agent / removes water from the product side of the reaction and will shift the equilibrium position to the right / product side. [1]

- (iii) Homogeneous catalyst - H₂SO₄ is readily available / commonly found. [1]

Heterogeneous catalyst -- can be reused / easily regenerated / can be separated easily. [1]

DSE13_01c

- (i) Chlorine can be produced industrially by electrolysis of brine / concentrated sodium chloride solution using flowing mercury cell / membrane cell. [1]

Cl⁻(aq) ions are discharged at the anode to give Cl₂(g). [1]



Membrane cell

H⁺(aq) ions are discharged at the cathode. With the removal of Cl⁻(aq) ions and H⁺(aq) ions, the resultant electrolytic solution contains NaOH(aq) in high concentration. [1]

OR, Overall reaction: $2\text{NaCl} + 2\text{H}_2\text{O} \longrightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH}$

Flowing mercury cell

Sodium amalgam produced at cathode reacts with water forming NaOH(aq). [1]



DSE14_01a

- (iii) It is to solve the problems of inadequate or shrinking supply of vitamin C. [1]

(iv) Any TWO: chlorine, hydrogen, sodium hydroxide, NaOCl, HCl, NaClO₃, ClO⁻, ClO₃⁻, bleaching solution. [1]

DSE14_01c

- (i) Haber process produces ammonia which can be used to manufacture fertilizers / explosives, e.f.c. (HNO₃, NH₄NO₃, NO₃⁻ / refrigerant) [1]

(ii) Natural gas remains the more convenient / cheap way to provide hydrogen as feedstock for production of ammonia in the Haber process. [1]

(iii) Provides a larger surface area that makes the catalyst more effective. [1]

(iv) Equilibrium position / yield [1]

Reaction rate / effective collision [1]

(v) Any unreacted reactants are reused / recycled and are allowed to react again. [1]

OR, Removing ammonia / liquefying ammonia from the product mixture so as to shift the equilibrium position to the produce side. [1]

OR, Further H₂ addition [1]

(vi) As the demand for mining the natural nitrate to produce fertilizers drops drastically, the mining work was no longer profitable / mining work might be closed / a high unemployment rate. [1]

DSE15_01a

- (ii) $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$ [1]

DSE15_01c

(i) Concentrated / saturated sodium chloride (NaCl) solution / brine [1]

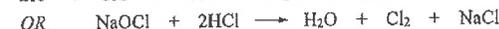
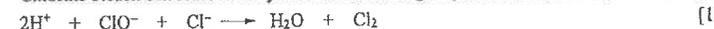
(ii) Site should be near the sea (because easy to get the raw materials.) / Easy transportation / Not too near residential places. [1]

(iii) $2\text{NaCl} + 2\text{H}_2\text{O} \longrightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH}$ [1]

(iv) Mercury is poisonous [1]

(v) In membrane cell, more pure sodium hydroxide can be obtained, but not for diaphragm cell / No impurity (NaCl) in sodium hydroxide obtained in membrane cell but in diaphragm cell / Less energy is required for membrane cell. [1]

(vi) Chlorine bleach can react with hydrochloric acid to give poisonous chlorine gas. [1]



DSE16_01a

(i) High(er) temperature will have a high(er) rate of reaction. [1]

But the (forward) reaction is exothermic, increasing the temperature will shift the equilibrium position to left / reactant side. / reaction has a lower yield / favors the backward reaction. [1]

Therefore, the operating temperature is set at 300 °C.

- OR As the (forward) reaction is exothermic, decreasing the temperature will shift the equilibrium position to right / product side / reaction has a higher yield. / lower temperature favours the reaction
- (iii) (1) carbon monoxide / CO and hydrogen / H₂ [1]
 (2) Methanol / CH₃OH [1]

DSE16_01b

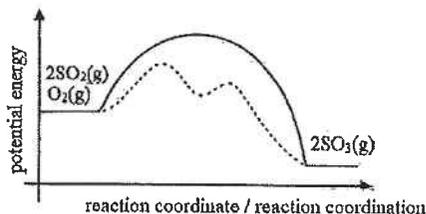
- (i) Fractional distillation of liquefied air [1]
 (ii) The hot gas from reaction chamber can help heat up the hydrogen and nitrogen / incoming gases / reactants / reactants mixture / cool down the product mixture
 It is to save energy. / to save fuel / conserve (recycle / reuse) energy / heat / reduce the cost of fuel / energy [1]
- (iii) mole ratio of N₂(g) to H₂(g) = $\frac{420000}{28} : \frac{96000}{2} = 1:3.2$ [1]
 N₂(g) is limiting reagent.
 mass of NH₃(g) produced = $\frac{420000}{28} \times 2 \times 17 \times 15\%$ [1]
 = 76.5 kg / 77 kg / 76500 g / 77000 g [1]
 (76 kg / 77.0 kg / 76.5 g : 0 mark)
- (iv) (1) 4NH₃ + 5O₂ → 4NO + 6H₂O [1]
 (2) 4NO₂ + O₂ + 2H₂O → 4HNO₃ [1]

DSE17_01a

- (i) (1) N₂ + 3H₂ → 2NH₃ [1]
 (2) The reaction mixture is cooled to condense ammonia to liquid. [1]
 OR, The reaction mixture is condensed / is cooled to liquid.
- (iii) Flammable / inflammable / toxic / poisonous [1]
 NOT accept harmful

DSE17_01b

- (i) [3]



1 mark for exothermic; i.e. energy of product is lower than that of reactants & E_a of the catalyzed reaction is lower.
 1 mark for two steps for the one with catalyst (i.e. two peaks) & one/multiple steps for the energy profile without catalyst
 1 mark for the labels of SO₂ & O₂ and SO₃ [Not accept: reactants & products]

- (ii) (1) Impurities in the reaction mixture may poison the catalyst. [1]
 [Accept: Adsorb / The active sites of the catalyst are occupied by impurities.
 NOT accept: the catalyst is poisoned by the reactants]
- (2) (I) Lowering the temperature makes the reaction proceed at a slower rate. [1]
 [NOT accept lower fuel cost]
 (II) The percentage conversion is already very high. / Increasing the pressure can only lead to a very small increase in the percentage conversion but very high cost is needed. [1]
 [Require to mention percentage conversion & cost.]
- (3) Oxygen is used in a slight excess because it is more cost-effective / cheaper to obtain / easier to obtain. [1]
 [Requires a comparative sense.]

DSE17_01c

- (i) CH₄ + H₂O → CO + 3H₂ [1]
 (ii) (1) 2Cl⁻ → Cl₂ + 2e⁻ [1]
 (2) Na⁺ + e⁻ → Na [1]
 OR Na⁺ + Hg + e⁻ → Na/Hg [1]
 (3) Mercury is poisonous. [1]
- (iii) Let rate = k [CO]^m [Cl₂]ⁿ
 From doubling [CO] while keeping [Cl₂] unchanged,
 2.83 = 2^m [1]
 m = 1.5 [accept 1.5, 1.501] [1]

DSE18_01a

- (i) Cathode / negative electrode: 2H⁺(aq) + 2e⁻ → H₂(g) [1]
 OR 2H₂O(l) + 2e⁻ → 2OH⁻(aq) + H₂(g)
 Anode / positive electrode 2Cl⁻(aq) → Cl₂(g) + 2e⁻ [1]
- (iii) Glucose [1]

DSE18_01b

- (i) (1) Cu / ZnO / Al₂O₃ / Cr₂O₃ [Mark the first one] [1]
 (2) May be due to higher activation energy / energy barrier. [1]
 (3) Number of moles of gaseous product is less than that of gaseous reactants. [1]
 Increasing the pressure will shift the equilibrium position to the right. [1]
 OR, increase in collision frequency / effective collision
 Make the reaction faster to reach equilibrium.
- (ii) (1) This reaction does not involve poisonous reagent / CO but the original one involves poisonous CO. [1]
 (2) It reduces the amount of atmospheric carbon dioxide and hence may alleviate global warming / greenhouse effect. [1]
- (iii) CH₃OH(g) + CO(g) → CH₃CO₂H(g) [1]

DSE19_01a

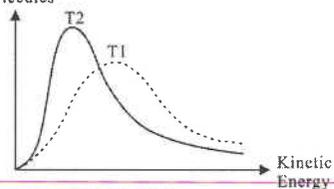
1. (a) (i) The Haber process produces ammonia / NH₃ which can make fertilisers to increase crop yield. 1
- (ii) (1) CH₄ + H₂O → CO + 3H₂ 1
- (2) It is because biomass is a renewable energy resource. 1
- (iii) • Comparing Trial 3 with Trial 2 (both same in [B(aq)], doubling the [A(aq)] leads to a double of the initial rate. Hence, the order of reaction with respect to A(aq) = 1. 1
- Comparing Trial 1 with Trial 2 (both same in [A(aq)], doubling the [B(aq)] leads to four times of the initial rate. Hence, the order of reaction with respect to B(aq) = 2. 1

DSE19_01b

- (b) (i) • Use concentrated sodium chloride solution / brine as electrolyte. 1
- Anode : 2Cl⁻(aq) → Cl₂(g) + 2e⁻ 1
- Cathode : 2H₂O(l) + 2e⁻ → H₂(g) + 2OH⁻(aq) 1
- The membrane is permeable to cations but not anions. 1
- (ii) Cl₂(g) + 2NaOH(aq) → NaOCl(aq) + NaCl(aq) + H₂O(l) 1
- (iii) Atom economy for Reaction (I) = 32 / 108.5 = 29.5 % 2
- Atom economy for Reaction (II) = 32 / 68 = 47.1 %
- Reaction (II) is greener as it has a higher atom economy.

DSE20_01a

1. (a) (i) • No toxic mercury (will be produced by) membrane cell but toxic mercury (may leak out from) flowing mercury cell. 1
- Less energy is required. 1
- Less maintenance is required. (1)
- (ii) Iron / iron(III) oxide / iron oxide / oxides of iron 1
- (iii) Number of Molecules 2

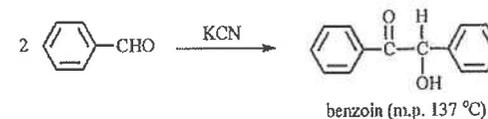


(1 mark for T₂ higher than T₁)
 1 mark for starting at zero and tail; T₁ > T₂ Okay if not labelling the axes.)

Green Chemistry

AL07(I)_08

14.6 g of benzoin was obtained by heating 15.9 g of benzaldehyde with potassium cyanide in a solvent-free condition.



- (a) Calculate the percentage yield of benzoin from benzaldehyde. (2 marks)
- (b) What is the function of potassium cyanide in this conversion? (1 mark)
- (c) Is this conversion an example of green chemistry? Explain. (1 mark)

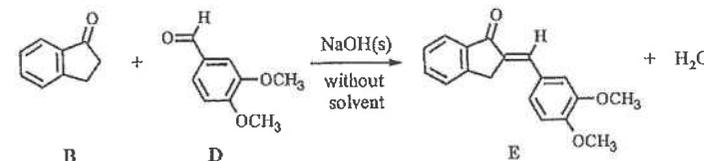
AL08(I)_10

Write an essay on the application of the principles of green chemistry in industry.

(20 marks)

ASL09(II)_05

Compound B (m.p. 39 °C) and compound D (m.p. of 42 °C) react in the presence of a small amount of NaOH(s) to give compound E. The E obtained can be purified by recrystallization from 90% ethanol.



- (a) Given that the relative molecular masses of B and D are 132.0 and 166.0 respectively, calculate the atom economy of the reaction. (2 marks)
- (b) In a typical experiment, 2.64 g of B and 3.32 g of D yielded 4.40 g of E. Calculate the percentage yield of E. (2 marks)
- (c) Give FOUR reasons why this reaction is considered as an example of green chemistry. (2 marks)

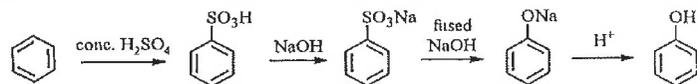
AL12 (I)_06

- (b) The manufacture of ammonia by the Haber process is considered as an example of green chemistry. Suggest TWO reason why.

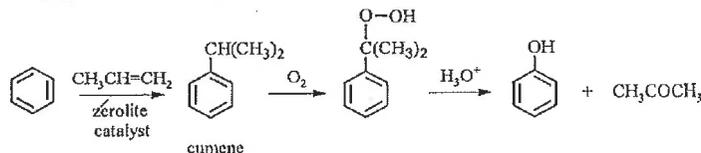
(2 marks)

AL13(II)_11 (modified)

Phenol can be synthesized from benzene via the following sulphonation route:



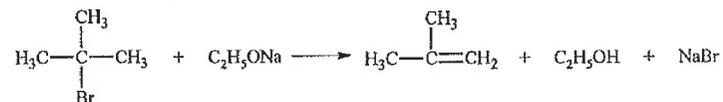
Nowadays, phenol is commonly synthesized from benzene via the cumene route as show below:



- (i) Suggest TWO reasons why the cumene route is considered greener than the sulphonation route. (2 marks)
- (ii) Suggest ONE industrial application of the CH_3COCH_3 formed in the cumene route. (1 mark)

DSE11SP_01c

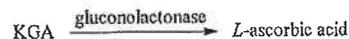
The reaction for the production of methylpropene from 2-bromo-2-methylpropane is represented by the following equation:



- (i) With reference to green chemistry, calculate the atom economy of the reaction. (2 marks)
- (ii) Apart from atom economy, suggest TWO other factors that scientists should consider in order to conduct a green production process. (2 marks)

DSE12PP_01a

- (iv) A method, with the use of a lactonase enzyme such as *gluconolactonase*, has been adopted for the conversion of KGA to *L*-ascorbic acid.

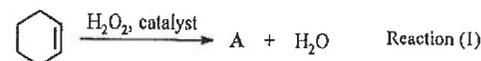


Suggest TWO reasons why this method is considered greener than the corresponding one in the above-shown Reichstein process. (2 marks)

64

DSE12_02a

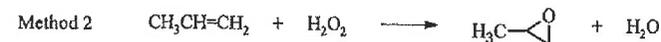
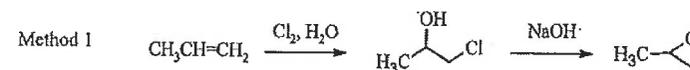
- (ii) Compound A is one of the monomers for making nylon-6,6 in industry. The following equations show two reactions that can produce A:



- (1) Reaction (1) is considered to be greener than Reaction (2). Suggest THREE reasons. (3 marks)
- (2) In what aspect are both reactions considered as NOT green? (1 mark)

DSE13_01c

Propylene oxide ($\text{H}_3\text{C}-\text{C}_2\text{H}_4\text{O}$) is a chemical commonly used in the plastic industry. Two methods for producing propylene oxide are shown below:



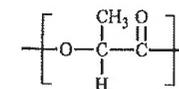
- (ii) The atom economy of Method 1 is 29.7%. Calculate the atom economy of Method 2. (1 mark)
- (iii) Discuss, from TWO different perspectives, whether Method 1 or Method 2 is greener. (2 marks)
- (iv) Comment on the following statement and explain your answer.

'A reaction with a high atom economy should also have a high yield.'

(2 marks)

DSE14_02c

- (iv) Some people suggest, from the perspective of environmental protection, switching from using polyethene (PE) and poly(ethylene terephthalate) (PET) to using polylactide (PLA) in making plastic bottles. The repeating unit of PLA is shown below:



- (1) It is known that PLA can be produced from the polymerization of lactic acid through esterification. Give the structure of lactic.

(1 mark)

65

- (2) PHB can be classified as polyester.
Based on the fact that PHB contains ester linkages, explain why it can be considered environmentally friendly in its disposal.

(1 mark)

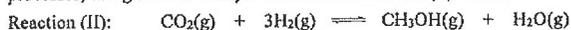
DSE18_01b

Reaction (I) below shows a process of producing methanol using catalyst at 100 atm and 250 °C in industry:



- (i) (1) Suggest a suitable catalyst for the reaction. (1 mark)
- (2) Suggest why the reaction would proceed slowly in the absence of a catalyst. (1 mark)
- (3) Explain why the operation pressure in industry for the reaction is set at 100 atm but not at atmospheric pressure. (2 marks)

- (ii) Methanol can also be produced from carbon dioxide, a side product of some industrial processes, using another catalyst as shown in Reaction (II) below:

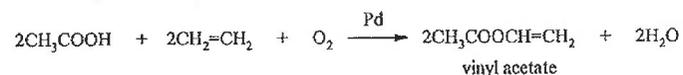


Based on the given information:

- (1) Suggest one reason why Reaction (II) can be considered as greener than Reaction (I). (1 mark)
- (2) Suggest a potential benefit of Reaction (II) to the environment. (1 mark)
- (iii) One of the industrial applications of methanol is to produce ethanoic acid. Write a chemical equation for the reaction involved. (1 mark)

DSE18_02a

- (i) The following chemical equation shows how vinyl acetate can be obtained.

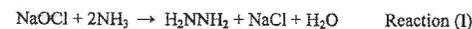


Give TWO reasons why this reaction can be considered as green.

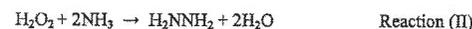
(2 marks)

DSE19_1b iii

- (iii) By using NaOCl, this chemical plant can produce hydrazine (H_2NNH_2), a propellant used in space vehicles:



However, instead of using NaOCl, H_2O_2 can also be used to produce hydrazine:



By calculating the respective atom economy of Reaction (I) and Reaction (II), compare which of them can be considered as greener.

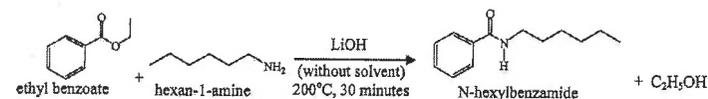
(Formula masses : NaOCl = 74.5, NH_3 = 17.0, H_2O_2 = 34.0, H_2NNH_2 = 32.0, NaCl = 58.5, H_2O = 18.0)

(2 marks)

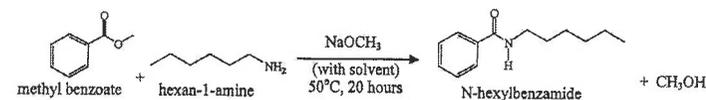
DSE20_1b

- (b) The two reactions below can produce N-hexylbenzamide:

Reaction (I):



Reaction (II):



- (i) Based on the above information, suggest one reason for each of the following:
- (1) Reaction (I) can be considered as greener than Reaction (II). (2 marks)
- (2) Reaction (II) can be considered as greener than Reaction (I). (2 marks)
- (ii) In Reaction (II), 3.00 g of methyl benzoate reacts with 2.23 g of hexan-1-amine to give 3.89 g of N-hexylbenzamide. Calculate the yield of this product. (Relative molecular masses : methyl benzoate = 136, hexan-1-amine = 101, N-hexylbenzamide = 205) (2 marks)
- (iii) The methanol produced in Reaction (II) can be used to manufacture ethanoic acid in industry by the following reaction:
- $$\text{CH}_3\text{OH(l)} + \text{CO(g)} \xrightleftharpoons[\text{catalyst}]{180^\circ\text{C}, 30 \text{ atm}} \text{CH}_3\text{COOH(l)} \quad \Delta H < 0$$
- (1) According to chemical equilibrium, explain why the operation pressure in industry for the reaction is set at 30 atm but not at atmospheric pressure. (3 marks)
- (2) Explain why the optimal operation conditions are set at 180°C and 30 atm. (3 marks)

Marking Scheme

AL07(I)_08

(a) % yield = $\frac{14.6}{15.9} \times 100\% = 91.8\%$ [2]

(b) Catalyst [1]

(c) Open-end questions: [1]

Yes. Any ONE of the followings:

1. The reaction does not involve the use of solvents
2. The reaction has a high atom economy
3. A catalyst is used.
4. No side product
5. One step reaction

No. The reaction requires the use of KCN which is highly toxic.

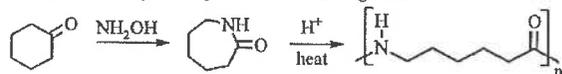
AL08(I)_10

Candidates are expected to discuss the application of at least four of the principles of green chemistry in industry.

(1) Atom economy: synthetic method should be designed to maximize the incorporation of all materials used in the process into the final product.

Atom economy industry process:

- Manufacture of nylon-6 by Beckmann rearrangement.



- Addition reactions, e.g. obtaining saturated fats by catalytic hydrogenation.
- Haber process in the manufacture of ammonia

(2) Less hazardous chemical synthesis: wherever practicable, synthetic method should be design to use and generate substances that possesses little or no toxicity to human health and the environment.

- Use of supercritical CO₂ in decaffeinating coffee and in dry cleaning: replacing harmful organic solvents such as CH₂Cl₂, benzene by non-polluting supercritical CO₂.

(3) Safe solvents and auxiliaries: the use of auxiliary substance (e.g. solvents, separating agents) should be made unnecessary wherever possible and innocuous when used.

- Solvent free syntheses: e.g. manufacture of PMMA by grinding monomers with a catalyst.

(4) Catalysis: catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

- Haber process in the manufacture of ammonia
- Biocatalysts and asymmetric catalysts.

(5) Design for energy efficiency: energy requirements of chemical process should be recognized for their environmental and economic impacts, and should be minimized. If possible synthetic methods should be conducted at ambient temperature and

pressure.

- Use of fuel cells.
- Replacing AlCl₃ by partially dealuminated zeolite Y catalyst.

ASL09(II)_05

(a) Atom economy = $\frac{\text{Relative molecular mass of desired products}}{\text{Relative molecular mass of all reactants}}$ [1]

= $\frac{132.0 + 166.0 - 18}{132.0 + 166.0} = 94.0\%$ [1]

(b) no. of moles of B used = $\frac{2.64}{132.0} = 0.02$ [½]

no. of moles of D used = $\frac{3.32}{166.0} = 0.02$

no. of moles of E obtained = $\frac{4.40}{280.0} = 0.0157$ [½]

% yield of reaction = $\frac{0.0157}{0.02} = 78.5\%$ [1]

(c) Any FOUR of the following: [2]

- The reaction has high atom economy
- The reaction has a high yield
- The reaction does not require the use of solvent
- A catalyst, NaOH(s), is used
- The other product, H₂O, is non-toxic

AL12 (I)_06

(b) Any TWO of the following: [2]

- The reaction in Haber process has very high atom economy (100%)
- The reactants (N₂ and H₂) are non-toxic and will pose no harm to the environment.
- The reaction takes place in gas phase. No solvent is required.
- The raw material (N₂) is available in larger amount in the atmosphere. Depletion is not a problem.
- The reaction does not require the use of any derivatives.

A catalyst (Fe) is used.

AL13(II)_11 (modified)

(i) Any TWO of the following: [2]

- The cumene route does not involve the use of corrosive acids (conc. H₂SO₄) / alkalis (NaOH)
- A catalyst (zeolite) is used in the cumene route.
- The cumene route has a higher atom economy.

(ii) Propanone, CH₃COCH₃, can be used as a solvent / to manufacture plastics, e.g. PMMA. [1]

DSE11SP_01c

- (i) Atom economy
- $$= \frac{\text{molar mass of desirable product}}{\text{sum of molar masses of all products}}$$
- $$= \frac{\text{molar mass of methylpropene}}{\text{molar mass of methylpropene} + \text{ethanol} + \text{sodium bromide}}$$
- $$= \frac{56}{56 + 46 + 102.9} \times 100\%$$
- [1]
[1]
[1]
- (ii) Examples of other factors (Any TWO): [2]
- Waste minimization at Source
 - Use of catalysts in place of reagents
 - Use of non-toxic reagents
 - Use of renewable resources
 - Use of solvent free or recyclable environmentally benign solvent system.

DSE12PP_01a

- (iv) This method uses a catalyst (the enzyme) instead of stoichiometric reagents. [1]
It uses less hazardous chemicals (e.g. MeOH / acid). [1]

DSE12_02a

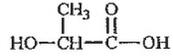
- (ii) (1) • The hydrogen peroxide used in Reaction (1) is less corrosive / hazardous when compared with the concentrated nitric acid used in Reaction (2). [1]
• The by-product H₂O produced in the Reaction (1) is less harmful / environmentally friendly when compared with the by-product N₂O produced in Reaction (2), which is an air pollutant. [1]
• A catalyst is used in Reaction (1) but not in Reaction (2). [1]
[Must be in comparison style]
- (2) Both reactions consume starting materials that possibly obtained from a non-renewable resource / petroleum. [1]

DSE13_01c

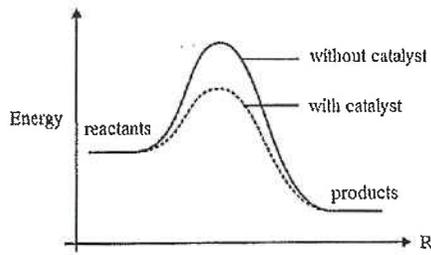
- (ii) Method 2:
- $$\text{Atom economy} = \frac{58}{76} = 76.32\%$$
- [1]
- (iii) Method 2 is greener. [2]
Any TWO of the following:
- It has a higher atom economy
 - It produces less waste (less side products) and less treatment is required / requires less steps.
 - Less hazardous chemicals are used such as method 1 uses (more) toxic Cl₂ / Method 1 uses more corrosive NaOH / Method 1 uses more toxic Cl₂.
- (Accept any reasonable answer and note for comparative sense.)

- (iv) The calculation of atom economy is based on a 100% completed reaction / complete conversion of reactants to products. [1]
Most reactions do not go to completion / There is loss during handling / The yield is related to extent of reaction (percentage conversion). [1]
Thus a reaction with high atom economy does not necessarily have a high yield.

DSE14_02c

- (iv) (1)  [1]
- (2) PLA is made from renewable resources, while PE and PET are made from non-renewable petroleum products. [1]
OR, PLA is biodegradable, while PET and PET are non-biodegradable.
- (3) PLA is made from agricultural products. Massive production of PLA may affect the supply of food. [1]

DSE15_01b

- (i) (1)  [3]
- (1 mark for each of the energy profiles – total 2 marks: Accept exothermic / endothermic; one peak or multiple peaks)
1 mark for the labels: Accept potential energy / enthalpy but NOT kinetic energy / energy level)
- (2) Catalyst can be poisoned. / Their active sites can be occupied by other chemicals making them inactive. [1]
- (ii) Any TWO of the following: [2]
- A (biological) catalyst / enzyme is used.
 - The reagent (O₂) used in non-toxic
 - The reactions take place in aqueous phase. (No organic solvents are used.)
 - The feedstock (sugars) is renewable.
 - The wastes formed are biodegradable.
 - The reaction is carried out at room temperature / pressure / requires less energy.

- (iii) Any TWO of the following: [2]
- The reactions in route (1) are carried out in dilute / aqueous solution while route 2 is not. / The ethanoic acid produced in route (1) is in form of dilute / aqueous solutions while route (2) is not. / In route (2), the ethanoic acid produced is purer / concentrated. / The recovery of the ethanoic acid from these solutions in route (1) requires much more energy than route (2). / The amount of ethanoic acid produced by the fermentation route / route (1) cannot meet the large demand of ethanoic acid but route (2) can.
 - The rate of fermentation / aerial oxidation in route (1) is slower.
 - Route (2) does not consume food but route (1) does.

DSE15_02a

- (iii) Conc. HNO_3 is corrosive. [1]
 NO_2 is poisonous / irritant. [1]

DSE16_01c

- (iii) Any 2 reasons of the above, with comparative sense 1 mark each [2]
- Need not to separate fructose from the mixture after hydrolysis of starch but the one with sucrose requires.
 - Higher atom economy as glucose is the only product from the enzymatic hydrolysis of starch. / atom economy of hydrolysis of starch is 100% while that of sucrose is 50% / less than 100%
 - Harmful / corrosive / irritating $\text{HCl}(\text{aq})$ is used in hydrolysis of sucrose while hydrolysis of starch involves enzyme which is biodegradable and less harmful

DSE16_02a

- (i) Cellulose is biodegradable / biodegradable / degrade readily by bacteria / enzymes / can undergo hydrolysis [1]

DSE17_01c

- (iv) (1) The atom economy is 100% in the reaction. / No solvent is required in the reaction. [1]
 [Accept: The atom economy is high]
- (2) The reactant / CO / Cl_2 are poisonous / toxic. [1]
 NOT accept harmful.

DSE17_02c

- (iii) (1) Production: Biomass is raw material / renewable resources [1]
 Disposal: PHB is biodegradable / degrade readily by bacteria / enzymes [1]
- (2) Disposal: PHB undergoes hydrolysis / decomposition in the presence of acids / alkalis. [1]

DSE18_01b

- (i) (1) $\text{Cu} / \text{ZnO} / \text{Al}_2\text{O}_3 / \text{Cr}_2\text{O}_3$ [Mark the first one] [1]
 (2) May be due to higher activation energy / energy barrier. [1]
 (3) Number of moles of gaseous product is less than that of gaseous reactants. [1]
 Increasing the pressure will shift the equilibrium position to the right. [1]
 OR, increase in collision frequency / effective collision
 Make the reaction faster to reach equilibrium.
- (ii) (1) This reaction does not involve poisonous reagent / CO but the original one involves poisonous CO . [1]
 (2) It reduces the amount of atmospheric carbon dioxide and hence may alleviate global warming / greenhouse effect. [1]
- (iii) $\text{CH}_3\text{OH}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CH}_3\text{CO}_2\text{H}(\text{g})$ [1]

DSE18_02a

- (i) Any TWO of the following: [2]
- Catalyst is used.
 - High atom economy / atom economy = $172 / 208 = 82.7\%$
 - Water generated possesses little or no toxicity to human health and the environment.

DSE19_1b

- (b) (i) • Use concentrated sodium chloride solution / brine as electrolyte. 1
 • Anode: $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ 1
 • Cathode: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ 1
 • The membrane is permeable to cations but not anions. 1
- (ii) $\text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{NaOCl}(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ 1
- (iii) Atom economy for Reaction (I) = $32 / 108.5 = 29.5\%$ 2
 Atom economy for Reaction (II) = $32 / 68 = 47.1\%$
 Reaction (II) is greener as it has a higher atom economy.

- (b) (i) (1) No solvent will be emitted to the environment for Reaction (I) but Reaction (II) will. / The side product, ethanol, of Reaction (I) is less toxic. / No toxic methanol will be produced in Reaction (I) but Reaction (II) will. / (A comparative sense) 1
- (2) Lower temperature is needed. / Higher atom economy. / (less energy is not accepted) / (A comparative sense) 1
- (ii) $3.00 \div 136 = 0.022 \text{ mol}$
 $2.23 \div 101 = 0.022 \text{ mol}$
 $(3.89 \div 205) \div 0.022 \times 100\%$ 1*
 $= 86\%$ 1
 (2 – 4 sign fig; range: 85.8 – 86.3)
 (1 mark for steps and 1 mark for answer)
- (iii) (1) Because increasing the / higher pressure can shift the equilibrium position to the right / higher yield. 1
- (2) • Higher temperature will have a higher rate of reaction. But the forward reaction is exothermic, increasing the temperature will shift the equilibrium position to the left / lower yield. 1
- Higher pressure (will shift the equilibrium position to the right but) extra cost is needed. 1