

HKDSE Chemistry Pastpaper Collection
Paper II
By Topic
Section 13,15

HKAL/HKASL Paper 1996-2013

HKCEE Paper 1990-2011

HKDSE Sample Paper 2011

HKDSE Practices Paper 2012

HKDSE Paper 2012-2022

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Characteristic Infra-red Absorption Wavenumber Ranges
(Stretching modes)

Bond	Compound type	Wavenumber range / cm^{-1}
C=C	Alkenes	1610 to 1680
C=O	Aldehydes, ketones, carboxylic acids and derivatives	1680 to 1800
C≡C	Alkynes	2070 to 2250
C≡N	Nitriles	2200 to 2280
O-H	Acid (hydrogen-bonded)	2500 to 3300
C-H	Alkanes, alkene, arenes	2840 to 3095
O-H	Alcohols (hydrogen-bonded)	3230 to 3670
N-H	Amines	3350 to 3500

Remarks:

Directions: Decide whether each of the two statements is true or false: if both are true, then decide whether or not the second statement is a correct explanation of the first statement. Then select one option from A to D according to the following table:

- A. Both statements are true and the 2nd statement is correct explanation of the Misstatement.
- B. Both statements are true but the 2nd statement is NOT a correct explanation of the 1st statement.
- C. The 1st statement is false but the 2nd statement is true.
- D. Both statements are false.

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:



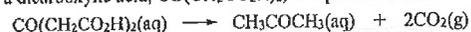
- (a) (i) The progress of the reaction can be monitored by a titrimetric method. Outline the experimental procedure. [For reference] (3 marks)
- (ii) State how the initial rate of the reaction can be determined from the titrimetric results. (2 marks)
- (iii) Suggest another method to monitor the progress 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:

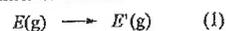


T/K	273	393	313	333	353
k / s^{-1}	2.46×10^{-5}	4.75×10^{-4}	5.76×10^{-3}	5.48×10^{-2}	?

- (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)

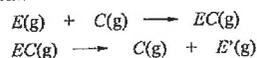
AL98(II)_03b

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:

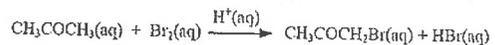
Initial concentration / mol dm^{-3}		Initial rate $\frac{d[\text{I}_2(\text{g})]}{dt} / \text{mol dm}^{-3} \text{ s}^{-1}$
$[\text{I}(\text{g})] / \text{mol dm}^{-3}$	$[\text{Ar}(\text{g})] / \text{mol dm}^{-3}$	
1.0×10^{-5}	1.0×10^{-3}	8.70×10^{-4}
2.0×10^{-5}	1.0×10^{-3}	3.48×10^{-3}
1.0×10^{-5}	5.0×10^{-4}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



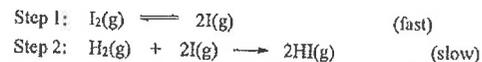
The table below lists the results of the experiment.

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:

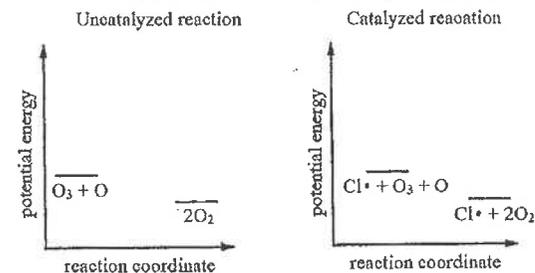


Combination of the above equations gives the overall equation for the depletion of ozone:



- (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.

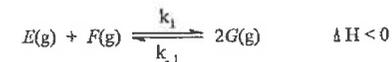
- (ii) Sketch the energy profiles for the uncatalyzed and catalyzed reactions.



- (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

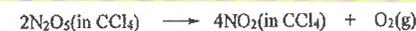
Consider the following system which comprises two single step reactions.



- (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

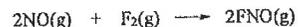
The decomposition of dinitrogen pentoxide in tetrachloromethane can be represented by the following equation:



- (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)

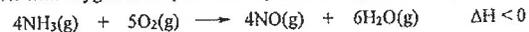
(iii) The rate equation for the above reaction is:
 $\text{rate} = k[\text{NO}(\text{g})][\text{F}_2(\text{g})]$

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.



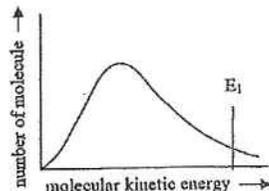
(i) $\text{NH}_3(\text{g})$ and $\text{O}_2(\text{g})$ are allowed to react in a vessel of constant volume. Find the rate of consumption of $\text{O}_2(\text{g})$ if the rate of formation of $\text{NO}(\text{g})$ is $1.24 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. (2 marks)

(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)

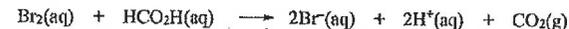
(ii) Explain why the rate of a catalyzed reaction would be different from that of an uncatalyzed

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)

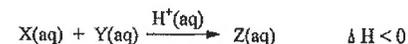
(c) Why is it necessary to keep the concentration of $\text{HCO}_2\text{H}(\text{aq})$ much higher than that of $\text{Br}_2(\text{aq})$? (2 marks)

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

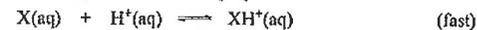
(e) Suggest how the order of the reaction with respect to $\text{HCO}_2\text{H}(\text{aq})$ can be determined. (1 mark)

ASL07(II)_03

Consider the acid-catalyzed reaction:



The following mechanism was proposed:



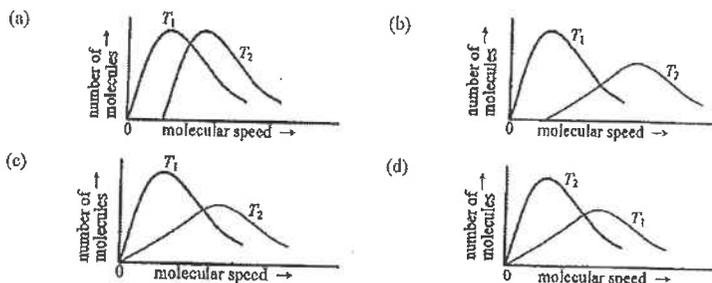
Based on this mechanism,

(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.

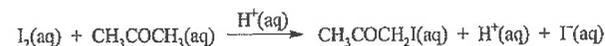
(3 marks)

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

(1 mark)

ASL09(II)_05

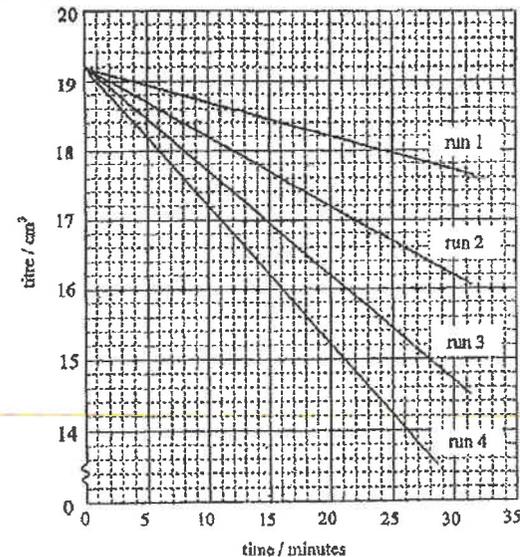
An experiment was devised to study the kinetics of the following acid-catalyzed reaction:



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

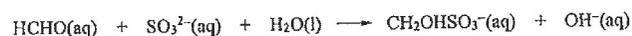
- (b) A student made the following remark:

'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

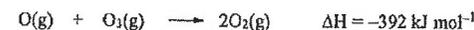
The reaction between A(g) and B(g) has a rate constant of $9 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Which one of the following is a possible rate equation for this reaction?

- 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)

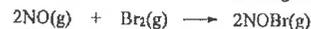
- (c) If chlorine free radicals ($\bullet\text{Cl}$) are present in the upper atmosphere, they will catalyze the conversion of ozone to diatomic oxygen leading to ozone depletion.
- (i) Given that the rate equation for the $\bullet\text{Cl}$ catalyzed ozone depletion is:
 $\text{rate} = k[\text{O}_3(\text{g})][\bullet\text{Cl}(\text{g})]$
 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)

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ASL12(II)_04

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



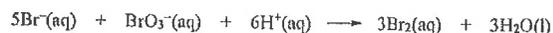
The table below lists the results obtained:

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.

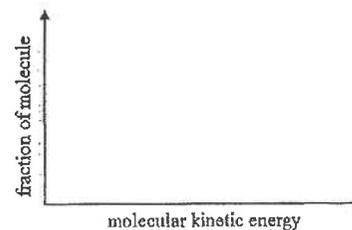
Trial	Initial concentration / mol dm^{-3}			Time taken for the red color to disappear / s
	Br ⁻ (aq)	BrO ₃ ⁻ (aq)	H ⁺ (aq)	
1	0.034	0.007	0.100	1026
2	0.017	0.007	0.100	2052
3	0.034	0.021	0.100	342
4	0.017	0.007	0.400	128

- (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 T₁ and T₂, where T₁ < T₂.



- (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:

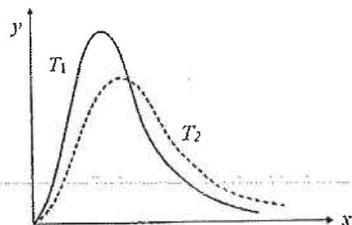
Trial	Initial concentration of $\text{NO}(\text{g})$ / mol dm^{-3}	Initial concentration of $\text{H}_2(\text{g})$ / mol dm^{-3}	Initial rate with respect to $\text{N}_2(\text{g})$ / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	2.50×10^{-2}	5.00×10^{-3}	1.20×10^{-6}
2	2.50×10^{-2}	1.00×10^{-2}	2.40×10^{-6}
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 $\text{NO}(\text{g})$ and that to $\text{H}_2(\text{g})$. (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 .

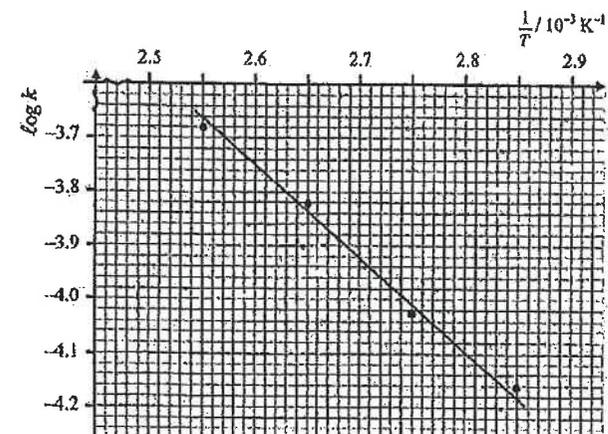


16

- (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)

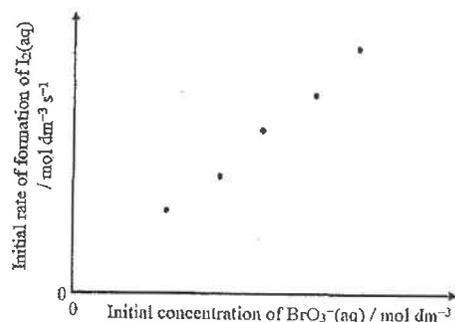
17

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 $\text{I}_2(\text{aq})$ / $\text{mol dm}^{-3} \text{ s}^{-1}$
	$\text{BrO}_3^-(\text{aq})$	$\text{I}^-(\text{aq})$	$\text{H}^+(\text{aq})$	
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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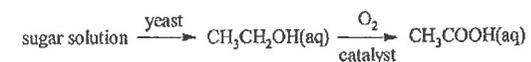
DSE15_01a

- (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: $\log k = \text{constant} - \frac{E_a}{2.3RT}$)

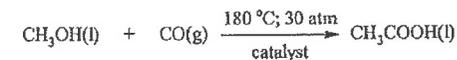
DSE15_01b

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

Route (1)



Route (2)

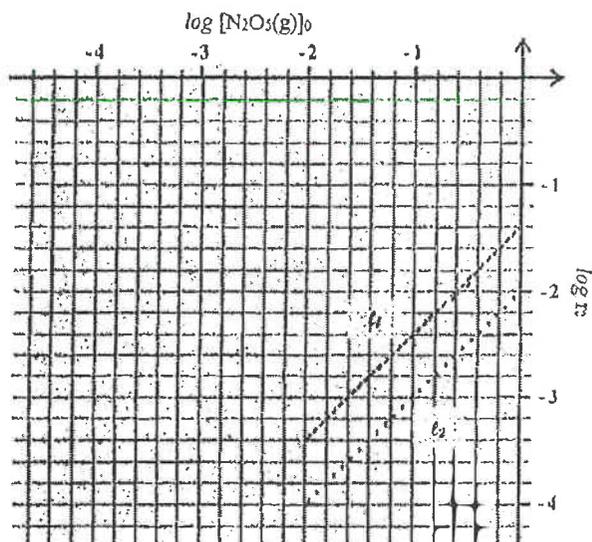


- (i) The reactions in both Routes (1) and (2) require the use of catalysts.
- (1) Draw, the same sketch, TWO labelled energy profiles for a reaction, one with a catalyst and the other one without catalyst. (3 marks)
- (2) Theoretically, catalysts are not consumed in reactions. Suggest why it is still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

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It is given that $\log r_0 = \log k + n \log [N_2O_5(g)]_0$, where k is the rate constant and n is the order of reaction with respect to $N_2O_5(g)$.

- Given that l_1 and l_2 have the same slope, what can you deduce in terms of chemical kinetics? (1 mark)
- From l_1 , deduce the order of reaction with respect to $N_2O_5(g)$. (2 marks)
- From l_2 , deduce the rate constant for the reaction at 345 K. (2 marks)
- 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)

DSE19_01a 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}

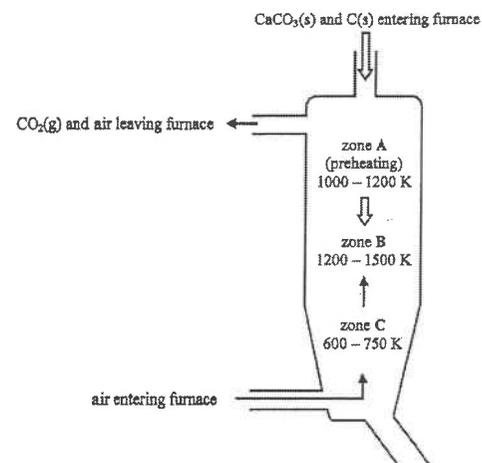
Deduce the order of reaction with respect to A(aq) and that with respect to B(aq). (2 marks)

DSE19_1c

- (c) In industry, CaO(s) is produced from the decomposition of $CaCO_3(s)$:

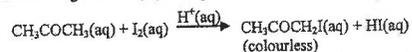


The diagram below shows an operating furnace for producing CaO(s) in an industrial plant. $CaCO_3(s)$ and C(s) enter the furnace from the top while air enters the furnace near the bottom.



- State one feedstock for $CaCO_3(s)$. (1 mark)
- 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)
- The operation pressure is set at about 1 atm. Give TWO reasons why a higher operation pressure is not preferred. (2 marks)
- The activation energy of the above decomposition of $CaCO_3(s)$ 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 $CaCO_3(s)$. (Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) (3 marks)
- According to chemical equilibrium, suggest why the decomposition of $CaCO_3(s)$ mainly occurs in zone B. (1 mark)

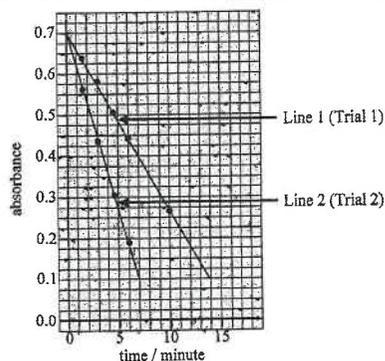
1. (c) Consider the following reaction ($\text{H}_2\text{SO}_4(\text{aq})$ as catalyst) and its rate equation :



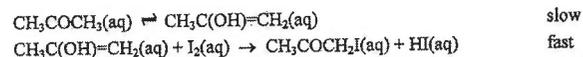
$$\text{Rate} = k_1[\text{I}_2(\text{aq})]^w[\text{CH}_3\text{COCH}_3(\text{aq})]^x[\text{H}^+(\text{aq})]^y \quad (\text{w, x and y are integers})$$

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 :

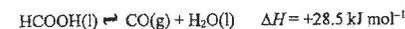


Draw an energy profile for the reaction. Label the axes.

(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.

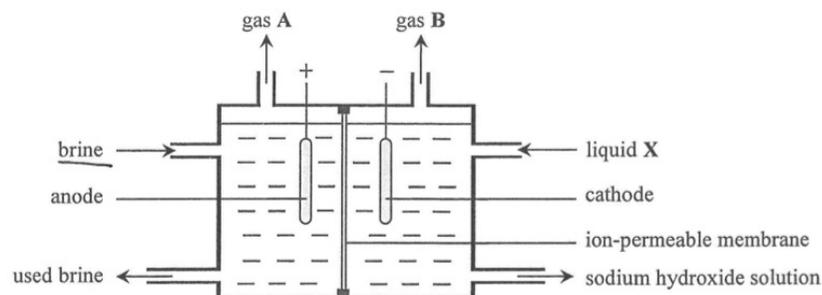
(2 marks)

(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)

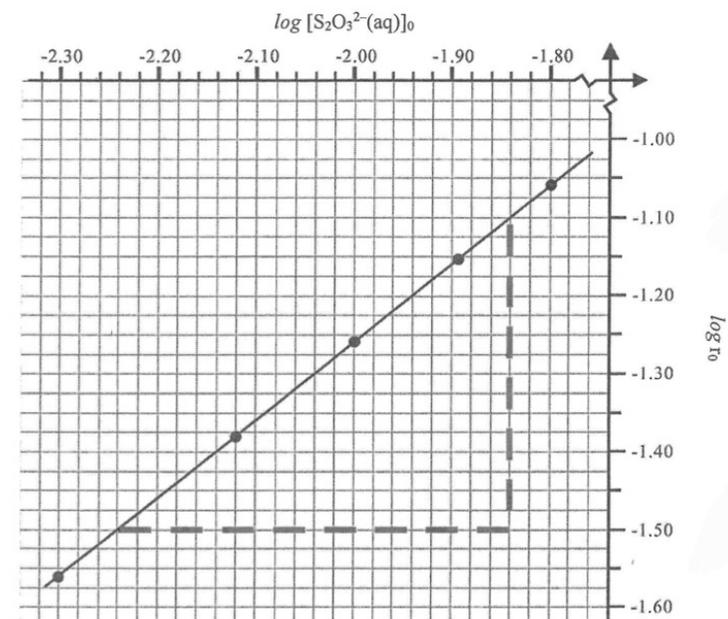
(iv) Suggest a chemical that can be manufactured from the reaction between A and sodium hydroxide solution.

(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} .

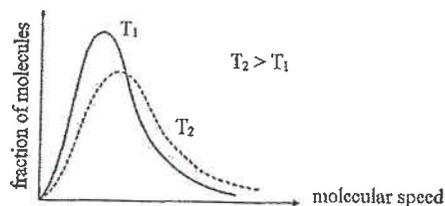
$$\left(\text{Gas constant } R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}; \text{ Arrhenius equation : } \log k = \text{constant} - \frac{E_a}{2.3RT}\right)$$

(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]

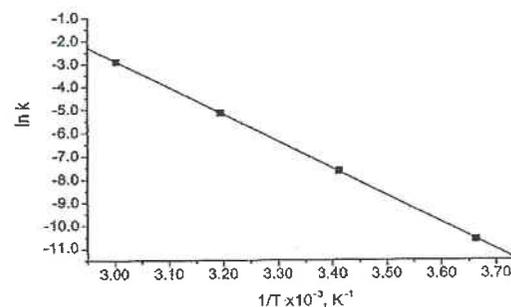
$E_a = +52.9 \text{ kJ mol}^{-1}$ (Range: 52.8 – 53.3) [1]

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)

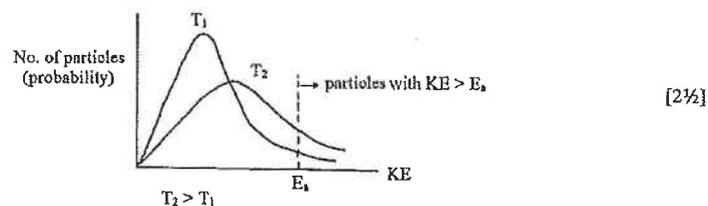
(1 mark for numerical answer, ½ marks for the unit)

(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

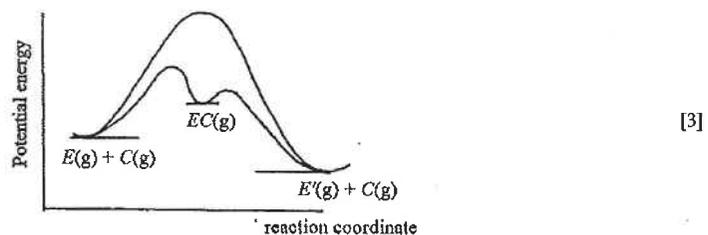
(i)



(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)



(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]

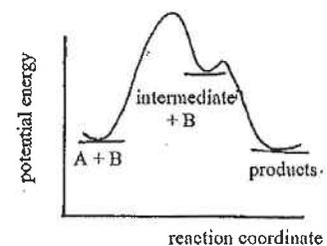
Under the same initial concentration of B, initial rate doubles when concentration of A is doubled. ∴ order w.r.t [A] = 1 [1]

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]

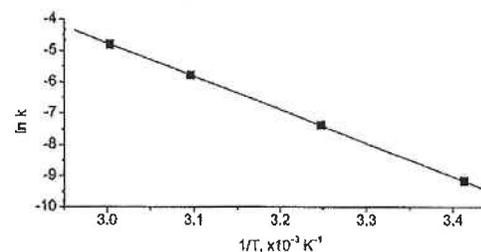
$$8.23 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} = k \times 0.05 \text{ mol dm}^{-3} \times 0.20 \text{ mol dm}^{-3}$$

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

(ii)

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]



(1 mark for a correct graph; 1 mark for labeling the axes. Deduce 1 mark if only 3 points are used.) [2]

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

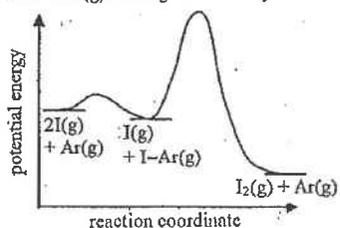
$$E_a = +88.5 \text{ kJ mol}^{-1} \quad (\text{Range: } 86 - 95)$$

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]

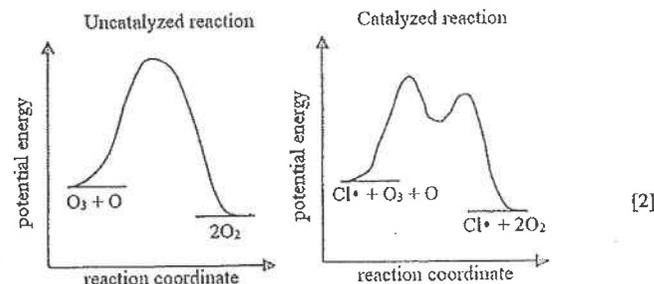
(b) $k = \frac{\text{rate}}{[CH_3COCH_3(aq)][H^+]}$ [1]
 Substitute a set of data (e.g. the first set) [1]
 $k = \frac{5.7 \times 10^{-5}}{0.30 \times 0.050} = 3.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [2]
 (Also accept 3.875×10^{-3} and 4.00×10^{-3}) [1]
 (1 mark for method; 1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

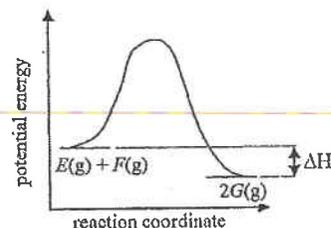
- (a) (i) Homogeneous catalyst because O_3 , O and $Cl\cdot$ are in the gaseous phase. [1]
 (ii)



- (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]

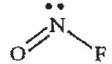
OR, Measure the volume of gas evolved because N_2O_5 and NO_2 are soluble in CCl_4 while O_2 is insoluble. [1]

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

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

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

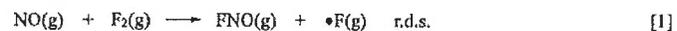
AL05(I)_02a

(i)  [1]

(ii) NO: +2 [½]

FNO: +3 [½]

(iii) Mechanism: [1]



ASL06(II)_10a

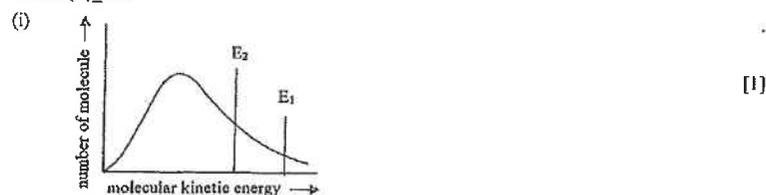
(i) rate of consumption of $O_2 = \frac{5}{4} \times 1.24 \times 10^{-4}$ [1]

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

(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]

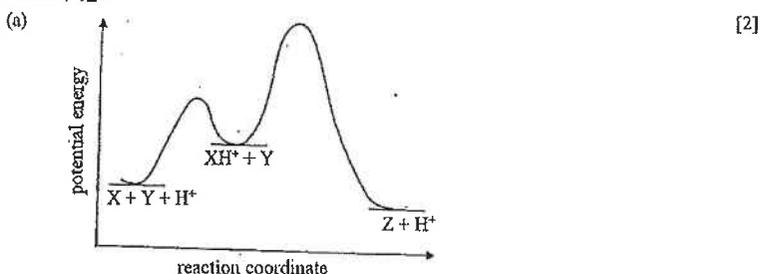
\therefore order w.r.t. $Br_2(aq)$ is 1. [1]

(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]

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 $\text{rate} = k'[I_2(aq)]^x$

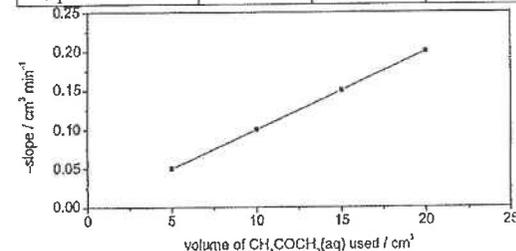
The titre decreases with time linearly, the rate of reaction is independent of $[I_2(aq)]$.

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.

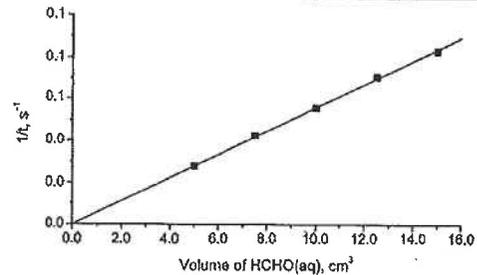
When nearly all of the $HSO_3^-(aq)$ and $SO_3^{2-}(aq)$ ions are reacted, there is excess $OH^-(aq)$ ions, the pH of the solution rises rapidly and phenolphthalein will turn pink.

- (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 $\text{HSO}_3^-(\text{aq}) / \text{SO}_3^{2-}(\text{aq})$ system is higher than the pH at which of methyl orange changes color. ∴ methyl orange will remain yellow throughout the experiment.

[1]

ASL11(I)_03

B

[1]

ASL11(II)_01

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

[1]

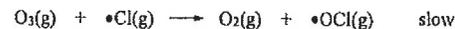
(b) $\ln k = \ln A - \frac{E_a}{RT}$

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

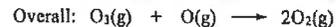
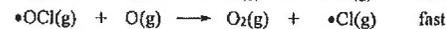
$$= +17.1(4) \text{ kJ mol}^{-1} \quad \text{unit must be present before award mark for the answer}$$

[1]

(c) (i) Mechanism



[2]



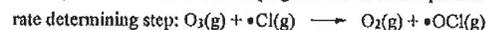
1 mark for having the mechanism agreeing with the rate equation

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

Explanation:

[1]

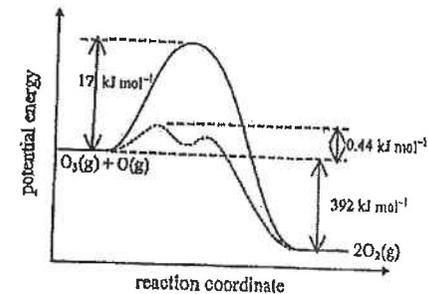
Adding the two mechanistic steps gives the overall equation. The proposed



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

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

[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: $\text{rate} = k[\text{NO}(\text{g})]^2[\text{Br}_2(\text{g})]$, 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 Br_2) 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]

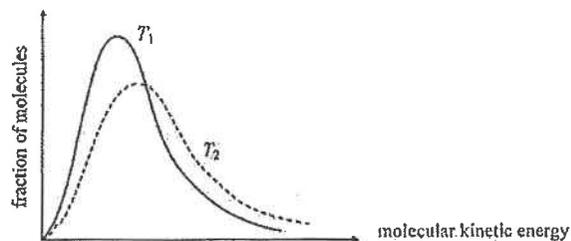
$E_a = +62.6 \text{ kJ mol}^{-1}$ [1]

(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]

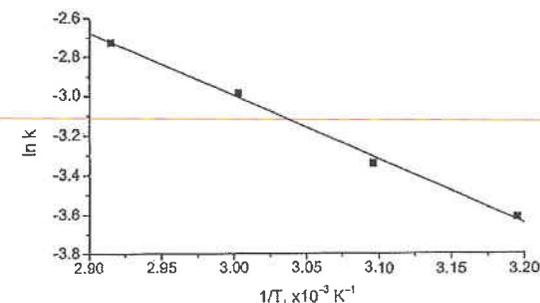
- The rate of reaction is proportional to the concentration of the reactant.
- The half-life of the reaction is constant.

(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, $[H_2]$ remains the same but $[NO]$ is halved, rate is decreased by a factor of 4. Therefore reaction order with respect to $[NO]$ is two. [1]

Compare experiments 1 & 2, $[NO]$ remains the same but $[H_2]$ is doubled, rate is also doubled. Therefore reaction order with respect to $[H_2]$ is one. [1]

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

(iii) $\text{rate} = k [NO]^2 [H_2]$ [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 $t = 0$

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

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

OR Titrate with standard $Na_2S_2O_3$ solution.

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

(iii) The initial rate is directly proportional to $[BrO_3^-(aq)]$. / The graph is linear / a straight line / $\text{rate} \propto [BrO_3^-(aq)]$ [1]

Therefore, the order of reaction with respect to $BrO_3^-(aq) = 1$ [1]

(iv) (1) $\text{Rate} = k [BrO_3^-(aq)] [I^-(aq)] [H^+(aq)]^y$

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

$y = 2$ [1]

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

(Accept other explanation.)

When initial $[I^-(aq)]$ increases by a factor of $0.30/0.15 = 2$ / doubles and initial $[H^+(aq)]$ increases by a factor of $0.20/0.10 = 2$ / double while keeping initial $[BrO_3^-(aq)]$ 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 $[H^+(aq)]$ is doubled.

(2) Rate of consumption of $BrO_3^-(aq) = 1/3 \times$ rate of formation of I_2

The initial rate with respect to $BrO_3^-(aq)$ 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 $[I_2(aq)]$. [1]

(2) $\text{Rate} = k [CH_3COCH_3(aq)] [H^+(aq)]$ [1]

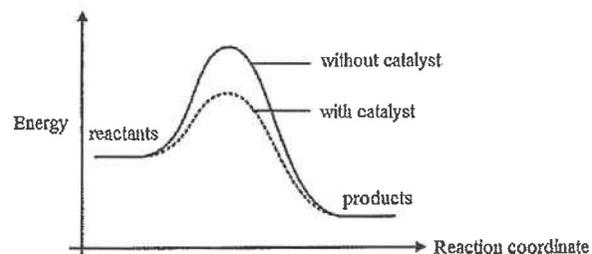
(ii) $\log \frac{k_2}{k_1} = -\frac{E_a}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \log 2 = -\frac{E_a}{2.3R} \left(\frac{1}{308} - \frac{1}{298} \right)$ [1]

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

DSE15_01b

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(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]

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]

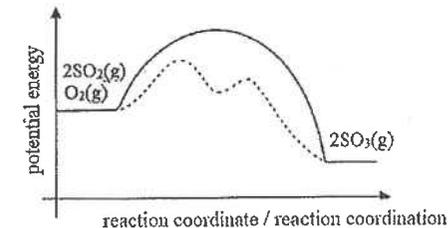
[Accept: A straight line is obtained. / [A] and time has a linear relationship /

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 = $k [CO]^m [Cl_2]^n$

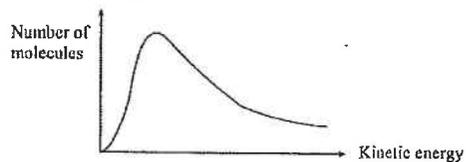
From doubling [CO] while keeping [Cl₂] unchanged, [1]

$2.83 = 2^m$

$m = 1.5$ [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 = $\log k$

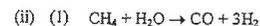
$$\log k_2 - \log k_1 = -\frac{E_a}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

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

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

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 = $-0.7 \div 8 = -0.0875$

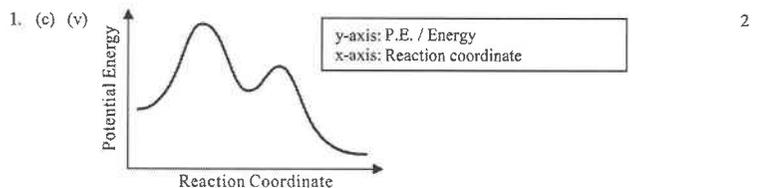
Trial 1 : slope of the plot = $-0.7 \div 16 = -0.04375$

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

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)

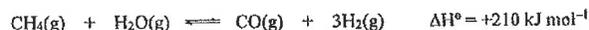
AL06(I)_09

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.

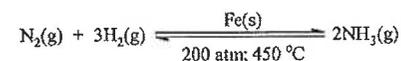
(2 marks)

AL12(I)_06

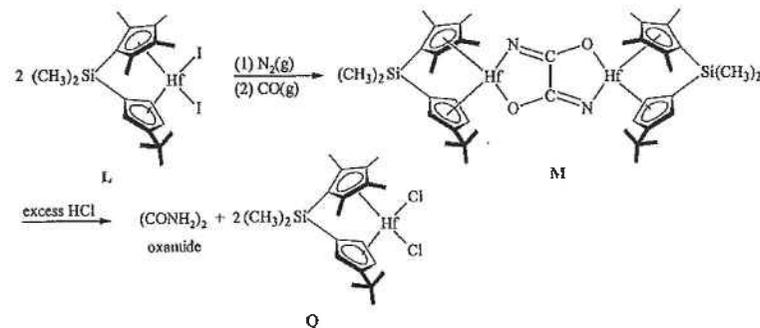
Read the passage below and answer the questions that follow.

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.

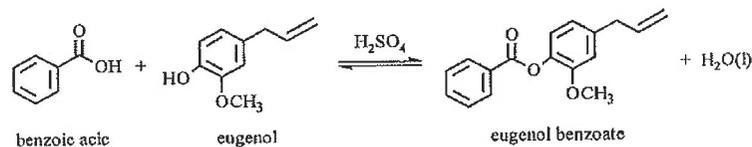
(3 marks)

(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)

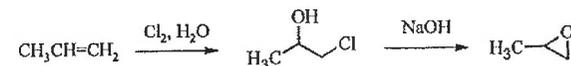
(iii) Eugenol benzoate can also be synthesized from the reaction of eugenol with benzoic acid in the presence of solid acid as a heterogeneous catalyst. With reference to the synthesis of eugenol benzoate, state ONE advantage of using a homogenous catalyst and ONE advantage of using heterogeneous catalyst.

(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.

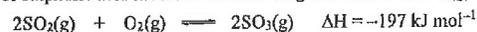
(1 mark)

- (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

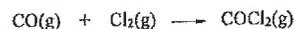
(1 mark)

(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)

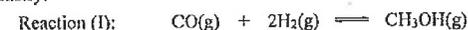
- (iii) Which one of the following species can be a raw material for manufacturing vitamin C in industry?

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)

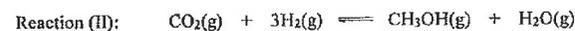
(2) Suggest why the reaction would proceed slowly in the absence of a catalyst.

(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)

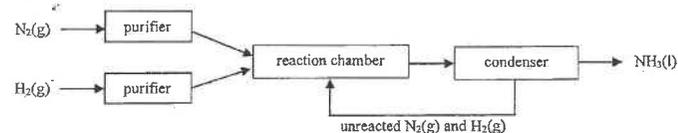
DSE20_01a

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.

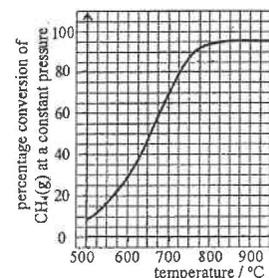


- (i) Explain why $N_2(g)$ and $H_2(g)$ need to be purified before going into the reaction chamber. (1 mark)
- (ii) Explain why the unreacted $N_2(g)$ and $H_2(g)$ are passed again to the reaction chamber. (1 mark)
- (iii) Why does ammonia, but not the other gases, become a liquid in the condenser ?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

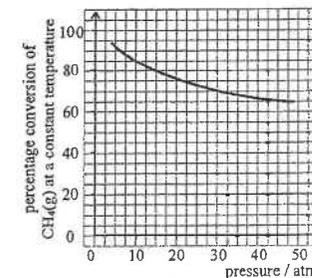
DSE21_01(C)

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]

(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

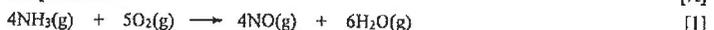
Manufacture of polymers, e.g. nylon, melamine, acrilan etc.

(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]

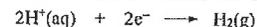
Separate crystal by filtration. [½]

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

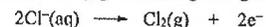
AL03(II)_02d

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]



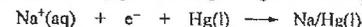
At anode: Cl⁻(aq) is discharged to give chlorine gas [1]



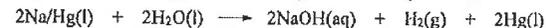
The Na⁺(aq) and OH⁻(aq) ions remaining in the solution constitute a NaOH(aq).

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]

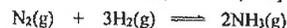
AL12(I)_06

- (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.)

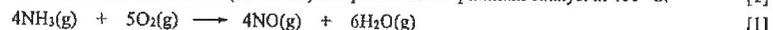
- (f) 2 moles of the HF complex are required for each mole of oxamide formed. The conversion can be very costly. [1]
 OR, The HF complex L cannot be regenerated in the reaction process.

DSE11SP_01b

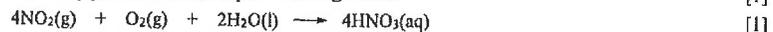
Purified N₂ and H₂ (ratio 1 : 3) are passed over iron catalyst at 450 °C and 200 atm pressure: [1]



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]

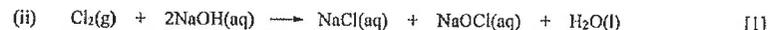


At the anode, Cl⁻(aq) is preferentially discharged because its concentration is high. [1]



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]



(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,

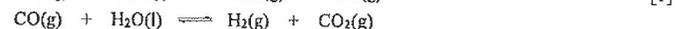
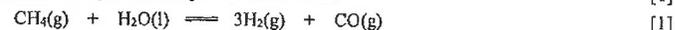
- Burning of H₂(g) gives water only.
- If there is a cheap source of electricity (e.g. photovoltaic cell), production of H₂(g) by electrolysis of brine can be a means of reducing air pollution problems. (Accept other reasonable answers.)

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 / formaldehyde / ethanoic acid / acetic acid / ether (dimethyl ether, MTBE) / as a solvent. [1]
 (Do not accept methanol as fuel, to produce "vinegar", or it is used to produce hydrogen / ethene)

(ii) $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$ (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.

OR, Further H₂ addition

(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]

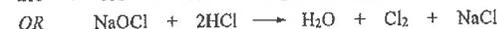
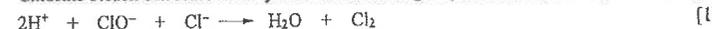
(ii) Site should be near the sea (because easy to get the raw materials.) / Easy transportation / Not too near residential places. [1]

(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

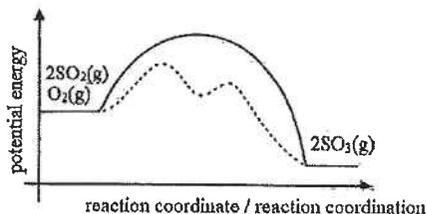
- (i) Fractional distillation of liquefied air [1]
 (ii) The hot gas from reaction chamber can help heat up the hydrogen and nitrogen / incoming gases / reactants / reactants mixture / cool down the product mixture
 It is to save energy. / to save fuel / conserve (recycle / reuse) energy / heat / reduce 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

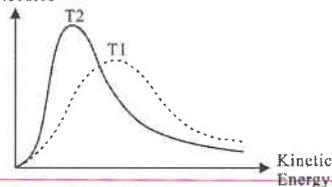
1. (a) (i) The Haber process produces ammonia / NH₃ which can make fertilisers to increase crop yield. 1
- (ii) (1) CH₄ + H₂O → CO + 3H₂ 1
- (2) It is because biomass is a renewable energy resource. 1
- (iii) • Comparing Trial 3 with Trial 2 (both same in [B(aq)], doubling the [A(aq)] leads to a double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

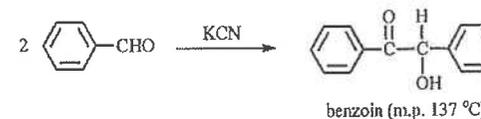


(1 mark for T₂ higher than T₁)
 1 mark for starting at zero and tail; T₁ > T₂ Okay if not labelling the axes.)

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)

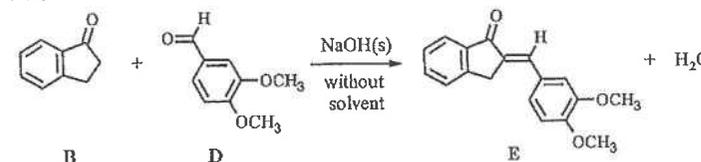
AL08(I)_10

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)

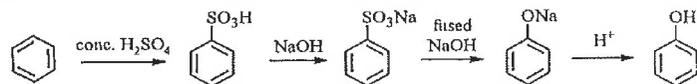
AL12 (I)_06

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

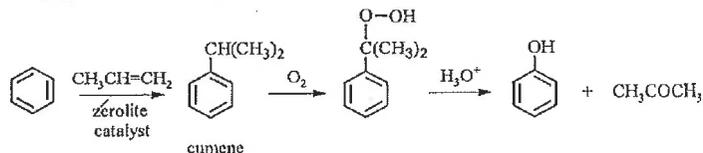
(2 marks)

AL13(II)_11 (modified)

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



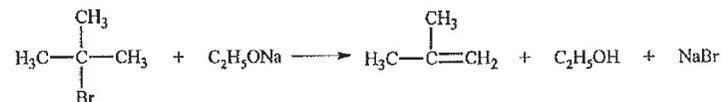
Nowadays, phenol is commonly synthesized from benzene via the cumene route as show below:



- (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

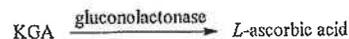
The reaction for the production of methylpropene from 2-bromo-2-methylpropane is represented by the following equation:



- (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.

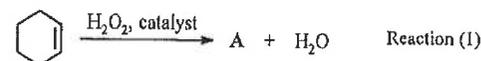


Suggest TWO reasons why this method is considered greener than the corresponding one in the above-shown Reichstein process. (2 marks)

64

DSE12_02a

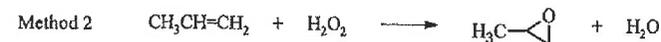
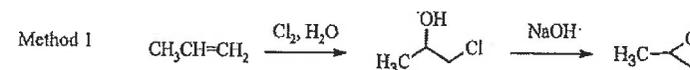
- (ii) Compound A is one of the monomers for making nylon-6,6 in industry. The following equations show two reactions that can produce A:



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



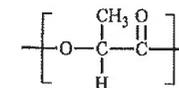
- (ii) The atom economy of Method 1 is 29.7%. Calculate the atom economy of Method 2. (1 mark)
- (iii) Discuss, from TWO different perspectives, whether Method 1 or Method 2 is greener. (2 marks)
- (iv) Comment on the following statement and explain your answer.

'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)

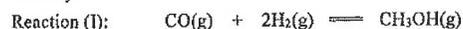
65

- (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)

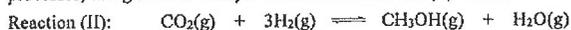
DSE18_01b

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:

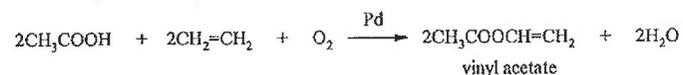


Based on the given information:

- (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.

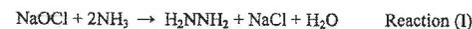


Give TWO reasons why this reaction can be considered as green.

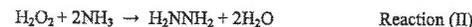
(2 marks)

DSE19_1b iii

- (iii) By using NaOCl, this chemical plant can produce hydrazine (H₂NNH₂), a propellant used in space vehicles:



However, instead of using NaOCl, H₂O₂ 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.

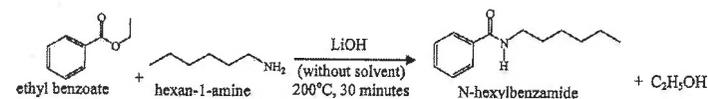
(Formula masses : NaOCl = 74.5, NH₃ = 17.0, H₂O₂ = 34.0, H₂NNH₂ = 32.0, NaCl = 58.5, H₂O = 18.0)

(2 marks)

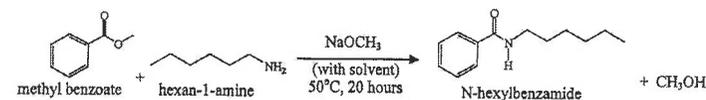
DSE20_1b

- (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.

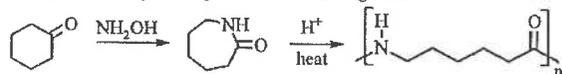
AL08(I)_10

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

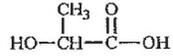
- (ii) (1) • The hydrogen peroxide used in Reaction (1) is less corrosive / hazardous when compared with the concentrated nitric acid used in Reaction (2). [1]
• The by-product H₂O produced in the Reaction (1) is less harmful / environmentally friendly when compared with the by-product N₂O produced in 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

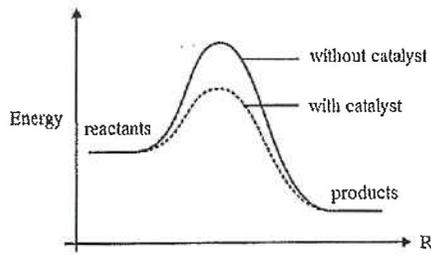
- (ii) Method 2:
- $$\text{Atom economy} = \frac{58}{76} = 76.32\%$$
- [1]
- (iii) Method 2 is greener. [2]
Any TWO of the following:
- It has a higher atom economy
 - It produces less waste (less side products) and less treatment is required / requires less steps.
 - Less hazardous chemicals are used 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 is 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 = $172 \div 208 = 82.7\%$
 - 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) $3.00 \div 136 = 0.022 \text{ mol}$
 $2.23 \div 101 = 0.022 \text{ mol}$
 $(3.89 \div 205) \div 0.022 \times 100\%$ f*
 $= 86\%$ 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

SECTION 15 Analytical Chemistry

Qualitative Analysis

AL96(II)_04b

For each of the following pairs of compounds, suggest a test to distinguish one compound from the other:

- (i) $\text{Na}_2\text{CO}_3(\text{s})$ and $\text{NaHCO}_3(\text{s})$ (2 marks)
- (ii) $\text{KCl}(\text{s})$ and $\text{MgCl}_2(\text{s})$ (2 marks)

AL98(I)_07a

Briefly describe how you would test for the presence of the all constitute ions and molecule in a sample of iron alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

(4 marks)

AL99(I)_07

- (a) Describe the procedure for a flame test. (3 marks)
- (b) Describe how to distinguish between a sodium salt and a potassium salt of the same anion by flame test. (1 mark)
- (c) Describe how to detect the presence of water of crystallization in an inorganic salt. (1 mark)

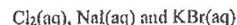
AL99(II)_01

For each of the following pairs of substances, suggest a chemical test to distinguish one from the other. For each test, give the reagent(s) used and the expected observation.

- (a) $\text{CsCl}(\text{s})$ and $\text{NH}_4\text{Cl}(\text{s})$ (2 marks)
- (b) $\text{Na}_2\text{SO}_3(\text{aq})$ and $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ (2 marks)

ASL00(I)_02

In the laboratory, there are three bottles labelled A, B and C. Each bottle contains one of the following reagents:



Three tests were carried out using the reagents in the bottles. The results are summarized in the table below:

Test	Observation
Mixing reagent in bottle A with reagent in bottle B	No observable change
Mixing reagent in bottle A with reagent in bottle C	Mixture turned brown
Mixing reagent in bottle B with reagent in bottle C	Mixture turned brown

- (a) Deduce which bottle contains $\text{Cl}_2(\text{aq})$. Write the relevant chemical equations. (3 marks)
- (b) If hexane is also provided, suggest how you would carry out an experiment to identify the contents of the other two bottles. (2 marks)
- (c) State ONE safety precaution which should be taken when performing the experiment you have suggested in (b). (1 mark)

AL00(I)_08

In order to establish the functional groups present in an acyclic compound F ($\text{C}_4\text{H}_6\text{O}$), three chemical tests were carried out. The test results are listed in the table below.

- (a) Complete the table by giving the inference of each test.

Test reagent	Test result	Inference
Acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$	Positive	Function group(s) that may be present:
Tollen's reagent	Negative	Functional group(s) absent:
Br_2 in CH_2Cl_2	Positive	Functional group(s) that may be present:

- (b) Based on the above information, draw four possible structure of F. (2 marks)

ASL00(II)_07

X, Y and Z are three isomeric cyclic compounds with molecular formula $\text{C}_6\text{H}_{10}\text{O}$. Two chemical tests were carried out on the compounds. The results are summarized in the table below:

Chemical test	X	Y	Z
Fehling's test	No observable change	Red precipitate	No observable change
Adding the compound to bromine water	No observable change	No observable change	Decolorization

- (a) What is the red precipitate formed in the Fehling's test? (1 mark)
- (b) Deduce a possible structure for each of the compounds, X, Y and Z. (5 marks)

ASL00(II)_11

Suggest a chemical test to distinguish one solution from the other in each of the following pairs. Equations should be given where appropriate.

- (a) $\text{Mg}(\text{NO}_3)_2(\text{aq})$ and $\text{Al}(\text{NO}_3)_3(\text{aq})$ (4 marks)
- (b) $\text{Na}_2\text{SO}_3(\text{aq})$ and $\text{Na}_2\text{SO}_4(\text{aq})$ (3 marks)

ASL01(I)_07

Suggest tests to show the identities of the cations and anion in $\text{KCl}(\text{s})$, and state the expected observation.

(4 marks)

AL02(II)_05c

Consider the substances listed below:

Butane	Benzoic acid	Dichlorodifluoromethane
Ethanoic acid	Hexane	Polystyrene
Propanone	Tetrachloromethane	Triethylamine

For each of the descriptions of physical properties from (a) to (h) below, choose from the above list, one substance which best fits the description.

- (i) A colorless, flammable gas
- (ii) A colorless liquid with a sour odour
- (iii) A colorless, water miscible, flammable liquid
- (iv) A colorless, non-flammable liquid
- (v) A colorless liquid with a fishy smell
- (vi) A colorless, water immiscible, flammable liquid
- (vii) A white solid which is insoluble in both cold and hot water
- (viii) A white solid which is insoluble in cold water, but soluble in hot water

(8 marks)

AL02(II)_01c

You are provided with a sample of blackboard chalk made from hydrated calcium sulphate(VI) powder.

- (i) The presence of calcium in the sample can be shown by conducting a flame test.
- (I) Give the essential steps in a flame test. (3 marks)
- (II) State the origin of the flame color. (1 mark)
- (ii) Devise an experiment, using chemicals and apparatus commonly available in a school laboratory, to determine the number of water of crystallization per formula unit of CaSO_4 in the sample of blackboard chalk. (4 marks)

AL03(I)_07

Outline how you would show the presence of Ba^{2+} and Ag^+ ions in a sample of water-soluble inorganic mixture. Give confirmatory test(s) for these ions if necessary.

(4 marks)

AL04(I)_07a

You are provided with three unlabeled bottles each containing one of the white powders listed below:

KBr(s) , $\text{SiO}_2(\text{s})$ and glucose

- (i) Outline the physical tests that you would perform to distinguish unambiguously the three substances from one another. (2 marks)
- (ii) Describe how you would carry out a chemical test to distinguish KBr(s) from glucose. (2 marks)

ASL05(I)_06

Compound A has the following composition by mass:

C 81.8%, H 6.1% and O 12.1%

Its relative molecular mass is in the range of 130 to 140.

- (a) Calculate the molecular formula of A. (3 marks)
- (b) A is an aromatic compound. It gives positive results when treated with Tollen's reagent. Deduce all functional groups present in A. (3 marks)
- (c) State a type of isomerism that A can exhibit. Illustrate your answer with the appropriate structures. (2 marks)

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AL05(II)_01

Each of six reagent bottles labeled A, B, C, D, E and F contained one of the following solutions.

$\text{AgNO}_3(\text{aq})$, $\text{BaCl}_2(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, $\text{NH}_3(\text{aq})$, $\text{NaOH}(\text{aq})$ and $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$

In an attempt to identify the contents of the bottles, a series of tests were conducted by mixing two of the solutions. The table below lists the observations in these tests.

Solution being mixed	Observations
A and C	A brown precipitate is formed
A and E	A white precipitate is formed
A and F	A brown precipitate is initially formed and the precipitate dissolves when F is in excess.
B and C	Only heat is liberated
B and D	A pale yellow precipitate is formed slowly
B and E	A white precipitate is formed

Identify, with explanation, the contents of the six reagent bottles based on the above information.

(8 marks)

AL07(I)_03

A mixture of $\text{Fe}^{3+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ is separated by paper chromatography using a mixture of propanone and 6M $\text{HCl}(\text{aq})$ as the mobile phase. Suggest how you would identify chemically the $\text{Fe}^{3+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ on the chromatographic paper.

(3 marks)

AL08(I)_08

Propenamide, the monomer of polypropenamide (also known as polyacrylamide), is a potential carcinogen. The melting point of propenamide is 84°C and its solubility in water is 2.16 g cm^{-3} at 30°C .

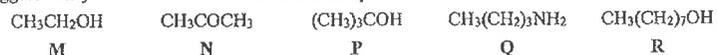
- (a) Polyacrylamide gel (PAAG) is polyacrylamide saturated with water. A sample of PAAG for breast augmentation is suspected to contain about 1% of propenamide. Suggest a chemical test to show the presence of propenamide in the sample. (2 marks)
- (b) Propenamide can be identified by converting it to a solid derivative and determining the melting point of the derivative. With the help of a chemical equation, suggest ONE solid derivative of propenamide suitable for this purpose. (1 mark)
- (c) Suggest an instrumental method for the further characterization of the derivative suggested in (b). State clearly the expected results. (2 marks)

(2 marks)

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AL08(I)_07

Compounds M, N, P, Q and R are all colorless liquids. Without the aid of instrumental analysis, suggest how you would differentiate the five compounds from one another.



ASL10(I)_05

State the expected observation(s) in each of the following experiments, and account for the observation with the aid of chemical equation(s).

Adding a solution of 2,4-dinitrophenylhydrazine to $\text{CH}_3\text{CH}_2\text{CHO}(\text{l})$.

(2 marks)

AL11(I)_07a

Copper(II) sulphate(VI) crystallizes from its aqueous solution as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$.

(i) The water of crystallization of the salt can be liberated upon heating. Suggest a chemical test to show that water is being liberated.

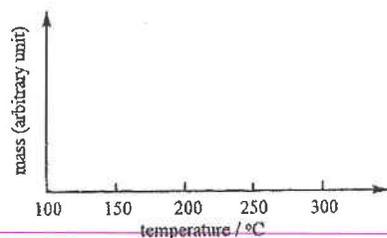
(1 mark)

(ii) Outline an experimental method to establish that the salt is a pentahydrate.

(3 marks)

(iii) When $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$ is heated slowly such that the temperature rises steadily, it will lose four water molecules at about 110°C , and then the last water molecule at about 250°C .

Using the axes below, sketch the change of mass when a sample of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$ is heated slowly.



(2 marks)

AL11(I)_07b

For each of the following pairs of species, suggest a chemical test to distinguish between them and write the chemical equation(s) of the reaction(s) involved.

(i) $\text{Ba}^{2+}(\text{aq})$ and $\text{Pb}^{2+}(\text{aq})$

(2 marks)

(ii) $\text{Cl}^-(\text{aq})$ and $\text{Br}^-(\text{aq})$

(2 marks)

ASL12(II)_06 (modified)

(a) Based on the information given below, deduce the structures of two isomeric compounds:

(1) Both compounds contain carbon, hydrogen and oxygen only.

(2) Both compounds have the same relative molecular mass of 58.0.

(3) Both compounds can react with 2,4-dinitrophenylhydrazine to give an orange precipitate.

(3 marks)

(b) Suggest a chemical test to distinguish between the two isomers in (a).

(2 marks)

AL13(I)_08b

For each of the following, given an example of its use in an inorganic experiment:

(i) A flame test

(1 mark)

(ii) Acidified $\text{BaCl}_2(\text{aq})$

(1 mark)

(iii) Starch solution

(1 mark)

DSE12_03a

Compound X (molar mass < 118 g) contains a $-\text{C}_6\text{H}_5$ group. Two chemical tests are performed on X and the results are as follows:

Test (1) : X turns acidified potassium dichromate solution green.

Test (2) : X gives a negative result when tested with 2,4-dinitrophenylhydrazine.

(i) With reference to the result of Test (1) only, suggest TWO functional groups that X may have.

(2 marks)

(ii) (1) What is the purpose of using 2,4-dinitrophenylhydrazine in Test (2)?

(1 mark)

(2) State the expected observation if X gives a positive result in Test (2).

(1 mark)

(iii) With reference to the results of both Test (1) and Test (2), suggest one functional group that may be present in X.

(1 mark)

DSE14_03a

Suggest a chemical test to show the presence of each of the following:

(i) $\text{HCl}(\text{g})$

(2 marks)

(ii) $\text{C}=\text{O}$ functional group

(2 marks)

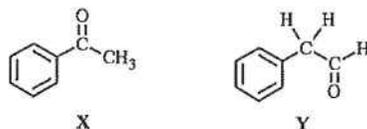
DSE15_03a

Suggest a chemical test to show the presence of Br^- (aq).

(2 marks)

DSE15_03b

Compounds X and Y shown below are isomers with relative molecular mass 120.



(i) Each of X and Y can react with 2,4-dinitrophenylhydrazine solution to give a similar observation. State the observation.

(1 mark)

(ii) Suggest a chemical test to distinguish between X and Y.

(2 marks)

DSE16_03a

Suggest a chemical test to show the presence of hypochlorite ions in an aqueous solution.

(2 marks)

DSE17_03a

Answer the following short questions:

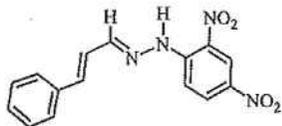
(i) Suggest a test to distinguish between sodium ions and potassium ions.

(2 marks)

(ii) Suggest a chemical test for detecting sulphur dioxide gas.

(2 marks)

(iii) An organic compound X reacts with 2,4-dinitrophenylhydrazine to form a yellow solid Z. The structure of Z is shown below:



Given that the molecular of X is $\text{C}_9\text{H}_8\text{O}$, draw the structure of X.

(1 mark)

DSE18_03a

Answer the following short questions:

(i) An ionic compound gives a brick red flame in a flame test. Suggest one cation the compound may contain.

(1 mark)

(ii) Suggest a chemical test to distinguish between K_2SO_3 (aq) and K_2SO_4 (aq).

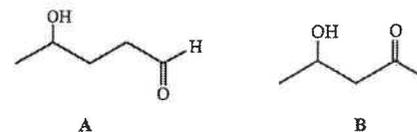
(2 marks)

DSE19_03a ii iii

(ii) Organic compounds can be extracted by suitable solvents from their aqueous solutions. The solvents should dissolve the organic compounds to be extracted without reacting with them. State one other property these solvents should have.

(1 mark)

(iii) Suggest a chemical test to show how compounds A and B below can be distinguished:



(2 marks)

DSE20_03a

3. (a) Answer the following short questions:

(i) Suggest how Na_2CO_3 (s) and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (s) can be distinguished.

(2 marks)

(ii) In an acidified medium, I_2 (aq) in a conical flask is titrated with Na_2SO_3 (aq) using starch solution as indicator. State the colour change at the end point of the titration.

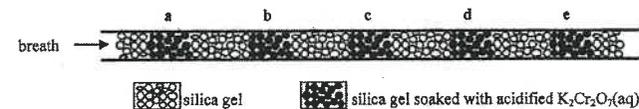
(1 mark)

(iii) Suggest a chemical test to show how hex-1-ene and hexanal can be distinguished.

(2 marks)

DSE20_03c i

(c) Road checking on ethanol intake of a driver can be done by having the driver exhale a breath into the tube as shown below:



(i) (1) Suggest the colour change of the silica gel soaked with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) if enough ethanol-contained breath is exhaled into the tube. Write a half equation for the colour change involved.

(2) A breath from driver A only changes colour at positions a and b; while a breath from driver B changes colour at positions a, b and c. Assuming the checking is performed in a fair manner, explain which driver has a higher ethanol intake.

(3) Suggest how the checking can be performed in a fair manner.

(4 marks)

Marking Scheme

AL96(II)_04b

- (i) Dissolve the solid in water, add $Mg(NO_3)_2(aq)$ or $Ca(NO_3)_2(aq)$ to the solutions. [1]
Only $Na_2CO_3(aq)$ give a white precipitate; but $NaHCO_3(a)$ does not. [1]
- (ii) Carry out a flame test, $KCl(s)$ give a lilac flame, while $MgCl_2(s)$ gives no characteristic flame color. [1]
OR, Add $NaOH(aq)$ to aqueous solution of the substance. [1]
Only $MgCl_2$ gives white precipitate, while KCl does not. [1]

AL98(I)_07a

- (i) NH_4^+ : Heat the sample with $NaOH(aq)$; [½]
Evolution of a gas with pungent smell, which can turn wet red litmus paper to blue indicates the presence of NH_4^+ . [½]
- (ii) Fe^{3+} : Add $KNCS(aq)$ [½]
Appearance of red color indicates the presence of Fe^{3+} [½]
OR, $NaOH$ -- forming brown precipitate
 $K_4[Fe(CN)_6](aq)$ -- appearance of deep blue color
- (iii) SO_4^{2-} : Add acidified $BaCl_2(aq)$ / $Ba(NO_3)_2(aq)$ to the solution of salt; [½]
Appearance of white precipitate indicate the presence of SO_4^{2-} [½]
- (iv) Water of crystallization
Heat a sample of salt; water vapor will turn anhydrous $CoCl_2$ from blue to pink / anhydrous $CuSO_4$ from white to blue. [½]

AL99(I)_07

- (a) Clean a platinum wire. [1]
Stick a sample of the salt on the Pt wire with conc. HCl. [1]
Heat the wire with the sample in a non-luminous flame. [1]
- (b) Na salt gives a persistent yellow flame [½]
K salt gives a lilac flame [½]
- (c) Heat the sample [½]
Water vapor will turn anhydrous $CoCl_2$ from blue to pink / anhydrous $CuSO_4$ from white to blue. [½]

AL99(II)_01

- (a) Heat the compounds separately with $NaOH(aq)$. [1]
 $NH_4Cl(s)$ gives an alkaline gas / a gas which forms white fumes with $HCl(g)$ but $CsCl(s)$ not. [1]
- (b) Treat the compounds separately with $HCl(aq)$. [1]
 $Na_2S_2O_3(aq)$ gives white / yellow precipitate of sulphur (+ SO_2) [½]
 $Na_2SO_3(aq)$ gives a gas with choking smell (SO_2) and a clear solution. [½]
OR, Only $Na_2S_2O_3(aq)$ gives a white / yellow precipitate.

ASL00(II)_07

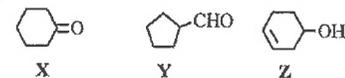
- (a) Bottle C [1]
Because solution A and B can only give brown mixture after mixing with solution C. [1]
 $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$ [½]
 $Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$ [½]
- (b) Add hexane in the solution A and B. [1]
The one can give a purple solution after mixing with solution C is $NaI(aq)$. [1]
- (c) Hexane is flammable and the experiment should be carried inside the fumehood. [1]

AL00(I)_08

- | (a) Test reagent | Test result | Inference | |
|----------------------------|-------------|--|-----|
| Acidified $K_2Cr_2O_7(aq)$ | Positive | Functional group(s) that may be present: | |
| | | - CH_2OH (primary alkanol) | [½] |
| | | $CHOH$ (secondary alkanol) | [½] |
| | | - CHO (aldehyde) | [½] |
| Tollens' reagent | Negative | Functional group(s) absent: | |
| | | - CHO (aldehyde) | [½] |
| Br_2 in CH_2Cl_2 | Positive | Functional group(s) that may be present: | |
| | | $C=C$ (alkene) | [½] |
| | | $C\equiv C$ (alkyne) | [½] |
- (b) $H_3C-C\equiv C-CH_2-OH$ $HC\equiv C-CH_2-CH_2-OH$ $HC\equiv C-CH(CH_3)-OH$ [2]
 $H_2C=C=CH-CH_2-OH$

ASL00(II)_07

- (a) Copper(I) oxide / $Cu_2O(s)$ [1]
- (b) D.B.E. of $C_6H_{10}O$ is 2. Compound X, Y and Z are cyclic compounds with one double bond. [1]
From the Fehling's test, only compound Y can give a red precipitate. Y should be a cyclic aldehyde, while others are not. [1]
Only compound Z can decolorize the bromine water. Compound Z, possess a carbon-carbon double bond, while others do not. [1]
Possible structure:



[3]

ASL00(I)_11

- (a) Dropwise addition of NaOH(aq) into two solutions respectively, until in excess. [1]
 Mg(NO₃)₂(aq) gives white precipitate while Al(NO₃)₃(aq) firstly forms white precipitate and it redissolves in excess NaOH(aq). [1]
- $$\text{Mg}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \longrightarrow \text{Mg}(\text{OH})_2(\text{s}) \quad [1]$$
- $$\text{Al}^{3+}(\text{aq}) + 3\text{OH}^{-}(\text{aq}) \longrightarrow \text{Al}(\text{OH})_3(\text{s}) \quad [1/2]$$
- $$\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^{-}(\text{aq}) \longrightarrow \text{Al}(\text{OH})_4^{-}(\text{aq}) \quad [1/2]$$
- (b) Dropwise addition of acidified KMnO₄(aq) into two solutions respectively. [1]
 Only Na₂SO₃(aq) can decolorize purple KMnO₄(aq), while Na₂SO₄(aq) cannot. [1]

$$5\text{SO}_3^{2-}(\text{aq}) + 2\text{MnO}_4^{-}(\text{aq}) + 6\text{H}^{+}(\text{aq}) \longrightarrow 5\text{SO}_4^{2-}(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \quad [1]$$

ASL01(I)_07

- By flame test / dip the sample on the platinum wire with conc. HCl and heat the sample in a non-luminous flame. [1]
 Potassium cations will give lilac flame in the flame test. [1]
 Add few drop of acidified silver nitrate solution in the KCl(aq). [1]
 White precipitate AgCl(s) is given. [1]

AL02(II)_05c

- | | | |
|---------------------------------|-------------------------|-----|
| (i) Butane | (ii) Ethanoic acid | [2] |
| (iii) Propanone / ethanoic acid | (iv) Tetrachloromethane | [2] |
| (v) Triethylamine | (vi) Hexane | [2] |
| (vii) Polystyrene | (viii) Benzoic acid | [2] |

AL02(II)_01c

- (i) (I) Clean a Pt wire / use a clean Pt wire (silica rod for flame test). [1]
 Stick sample of the salt onto the Pt wire with concentrated HCl. [1]
 Heat the wire with the sample in a non-luminous Bunsen flame. [1]
 (II) Electron transition from a higher energy level to a lower energy level leads to the emission of a photo with wavelength in the visible (red) region. [1]
- (ii) Heat a sample of the blackboard chalk (with a known mass) in a crucible until there is no further reduction in mass. [1]
 Assuming that the initial mass and the final mass of the sample are m₁ and m₂ respectively. [1]
- $$\text{moles of CaSO}_4 = \frac{m_2}{40 + 32 + 16 \times 4} = \frac{m_2}{136} \quad [1/2]$$
- $$\text{moles of H}_2\text{O} = \frac{m_1 - m_2}{18} \quad [1/2]$$
- moles of water of crystallization per formula unit of CaSO₄
- $$= \frac{m_1 - m_2}{18} / \frac{m_2}{136} \quad [1]$$

AL03(I)_07

- Dissolve the mixture in deionized water (water free from Cl⁻ ions)
 Add HCl(aq) to the solution. The silver ions in the solution will react with Cl⁻(aq) ions to form a white precipitate. [1]
 Confirmatory test for Ag⁺ ions: AgCl(s) is solution in aqueous ammonia. [1]
 Filter the mixture obtained. Add (NH₄)₂SO₄(aq) / H₂SO₄(aq) to the filtrate. Formation of a white precipitate shows the presence of Ba²⁺(aq) ions. [1]
 Confirmatory test for Ba²⁺ ions: apple green color in a flame test. [1]

AL04(I)_07a

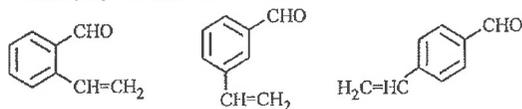
- (i) Add water to the white powder. Only SiO₂(s) is insoluble. [1]
 Test the electrical conductivity of the solutions obtained. [1/2]
 KBr(aq) conducts, but glucose solution does not. [1/2]
 OR, Conduct a flame test. Only KBr(s) gives a lilac flame.
 OR, Determine the melting points of the solid. KBr(s) has a very high melting point.
 OR, Use IR spectroscopy. Only glucose shows absorption peak at 2800 -- 3400 cm⁻¹.
- (ii) Heat the solids strongly. Only glucose becomes char. [2]
 OR, Add conc. H₂SO₄. Glucose gives a black mass, while KBr(s) gives brown fumes.
 OR, Add acidified AgNO₃(aq). KBr(aq) gives a pale yellow precipitate.
 OR, Treat compounds with Tollens' reagent. Only glucose gives a silver mirror.

ASL05(I)_06

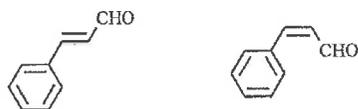
- (a) mole ratio of C : H : O = $\frac{81.8}{12} : \frac{6.1}{1} : \frac{12.1}{16} = 6.81 : 6.1 : 0.756 = 9 : 8 : 1$ [1]
 empirical formula is C₉H₈O
 molecular formula is (C₉H₈O)_n [1]
 $130 < n(9 \times 12 + 8 + 16) < 140$
 $\therefore n = 1$
 molecular formula is C₉H₈O [1]
- (b) A reacts with Tollens' reagent. \therefore A possess an aldehyde functionality / the -CHO group. [1]
 A is an aromatic compound with molecular formula C₉H₈O. It has a double-bond equivalence of 6. [1]
 A is likely to possess a C=C bond or alicyclic structure. [1]

(c) Possible types of isomerism: Position isomerism: [1]

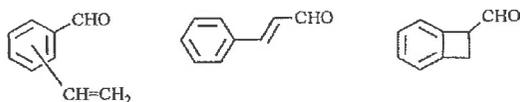
Structure (Any TWO of the following)



OR, Geometrical isomers:
Structure



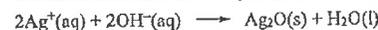
OR, Structural isomerism (Any TWO of the following)



AL05(II)_01

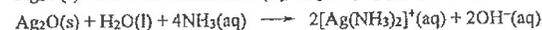
A is $\text{AgNO}_3(\text{aq})$ [1]

C and F are alkali because $\text{AgNO}_3(\text{aq})$ reacts with alkalis to give brown $\text{Ag}_2\text{O}(\text{s})$. [1]



C is $\text{NaOH}(\text{aq})$, while F is $\text{NH}_3(\text{aq})$. [1]

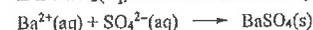
$\text{Ag}_2\text{O}(\text{s})$ reacts with excess $\text{NH}_3(\text{aq})$ to give $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$.



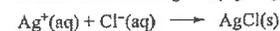
B is $\text{H}_2\text{SO}_4(\text{aq})$ as it undergoes neutralization with C. (Heat is evolved) [1]



E is $\text{BaCl}_2(\text{aq})$ as it reacts with $\text{SO}_4^{2-}(\text{aq})$ ions (in B) to give a white precipitate. [1]



E also reacts with $\text{AgNO}_3(\text{aq})$ to give a white precipitate $\text{AgCl}(\text{s})$ [1]



D is $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ because it reacts with acid (B) to give a pale yellow precipitate. [1]



The six solutions are

A : $\text{AgNO}_3(\text{aq})$ B : $\text{H}_2\text{SO}_4(\text{aq})$ C : $\text{NaOH}(\text{aq})$ D : $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ E : $\text{BaCl}_2(\text{aq})$ [1]

F : $\text{NH}_3(\text{aq})$

[1]

AL07(I)_03

Place the chromatographic paper in the atmosphere of ammonia. [1]

$\text{Fe}^{3+}(\text{aq})$ reacts with $\text{OH}^-(\text{aq})$ to give brown $\text{Fe}(\text{OH})_3(\text{s})$ [1]

$\text{Cu}^{2+}(\text{aq})$ reacts with $\text{NH}_3(\text{aq})$ to give deep blue complex $[\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$. [1]

AL08(I)_08

(a) Add $\text{Br}_2/\text{H}_2\text{O}$ or Br_2/CCl_4 [1]

The presence of propenamide causes the reddish brown reagent to turn colorless. [1]

OR, Add ICl/CHCl_3

The presence of propenamide causes the reddish brown reagent to turn colorless. (accept other test for alkene)

(b) $\text{Br}_2 + \text{CH}_2=\text{CHCONH}_2 \longrightarrow \text{CH}_2\text{BrCHBrCONH}_2$ [1]

(c) Mass spectrometry [1]

Expected result: There are three peaks for the molecular-ion at $m/z = 229, 231$ and [1]

233 respectively. The intensities of the three peaks should be in the ratio of 1 : 2 : 1. (relative abundance of the isotopes of bromine ^{79}Br and ^{81}Br is 1 : 1).

(Also accept compare the fragmentation patterns of the derivative obtained with that of an authentic sample).

OR, NMR spectroscopy [1]

Run NMR spectrum of the derivative and that of an authentic sample of the derivative. Compare the two spectra. [1]

AL08(II)_07

Q is the compound with a fishy smell (foul smell) / Only Q is basic [1]

R is the only compound which is immiscible with water. [1]

Only N reacts with 2,4-dinitrophenylhydrazine to give a red precipitate. [1]

M is more readily oxidized by $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ than P. [2]

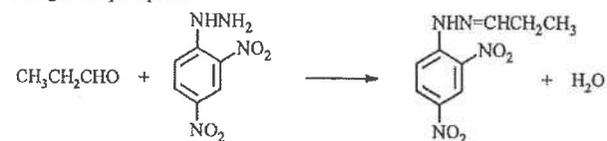
(or when M and P are treated with conc. HCl/ZnCl_2 (Lucas Reagent), P reacts more readily to give a cloudy mixture.)

(or when M and R are treated with I_2 in NaOH (iodoform test), only M give yellow precipitate.)

(award 1 mark for distinguishing one compound from the others.)

ASL10(I)_05

Orange / red precipitate [1]



AL11(I)_07a

- (i) Treat the vapor with anhydrous CoCl_2 / dry cobalt(II) chloride paper. A change of color from blue to pink shows the presence of water. [½]
OR, Treat the vapor with anhydrous CuSO_4 . A change of color from white to blue shows the presence of water. [½]

- (ii) Weigh an empty crucible and its lid (m_1). [½]
Put a sample of the salt in the crucible and weigh the crucible, its content and the lid (m_2). [½]

Heat the crucible and its content, not completely covered by the lid, to allow water vapor to escape until the sample turns white. [½]

Allow the crucible and its content to cool in a desiccator and then weigh the crucible, its content and the lid.

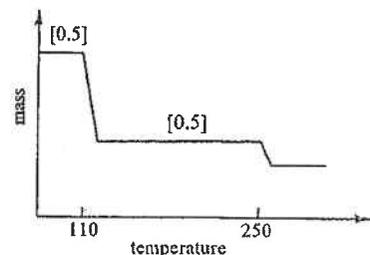
Repeat the heating and weighing processes until a constant mass (m_3) is reached. [½]

No. of molecules of water of crystallization

$$= \frac{(m_2 - m_3)}{(m_3 - m_1)} \times \frac{(63.5 + 32.1 + 16 \times 4)}{(2 \times 1 + 16)} \quad [½]$$

Should be equal to 5. [½]

- (iii) [2]



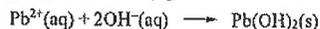
(1 mark for showing two 'steps' in the curve; 1 mark for showing that the heights of two 'steps' are in 4 : 1 ratio.)

AL11(I)_07b

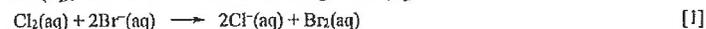
- (i) Adding of dil. $\text{HCl}(\text{aq})$ to two solutions. The one gives white precipitate is $\text{Pb}^{2+}(\text{aq})$, the one does not give white precipitate is $\text{Ba}^{2+}(\text{aq})$. [1]



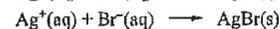
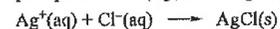
OR Adding few drops of $\text{NaOH}(\text{aq})$ / $\text{NH}_3(\text{aq})$ [not in excess] into the two solutions. The one gives white precipitate is $\text{Pb}^{2+}(\text{aq})$, the one has no precipitate is $\text{Ba}^{2+}(\text{aq})$.



- (ii) Adding of chlorine water into the two solutions. The one gives brown solution is $\text{Br}^{-}(\text{aq})$, the one has no observable change is $\text{Cl}^{-}(\text{aq})$. [1]



OR Adding acidified $\text{AgNO}_3(\text{aq})$ into the two solutions. The one gives white precipitate is $\text{Cl}^{-}(\text{aq})$, the one give pale yellow precipitate is $\text{Br}^{-}(\text{aq})$.

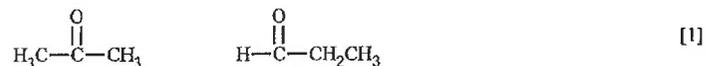


ASL12(II)_06 (modified)

- (a) Both compounds contain $\text{C}=\text{O}$ carbonyl group because they give positive result with 2,4-dinitrophenylhydrazine. [1]

A carbonyl group has a mass unit of 28. $(58 - 28) = 30$. These compounds can have 2 other C atoms. Their formula should be $\text{C}_3\text{H}_6\text{O}$.

Possible structure



- (b) Reagents: $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ / $\text{H}^{+}(\text{aq})$ [1]

Observation: Only propanal will turn the color of the reaction mixture from orange to green. [1]

(Also accept Tollens' test; Fehling's reagent; iodoform reaction etc.)

(1 mark for reagents; 1 mark for observation)

AL13(I)_08b

- (i) Identification of some metal and their ions, e.g. Na (golden yellow flame), K (lilac flame), Ca (brick red flame) etc. [1]

- (ii) Confirmation of $\text{SO}_4^{2-}(\text{aq})$ ions. [½]



- (iii) Testing of iodine [½]



DSE12_03a

- (i) hydroxyl (group) / $-\text{OH}$ / alcohol [1]

aldehyde (group) / $-\text{CHO}$ / aldehyde [1]

- (ii) (1) Test for aldehyde (group) or ketone (group) / carbonyl (group) / aldehyde (group) and ketone (group). [1]

(2) 2,4-dinitrophenylhydrazine reacts with aldehyde or ketone to give yellow, orange or red precipitate. [1]

- (iii) hydroxyl (group) / $-\text{OH}$ [1]

DSE14_03a

- (i) Place HCl(g) near NH₃(g / conc.) [1]
 Dense white fume is observed. [1]
OR Dissolve HCl(g) in deionized water.
 + Na₂CO₃ (s/aq) give a gas
 + AgNO₃/H⁺ gives a white ppt.
OR HCl + Na₂CO₃(aq) gives a gas
 HCl + AgNO₃/H⁺ gives a white ppt
- (ii) Add 2,4-dinitrophenylhydrazine [1]
 Yellow / orange / red precipitate is formed. [1]

DSE15_03a

- Addition of (acidified) silver nitrate solution (acidified by nitric acid). [1]
 Pale yellow precipitate formed (which is insoluble in aqueous ammonia) [1]
 [Add Cl₂(aq). Next, add an organic solvent. The solution turns brown. The organic solvent becomes orange/brown.]

DSE15_03b

- (i) yellow / orange / red precipitate (solid/ppt) [1]
 (ii) Add acidified K₂Cr₂O₇(aq). [1]
 Only Y turns the solution from orange to green. [1]
OR Only Y turns MnO₄⁻/H⁺ from purple to colourless.
OR Only Y gives a silver mirror in Tollens' test.
OR Only X gives a yellow precipitate with I₂/NaOH(aq).

DSE16_03a

- Add a few drops of HCl(aq) / a dilute acid / acid. [1]
 Pale (yellowish-)green gas evolved / which turns (moist) blue litmus paper red and then bleaches it / gas evolved which turns colorless iodide solution brown / yellow / orange. / a yellow gas is evolved which turns blue litmus paper red and then bleaches it. [1]

WITHOUT the use of dilute acid

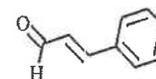
Reasonable test of the bleaching property with correct observation

- e.g. use a red litmus paper; red → (blue) → white (NOT colorless)
 use a blue litmus paper; blue → white (NOT colorless)
 use a pH paper; yellow → (green / blue) → white (NOT colorless)
 use litmus solution; purple → (blue) → colorless (NOT white)
 blue → colorless (NOT white)
 colored flowers (petals); decolorize

DSE17_03a

- (i) Flame test(s) are carried out. [1]
 Sodium ions give an intense golden yellow flame while potassium ions give a lilac flame. [1]
- (ii) Add a piece of filter paper which is soaked with acidified K₂Cr₂O₇ to the gas, the paper turns from orange to green. [1]
OR Pass the gas to Cr₂O₇²⁻/H⁺ (or MnO₄⁻/H⁺).
 The solution turns from orange to green (or purple to colorless / pale pink) [No acidification: 0 mark]
OR It decolorizes petals temporarily.
OR It turns Br₂(aq) from brown / orange to colorless.
 1 mark for correct reagent and 1 mark for correct observation

(iii)



[1]

DSE18_03a

- (i) calcium (ion) / Ca²⁺ [1]
 (ii) Add Ba(NO₃)₂(aq) acidified with HNO₃(aq) to the sample, white precipitate forms for K₂SO₄(aq) whereas no precipitate will form for K₂SO₃(aq). [1]

[Accept other answers: 1 mark for the reagent and 1 mark for the observation]

Reagent	Observation
H ⁺ (aq) / acid	Only SO ₃ ²⁻ gives a gas, SO ₂ , with pungent smell
Cr ₂ O ₇ ²⁻ /H ⁺ (aq)	Only SO ₃ ²⁻ turns the solution from orange to green
MnO ₄ ⁻ /H ⁺ (aq)	Only SO ₃ ²⁻ turns the solution from purple to colorless
I ₂ (aq)	Only SO ₃ ²⁻ turns the solution from brown to colorless

Not accept Br₂ / Br₂(l)

DSE19_03a

3. (a) (i) • IR Peak at 2070 – 2250 cm⁻¹ corresponds to C≡C. 1
 • Relative molecular mass of 40.0 confirms it to be HC≡CCH₃. 1
- (ii) immiscible with water / low boiling point / easily evaporate 1
- (iii) • Heat with Tollen's reagent. 1
 • Only A gives silver mirror. 1

3. (a) (i) Heat the solid samples in a test tube and place a piece of anhydrous/dry cobalt chloride paper near the mouth of the tube. The anhydrous/dry cobalt chloride paper turns from blue to pink. The solid is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(s)$. The colour of cobalt chloride paper does not change for $\text{Na}_2\text{CO}_3(s)$.
(A comparative sense)
(OR)
Heat both samples.
Condensed liquid can only be found in $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(s)$.
(OR)
Heat both samples.
Only $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(s)$ will have condensed liquid that can turn anhydrous/dry copper(II) sulphate from white to blue.
(A comparative sense)
- (ii) From blue to colourless 1
- (iii) Hex-1-ene turns Br_2 (in organic solvent/aq) (not accept $\text{Br}_2(l)$) from reddish-brown to colourless but hexanal does not. (1)
(OR) (1)
Warm hexanal with Tollen's reagent. 1
It gives a silver mirror but hex-1-ene does not. 1
(A comparative sense)
(1 mark for the reagent and 1 mark for observation)
(Accept other possible chemical tests with comparative sense.
Hexanal :
 $\text{Cr}_2\text{O}_7^{2-}(\text{aq})/\text{H}^+(\text{aq})$: from orange to green but hex-1-ene does not
2,4-dinitrophenylhydrazine: a yellow / red / orange precipitate but hex-1-ene does not)
(Not accept)
Hex-1-ene :
 $\text{MnO}_4^-(\text{aq})/\text{H}^+(\text{aq})$: from purple to colourless)

DSE20_03c i

3. (c) (i) (1) orange to green 1
 $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(l)$ 1
- (2) Driver B has a higher ethanol intake because the breath can also change the colour of the gel in position c while Driver A cannot.
(A comparative sense and similar meaning)
- (3) (Exhale the) same amount / volume / strength of breath (into the tube). 1
- (ii) No. of mole of ethanol = $0.025 \times 4.38 \times 10^{-3} \times 3 = 0.0003285 \text{ mol}$ (0.00033 / 0.000329) 1*
Mass of the ethanol = 0.0003285×46 (x 46) 1*
= 0.01511 g = 15.11 mg
The mass of ethanol in 100 cm³ of serum sample = $15.11 \text{ mg} \div 10 \times 100$ (+10 x 100) 1*
= 151.1 mg
(The mass is) 151.1 mg (which exceeds 55 mg. The driver would be found) guilty. 1
(Range of answer: 150 – 152, max. 3 dec. places)

Separation and Purification Methods

AL97(I)_08

You are provided with a mixture of two liquids, hexan-1-amine (U) and ethyl ethanoate (W). Outline an experimental procedure, based on a solvent extraction process, to enable U to be separated from W.

(3 marks)

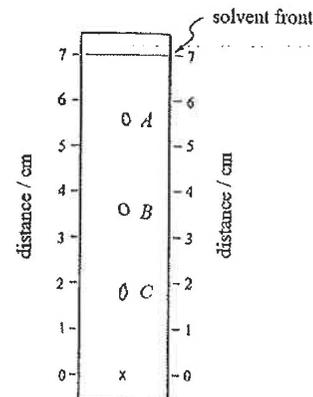
AL98(I)_08

You are provided with a mixture of two liquids, heptanoic acid and hexan-3-one. Outline an experimental procedure, based on a solvent extraction process, to isolate pure heptanoic acid in good yield.

(3 marks)

AL99(I)_02c

A mixture of amino acids, A, B and C, was separated by paper chromatography using an appropriate solvent. The chromatogram obtained is shown below:

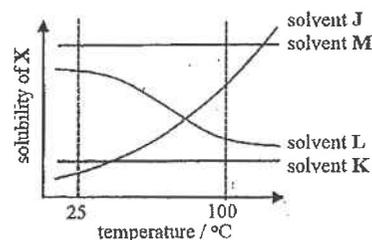


(x is the starting point of the mixture.)

- (i) Briefly describe the principle underlying the separation of A, B and C by paper chromatography. (2 marks)
- (ii) The amino acid spots are invisible to naked eyes. Suggest how to make them visible. (1 mark)
- (iii) Calculate the R_f value for A. (1 mark)

AL01(I)_08a

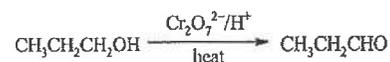
The graph shows the solubility curves of a solid organic compound X in four mutually miscible solvents J, K, L and M.



- (i) (I) Which solvent among J, K, L and M is the best for the recrystallization of X? (1 mark)
- (II) You are provided with a sample of X contaminated with some colored impurities. Outline the procedure to purify X by recrystallization. (3 marks)
- (ii) Decide which two of these solvents form the best solvent system for the recrystallization of X at 25°C. (1 mark)

AL01(I)_08b

In an experiment to prepare propanal from propan-1-ol,



a side-product N ($\text{C}_6\text{H}_{12}\text{O}_2$) was formed

- (i) What is N? Suggest how N is formed. (2 marks)
- (ii) Suggest one method to separate propanal from a mixture of propanal and N. (1 mark)
- (iii) Suggest two methods to confirm the identity of propanal. (2 marks)

ASL01(II)_11

2-chloro-2-methylpropane can be prepared by reacting 2-methylpropan-2-ol with concentrated hydrochloric acid.



This preparation consists of four stages as outlined below:

- Stage 1:* Add concentrated hydrochloric acid slowly into a vessel containing 2-methylpropan-2-ol while shaking until the acid is in excess.
- Stage 2:* Allow the mixture to settle into two layers. Separate the organic layer and add to it sodium hydrogencarbonate solution to neutralize the excess acid.
- Stage 3:* Transfer the organic layer obtained at the end of *Stage 2* into a conical flask. Add enough anhydrous sodium sulphate(VI) and swirl the flask.
- Stage 4:* Filter off sodium sulphate(VI) from the mixture obtained in *Stage 3*. Distil the filtrate and collect 2-chloro-2-methylpropane in the temperature range from 47°C to 53°C.

- (a) A turbid mixture is formed in *Stage 1*. Explain. (2 marks)
- (b) How can one know that the excess acid has been neutralized in *Stage 2*? (1 mark)
- (c) Why is anhydrous sodium sulphate(VI) used in *Stage 3*? State the expected observation at the end of this stage. (2 marks)
- (d) Draw a labelled diagram for the experimental set-up that is used in the distillation process in *Stage 4*. (2 marks)
- (e) The boiling point of 2-methylpropan-2-ol is 82°C. Explain why the boiling point of 2-methylpropan-2-ol is higher than that of 2-chloro-2-methylpropane. (1 mark)

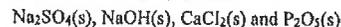
AL02(I)_08a

In an attempt to prepare 1-methylcyclopentene, 1-methylcyclopentanol was allowed to react with phosphoric(V) acid. The reaction mixture was then subjected to simple distillation, a side-product

- (i) Draw a labelled diagram to show the set-up of apparatus used in a simple distillation. (2 marks)
- (ii) Suggest a chemical test, giving the expected observation, to show the presence of an alkene in the distillate. (2 marks)
- (iii) The distillate was known to contain a small amount of unreacted 1-methylcyclopentanol. Suggest a method to separate it from the desirable product. (1 mark)
- (iv) Is 1-methylcyclopentene the only compound obtained after the suggested separation method in (iii)? Explain. (1 mark)

AL03(I)_08b

The following compounds can be used as drying agents:

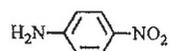


Choose, from the above, one compound which is most suitable and effective

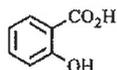
- (i) for drying a solution of $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ in CHCl_3 . (1 mark)
- (ii) for drying a moist solid sample of $\text{C}_6\text{H}_5\text{CO}_2\text{H}$. (1 mark)

AL03(II)_05

A student carried out an experiment to extract 4-nitrophenylamine and 2-hydroxybenzoic acid from a solution of the two compounds in ethoxyethane. The solution contained 1.5 g each of the compounds in 20 cm³ of ethoxyethane.



4-nitrophenylamine



2-hydroxybenzoic acid

The student shook the solution with 12 cm³ of 0.50 M $\text{NaHCO}_3(\text{aq})$ in a separating funnel. The mixture in the separating funnel was allowed to settle, and the aqueous layer was then separated from the organic layer. Evaporation of the aqueous layer gave a solid residue, which was water-soluble and had a melting point higher than 200 °C. Evaporation of the organic layer gave another solid residue, which melted over a wide temperature range of 140 °C to 160 °C.

- (a) Why was $\text{NaHCO}_3(\text{aq})$ used in the extraction? (1 mark)
- (b) While the student was shaking the separating funnel, the stopper of the funnel popped out, spilling part of the mixture on the bench. With the help of equation(s), explain why this happens. (2 marks)
- (c) Was the solid residue obtained from the organic layer a pure compound? Support your answer by stoichiometric calculation. (3 marks)
- (d) State TWO reasons why ethoxyethane is commonly used to extract organic compounds from an aqueous solution. (2 marks)
- (e) State ONE safety precaution necessary in the evaporation of ethoxyethane. (1 mark)

AL04(I)_08

- (a) A sample of N-phenylethanamide is contaminated with some colored impurities. Outline the procedures for the purification of this sample by recrystallization from water. (3 marks)
- (b) Draw a labelled diagram for the assembly of apparatus used in simple distillation. (2 marks)

97

AL04 (II)_03d

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

- (ii) Chile saltpetre also contains a small amount of sodium iodate(V), which is a source of iodine.
- (I) Suggest one way to isolate $\text{NaNO}_3(\text{s})$ from an aqueous solution of Chile saltpetre. (1 mark)
- (II) After removing $\text{NaNO}_3(\text{s})$ from an aqueous solution of Chile saltpetre, the $\text{NaIO}_3(\text{aq})$ that remains is divided into two parts. One part is treated with $\text{NaHSO}_3(\text{aq})$ to reduce $\text{NaIO}_3(\text{aq})$ to $\text{I}^-(\text{aq})$. The resultant mixture is then mixed with the unreacted part of $\text{NaIO}_3(\text{aq})$ to give iodine. Use equations to describe the conversion of NaIO_3 to I_2 in the above process. (2 marks)
- (III) Suggest one method that can be used to purify a sample of sodium iodine. (1 mark)

ASL04(II)_10

Preparation of benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$) involves heating methyl benzoate ($\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$) with excess sodium hydroxide solution under reflux for some time. The resultant mixture contains sodium benzoate and methanol.



- (a) Draw a labelled diagram for the set-up used for heating methyl benzoate with sodium hydroxide solution under reflux. (2 marks)
- (b) Suggest how a crude sample of benzoic acid can be obtained from the resultant mixture. (2 marks)
- (c) The crude sample of benzoic acid can be purified by recrystallization from hot water. Outline the procedures in the recrystallization process. (2 marks)
- (d) In an experiment, 3.0 g of methyl benzoate gave 1.9 g of benzoic acid. Calculate the percentage yield of benzoic acid. (2 marks)

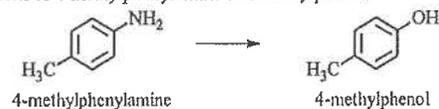
AL05(I)_07a

- (i) Draw a labelled diagram for the assembly of apparatus that you would use to determine the boiling point of propan-2-ol. (2 marks)
- (ii) Suggest one hazard warning label which should be displayed on a bottle of propan-2-ol. (1 mark)

98

AL05(I)_08c

Consider the conversion of 4-methylphenylamine to 4-methylphenol:



- (ii) The identity of the 4-methylphenol obtained can be confirmed from the melting point of its solid derivative.
With the help of an equation, suggest a derivative of 4-methylphenol that would be suitable for this purpose. (2 marks)
- (iii) Suggest a method to purify the derivative in (ii) for melting point determination. (1 mark)

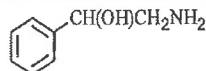
AL06(I)_08b

State a possible consequence from each of the following poor laboratory techniques:

- (i) draining the lower layer from a separating funnel without removing the stopper (1 mark)
- (ii) determining the melting point of a compound without completely removing the solvent after recrystallization. (1 mark)

AL06(II)_05b

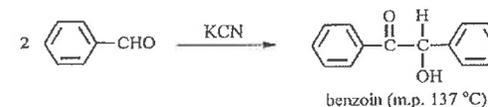
Compound B is a strong stimulant. Its structural formula is as follows:



- (i) It is known that among the two stereoisomers, only B has stimulant activity while the other one does not. Why? (1 mark)
- (ii) A person is suspected to have taken stimulant B. A urine sample of the person is sent for analysis. Suggest a method to establish whether B is present in the urine sample. (2 marks)

AL07(I)_08

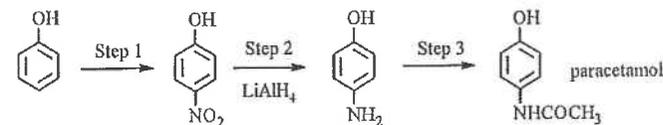
14.6 g of benzoin was obtained by heating 15.9 g of benzaldehyde with potassium cyanide in a solvent-free condition.



- (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)
- (d) Devise an experimental procedure to remove potassium cyanide from the crude product. (2 marks)
- (e) The benzoin obtained can be purified by recrystallization. Suggest three criteria for an appropriate solvent for the recrystallization. (3 marks)
- (f) Cyanide waste is usually treated with oxidizing agents. Explain whether acidified $\text{KMnO}_4(\text{aq})$ is suitable for such a purpose. (1 mark)

AL07(II)_07

Paracetamol is an over-the-counter analgesic drug. It can be synthesized from phenol in three separate steps as shown below:

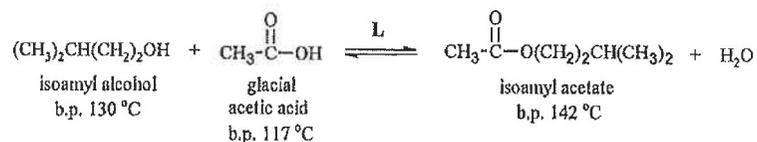


- (a) Consider Step 1.
(i) Give the reagent(s) used and the reaction conditions. (Out-of-syllabus) (1 mark)
- (ii) The reaction also gives 2-nitrophenol. The 4-nitrophenol formed can be separated from 2-nitrophenol by chromatography using powdered silica as the stationary phase, and a mixture of ethyl ethanoate and cyclohexane as the mobile phase.
Which of the two compounds, 2-nitrophenol or 4-nitrophenol, would move faster in this chromatography? Explain. (Partial out-of-syllabus) (3 marks)
- (b) Name the type of reaction for the transformation in Step 2. (1 mark)

- (c) For Step 3, give the reagent(s) used and the reaction conditions. (1 mark)
- (d) Outline the recrystallization procedure for the purification of a crude product of paracetamol by water. (3 marks)

ASL09(I)_04

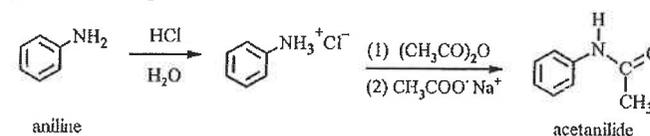
3-Methyl-1-butyl ethanoate, commonly known as isoamyl acetate, is a naturally occurring compound having a distinctive pleasant banana odor and is used in food flavoring. In an experiment to prepare the compound, 5.0 cm³ of isoamyl alcohol is allowed to react with 15.0 cm³ of glacial acetic acid in the presence of a reagent L.



- (a) Suggest what reagent L may be and give the reaction conditions for this preparation. (1 mark)
- (b) Calculate the mole ratio of isoamyl alcohol to glacial acetic acid used in this preparation. (Given: density of isoamyl alcohol = 0.81 g cm⁻³; density of glacial acetic acid = 1.05 g cm⁻³) (2 marks)
- (c) Draw a labelled diagram of the assembly of apparatus used in this preparation. (2 marks)
- (d) What are the major compounds present in the resulting mixture at the end of this preparation? (2 marks)
- (e) Outline the procedure to isolate isoamyl acetate from the resulting mixture. (It is known that isoamyl acetate cannot be effectively separated from the resulting mixture by fractional distillation.) (2 marks)
- (f) Suggest why isoamyl alcohol is NOT used in excess in this preparation. (1 mark)

ASL10(I)_10

Acetanilide (N-phenylethanamide) is a white solid. It can be synthesized from aniline (phenylamine) according to the reaction scheme:



- (a) The crude product from the above synthesis is collected by suction filtration. Draw a labelled diagram of the assembly of apparatus used. (2 marks)
- (b) The crude product appears yellow due to the presence of impurities. Outline the experimental procedure for the purification of the crude product by recrystallization from an ethanol-water mixture. (3 marks)
- (c) Suggest a method to verify or not the recrystallized sample of acetanilide is pure. (1 mark)

ASL10(II)_06

Caffeine is a component of many over-the-counter analgesics.



- (a) With reference to its structure, explain why caffeine is basic. (2 marks)
- (b) A brand of analgesic tablets contains aspirin, caffeine and a binder. The binder is insoluble in aqueous acids or alkalis, and in common organic solvents.



Outline an experimental procedure to isolate caffeine and aspirin separately from the tablets. (4 marks)

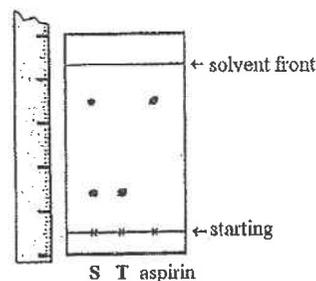
AL12 (I)_07

Outline how you would separate NH₄Cl(s), NaCl(s) and PbCl₂(s) from a mixture of the three compounds.

(3 marks)

AL12 (I)_08

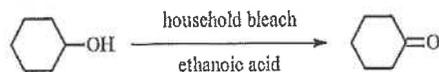
An aspirin sample **S** was contaminated with an organic base **T**. A thin layer chromatography with silica as the stationary phase and ethyl ethanoate as the mobile phase was conducted to analyze **S**. The result obtained is shown below:



- (a) (i) Calculate the R_f value of aspirin. (1 mark)
- (ii) Explain why aspirin and **T** have different R_f values. (1 mark)
- (b) Suggest how aspirin can be isolated from **S** without using chromatography. (2 marks)

ASL13(I)_09 (modified)

In an experiment to prepare cyclohexanone from cyclohexanol, a household bleach, containing 5.25% of sodium chlorate(I) by mass, was used as the oxidizing agent.



Density:	0.948 g cm ⁻³	0.947 g cm ⁻³
Solubility in water:	3.6 g / 100 cm ³	Very slightly soluble
Melting point:	25 °C	-16 °C
Boiling point:	160 °C	156 °C

5.0 cm³ of cyclohexanol and 3 cm³ of ethanoic acid were placed in a 250 cm³ conical flask. A 25 cm³ portion of the household bleach was added to the conical flask with vigorous stirring. Then additional 25 cm³ portions of bleach were successively added into the reaction mixture until all cyclohexanol had reacted.

- (a) (i) Assuming that the density of the household bleach is 1.0 g cm⁻³, calculate the molarity of NaClO in the bleach used. (Formula mass of NaClO = 74.5) (1 mark)

- (ii) Given that the mole ratio between cyclohexanol and NaClO is 1 : 1, calculate the minimum number of 25 cm³ portions of household bleach required for the complete reaction of cyclohexanol.

(Relative molecular mass of cyclohexanol = 100.0)

(2 marks)

- (b) What would be observed in the reaction mixture with the formation of cyclohexanone? (1 mark)
- (c) Suggest how chromatography can be used to show that all cyclohexanol has reacted. (1 mark)
- (d) You are provided with Na₂S₂O₃(aq) and NaHCO₃(aq). Outline the procedure for isolating cyclohexanone from the reaction mixture, and explain why these two chemicals are used. (3 marks)
- (e) Draw the experimental set-up for the purification of the cyclohexanone isolated in (d). (2 marks)

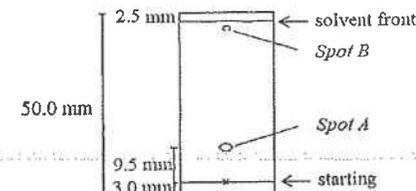
DSE12PP_03a

A colorless compound **X** (C₉H₈O₂) is obtainable from cinnamon. **X** has a melting point of 134 °C and is insoluble in water.

An experiment to extract **X** from an impure sample, which contains non-polar organic impurities, involves the following five steps:

Step 1:	Dissolve the sample in excess NaOH(aq).
Step 2:	Shake the solution from Step 1 with hexano and discard the organic layer.
Step 3:	Add HCl(aq) to the aqueous layer obtained until a white precipitate forms and the solution becomes acidic.
Step 4:	Collect the white precipitate by filtration.
Step 5:	Using ethanol as solvent, recrystallize the precipitate collected to obtain X .

- (i) From the above experimental steps, suggest ONE functional group present in **X**. (1 mark)
- (ii) Name the apparatus used in Step 2. (1 mark)
- (iii) Briefly explain the purpose of carrying out Steps 1, 2 and 3 respectively. (3 marks)
- (v) Another sample of **X** is contaminated with a colorless organic compound. The sample is analyzed by thin-layer chromatography (TLC), and the result is shown below:



- (1) Suggest ONE method that can be used to make the two spots on the chromatographic plate become visible. (1 mark)
- (2) Given that *Spot A* corresponds to X, calculate the R_f of X. (1 mark)
- (3) Based on the TLC results, suggest ONE method to separate X from the contaminated sample. (1 mark)

DSE13_03a

Outline how hex-1-ene can be obtained from a mixture of hex-1-ene, octane and water by physical methods.

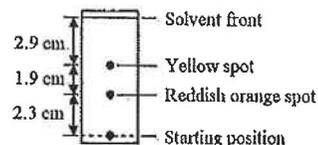
(Boiling points: hex-1-ene = 63°C, octane = 125°C, water = 100°C)

(4 mark)

DSE13_03c

The main pigments in a certain brand of tomato paste are lycopene (reddish orange) and β -carotene (yellow). In order to isolate lycopene from the tomato paste, an experiment involving solvent extraction, thin-layer chromatography (TLC) and column chromatography was performed.

(i) The result of TLC is shown below:



Calculate the R_f value for the lycopene spot.

(1 mark)

(ii) With reference to the result of TLC, explain whether the first-collected colored fraction in the column chromatography is lycopene or β -carotene, if the same stationary phase and mobile phase are used.

(1 mark)

DSE14_03a

Which of the following chemicals is most suitable for drying ethyl ethanoate?

Anhydrous magnesium sulphate, concentrated sulphuric acid, solid sodium hydroxide.

(1 mark)

DSE14_03c

Under room temperature, T ($C_8H_8O_2$) is a colorless oily liquid and is immiscible with water. Moreover, T does not react with $NaHCO_3(aq)$.

(i) A sample of T contains an organic acid as impurity. Outline the experimental steps for purifying the sample by using $NaHCO_3(aq)$ and pentane.

(2 marks)

DSE15_03a

Suggest how copper powder can be obtained from a mixture of copper powder and iron(III) oxide by chemical method.

(2 marks)

DSE16_03c

X and Y are isomeric compounds with their structures shown below:



(ii) The melting point of X is 50 °C while that of Y is 77 °C. Both of them are insoluble in water but soluble in dichloromethane. When treated with dilute $Na_2CO_3(aq)$, no reaction occurs for X but reaction occurs for Y to form a soluble salt.

(1) You are provided with dilute $Na_2CO_3(aq)$ and dilute $H_2SO_4(aq)$. Outline an experimental procedure, based on solvent extraction, to separate solid Y from a solution of X and Y in dichloromethane.

(4 marks)

(2) Suggest how you can identify that the solid obtained in (1) is pure compound Y.

(1 mark)

DSE17_03c

Many plants contain useful organic compounds which can be obtained by extraction using suitable solvents.

(i) The leaf of a certain plant contains a useful organic compound S. S can dissolve gradually in a warm organic solvent, and can be extracted from the leaves by using this solvent.

(1) 'Heating under reflux' is a method commonly used to carry out this kind of extraction. State the advantage of this method.

(1 mark)

(2) After extraction, the solvent can be removed from the extract by simple distillation. Draw a labelled diagram for the set-up required for this simple distillation.

(2 marks)

(3) S obtained from the extraction may contain other organic impurities. Suggest a method for separating S from these impurities.

(1 mark)

DSE18_03a

- (iii) What is meant by the 'R_f value' of a substance in a paper chromatogram? (2 marks)

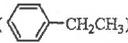
DSE18_03c

A liquid mixture consists of two organic compounds X and Y:

	X	Y
Molecular formula	C ₄ H ₆ O	C ₄ H ₈ O
Boiling point / °C	81.4	79.6

- (i) Explain why fractional distillation is NOT a suitable method to separate X from the mixture. (1 mark)

DSE19_03c i

3. (c) Chlorine reacted with ethylbenzene () under sunlight to give a mixture of different chlorinated compounds.

- (i) Thin layer chromatography (TLC) was used to separate a small amount of the mixture.
- (1) Explain briefly why chromatography can be used to separate a mixture.
- (2) Based on the result in TLC, suggest a method to separate a large amount of the mixture.

(3 marks)

DSE20_03b i ii iii

- (b) In order to determine the sodium contents (existing as NaCl) in a bacon sample, its Cl⁻ contents should first be found. 2.0 g of the bacon sample was added to 2.50 cm³ of 1.0 M AgNO₃(aq). After that, excess dilute HNO₃(aq) was added to the mixture obtained. The AgCl(s) formed was then removed by filtration. The excess AgNO₃(aq) remaining in the filtrate was then titrated with 0.10 M KSCN(aq) to give AgSCN(s) in the presence of a suitable indicator until the end point was reached. All steps were repeated several times and the mean volume of the KSCN(aq) used to reach the end point was 9.42 cm³.

- (i) Why was excess dilute HNO₃(aq) added to the mixture? (1 mark)
- (ii) Draw a diagram for the set-up to be used in the titration, labelling all apparatus and reagents. (2 marks)
- (iii) Assuming that all Cl⁻ comes from NaCl in the bacon sample, calculate the percentage by mass of sodium in the bacon sample. (Relative atomic masses: Na = 23.0, Cl = 35.5, Ag = 107.9) (4 marks)

Working Scheme

1. (i) (1) Add ether solvent (1) (1)
(2) Shake in a separating funnel (1) (1)
(3) Lower layer will contain CH₂BrCH₂Br (1) (1)
(4) Shake the upper layer with excess NaOH(aq) (1) (1)
(5) and then extract with ether. The ether layer will contain CH₃CH₂Br (1) (1)

1. (ii) (1) Add ethanolic silver nitrate solution / silver nitrate (1) (1)
(2) Shake in separating funnel (1) (1)
(3) Ether layer contains bromine. Lower layer contains CH₃CH₂Br (1) (1)
(4) Add dilute NaOH(aq) to separate layer (1) (1)
(5) Shake with ether (1) (1)
(6) Wash ether to obtain bromoethane (1) (1)

1. (iii) (1) Touch a thin film of water on the chromatography paper. (1) (1)
(2) The solid acids distribute themselves between the stationary phase (water on the paper) and the moving phase (the solvent / alcohol). (1) (1)
(3) A has a highest solubility in the moving phase, so its motion is fastest. (1) (1)
(4) C has the lowest solubility in the moving phase, so its motion is slowest. (1) (1)

1. (iv) (1) Spray chromatography paper with suitable reagent which reacts with various acids to give purple-colored compounds. (1) (1)
(2) Alternatively using UV radiation / iodine paper to detect the organic acid spots. (1) (1)
(3) $\frac{2.0}{20} = 0.1$ (Range: 0.77 to 0.83) (1) (1)

1. (v) (1) Add dilute HNO₃ (1) (1)
(2) Add water-soluble NaCl until it just dissolves. (1) (1)
(3) Shake with a red litmus changed to orange-red color. (1) (1)
(4) Filter solution to remove chemical particles. (1) (1)
(5) Reduce solution to cool to room temperature. Transfer filtrate in the flask with a spatula. (1) (1)
(6) Calculate X by formula. (1) (1)

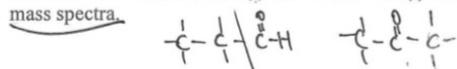
1. (vi) (1) Add NaOH (1) (1)
(2) Add water-soluble NaCl until it just dissolves. (1) (1)
(3) Shake with a red litmus changed to orange-red color. (1) (1)
(4) Filter solution to cool to room temperature. Transfer filtrate in the flask with a spatula. (1) (1)
(5) Calculate X by formula. (1) (1)
(6) Add NaOH (1) (1)
(7) Add water-soluble NaCl until it just dissolves. (1) (1)
(8) Shake with a red litmus changed to orange-red color. (1) (1)
(9) Fractional distillation / chromatography (1) (1)

Answer ALL parts of the question.

3. (a) Answer the following short questions :

(i) Suggest a chemical test to show how $\text{SO}_2(\text{g})$ and $\text{CO}_2(\text{g})$ can be distinguished. (2 marks)

(ii) Illustrate how $\text{CH}_3\text{CH}_2\text{CHO}(\text{l})$ and $\text{CH}_3\text{COCH}_3(\text{l})$ can be distinguished from their respective mass spectra. (2 marks)



(iii) Which one of the following chemicals is the most suitable for drying ethyl butanoate?
concentrated sulphuric acid, solid sodium hydroxide, anhydrous sodium sulphate (1 mark)

(b) A solid sample consists of a compound Y and a small amount of an impurity Z. The following steps were performed in an experiment to obtain pure Y(s) from this solid sample.
(Given : Y is more soluble in deionised water at 80 °C than at 25 °C.)

Step (1) : 1.40 g of this solid sample was added to 50 cm³ of deionised water and heated to 80 °C.

Step (2) : Water-insoluble activated charcoal was then added to remove Z. The mixture obtained was filtered when it was still hot.

Step (3) : The hot filtrate obtained was allowed to cool slowly to 25 °C. Y(s) was formed.

Step (4) : The cooled mixture was filtered to collect Y(s). After washing and drying, 0.75 g of Y(s) was collected.

(i) It is given that no more than 3.04 g of Y(s) can dissolve in 100 cm³ of deionised water at 80 °C. Show, by calculation, that all of Y in this solid sample should have dissolved in Step (1). (1 mark)

(ii) Explain why the mixture was filtered in Step (2). (1 mark)

(iii) Name the process of the formation of Y(s) in Step (3). (1 mark)

(iv) Suggest one reason why the mass of Y(s) collected in Step (4) was smaller than the mass of Y in this solid sample. (1 mark)

(v) Y and Z can be separated by chromatography. Thin layer chromatography (TLC) and column chromatography were performed separately with this solid sample using the same stationary phase and mobile phase.
(Given : R_f value of Y is greater than that of Z.)

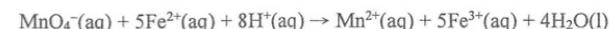
(1) Sketch a labelled chromatogram of TLC to show the expected result.

(2) Explain whether the first-collected fraction in the column chromatography is Y or Z. (3 marks)

(c) The major ingredient in a certain brand of iron supplement tablets is FeSO₄. Several pieces of these iron supplement tablets were dissolved in deionised water to obtain an aqueous solution S. The concentration of $\text{Fe}^{2+}(\text{aq})$ ions in solution S was determined by using the following two methods :

(i) **Method (I) : using volumetric analysis**

The chemical equation for the reaction involved in the titration is as follows :



25.00 cm³ of solution S was acidified and then titrated with 0.0041 M $\text{KMnO}_4(\text{aq})$. The mean volume of the $\text{KMnO}_4(\text{aq})$ required to reach the end point was 32.35 cm³.

(1) The colour of the reaction mixture changed from pale yellow to pale pink at the end point of the titration. Explain the colour change.

(2) Calculate the concentration of $\text{Fe}^{2+}(\text{aq})$ ions in solution S. (4 marks)

(ii) **Method (II) : using colorimetry**

$\text{Fe}^{2+}(\text{aq})$ can completely react with a colourless organic reagent to form an orange-red species W(aq).

(Given : number of moles of $\text{Fe}^{2+}(\text{aq})$ reacted : number of moles of W(aq) formed = 1 : 1)

Step (1) : Several standard $\text{FeSO}_4(\text{aq})$ solutions of various concentrations were separately treated with the colourless organic reagent to form the corresponding orange-red solutions of W(aq).

Step (2) : The absorbances of these solutions of W(aq) were measured using a colorimeter and a calibration curve was plotted.

Step (3) : Solution S was diluted 100 times. A sample of this diluted solution was treated in the same way as described in Step (1) to give a solution T which contains W(aq).

Step (4) : The absorbance of solution T was measured.

(1) Sketch the calibration curve in Step (2) and label the axes. On this sketch, show how the concentration of W(aq) in solution T can be found.

(2) Hence, suggest how the concentration of Fe²⁺(aq) ions in solution S can be determined. (4 marks)

MARKING SCHEME

Q10) What is meant by the 'forward' of a reaction in a paper chromatogram? (2 marks)

DEEDR 104

A liquid mixture consists of two organic compounds X and Y.

	X	Y
Molecular formula	C_4H_8O	$C_4H_8O_2$
Boiling point / °C	81.3	76.6

Q1) Explain why fractional distillation is NOT a suitable method to separate X from the mixture. (1 mark)

DEEDR 104a

Q2) The liquid mixture is analysed using ^{13}C -NMR. The spectrum is given below in Figure 1. (2 marks)

Q3) The liquid chromatography (L.C.) method is used to separate a small amount of the mixture. (1 mark)

Q4) Explain how the chromatography can be used to separate the mixture. (2 marks)

Q5) Refer to the result in L.C. suggest a method to separate a large amount of the mixture. (1 mark)

DEEDR 104a (ii)

Q6) In order to separate the mixture mixture (boiling at 80°C) in a liquid mixture, the mixture should first be heated to 80°C and the lower boiling component is 40°C and 60°C. Explain why that mixture will be separated. (2 marks)

Q7) Why was excess $NaOH(aq)$ added to the mixture? (1 mark)

Q8) Draw a diagram for the setup to be used for the reaction. Label the apparatus and reagents. (2 marks)

Q9) Suggest the full name of the compound from the chromatography. Justify the percentage by mass of carbon in the compound. (2 marks)

Marking Scheme

AL97(I)_08
 Add ether and dil HCl [1]
 Shake in a separating funnel [½]
 Ether layer will contain $CH_3CO_2C_2H_5$ [½]
 Basify the aqueous layer with excess $NaOH(aq)$ [½]
 and then extract with ether. The ether layer will contain $CH_3(CH_2)_5NH_2$. [½]

AL98(I)_08
 Add ether and dilute $NaHCO_3(aq)$ / $Na_2CO_3(aq)$. [1]
 Shake in a separating funnel. [½]
 Ether layer contains hexan-3-one; aqueous layer contains $CH_3(CH_2)_5COONa$. [½]
 Add dilute HCl to aqueous layer generate $CH_3(CH_2)_5COOH$. [½]
 Extract with ether. [½]
 Distill ether to obtain heptanoic acid. [½]

AL99(I)_02c
 (i) There is a thin film of water on the chromatography paper. [½]
 The amino acids distribute themselves between the stationary phase (water on the paper) and the moving phase (the solvent / eluent) [1]
 A has the highest solubility in the moving phase. ∴ Its motion is fastest. [½]
 OR, C has the lowest solubility in the moving phase. ∴ Its motion is slowest. [½]
 (ii) Spray chromatography paper with ninhydrin solution which reacts with amino acids to give purple-colored compounds. [1]
 (Also accept using UV radiation / iodine vapor to detect the amino acid spots.)
 (iii) $R_f = \frac{5.6}{7.0} = 0.8$ (Range: 0.77 to 0.83) [1]

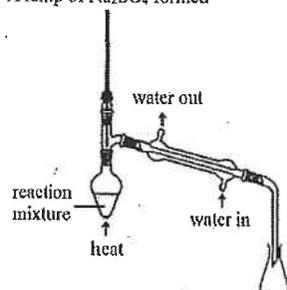
AL01(I)_08a
 (i) (I) J [1]
 (II) Add warm solvent J to X until X just dissolves. [½]
 Heat with activated charcoal to remove colored impurities [1]
 Filter when hot to remove charcoal particles [½]
 Allow solution to cool to room temperature / scratch filtrate in the flask with a spatula. [½]
 Collect X by filtration [1]
 (ii) J and M [1]

AL01(I)_08b
 (i) propyl propanoate / $CH_3CH_2COOCH_2CH_2CH_3$ [1]
 Some propan-1-ol was oxidized to propanoic acid which reacts with excess propen-1-ol to give the ester [1]
 (ii) Fractional distillation / chromatography [1]

- (iii) Any TWO of the following: [2]
- boiling point determination
 - Treat propanal with 2,4-dinitrophenylhydrazine / Brady's reagent, then determine the m.p. of the crystals formed.
 - Compare IR spectrum (finger print) of the propanal with that of an authentic sample.
 - Compare mass spectrum (finger print) of the propanal with that of an authentic sample.
 - Compare the H-NMR of the propanal with that of an authentic sample.

ASL01(H)_11

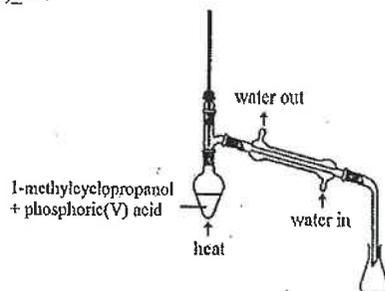
- (a) Product $(\text{CH}_3)_2\text{CCl}$ is insoluble (immiscible) in the mixture of $(\text{CH}_3)_2\text{COH}$ and $\text{HCl}(\text{aq})$. [1]
After shaking, an emulsion is formed which decrease the light transmittance. [1]
- (b) Add $\text{NaHCO}_3(\text{aq})$ until no gas bubble formed. [1]
- (c) To absorb water in the organic layer. [1]
A lump of Na_2SO_4 formed [1]
- (d) [2]



- (e) Both of them are simple molecule, while 2-methylpropan-2-ol molecules are held by strong hydrogen bond, while 2-chloro-2-methylpropane molecules are held by weak van der Waals' force. [1]

AL02(I)_08a

- (i) [2]



- (ii) Treat distillate with Br_2 in an appropriate solvent (e.g. CCl_4 or water). [1]
Observation: orange color of Br_2 solution changes to colorless. [1]
OR, Treat distillate with neutral KMnO_4
Observation: a brown precipitate is formed.
- (iii), Fractional distillation [1]
- (iv) No, the product contains another alkene such as [1]



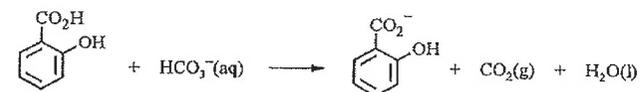
- OR, Gas chromatography
Yes, different compounds have different retention times.
 \therefore pure 1-methylcyclopentene can be isolated.

AL03(I)_08b

- (i) $\text{Na}_2\text{SO}_4(\text{s})$ [1]
- (ii) $\text{Na}_2\text{SO}_4(\text{s}) / \text{CaCl}_2(\text{s}) / \text{P}_2\text{O}_5(\text{s})$ [1]

AL03(II)_05

- (a) To convert 2-hydroxybenzoic acid to the carboxylate salt which is soluble in water. [1]
- (b) Carbon dioxide is formed. [1]



Pressure therefore builds up inside the separating funnel. [1]

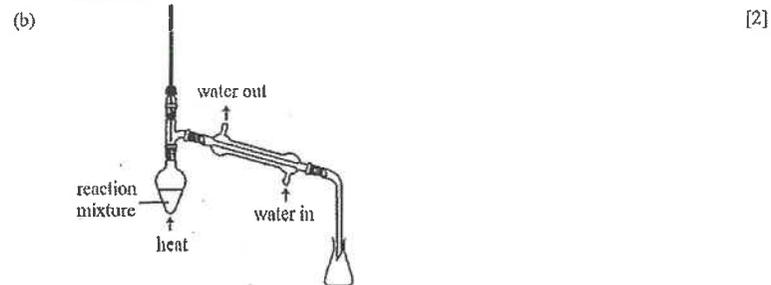
OR, Ethoxyethane is highly volatile. Vaporization of ethoxyethane leads to the building up of pressure in the funnel.



- (c) no. of mole of 2-hydroxybenzoic acid = $\frac{1.5}{138} = 0.011$ [1]
no. of mole of $\text{NaHCO}_3 = 0.5 \times 12 \times 10^{-3} = 6 \times 10^{-3}$ [1]
no. of mole of 2-hydroxybenzoic acid > no. of moles of NaHCO_3
(0.011 - 0.006) = 0.005 mol of 2-hydroxybenzoic acid will remain in the organic layer. The residue is therefore not a pure compound. [1]
- (d) Any TWO of the following: [2]
Ethoxyethane has a small dipole moment. It is a good solvent for most organic compounds.
Ethoxyethane is immiscible with water.
Ethoxyethane is volatile. It can easily be removed by distillation.
Ethoxyethane is chemically unreactive.
- (e) Avoid naked flame / extraction should be carried out in a fume cupboard. [1]

AL04(I)_08

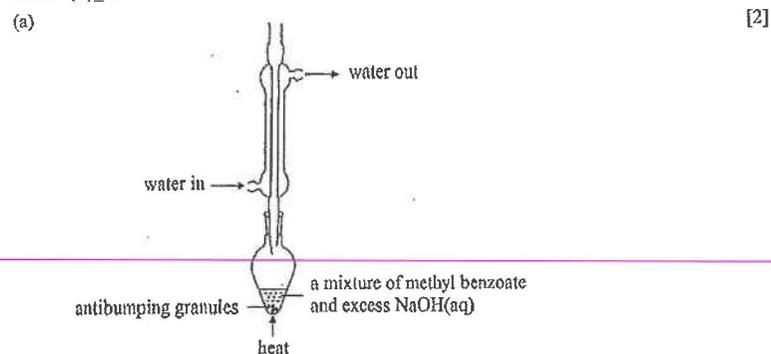
- (a) Dissolve *N*-phenylethanamide in minimum volume of hot water. [1]
Heat the solution with activated charcoal. [1]
Filter the mixture while hot using a short stem funnel. [½]
 Allow filtrate to cool to room temperature. Collect *N*-phenylethanamide crystal by filtration. [½]



AL04 (II)_03d

- (ii) (I) Fractional crystallization [1]
 (II) $\text{IO}_3^- + 3\text{HSO}_3^- \rightarrow \text{I}^- + 3\text{SO}_4^{2-} + 3\text{H}^+$ [1]
 $5\text{I}^- + \text{IO}_3^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$ [1]
 (III) Sublimation [1]

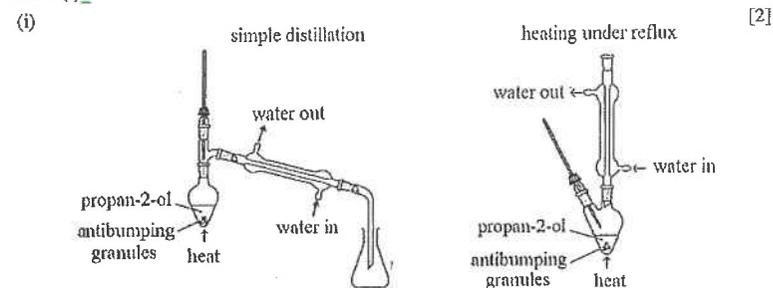
ASL04(II)_10



- (b) Add $\text{H}_2\text{SO}_4(\text{aq})$ and filter [1]
 (c) Dissolve crude sample in minimum amount of hot water. [1]
 Filter mixture while hot. [1]
 Allow filtrate to cool and collect crystals by filtration. [1]

- (d) no. of moles of methyl benzoate = $\frac{3.0}{136.0} = 0.022$ [½]
 no. of moles of benzoic acid = $\frac{1.9}{122.0} = 0.0156$ [½]
 $\% \text{ yield} = \frac{0.0156}{0.022} \times 100\% = 70.8\%$ [1]

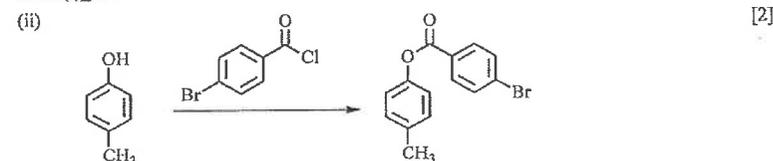
AL05(I)_07a



(1 M for a correct set-up and showing the bulb of the thermometer is slightly above the liquid level, 1 M for labels)

- (ii) Flammable [1]

AL05(I)_08c



- (iii) Recrystallization [1]

AL06(I)_08b

- (i) Without releasing the pressure, the liquid in the separating funnel will not drain out of the funnel. [1]
 (ii) The m.p. determined will be lower than the expected value. [1]

AL06(II)_05b

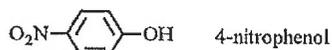
- (i) The neuroreceptor is likely to be chiral. The reaction between compound B and the neuroreceptor is stereospecific. [1]
 (ii) Conduct a chromatographic study. [1]
 Compare the R_f value of the suspected stimulant with that of an authentic sample of B. [1]

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 following: [1]
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.
- (d) Extract benzoin with an appropriate organic solvent, such as ethoxyethane. [1]
Wash the organic layer with water to remove KCN. [1]
- (e) THREE of the following: [3]
1. Benzoin should have a high solubility in the solvent while the impurities should not.
 2. The solubility of benzoin in the solvent should be high at elevated temperature but low at room temperature.
 3. The solvent should be volatile.
 4. The solvent should not react with benzoin.
- (f) No. CN⁻ reacts with H⁺ to give toxic HCN. [1]

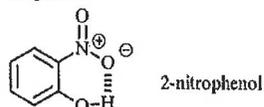
AL07(II)_07

- (a) (i) Diluted HNO₃; temperature <20 °C (stir reaction mixture for 2 hours). [1]
(accept conc. HNO₃ / mixture of conc. HNO₃ and conc. H₂SO₄)
- (ii) 2-nitrophenol moves faster [1]



4-nitrophenol has a large dipole moment and has a greater affinity for the polar silica / form intermolecular hydrogen bonds only, it has stronger attraction for silica. [1]

Intramolecular hydrogen bond occurs in 2-nitrophenol, but not in 4-nitrophenol. [½]



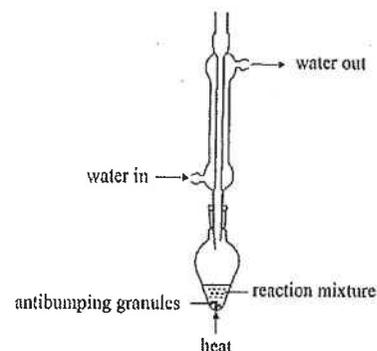
2-nitrophenol is less polar and is more soluble in organic solvent (i.e. the mobile phase). [½]

- (b) Reduction [1]
- (c) CH₃COCl; at room temperature / warm. (Formation of amide) [1]

- (d) Dissolve the sample in minimum amount of hot water. [1]
Filter, when hot, to remove any insoluble impurities. [1]
Allow the saturated solution to cool slowly and collect crystals of paracetamol by filtration. [1]

ASL09(I)_04

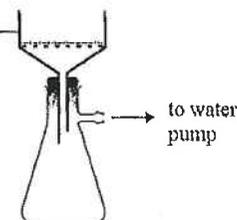
- (a) Concentrated H₂SO₄ / conc. H₃PO₄ / P₄O₁₀ [½]
Reflux [½]
- (b) no. of moles of isoamyl alcohol = $\frac{5.0 \times 0.81}{88} = 0.046$ [1]
no. of moles of acetic acid = $\frac{15.0 \times 1.05}{60} = 0.26$ [½]
Mole ratio of isoamyl alcohol : acetic acid = 1 : 5.7 [½]
- (c) [2]



- (d) Isoamyl acetate; acetic acid; water [1]
- (e) Shake mixture with NaHCO₃(aq) in a separating funnel until no more gas is evolved. [1]
Extract isoamyl acetate from the organic layer using ethoxyethane (diethyl ether). [½]
Remove ethoxyethane (diethyl ether) by simple distillation. [1]
(f) It is difficult to remove isoamyl alcohol from isoamyl acetate as both substance do not react with alkali / their difference in boiling point is small. [1]

ASL10(I)_10

- (a) Buchner funnel [1]



- (b) Dissolve the crude product in minimum volume of hot ethanol-water mixture. [1]
 Heat the solution with activated charcoal (to remove the color impurities). [1]
 Filter the hot mixture (using a short-stem funnel). [½]
 Allow the filtrate to cool to room temperature to obtain acetanilide. [½]
- (c) Any ONE of the following: [1]
 1. Determine the melting point of the product and compare the result with literature data.
 2. Use the method of mixed melting point.

ASL10(II)_06

- (a) Caffeine has amine / imine functional group. [1]
 The lone pair on the N atoms can readily be donated to H⁺(aq) to form salt. [1]
- (b) (use mortar and pestle to) grind analgesic tablets into fine powder. [½]
 Add CH₂Cl₂ (any appropriate organic solvent) to dissolve caffeine and aspirin. [½]
 Remove the (undissolved) binder by filtration. [½]
 Add NaOH(aq) to filtrate. Aspirin will react to give a salt and dissolve in the aqueous layer. [½]
 Using a separating funnel, separate the organic layer from the aqueous layer. (Dry the organic layer with MgSO₄(s).) [½]
 Remove CH₂Cl₂ from organic layer by simple distillation to obtain caffeine. [½]
 Add acid (HCl(aq)) dropwise to the aqueous layer (to pH~3) to regenerate aspirin. [½]
 Cool the mixture and then filter to obtain aspirin. [½]
 (1.5 marks for removing binder; 1.5 marks for isolation of the first ingredient; 1 mark for the second ingredient.)

AL12 I (7)

- Heat the mixture. Only NH₄Cl(s) will sublime. [1]
 It can be collected on a cold surface. [½]
 Add water to the remaining solid mixture. [½]
 PbCl₂(s) is insoluble. It can be collected by filtration. [½]
 NaCl(s) can be obtained from its solution by filtration. [½]
 OR, Add water to the mixture to dissolve NaCl(s) and NH₄Cl(s). [½]
 Remove undissolved PbCl₂(s) by filtration.
 Separate NaCl(s) and NH₄Cl(s) from the solution by fractional crystallization / by (ion-exchange) chromatography.

AL12 (I)_08

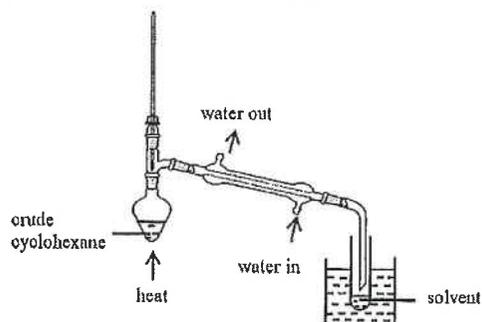
- (a) (i) $R_f = \frac{30}{38} = 0.79$ [1]
 (ii) Any one of the following: [1]
 - Aspirin is more soluble in ethyl ethanoate than T.
 - T adsorbs more strongly to the stationary phase than aspirin does.
 - Aspirin and T distribute differently between the stationary phase and the mobile phase.
- (b) Dissolve the sample in an organic solvent such as CH₂Cl₂. [½]
 Extract the solution obtained with an aqueous alkaline solution (e.g. NaOH / Na₂CO₃ / NaHCO₃). [½]
 Collect the aqueous layer / decant the organic layer. [½]
 Add HCl(aq) to the aqueous layer to regenerate aspirin and then collect the aspirin formed by filtration. [½]
 OR, Dissolve the sample in an organic solvent such as CH₂Cl₂.
 Extract the solution obtained with an aqueous acid (e.g. HCl).
 Collect the organic layer / decant the aqueous layer.
 Obtain aspirin from the organic layer by crystallization.

ASL13(I)_09

- (a) (i) $\text{Molarity of NaClO} = \frac{5.25 \times 1000}{74.5 \times 100} = 0.705 \text{ M}$
 (acceptable range: 0.70 to 0.71 M) [1]
- (ii)  [1]
 $\text{no. of moles of cyclohexanol used} = \frac{5.0 \times 0.948}{100} = 0.0474$ [½]
 $\text{no. of mole of NaClO in } 25 \text{ cm}^3 \text{ of bleach} = 0.705 \times 25 \times 10^{-3} = 0.0177$ [½]
 $\text{Minimum no. of portions of bleach used} > \frac{0.0474}{0.0177} = 3$ [½]
- (b) Two immiscible layers / turbid / cloudy [1]
- (c) Use TLC / GC / other appropriate chromatographic methods. Disappearance of the characteristic absorption peak for cyclohexanol indicates that all cyclohexanol has been reacted. [1]
- (d) Using a separating funnel, separate the aqueous layer from the organic layer (upper layer). [½]
 Shake the organic layer with Na₂S₂O₃(aq) and collect the upper / organic layer. [1]
 Na₂S₂O₃(aq) reacts with excess NaClO(aq). [½]
 Shake the collected organic layer with NaHCO₃(aq) until no more gas evolves from the mixture. [½]
 NaHCO₃(aq) reacts with the CH₃COOH in the mixture. [½]

(e) Diagram (simple distillation / fractional distillation)

[2]



DSE12PP_03a

- (i) Carboxylic acid / carboxyl group (because X is soluble in NaOH(aq)) [1]
(Also accept phenol).
- (ii) Separating funnel [1]
- (iii) Step 1: Allow X to dissolve in NaOH(aq) to give (carboxylate) anions / a salt. [1]
Step 2: Allow the non-polar impurities to dissolve in hexane while the (carboxylate) anions / salt to stay in the aqueous layer. [1]
OR, Separate the non-polar impurities (in hexane) from the salt of X.
Step 3: Regenerate the (carboxylic) acid (which is insoluble in water) by adding acid. [1]
- (v) (1) Put the chromatographic plate into a jar that is saturated with iodine vapor. The spot will appear brown. [1]
OR, Irradiate the plate with UV. The stationary phase is fluorescent while the two spots are not.
(2) $R_f = \frac{\text{distance travelled by X}}{\text{distance travelled by solvent}} = \frac{9.5}{(50 - 3 - 2.5)}$ [1]
 $R_f = 0.21$ [1]
(3) Column chromatography (using the same moving phase and stationary phase) [1]

DSE13_03a

- Use separating funnel to remove water (the lower liquid layer) from the mixture. [1]
The remaining upper / organic layer (remaining in the funnel) is hex-1-ene and octane. [1]
Carry out fractional distillation / distillation on the upper layer. [1]
The first distilled collected is hex-1-ene. The second distillate collected is octane. [1]

DSE13_03c

- (i) $R_f = \frac{2.3}{2.3 + 1.9 + 2.9} = \frac{2.3}{7.1} = 0.32$ [1]

(Accept also 0.324 and 0.3239 BUT NOT 0.3)

- (ii) β -Carotene [1]
Lycopene has a smaller R_f value / lycopene moves slower. [1]
Lycopene takes a longer time to reach the bottom of the column.

DSE14_03a

(anhydrous) magnesium sulphate [1]

DSE14_03c

- (i) Dissolve the sample in pentane and shake the solution with NaHCO₃(aq) in a separating funnel. [1]
Collect the organic layer and carry out fractional distillation / distillation. [1]
[Only fractional distillation / distillation: 0 mark]

DSE15_03a

- Add dilute HCl(aq) / dilute H₂SO₄(aq) / very dilute HNO₃(aq) to the mixture (for dissolving the Fe₂O₃). [1]
Collect the copper powder from filtering the mixture obtained. [1]

DSE16_03c

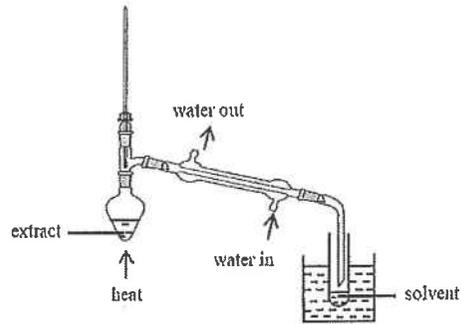
- (ii) (1) • Na₂CO₃(aq) is added to the dichloromethane solution of X and Y. [1]
• The mixture is shaken in a separating funnel. [1]
The mixture in the separating funnel is allowed to settle, and the aqueous layer was then separated from the organic layer.
• Dilute H₂SO₄(aq) is added to the aqueous layer / upper layer / lower aqueous layer / (until no more precipitate is formed.) / (the solution becomes acidic). [1]
• Solid Y can be obtained by filtration. [1]
- (2) Measure the melting point of the solid obtained. [1]
If the melting point of the solid is 77°C / a sharp m.p. measured / a narrow melting point range, it may be pure compound Y. [1]
(mixed melting point technique → sharp melting point / m.p. 77 °C;
OR compare the IR spectrum / mass spectrum / NMR spectrum of the solid obtained with that of authentic sample, if they are identical → pure
OR run a TLC / paper chromatography for the sample; if only one spot is detected on the chromatogram → pure)

DSE17_03c

- (i) (1) The solvent / product will not lose due to heating. [1]

DSE20_3b

(2)



[2]

1 mark for correct experimental set-up, 1 mark for correct labels
 Experimental set-up: 0 mark for closed system, wrong position of thermometer / delivery tube etc.
 [Accept: No cold water to condense the solvent.]
 1 mark for labelling heat, water in and water out

(3) (column) chromatography / thin layer chromatography / TLC / GCMS [1]

DSE18_03a

(iii) 'R_f value' of a substance is the ratio between the migration distance of the substance and the migration distance of the solvent front during chromatography. [2]
 1 mark: indicating ratio; 1 mark: other parts correct
 Can be represented by labelled diagram indicating 2 distances and correct mathematical expression.

DSE18_03c

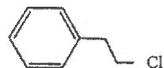
(i) Boiling points of X and Y are too close. [1]

DSE19_03c

(c) (i) (1) • Different substances have different adsorptivity to the stationary phase. 1
 • They have different solubility in mobile phase. 1

(2) column chromatography 1

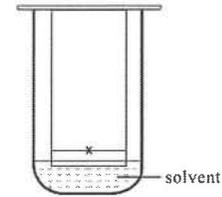
(ii) The chemical species for the peak at m/z = 91 may be C₆H₅CH₂⁺. 1
 The chemical species for the peak at m/z = 140 may be C₆H₅CH₂CH₂³⁵Cl⁺. 1
 (or m/z = 142 may be C₆H₅CH₂CH₂³⁷Cl⁺)
 Possible structure :



(iii) (1) High levels of dioxins may cause cancer. 1

(2) Modern instrumentation is accurate and sensitive enough to measure very low levels of dioxins. 1

(b) (i)



2

(1 mark for labelling: solvent
 1 mark for the drawing: pencil line above solvent, spot of mixture, TLC plate and a container)

(ii) $R_f = 45 / (130 - 10 - 20) = 0.45$ 1
 (Only mark the answer.)

(iii) Aspirin and Caffeine 1

(iv) (1) IR spectrum of Aspirin shows (strong absorption) peak at 2500 (cm⁻¹) to 3300 (cm⁻¹) / corresponding to O-H group of carboxylic acid while that of caffeine does not. 1
 (A comparative sense)

(2) m/z = 43 corresponds to a CH₃CO⁺ ion. 1

(Accept CH₃CO⁺
 Not accept CH₃CO⁺, CH₃CO)
 Both aspirin and acetaminophen have this fragment, only this information cannot help confirm which one of the three chemicals the sample is.

Quantitative Analysis

AL96(I)_04c

In a titration experiment, a H_2O_2 solution was diluted 25 times. 25 cm^3 of the diluted H_2O_2 solution, in the presence of excess dilute H_2SO_4 , required 26.45 cm^3 of 0.00995 M KMnO_4 solution for titration.

- (i) Describe, with experimental details, how you would dilute the H_2O_2 solution. (3 marks)
- (ii) Write a balanced equation for the reaction involved in the titration. (1 mark)
- (iii) Describe the color change at the end point of the titration. (1 mark)
- (iv) Calculate the molarity of the diluted H_2O_2 solution. (2 marks)
- (v) What reagent would be used to standardize the KMnO_4 solution in this experiment? (1 mark)

AL96(I)_04d

In an experiment to determine the concentration of H_2O_2 contained in a rainwater sample, 5.0 cm^3 of the sample were mixed with an excess of a certain transition metal complex solution, giving a colored mixture. The absorbance of the mixture was measured by a colorimeter and was found to be 0.0273. When 5.0 cm^3 of $1.46 \times 10^{-6} \text{ M H}_2\text{O}_2$ (instead of the rainwater sample) were treated in the same way, an absorbance of 0.0398 was recorded.

- (i) Calculate the concentration of H_2O_2 in the rainwater sample assuming that concentration is directly proportional to absorbance. (2 marks)
- (ii) Why is the method of titration not suitable for the determination of the concentration of H_2O_2 in the rainwater sample? (1 mark)
- (iii) Why is it not suitable to collect the rainwater sample for this experiment in an iron container? (1 mark)

AL98(I)_07 [Similar as DSE13]

The sulphur dioxide content in white wine was determined by an experiment described below:

1. 25.0 cm^3 of a sample of white wine was transferred to a conical flask
 2. 15 cm^3 of 1 M NaOH(aq) was added to the flask and the mixture was allowed to stand for 15 minutes.
 3. 15 cm^3 of $2 \text{ M H}_2\text{SO}_4\text{(aq)}$ was added to the flask and the resulting solution was quickly titrated with $0.0050 \text{ M I}_2\text{(aq)}$.
 4. 12.9 cm^3 of the $\text{I}_2\text{(aq)}$ was required to reach the titration end point.
- (a) What is the purpose of adding the $2 \text{ M H}_2\text{SO}_4\text{(aq)}$? (1 mark)

- (b) Why should the titration be carried out quickly? (1 mark)
- (c) Briefly describe how the end point of the titration can be determined. (2 marks)
- (d) Calculate the sulphur dioxide content, in mg dm^{-3} , in the sample of white wine. (2 marks)

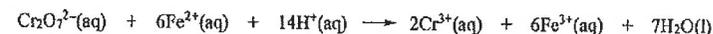
AL00(I)_03

In a titration experiment, 25.00 cm^3 of acidified $\text{FeSO}_4\text{(aq)}$ required 32.15 cm^3 of $0.0203 \text{ M K}_2\text{Cr}_2\text{O}_7\text{(aq)}$ for complete reaction.

- (a) Write a balanced equation for the reaction involved. (1 mark)
- (b) Calculate the concentration, in mol dm^{-3} , of the $\text{FeSO}_4\text{(aq)}$. (2 marks)

ASL00(I)_03

The waste water from an electroplating factory contains chromium in the form of dichromate(VI) ions. In order to remove chromium from the waste water, green vitriol, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, was first added to reduce the dichromate(VI) ions to chromium(III) ions:



The chromium(III) ions formed were then precipitated as hydroxide.

- (a) Suggest ONE reason why it is necessary to remove chromium from the waste water. (1 mark)
- (b) A sample of the waste water of volume $1.0 \times 10^5 \text{ dm}^3$ contains $1.2 \times 10^{-4} \text{ mol dm}^{-3}$ of dichromate(VI) ions. Calculate the minimum mass of green vitriol required in the waste water treatment process. (3 marks)
- (c) Suggest an appropriate reagent for the precipitation reaction. (1 mark)
- (d) Name TWO chemicals present in the precipitate formed. (2 marks)

ASL00(II)_12 [Similar as DSE13]

Sulphur dioxide is used to preserve wines. In an experiment to determine the sulphur dioxide content of a white wine, 25.00 cm^3 of a sample of the wine was titrated against 0.00480 M iodine solution. 14.80 cm^3 of the iodine solution was required to reach the end point.

- (a) Explain why sulphur dioxide can be used to preserve wines. (1 mark)
- (b) In the titration, sulphate(VI) ions and iodide ions were formed. Using two half equations, establish the overall equation for the reaction involved. (2 marks)

- (c) What indicator should be used in the titration? State the color change of the indicator at the end point.
(2 marks)
- (d) Calculate the concentration of sulphur dioxide, in mg dm^{-3} , in the sample of white wine.
(2 marks)

ASL00(HI)_13 [Similar as DSE18]

A brand of mould-killer contains sodium chlorate(I) as the active ingredient. In an experiment to determine the sodium chlorate(I) content, 25.00 cm^3 of the mould-killer was treated with excess potassium iodide solution in the presence of an acid. The iodine liberated was then titrated against 0.680 M sodium thiosulphate solution, 31.10 cm^3 of the sodium thiosulphate solution was required to reach the end point.

- (a) Write chemical equations for
- the reaction of sodium chlorate(I) with potassium iodide solution under acidic condition, and
(1 mark)
 - the reaction of iodine with sodium thiosulphate solution.
(1 mark)
- (b) What indicator should be used in the titration? State the color change of the indicator at the end point.
(2 marks)
- (c) Calculate the concentration of sodium chlorate(I), in g dm^{-3} , in the sample of mould-killer.
(3 marks)

ASL01(I)_03

In an experiment to determine the percentage by mass of iron in an iron wire, 0.160 g of a sample of the iron wire was added to 50 cm^3 of 2 M sulphuric(VI) acid. The solution obtained was then titrated against 0.0215 M potassium manganate(VII) solution. 24.30 cm^3 of the potassium manganate(VII) solution was required to reach the end-point.

- (a) What would be observed when the iron wire was added to the sulphuric(VI) acid?
(1 mark)
- (b) Write the ionic equation for the reaction taking place during the titration. Hence, calculate the percentage by mass of iron in the sample of the iron wire.
(4 marks)
- (c) Suggest how the end-point of the titration can be detected.
(1 mark)

ASL01(I)_07

Office paper contains calcium carbonate (up to 50%) as an additive to enhance its brightness, whiteness and opacity. Devise an experiment to estimate the percentage by mass of calcium carbonate in a sample of office paper.

(4 marks)

AL01(II)_01

A standard iodine solution was prepared by dissolving 0.953 g of $\text{KIO}_3(\text{s})$ in excess $\text{KI}(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ and then making up the solution to 250.0 cm^3 .

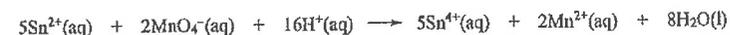
- (a) Why are standard iodine solutions not prepared directly from solid iodine?
(1 mark)
- (b) Calculate the molarity of the standard iodine solution.
(2 marks)
- (c) 25.00 cm^3 of the standard iodine solution was titrated against $0.0981 \text{ M Na}_2\text{S}_2\text{O}_3(\text{aq})$, 27.25 cm^3 of the $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ was required to reach the end-point.
- Deduce the stoichiometry of the reaction of $\text{I}_2(\text{aq})$ with $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$, and write a balanced equation for the reaction.
(3 marks)
 - Suggest an appropriate indicator for the titration and state the color change at the end-point.
(1 mark)

AL02(I)_07

An experiment was carried out to determine the percentage by mass of tin in a sample of bronze, an alloy of copper and tin:

15.03 g of the finely divided sample was warmed with excess 1 M sulphuric acid to convert all the tin to tin(II) sulphate(VI). The mixture was filtered to remove copper which did not undergo reaction. The colorless filtrate was then diluted to 250 cm^3 with deionized water. Four portions of the diluted tin(II) sulphate(VI) solution, each of volume 25.00 cm^3 , were titrated against 0.0205 M potassium manganate(VII) solution. The titres were 23.90 cm^3 , 23.35 cm^3 , 23.40 cm^3 and 23.35 cm^3 .

The equation for the reaction involved in the titration is as follows:



- (a) Describe how the end point of the titration can be detected.
(1 mark)
- (b) Calculate the reasonable volume of titre used in this titration.
(1 mark)
- (c) Calculate the percentage by mass of tin in the sample of bronze.
(3 marks)

ASL02(II)_10 [Similar as DSE15]

A chemist carried out an experiment to determine the percentage by mass of nitrogen in a sample of nitrogenous fertilizer, which contained ammonium ions as the only source of nitrogen. The experiment consisted of three stages:

Stage 1: 1.64 g of the sample was dissolved in deionized water and then made up to 250.0 cm³.

Stage 2: 25.00 cm³ of this solution was heated with 25.00 cm³ of 0.105 M sodium hydroxide solution until no more ammonia gas was evolved.

Stage 3: The resultant solution was titrated against 0.123 M hydrochloric acid. 10.80 cm³ of the acid was required to reach the end point.

- (a) Write a chemical equation for the reaction that occurred in *Stage 2*.
(1 mark)
- (b) Suggest a suitable indicator for the titration in *Stage 3*. State the color change at the end point.
(2 marks)
- (c) Calculate the percentage by mass of nitrogen in the sample.
(5 marks)

AL03(I)_01 modified

Phosphoric acid, H₃PO₄(aq), a weak acid, ionizes in three stages to give H₂PO₄⁻(aq), HPO₄²⁻(aq) and PO₄³⁻(aq).

- (a) Write an chemical equations to show the stepwise formation of H₂PO₄⁻(aq), HPO₄²⁻(aq) and PO₄³⁻(aq).
(3 marks)
- (b) Explain why the ability of phosphoric acid to dissociate H⁺(aq) in each step progressively decreases.
(1 mark)
- (c) Sketch the expected pH titration curve when H₃PO₄(aq) is titrated with NaOH(aq).
(3 marks)

ASL03(II)_12 (I)

An experiment, consisting of the following two stages, was carried out to determine the content of ascorbic acid in a sample of grapefruit juice.

Stage 1: Excess KI(aq) and H₂SO₄(aq) were added to 100.0 cm³ of 0.0240 M KIO₃(aq). The mixture was then diluted to 250.0 cm³ using deionized water to give a standard iodine solution.

Stage 2: 25.0 cm³ portions of the grapefruit juice were titrated against the standard iodine solution. The mean titre was 18.0 cm³.

- (a) The reaction in *Stage 1* can be represented by the following equation:

$$\text{IO}_3^-(\text{aq}) + 5\text{I}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 3\text{I}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
 Calculate the molarity of the standard iodine solution prepared.

(2 marks)

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- (b) Suggest how the end point of the titration in *Stage 2* can be detected.
(2 marks)
- (c) The reaction of ascorbic acid, C₆H₈O₆(aq), with iodine can be represented by the following equation:

$$\text{C}_6\text{H}_8\text{O}_6(\text{aq}) + \text{I}_2(\text{aq}) \longrightarrow \text{C}_6\text{H}_6\text{O}_6(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq})$$
 Calculate the mass of ascorbic acid in 1.0 dm³ of the sample of grapefruit juice.
(3 marks)
- (d) Ascorbic acid is used as a preservative in packaged fruit juice. Suggest how ascorbic acid works.
(1 mark)

ASL03(II)_12 (II) [Similar as DSE18]

A sample of household bleach contains sodium chlorate(I) as the active ingredient. An experiment, consisting of the following three stages, was carried out to determine the concentration of sodium chlorate(I) in a sample of the bleach.

Stage 1: 25.0 cm³ of the sample of bleach was diluted to 250.0 cm³ with deionized water.

Stage 2: 25.0 cm³ of the diluted sample was transferred to a conical flask. Excess KI(aq) and H₂SO₄(aq) were then added.

Stage 3: The mixture in *Stage 2* was titrated against 0.105 M Na₂S₂O₃(aq). 18.0 cm³ of Na₂S₂O₃(aq) was required to reach the end point.

- (a) Outline the procedure for diluting the sample of bleach in *Stage 1*.
(2 marks)
- (b) Write a chemical equation for the reaction in *Stage 2*.
(1 mark)
- (c) Suggest how the end point of the titration in *Stage 3* can be detected.
(2 marks)
- (d) Calculate the concentration of sodium chlorate(I), in g dm⁻³, in the sample of bleach.
(3 marks)

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AL04(I)_07

A student proposed a method to determine the concentration of citric acid in a sample of lemon juice by titration with standard sodium hydroxide solution. The method proposed consists of the following experimental procedures:

1. Prepare a standard sodium hydroxide solution by dissolving a known mass of sodium hydroxide pellets in deionized water and then make it up to 250.0 cm³.
2. Transfer a known volume of the sample of lemon juice to a clean conical flask.
3. Fill a burette, which has been well rinsed with deionized water beforehand, with the standard sodium hydroxide solution.
4. Titrate the lemon juice in the flask with sodium hydroxide solution using methyl orange as the indicator.
5. Using this titration result, calculate the concentration of citric acid in the sample.

Point out four inappropriate practices in the method. Explain why they are inappropriate and suggest corrections for them.

(6 marks)

AL04(II)_04 [Similar as DSE11SP]

- (a) Under acidic conditions, ethanol reacts with dichromate(VI) ions quantitatively to give ethanoic acid and chromium(III) ions.

Write an equation for the reaction of ethanol with dichromate(VI) ions under acidic conditions.

(1 mark)

- (b) In an experiment to determine the concentration of ethanol in a brand of spirit, 10.0 cm³ of a sample of the spirit was diluted to 250.0 cm³. 25.0 cm³ portions of the diluted spirit were withdrawn. To each portion, 25.0 cm³ of 0.156 M K₂Cr₂O₇(aq) and excess dilute H₂SO₄(aq) were added. The mixtures obtained were allowed to stand at room temperature for about an hour. The excess K₂Cr₂O₇ in each mixture was then titrated against 0.118 M (NH₄)₂Fe(SO₄)₂(aq) with an appropriate indicator. The mean titre was 12.23 cm³.

Calculate the concentration of ethanol, in mol dm⁻³, in this brand of spirit.

(4 marks)

ASL04(II)_08 [Similar as DSE118]

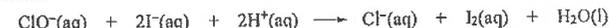
Household bleach contains NaClO as the active ingredient. In an experiment to determine the concentration of NaClO in a brand of household bleach, a sample of the bleach was diluted 50 times using deionized water. To 25.00 cm³ of the diluted bleach, excess KI(aq) and H₂SO₄(aq) were added. The mixture was then titrated against 0.0552 M Na₂S₂O₃(aq). 16.00 cm³ of the Na₂S₂O₃(aq) was required to reach the end point.

- (a) Describe how the sample of bleach can be diluted using apparatus available in a school laboratory.

(3 marks)

- (b) Suggest how the end point of the titration can be detected. (2 marks)

- (c) The reaction of ClO⁻(aq) with I⁻(aq) under acidic conditions can be represented by the equations:



From the titration result, calculate the concentration of ClO⁻(aq), in mol dm⁻³, in this brand of bleach.

(3 marks)

AL05(II)_01

X is a trivalent metal. When treated with hydrochloric acid, X(s) gives hydrogen, while its oxide X₂O₃(s) undergoes neutralization.

- (a) Write the chemical equation for the reaction of X(s) with HCl(aq) and that of X₂O₃(s) with HCl(aq).

(2 marks)

- (b) 16.5 g of a mixture of X(s) and X₂O₃(s) is allowed to react with 6.0 M HCl(aq). 95.4 cm³ of the acid is required for both the metal and its oxide to undergo complete reaction.

Deduce respectively the greatest possible value and the smallest possible value of the relative atomic mass of X.

(4 marks)

- (c) With reference to the Periodic Table, deduce what X may be.

(1 mark)

ASL05(II)_11

An experiment was carried out to determine the amount of K₂Cr₂O₇ required to oxidize the organic matter present in a water sample. This provides an indication of the extent of organic pollution of the sample. The experiment consists of the following two stages:

Stage 1: 2.50 cm³ of 0.0100 M K₂Cr₂O₇(aq) and excess H₂SO₄(aq) were added to 100.0 cm³ of the sample. The mixture was heated under reflux until all the organic matter it contained was oxidized to CO₂(g) and H₂O(l). The resultant mixture was then allowed to cool to room temperature.

Stage 2: The unreacted K₂Cr₂O₇ in the resultant mixture was titrated against 0.0124 M (NH₄)₂Fe(SO₄)₂(aq). 7.60 cm³ of the (NH₄)₂Fe(SO₄)₂(aq) was required to reach the end point.

- (a) Draw a labelled diagram of the set-up used for heating the mixture under reflux in *Stage 1*. (2 marks)

- (b) Write an ionic equation for the reaction which occurred in *Stage 2*. (1 mark)

- (c) Calculate the number of moles of K₂Cr₂O₇ required to oxidize all of the organic matter present in 1.0 dm³ of the sample.

(4 marks)

AL06(I)_02

Hard water contains $Mg^{2+}(aq)$ and $Ca^{2+}(aq)$ ions.

- (a) Name a mineral that provides $Ca^{2+}(aq)$ ions in hard water. (1 mark)
- (b) An experiment as described below was carried out to determine the total hardness in a sample of hard water.

"50.0 cm^3 of the sample was allowed to pass through an ion-exchange column, in which the metal ions present in the sample were totally exchanged by hydrogen ions. The eluent collected required 15.0 cm^3 of 0.020 $mol\ dm^{-3}$ $KOH(aq)$ for complete neutralization."

Assuming that the metal ions present in the sample are $Mg^{2+}(aq)$ and $Ca^{2+}(aq)$ only, calculate the total hardness, in $mol\ dm^{-3}$, of the sample.

(2 marks)

AL06(II)_07

The extent of oxidation of an oil can determined by iodometric analysis.

In a typical experiment, 4.85 g of a sample of oil is treated with excess $KI(aq)$ and $H_2SO_4(aq)$. The iodine liberated required 21.20 cm^3 of 0.012 $mol\ dm^{-3}$ $Na_2S_2O_3(aq)$ for complete reaction.

Given that when treated with acidified $KI(aq)$, 1 mol of peroxide liberates 1 mol of I_2 , calculate the number of moles of O_2 absorbed per kg of the oil.

(3 marks)

ASL06(II)_09c

A student carried out an experiment to determine the percentage by mass of iron in an iron wire. A sample of 0.212 g of the iron wire was added to 100 cm^3 of 2 M sulphuric acid. The solution obtained was then titrated against 0.0208 M potassium manganate(VII) solution. 34.70 cm^3 of the potassium manganate(VII) solution was required to reach the end-point.

- (i) Write the ionic equation for the reaction taking place during the titration. (1 mark)
- (ii) Calculate the percentage by mass of iron in the iron wire sample. (3 marks)
- (iii) State one assumption for the experiment. (1 mark)
- (iv) Could hydrochloric acid be used instead of sulphuric(VI) acid in this experiment? Explain your answer. (1 mark)

AL07(I)_07

- (a) What is meant by 'primary standard' in titrimetric analysis? (1 mark)
- (b) Give one reason why each of the following chemicals is not used as a primary standard.
- (i) liquid bromine (1 mark)
- (ii) potassium hydroxide pellets (1 mark)

ASL07(II)_03

In an experiment to determine the percentage by mass of copper in a sample of copper ore, 3.00 g of the sample was warmed with excess $HNO_3(aq)$ to convert all copper-containing substances to $Cu^{2+}(aq)$ ions. The resulting solution was boiled to remove all nitrogen oxides formed. Upon cooling, the solution was diluted to 250.0 cm^3 . 25.00 cm^3 of the diluted solution was withdrawn and then treated with excess $KI(aq)$ to liberate $CuI(s)$ and $I_2(aq)$. The titration of the $I_2(aq)$ liberated required 25.80 cm^3 of 0.102 M $Na_2S_2O_3(aq)$.

- (a) Write chemical equation for
- (i) The reaction of $Cu^{2+}(aq)$ and $I^- (aq)$, and (1 mark)
- (ii) The reaction of $I_2(aq)$ with $Na_2S_2O_3(aq)$. (1 mark)
- (b) Calculate the percentage by mass of copper in the sample of copper ore. (3 marks)
- (c) State one assumption made in the experiment. (1 mark)

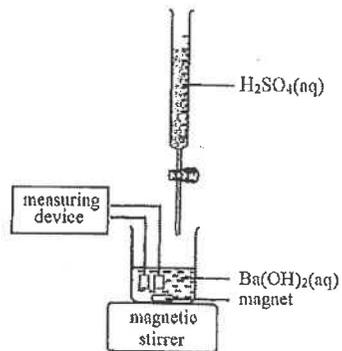
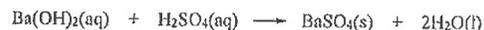
ASL09(II)_03

In an experiment to determine the relative atomic mass of magnesium, 0.420 g of magnesium ribbon was added to 25.0 cm^3 of 0.955 $mol\ dm^{-3}$ $H_2SO_4(aq)$. When effervescence ceased, the resulting mixture was diluted to 250.0 cm^3 with deionized water. 25.0 cm^3 portions of the diluted solution were withdrawn and titrated against 0.0941 $mol\ dm^{-3}$ $NaOH(aq)$ using methyl orange as indicator. The mean titre was 16.48 cm^3 .

- (a) State the color change at the end point of the titration. (1 mark)
- (b) Based on the titration results, calculate the relative atomic mass of magnesium. (4 marks)
- (c) Assuming that the experimental error is negligible, suggest ONE reason why the relative atomic mass of magnesium calculated in (b) is different from that found in the Periodic Table. (1 mark)

AL10(I)_07

The diagram on the right shows the set-up of a titrimetric experiment involving the following reaction:



- (a) What physical parameter of the reaction mixture is measured by this set-up? (1 mark)
- (b) $\text{H}_2\text{SO}_4(\text{aq})$ is added gradually to $\text{Ba(OH)}_2(\text{aq})$ until in excess. Sketch a graph to show the variation of measured physical parameter with the volume of $\text{H}_2\text{SO}_4(\text{aq})$ added. Explain your answer. (2 marks)

AL11(I)_01

A water-soluble solid sample A contains iron(II) ions. The percentage by mass of iron(II) ions in A can be determined from the experimental data listed below:

25.00 cm³ of 0.0326 mol dm⁻³ Na₂C₂O₄(aq), after acidification, requires 24.35 cm³ of a certain KMnO₄(aq) for complete reaction.

An aqueous solution of 0.863 g of A, after acidification, requires 31.85 cm³ of the same KMnO₄(aq) for complete reaction.

- (a) Write chemical equations for the above two reactions. (2 mark)
- (b) Calculate the percentage by mass of iron(II) ions in A. (Assume that A does NOT contain any other species that react with KMnO₄(aq).) (3 marks)
- (c) Suggest why KMnO₄(s) is NOT used as a primary standard. (1 mark)

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AL12(I)_07

Iodine-thiosulphate titrations involve the following reaction and the use of starch indicator.

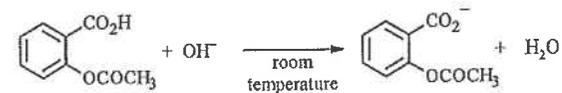


Suggest why

- (a) starch indicator is only added near the end-point, and (1 mark)
- (b) such titrations are NOT carried out under strongly acidic conditions. (1 mark)

AL12(I)_08

A commercial aspirin sample U was known to contain about 90% by mass of aspirin, while the rest was an inert binder. Based on the following reaction, a student designed an experiment and performed it at room temperature to determine the percentage by mass of aspirin in U.



The student added 2.25 g of U to 25.00 cm³ of 3.05 mol dm⁻³ NaOH(aq), and then back titrated the excess NaOH(aq) with 2.50 mol dm⁻³ HCl(aq). The volume of HCl(aq) used was 23.10 cm³.

- (a) Suggest an indicator for the titration. (1 mark)
- (b) From the student's experimental results, calculate the percentage by mass aspirin in U. Suggest why the calculated percentage by mass of aspirin deviated greatly from 90%. (relative molecular mass of aspirin = 180.0) (4 marks)
- (c) Suggest ONE improvement to the design of the experiment to find the percentage by mass of aspirin in U. (1 mark)

AL12(II)_01

Metal M forms a water-soluble bromide MBr₂. The following gravimetric analysis experiment was conducted to determine the formula mass of MBr₂.

A solution of MBr₂ was prepared by dissolving 0.400 g of MBr₂(s) completely in deionized water. The solution was acidified with HNO₃(aq) and then treated with excess AgNO₃(aq). The AgBr(s) formed was separated from the mixture by filtration, washed and dried. Its mass was found to be 0.816 g.

- (a) Given that the cation of M in MBr₂ does NOT react with Ag⁺(aq) ions, calculate the formula mass of MBr₂. (3 marks)
- (b) Calculate the relative atomic mass of M, and deduce what M is. (2 marks)

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- (c) M also forms a water-soluble fluoride MF₂. Can the formula mass of MF₂ be determined by gravimetric analysis using AgNO₃(aq) as the precipitating agent? Explain. (1 mark)

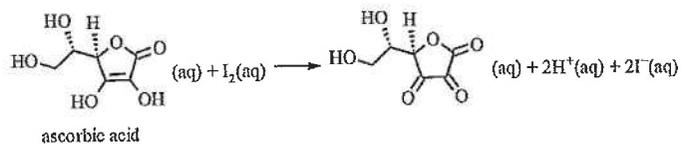
ASL13(II)_01

Orange juice contains ascorbic acid, also known as vitamin C. The following titrimetric experiment was conducted to estimate the amount of ascorbic acid in a sample of orange juice:

A standard iodine solution was prepared by dissolving 2 g of KI(s) in 100.0 cm³ of 0.0100 mol dm⁻³ KIO₃(aq), adding in 25 cm³ of 1 mol dm⁻³ H₂SO₄(aq) and then making up the resulting solution to 250.0 cm³ with deionized water.

Several aliquots of 25.00 cm³ of the sample of orange juice were titrated with the standard iodine solution. The mean titre was 7.60 cm³.

- (a) (i) Write the chemical equation for the reaction of KIO₃ with KI under acidic conditions. (1 mark)
- (ii) Suggest why the standard iodine solution was NOT prepared by weighing a sample of I₂(s) and then dissolving it in a known volume of KI(aq). (1 mark)
- (iii) Calculate the concentration of the standard iodine solution prepared. (1 mark)
- (b) Suggest how the end point of the above titration can be detected. (2 marks)
- (c) The reaction of I₂(aq) with ascorbic acid can be represented by the following equation:



- (i) From the titration results, calculate the mass of ascorbic acid in 100.0 cm³ of this sample of orange juice. (Relative molecular mass of ascorbic acid = 176.0) (3 marks)
- (ii) State ONE assumption in this experiment. (1 mark)

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DSE11SP_03b [Similar as AL04]

In an experiment to determine the concentration of ethanol in a brand of spirit, 10.0 cm³ of a sample of the spirit was diluted to 250.0 cm³. 25.0 cm³ portions of the diluted spirit were withdrawn. To each portion, 25.0 cm³ of 0.156 M K₂Cr₂O₇(aq) and excess dilute H₂SO₄ were added. The mixtures obtained were allowed to stand at room temperature overnight. The excess K₂Cr₂O₇ in each mixture was then titrated against 0.118 M (NH₄)₂Fe(SO₄)₂(aq) with an appropriate indicator. The mean titre was 12.23 cm³.

- (i) Write an equation for the reaction of ethanol with dichromate ions under acidic condition. (1 mark)
- (ii) Give TWO properties of (NH₄)₂Fe(SO₄)₂ rendering it to be used as primary standard in volumetric analysis. (2 marks)
- (iii) Suggest a method to test whether the oxidation of ethanol has been completed. (2 marks)
- (iv) Calculate the concentration of ethanol, in mol dm⁻³, in this brand of spirit. (5 marks)

DSE12PP_03b [OUT, for reference]

The percentage by mass of barium (Ba) in a barium salt can be determined by gravimetric method. In one such experiment, 0.305 g of a sample a barium salt was dissolved completely in about 100 cm³ of deionized water. Excess dilute sulphuric acid was then added to the solution to precipitate out barium sulphate. After filtration and appropriate treatment, the barium sulphate was found to have a mass of 0.291 g.

- (i) State TWO necessary treatment on the filtered barium sulphate precipitate before its mass is determined. (2 marks)
- (ii) Calculate the percentage by mass of barium in the sample. (3 marks)
- (iii) State TWO conditions under which gravimetric method is suitable for quantitative analysis. (2 marks)

DSE12_03c [OUT, for reference]

An aqueous solution only contains HCl(aq) and HI(aq). Based on the fact that AgCl(s), but not AgI(s), can dissolve in excess NH₃(aq), you are required to plan a gravimetric analysis to determine the mole ratio of Cl⁻(aq) to I⁻(aq) in the solution.

- (i) Suggest TWO reagents, other than deionized water, that should be used in the analysis. (2 marks)
- (ii) Outline the experimental steps involved in the analysis. (4 marks)
- (iii) Outline the steps in the calculation of the mole ratio of Cl⁻(aq) to I⁻(aq) in the solution using the data obtained from (ii) above. (2 marks)

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DSE13_03b [Similar as AL98, ASL00]

Both white wine and red wine contain SO₂ preservative which is fixed in different forms. A volumetric analysis experiment was performed to determine the total concentration of SO₂ in a sample of white wine. In the experiment, 25.00 cm³ of the wine sample was transferred to a conical flask. Following certain stipulated procedure, NaOH(aq) and H₂SO₄(aq) were successively added to the flask to liberate all SO₂ from the wine. The resultant solution was immediately titrated with 0.00412 mol dm⁻³ I₂(aq) using freshly prepared starch solution as indicator. The experiment was repeated several times, and the mean volume of I₂(aq) required to reach the end point was 10.50 cm³.

- (i) A reaction must fulfill certain conditions in order that it can be used in volumetric analysis. State ONE such condition. (1 mark)
- (ii) Explain why the resultant solution needed to be titrated immediately. (1 mark)
- (iii) State the expected color change at the end point of the titration. (1 mark)
- (iv) The chemical equation for the reaction involved in the titration is as follows:
$$\text{SO}_2(\text{aq}) + \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{HI}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq})$$

Calculate the total concentration of SO₂(aq), in mg dm⁻³, in the white wine sample. (4 marks)
- (v) Explain whether the total concentration of SO₂ in a sample of red wine can be determined in such an experiment. (1 mark)

DSE14_03b [OUT, for reference]

A powdered limestone sample mainly consists of CaCO₃, and a small amount of MgCO₃ and FeCl₃. The following steps were performed in an experiment to determine the percentage of CaCO₃ by mass in the sample.

- Step 1: 2.025 g of the limestone sample was added to excess amount of 6 M HCl(aq).
- Step 2: The mixture obtained was gently heated until no signs of further reaction. It was then allowed to cool to room temperature
- Step 3: The cooled mixture was diluted with distilled water, and made slightly alkaline by adding NH₃(aq) to precipitate the Fe³⁺(aq) ions present.
- Step 4: The mixture obtained was filtered to collect the filtrate.
- Step 5: Excess ammonium oxalate solution, (NH₄)₂C₂O₄(aq), was added to the filtrate, and the mixture obtained was then made slightly alkaline by using NH₃(aq) to selectively precipitate the calcium oxalate formed.
- Step 6: The mixture was filtered. After washing and drying, 2.374 g of calcium oxalate solid was collected.

- (i) Why is it necessary to heat the mixture in Step 2? (1 mark)
- (ii) (1) How does one know when the reaction involved in Step 2 has been completed? (1 mark)

- (2) State the observation in Step 3. (1 mark)
- (iii) It is given that magnesium oxalate is soluble in alkaline solutions but calcium oxalate is not. Calculate the percentage of CaCO₃ by mass in the limestone sample. (3 marks)
- (iv) State the quantitative analysis method used in this experiment. (1 mark)

DSE15_03c [Similar as ASL02]

An experiment consisting of the following four steps was performed to determine the amount of nitrogen in a milk powder sample:

- Step (1): 3.00 g of the milk powder sample was heated with excess concentrated sulphuric acid so as to turn all nitrogen in it into (NH₄)₂SO₄(aq).
- Step (2): The reaction mixture obtained was heated with excess NaOH(aq) to liberate NH₃(g). All NH₃(g) liberated was then absorbed by 50.00 cm³ of 1.00 M HCl(aq).
- Step (3): The solution formed was diluted to 250.0 cm³ with deionized water.
- Step (4): 25.00 cm³ portions of the diluted solution were titrated with 0.100 M KOH(aq) using methyl orange as an indicator. An average of 13.55 cm³ of the KOH(aq) was required to reach the end point.

- (i) Write the chemical equations for the following reactions in Step (2):
- (1) The reaction of (NH₄)₂SO₄(aq) with NaOH(aq) (1 mark)
- (2) The reaction of NH₃(g) with HCl(aq) (1 mark)
- (ii) State the color change at the end point of the titration in Step (4). (1 mark)
- (iii) Calculate the percentage by mass of nitrogen in the milk powder sample. (4 marks)
- (iv) In finding out the protein content in a milk powder sample, a common method is to determine the amount of nitrogen, but not to directly determine the amount of protein in the sample. Suggest one limitation of this common method. (1 mark)

DSE16_03a

Given one property of solid sodium hydroxide making it NOT suitable to be weighed for preparing a standard solution.

(1 mark)

DSE16_03b

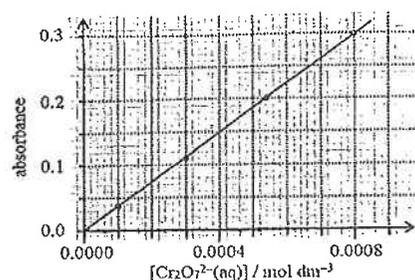
The concentration of a $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ sample A was determined by volumetric analysis; while the concentration of another $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ sample B was determined by colorimetry.

- (i) 25.00 cm^3 of sample A was transferred to a conical flask and acidified with dilute $\text{H}_2\text{SO}_4(\text{aq})$. Then the mixture was titrated with $0.0642 \text{ mol dm}^{-3} \text{ Fe}^{2+}(\text{aq})$ solution with a suitable indicator. It required 26.88 cm^3 of the $\text{Fe}^{2+}(\text{aq})$ solution to reach the end point.

(1) Write a balanced equation for the reaction involved. (1 mark)

(2) Calculate the concentration of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ in A. (2 marks)

- (ii) In colorimetry, various standard $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ solution were first prepared, and then the absorbance of these solutions were measured with a colorimeter installed with a blue filter. The calibration curve below shows the variation of absorbance with the concentration of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ions.



(1) Suggest why a blue filter was used. (1 mark)

(2) With reference to the above calibration curve, state the relationship between absorbance and $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})]$. (1 mark)

(3) Sample B was diluted 100 times. The absorbance of the diluted solution was measured as 0.26 by the colorimeter. Based on the information given from the above calibration curve, calculate the concentration of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ in B. (2 marks)

- (iii) Explain whether volumetric analysis or colorimetry is more appropriate in determining the concentration of a very dilute $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$, such as around $10^{-4} \text{ mol dm}^{-3}$. (1 mark)

DSE17_03b

Hydroxylamine (HONH_2) reacts with $\text{Fe}^{3+}(\text{aq})$ ions under acidic conditions to form products including $\text{Fe}^{2+}(\text{aq})$ ions and an oxide of nitrogen. An experiment, consisting of the following two steps, was carried out to deduce the oxidation number of N in the oxide.

Step (1): An aqueous solution containing 0.875 g of HONH_2 and excess $\text{Fe}_2(\text{SO}_4)_3$ was heated under an acidic condition until the reaction was complete. The resulting solution was then dilute to 250.0 cm^3 .

Step (2): 25.00 cm^3 of the diluted solution was acidified with excess $\text{H}_2\text{SO}_4(\text{aq})$ and then titrated with $0.0282 \text{ mol dm}^{-3} \text{ KMnO}_4(\text{aq})$ until the end point was reached. The chemical equation for the reaction involved is as follows:



(i) State the color change at the end point of the titration. (1 mark)

(ii) Four trials of the titration were carried out and the results are listed below:

Trial	1	2	3	4
Volume of $\text{KMnO}_4(\text{aq})$ used / cm^3	38.34	37.62	37.58	37.60

(1) Calculate a reasonable average of the volume of $\text{KMnO}_4(\text{aq})$ used in the titration. (1 mark)

(2) Based on the experimental results, calculate the mole ratio of $\text{HONH}_2(\text{aq}) : \text{Fe}^{3+}(\text{aq})$ required for the completion of the reaction in Step (1). (Relative atomic masses: $\text{H} = 1.0$, $\text{N} = 14.0$, $\text{O} = 16.0$) (3 marks)

(3) Given that the oxidation number of N in HONH_2 is -1 , and the oxidation numbers of H and O remain unchanged, deduce the oxidation number of N in the oxide. (2 marks)

(iii) According to (ii)(3), suggest a reasonable empirical formula for the oxide. (1 mark)

DSE18_03b [Similar as ASL00, 03, 04]

An experiment was performed to determine the percentage by mass of $\text{NaClO}_3(\text{s})$ in a sample. 1.63 g of the sample was dissolved in deionized water and then made up to 250.0 cm^3 . 10.00 cm^3 of the solution was transferred to a conical flask. Then 10 cm^3 of $1 \text{ M KI}(\text{aq})$ and 20 cm^3 of $6 \text{ M HCl}(\text{aq})$ were added in the flask. The resulting mixture was titrated with $0.112 \text{ M Na}_2\text{S}_2\text{O}_3(\text{aq})$, adding starch solution as indicator at appropriate time. The titration was repeated several times, and the mean volume of $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ required to reach the end point was 27.88 cm^3 .

(i) Describe how the sample dissolved in deionized water can be made up to 250.0 cm^3 . (2 marks)

(ii) It is known that in the conical flask, $\text{ClO}_3^-(\text{aq})$ reacts with $\text{I}^-(\text{aq})$ in the presence of $\text{H}^+(\text{aq})$ to form $\text{I}_2(\text{aq})$ and $\text{Cl}^-(\text{aq})$. Write an ionic equation for the reaction. (1 mark)

(iii) State the color change at the end point of the titration. (1 mark)

- (iv) The chemical equation for the titration reaction is as follows:



Assuming that no other species in the sample would react with $I^-(aq)$, calculate the percentage by mass of $NaClO_3(s)$ in the sample.

(Relative atomic masses: O = 16.0, Na = 23.0, Cl = 35.5)

DSE19_03b

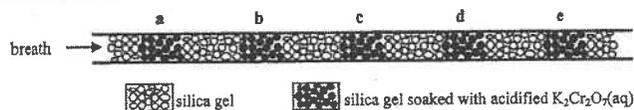
(3 marks)

- (b) In order to determine the sodium contents (existing as NaCl) in a bacon sample, its Cl^- contents should first be found. 2.0 g of the bacon sample was added to 2.50 cm³ of 1.0 M $AgNO_3(aq)$. After that, excess dilute $HNO_3(aq)$ was added to the mixture obtained. The $AgCl(s)$ formed was then removed by filtration. The excess $AgNO_3(aq)$ remaining in the filtrate was then titrated with 0.10 M $KSCN(aq)$ to give $AgSCN(s)$ in the presence of a suitable indicator until the end point was reached. All steps were repeated several times and the mean volume of the $KSCN(aq)$ used to reach the end point was 9.42 cm³.

- (i) Why was excess dilute $HNO_3(aq)$ added to the mixture ? (1 mark)
- (ii) Draw a diagram for the set-up to be used in the titration, labelling all apparatus and reagents. (2 marks)
- (iii) Assuming that all Cl^- comes from NaCl in the bacon sample, calculate the percentage by mass of sodium in the bacon sample. (Relative atomic masses: Na = 23.0, Cl = 35.5, Ag = 107.9) (4 marks)

DSE20_03cii

- (c) Road checking on ethanol intake of a driver can be done by having the driver exhale a breath into the tube as shown below :



- (i) (1) Suggest the colour change of the silica gel soaked with acidified $K_2Cr_2O_7(aq)$ if enough ethanol-contained breath is exhaled into the tube. Write a half equation for the colour change involved.
- (2) A breath from driver A only changes colour at positions a and b; while a breath from driver B changes colour at positions a, b and c. Assuming the checking is performed in a fair manner, explain which driver has a higher ethanol intake.
- (3) Suggest how the checking can be performed in a fair manner. (4 marks)
- (ii) In a certain country, a driver would be found guilty if the ethanol content in his / her blood exceeds '55 mg of ethanol per 100 cm³ of serum'. 10.0 cm³ of a treated serum sample obtained from the blood of a driver requires 4.38 cm³ of 0.025 mol dm⁻³ $K_2Cr_2O_7(aq)$ in an acidified medium for complete reaction. Given that the mole ratio of $C_2H_5OH(aq)$ to $K_2Cr_2O_7(aq)$ is 3 : 1 in the reaction, calculate the mass of C_2H_5OH , in mg, in the serum sample. Determine whether the driver would be found guilty. (Relative atomic masses : H = 1.0, C = 12.0, O = 16.0) (4 marks)

Marking Scheme

AL96(I)_04c

- (i) Transfer the given H_2O_2 solution to beaker. [1]
Pipette 10 cm³ of H_2O_2 solution to a 250 cm³ volumetric flask. [1]
Dilute the solution by adding water until the bottom of the meniscus reach the graduation mark. [1]
- (ii) $2MnO_4^- + 5H_2O_2 + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2 + 8H_2O$ [1]
- (iii) A permanent pink color appears at the end point / colorless to pink.
- (iv) $\frac{\text{mole of } H_2O_2}{5} = \frac{\text{mole of } MnO_4^-}{2}$
 $\frac{25 \times 10^{-3} \times [H_2O_2]}{5} = \frac{26.45 \times 10^{-3} \times 0.00995}{2}$ [1]
 $[H_2O_2] = 0.263 \text{ M}$ [1]
- (v) Sodium ethanedioate (oxalate) / ammonium iron(II) sulphate(VI) [1]

AL96(I)_04d

- (i) $[H_2O_2]$ in the sample = $\frac{1.46 \times 10^{-6}}{0.0398} \times 0.0273 = 1.00 \times 10^{-6} \text{ M}$ [2]
- (ii) The concentration of H_2O_2 in rainwater is too low to be determined by titrimetric method. [1]
- (iii) Fe can be oxidized by H_2O_2 [1]
OR, Transition metal ions can catalyze the decomposition of H_2O_2 .

AL98(I)_07

- (a) To convert all sulphite to SO_2 / to prevent the disproportionation of I_2 in alkaline medium. [1]
- (b) SO_2 / I_2 is volatile [1]
- (c) Add starch solution [1]
End point : solution changes from colorless to blue [1]
- (d) $SO_2 + I_2 + 2H_2O \longrightarrow 2I^- + SO_4^{2-} + 4H^+$
 $I_2 \equiv SO_2 \equiv SO_3^{2-}$
 $[SO_2(aq)] = \frac{0.005 \times 12.9}{25} = 2.58 \times 10^{-3} \text{ M}$ [1]
 $[SO_2(aq)] = 2.58 \times (32.1 + 16 \times 2) = 165 \text{ mg dm}^{-3}$ [1]

AL00(I)_03

- (a) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$ [1]
- (b) Mole of $Cr_2O_7^{2-}(aq) = 0.0203 \times 32.15 \times 10^{-3} = 6.526 \times 10^{-4}$ [1]
 $[FeSO_4(aq)] = \frac{6 \times 6.526 \times 10^{-4}}{25 \times 10^{-3}} = 0.157 \text{ mol dm}^{-3}$ [1]

ASL00(I)_03

- (a) Chromium(VI) is toxic. [1]
 (b) No. of mole of $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) = 1.2 \times 10^{-4} \times 1 \times 10^5 = 12$ [1]
 No. of mole of $\text{Fe}^{2+}(\text{aq})$ required = $12 \times 6 = 72$ [1]
 Mass of green vitriol = $72 \times 277.8 = 20001.6 \text{ g} = 20 \text{ kg}$ [1]
 (c) Sodium hydroxide / ammonia [1]
 (d) Cr(III) cation and hydroxide anion [1]

ASL00(II)_12

- (a) Sulphur dioxide is used as anti-oxidant / reductant to prevent air oxidation of ethanol. [1]
 (b) $\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^-$ [½]
 $\text{I}_2(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$ [½]
 $\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq})$ [1]
 (c) Starch solution. Change from colorless to dark blue at the end point. [2]
 (d) $\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq})$ [1]
 No. of mole of $\text{SO}_2(\text{aq}) = \text{no. of mole of } \text{I}_2(\text{aq}) \text{ used}$
 $= 14.8 \times 10^{-3} \times 0.0048 = 7.104 \times 10^{-5}$ [1]
 $[\text{SO}_2(\text{aq})] = \frac{7.104 \times 10^{-5} \times 64}{25 \times 10^{-3}} = 0.182 \text{ g dm}^{-3} = 182 \text{ mg dm}^{-3}$ [1]

ASL00(II)_13

- (a) (i) $\text{OCl}^-(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$ [1]
 (ii) $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \longrightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ [1]
 (b) Starch solution. [1]
 Color changes from dark blue to colorless at the end point. [1]
 (c) mole of $\text{I}_2(\text{aq})$ formed = $\frac{1}{2} \times \text{mole of } \text{S}_2\text{O}_3^{2-} \text{ used}$ [1]
 $= \frac{1}{2} \times 31.1 \times 10^{-3} \times 0.680 = 1.06 \times 10^{-2}$ [1]
 mole of $\text{OCl}^-(\text{aq}) = \text{mole of } \text{I}_2(\text{aq}) \text{ formed} = 1.06 \times 10^{-2}$ [1]
 $[\text{NaOCl}(\text{aq})] = \frac{1.06 \times 10^{-2} \times 74.5}{25 \times 10^{-3}} = 31.6 \text{ g dm}^{-3}$ [1]

ASL01(I)_03

- (a) A colorless bubbles and green iron(II) solution are given. [1]
 (b) $\text{MnO}_4^-(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) + 8\text{H}^+(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + 5\text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ [1]
 mole of $\text{Fe}^{2+}(\text{aq}) = 5 \times 24.3 \times 10^{-3} \times 0.0215 = 2.612 \times 10^{-3}$ [1]
 mass of Fe(s) = $2.612 \times 10^{-3} \times 55.8 = 0.146 \text{ g}$ [1]
 $\% \text{ by mass} = \frac{0.146}{0.160} \times 100\% = 91.1\%$ [1]
 (c) First appearance of permanent pink color [1]

ASL01(I)_07

- Weigh a piece of office paper. [½]
 Immerse paper in excess HCl(aq). [½]
 When no CO_2 evolves from the mixture, decant acid and wash paper with distilled water. [1]
 Dry the paper in an oven (110°C). [½]
 Weigh the paper again. [½]
 $\% \text{ by mass of } \text{CaCO}_3 = \frac{\text{change in mass of paper}}{\text{original mass of paper}} \times 100\%$ [1]

Alternative answers

- Weigh a piece of office paper. [½]
 Immerse in a known volume of standard HCl (excess). [1]
 Titrate excess HCl using standard KOH (aq) / NaOH (aq). [1]
 Calculate mass of CaCO_3 from the titration result. [½]
 $\% \text{ by mass of } \text{CaCO}_3 = \frac{\text{mass of } \text{CaCO}_3}{\text{original mass of paper}} \times 100\%$ [1]

Alternative answers

- Weigh a piece of office paper [½]
 Burn the paper completely (in a crucible) [1]
 Weigh the CaO (s) produced, (m) [½]
 $\text{mass of } \text{CaCO}_3 = \frac{m}{40 + 16} \times 100\%$ [1]
 $\% \text{ by mass of } \text{CaCO}_3 = \frac{\text{mass of } \text{CaCO}_3}{\text{original mass of paper}} \times 100\%$ [1]

AL01(II)_01

- (a) $\text{I}_2(\text{s})$ is volatile. It is difficult to weigh accurately a sample of $\text{I}_2(\text{s})$. [1]
 OR, $\text{I}_2(\text{s})$ reacts readily with reducing agents in the environment. $\text{I}_2(\text{s})$ in the laboratory usually contains impurities.
 (b) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$ [1]
 $\text{IO}_3^- \equiv 3\text{I}_2$
 $[\text{I}_2(\text{aq})] = 3 \times \frac{0.953}{214} \times 4 = 0.0534 \text{ M}$ [1]
 (c) (i) mole of I_2 used = $0.0534 \times 25 \times 10^{-3} = 1.335 \times 10^{-3}$ [½]
 mole of $\text{S}_2\text{O}_3^{2-}$ used = $0.0981 \times 27.25 \times 10^{-3} = 2.673 \times 10^{-3}$ [½]
 $\text{I}_2 : \text{S}_2\text{O}_3^{2-} = 1.335 \times 10^{-3} : 2.673 \times 10^{-3} = 1 : 2$ [1]
 Equation: $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$ [1]
 (ii) Starch solution; color change: from blue to colorless [1]

AL02(I)_07

- (a) No indicator is required. When the equivalence point is reached, the addition of a further drop of $\text{KMnO}_4(\text{aq})$ will give a permanent pale pink color (end point) [1]
 (b) mean titre = $\frac{23.35 + 23.40 + 23.35}{3} = 23.37 \text{ cm}^3$ [1]

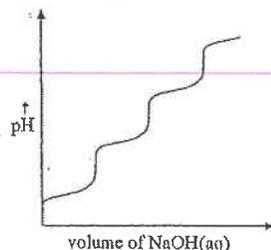
- (c) mole of MnO_4^- (aq) used = $0.0205 \times 23.37 \times 10^{-3} = 4.79 \times 10^{-4}$ [1]
 mole ratio of MnO_4^- (aq) : Sn^{2+} (aq) = 5 : 2
 mole ratio of Sn^{2+} (aq) in $250 \text{ cm}^3 = 4.79 \times 10^{-4} \times \frac{5}{2} = 0.00120$
 mole ratio of sample in sample bronze = $0.00120 \times \frac{250}{25} = 0.0120$ [1]
 % by mass of tin in the sample = $\frac{0.0120 \times 118.7}{15.03} = 9.46\%$ [1]
 [deduct 1 mark if 23.90 cm^3 is included in the calculation of the mean titre, i.e. % by mass of tin is 9.51']

ASL02(II)_10

- (a) $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$ [1]
 (b) Methyl red / methyl orange; from yellow to orange [2]
 Phenolphthalein; from pink to colorless
 (c) mole of $\text{NaOH}(\text{aq})$ remained = $0.123 \times 10.8 \times 10^{-3} = 1.328 \times 10^{-4}$ [1]
 mole of $\text{NaOH}(\text{aq})$ reacted
 = $0.105 \times 25 \times 10^{-3} - 1.328 \times 10^{-4} = 1.297 \times 10^{-3}$ [1]
 mole of $\text{NH}_4^+(\text{aq}) = 1.297 \times 10^{-3} \times \frac{250}{25} = 1.297 \times 10^{-2}$ [1]
 mass of N = $1.297 \times 10^{-2} \times 14 = 0.1815$ [1]
 % by mass of N = $\frac{0.1815}{1.64} \times 100\% = 11.1\%$ [1]

AL03(I)_01 modified

- (a) $\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}^+(\text{aq})$ [1]
 $\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{H}^+(\text{aq})$ [1]
 $\text{HPO}_4^{2-}(\text{aq}) \rightleftharpoons \text{PO}_4^{3-}(\text{aq}) + \text{H}^+(\text{aq})$ [1]
 (b) After the removal of a hydrogen ion, the remaining species has an additional negative charge that attracts the remaining hydrogen ions more strongly. [1]
 (c)



(2 mark for a curve showing the neutralization of H_3PO_4 , H_2PO_4^- and HPO_4^{2-} ,
 1 mark for labeling the axes.) [3]

ASL03(II)_12 (I)

- (a) $[\text{I}_2(\text{aq})] = \frac{0.0243 \times 3}{2.5} = 0.0288 \text{ mol dm}^{-3}$ [2]
 (b) Use starch solution as indicator [1]
 Add iodine solution until a blue color is developed [1]
 (c) Formula mass of ascorbic acid = 176 [1]
 mass of ascorbic acid in 1.0 dm^3 of grapefruit juice
 = $\frac{0.0288 \times 18}{25} \times 176 = 3.65 \text{ g}$ [2]
 (d) As an anti-oxidant [1]

ASL03(II)_12 (II)

- (a) Use a pipette to transfer 25.0 cm^3 of the bleach to a 250.0 cm^3 volumetric flask. [1]
 Add deionized water to the flask until the bottom of the meniscus reaches the mark on the flask. [1]
 (b) $2\text{H}^+(\text{aq}) + \text{ClO}^-(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{I}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ [1]
 (c) Add $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ until the liquid in the conical flask turns pale yellow. [1]
 Add starch solution and continue the titration until the color of the liquid changes from blue to colorless. [1]
 (d) $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ [1]
 $[\text{ClO}^-(\text{aq})] = \frac{0.105 \times 18}{2 \times 25} = 0.0378 \text{ mol dm}^{-3}$ [1]
 $[\text{NaClO}(\text{aq})] = 0.0378 \times (23 + 35.5 + 16) \times 10 = 28.2 \text{ g dm}^{-3}$ [1]

AL04(I)_07

- Step 1:
 A standard $\text{NaOH}(\text{aq})$ should not be prepared using the method as described. [½]
 Explanation: $\text{NaOH}(\text{s})$ is hygroscopic. [½]
 Correction: It is necessary to standardize the $\text{NaOH}(\text{aq})$ before use. [½]
 Step 3:
 The burette should not be rinsed with water only. [½]
 Explanation: Water that remains in the burette will cause a dilution of the $\text{NaOH}(\text{aq})$. [½]
 Correction: The burette needs to be rinsed with deionized water and then with the $\text{NaOH}(\text{aq})$ prepared. [½]
 Step 4:
 Methyl orange is not a suitable indicator. [½]
 Explanation: The experiment involves a titration of a weak acid with a strong alkali. pH at the end point is about 8 to 9. [½]
 Correction: Phenolphthalein should be used. [½]
 Step 5:
 Calculation should not be based on the result of one titration only. [½]
 Explanation: There may be errors in the titration. [½]
 Correction: Repeat the titration at least 3 times. Use the mean titre for the calculation. [½]

AL04(II)_04

- (a) $3\text{CH}_3\text{CH}_2\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ \longrightarrow 3\text{CH}_3\text{COOH} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O}$ [1]
- (b) $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$ [1]
- moles of Fe^{2+} used in titration = $0.118 \times 12.23 \times 10^{-3}$
- moles of excess $\text{Cr}_2\text{O}_7^{2-} = \frac{1}{6} \times 0.118 \times 12.23 \times 10^{-3} = 2.405 \times 10^{-4}$ [1]
- moles of excess $\text{Cr}_2\text{O}_7^{2-}$ added = $0.156 \times 25 \times 10^{-3} = 3.9 \times 10^{-3}$ [1]
- moles of excess $\text{Cr}_2\text{O}_7^{2-}$ that reacts with $\text{CH}_3\text{CH}_2\text{OH}$
 $= 3.9 \times 10^{-3} - 2.405 \times 10^{-4} = 3.659 \times 10^{-3}$ [1]
- $[\text{CH}_3\text{CH}_2\text{OH}]$ in the brand of spirit = $\frac{3.659 \times 10^{-3} \times 10}{10 \times 10^{-3}} \times \frac{3}{2} = 5.49 \text{ mol dm}^{-3}$ [1]

ASL04(II)_08

- (a) Use a graduated pipette to transfer 5.0 cm^3 of the household bleach to a 250.0 cm^3 volumetric flask. [1]
 Add deionized water to the flask until the bottom of the meniscus reaches the mark on the flask. [1]
- (b) Add $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ until the color of the solution in the flask becomes pale yellow. [1]
 Add starch indicator and continue the titration until the solution becomes colorless. [1]
- (c) $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \longrightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ [1]
- moles of ClO^- in 25 cm^3 of the diluted bleach = $\frac{1}{2} \times 0.0552 \times 16 \times 10^{-3}$ [1]
- $[\text{NaClO}]$ in the bleach = $\frac{\frac{1}{2} \times 0.0552 \times 16 \times 10^{-3} \times 10}{5 \times 10^{-3}} = 0.883 \text{ mol dm}^{-3}$ [1]

AL05(II)_01

- (a) $2\text{X}(\text{s}) + 6\text{HCl}(\text{aq}) \longrightarrow 2\text{XCl}_3(\text{aq}) + 3\text{H}_2(\text{g})$ [1]
 $\text{X}_2\text{O}_3(\text{s}) + 6\text{HCl}(\text{aq}) \longrightarrow 2\text{XCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$ [1]
- (b) According to the equations, $2\text{X} \equiv \text{X}_2\text{O}_3$
 For complete reaction with 6 mole of HCl, the mass of X(s) required is less than that of X_2O_3 .
 Greatest possible value of RAM of X can be calculated by assuming that the sample contains X only.
 moles of HCl(aq) used = $0.0954 \times 6 = 0.5724$
 Since the sample consists of pure X & 1 mole of X reacts with 3 moles of HCl
 moles of X = $\frac{0.5724}{3} = 0.1908$ [1]
 Greatest possible RAM of X = $\frac{16.5}{0.1908} = 86.5$ [1]

Smallest possible value of RAM of X can be calculated by assuming that the sample contains X_2O_3 only.

Since 1 mole of X_2O_3 reacts with 6 moles of HCl [1]

$$\text{moles of } \text{X}_2\text{O}_3 = \frac{0.5724}{6} = 0.0954$$

Let the RAM of X be A

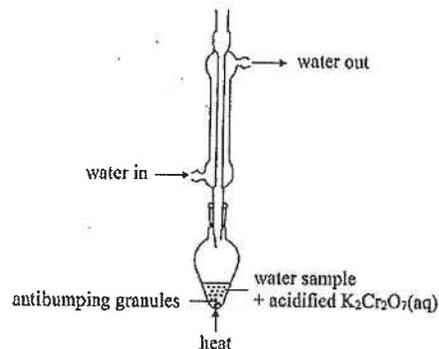
$$\frac{16.5}{2A + 16 \times 3} = 0.0954 \quad [1]$$

Smallest possible RAM of X = 62.5

- (c) The only trivalent metal with RAM in the range of 62.5 to 86.5 is gallium, Ga [1]

ASL05(II)_11

- (a) [1]



- (b) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) + 14\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{Fe}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$ [1]
- (c) moles of $\text{Cr}_2\text{O}_7^{2-}$ originally added = $0.010 \times 2.5 \times 10^{-3} = 2.5 \times 10^{-5}$ [1]
 moles of $\text{Cr}_2\text{O}_7^{2-}$ remaining = $\frac{1}{6} \times 0.0124 \times 7.6 \times 10^{-3} = 1.57 \times 10^{-5}$ [1]
 moles of $\text{Cr}_2\text{O}_7^{2-}$ consumed = $2.5 \times 10^{-5} - 1.57 \times 10^{-5} = 9.3 \times 10^{-6}$ [1]
 mole of $\text{K}_2\text{Cr}_2\text{O}_7$ required to oxidize all organic matter in 1 dm^3 of water sample
 $= 9.3 \times 10^{-6} \times 10 = 9.3 \times 10^{-5}$ [1]

AL06(I)_02

- (a) Limestone / marble / chalk / anhydrite / gypsum / fluorite [1]
- (b) moles of $\text{H}^+(\text{aq})$ exchanged = $0.020 \times 15 \times 10^{-3} = 3.0 \times 10^{-4}$ [1]
 moles of $\text{Ca}^{2+}(\text{aq}) / \text{Mg}^{2+}(\text{aq})$ exchanged = $\frac{3.0 \times 10^{-4}}{2} = 1.5 \times 10^{-4}$
 Total hardness of the water sample = $\frac{1.5 \times 10^{-4}}{50 \times 10^{-3}} = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ [1]

AL06(II)_07

Given that when treated with acidified KI(aq), 1 mol of peroxide liberates 1 mol of I₂



$$\text{mole of S}_2\text{O}_3^{2-} \text{ used} = 0.012 \times 21.2 \times 10^{-3} = 2.54 \times 10^{-4} \quad [1]$$

$$\text{Mole of O}_2 \text{ absorbed per kg of oil} = \frac{2.54 \times 10^{-4}}{4.85 \times 10^{-3}} = 26.2 \times 10^{-2} \quad [2]$$

ASL06(II)_09c



(ii) moles of Fe²⁺ present = 5 × moles of MnO₄⁻ reacted
 = 5 × 34.7 × 10⁻³ × 0.0208 = 3.609 × 10⁻³ = moles of Fe [1]

mass of Fe present in the sample = 3.609 × 10⁻³ × 55.8 = 0.201 g [1]

% by mass of Fe = $\frac{0.201}{0.212} \times 100\% = 94.8\%$ [1]

(iii) The impurities in the iron sample have no reaction with MnO₄⁻.
 No air oxidation of Fe²⁺ to Fe³⁺. [1]

(iv) Not appropriate. MnO₄⁻ might oxidize Cl⁻ in the solution. [1]

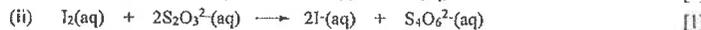
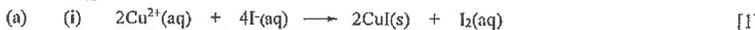
AL07(I)_07

(a) Primary standard: a standard solution of the substance can be prepared by dissolving a known mass of the substance in a solvent and making up the solution to a known volume. [1]

(b) (i) Br₂(l) is volatile. It is difficult to weigh a sample of Br₂(l) accurately. [1]

(ii) KOH(s) absorbs water moisture/absorbs CO₂. [1]

ASL07(II)_03



(b) ∴ no. of mole of Cu²⁺ = no. of mole of S₂O₃²⁻ [1]

mass of Cu²⁺ in the sample = 25.8 × 10⁻³ × 0.102 × 63.5 = 1.67 g [1]

% by mass of Cu in the ore = $\frac{1.67}{3} \times 100\% = 55.7\%$ [1]

(c) Open-ended question. Possible answers [1]

The impurities in the sample do not react with KI(aq) to give I₂(aq)

Cu²⁺(aq) reacts quantitatively with I⁻(aq) to give CuI(s) and I₂(aq).

ASL09(II)_03

(a) Red to orange [1]

(b) moles of NaOH used in the titration = 0.0941 × 16.48 × 10⁻³ = 1.55 × 10⁻³ [1]

moles of H⁺ originally present = 0.955 × 25 × 10⁻³ × 2 = 0.0478 [1]

moles of H⁺ that react with Mg = 0.0478 - 1.55 × 10⁻³ = 0.0322 [1]



moles of Mg in the ribbon = $\frac{0.0322}{2} = 0.0161$ [1]

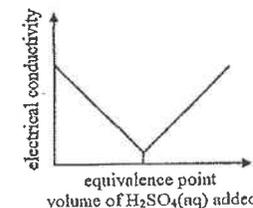
relative atomic mass = $\frac{0.420}{0.0161} = 26.05$ [1]

(c) Some of the Mg has been oxidized to MgO [1]

AL10(I)_07

(a) Electrical conductivity [1]

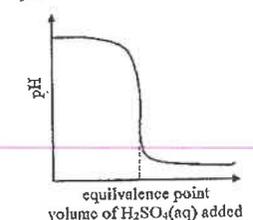
(b) [1]



Electrical conductivity decreases before the equivalence point because the concentration of the highly conducting OH⁻(aq) decreases as it reacts with H⁺(aq) to give H₂O(l). [½]

After the equivalent point, the increase in conductivity is due to the increase in [H⁺(aq)]. [½]

OR pH [1]



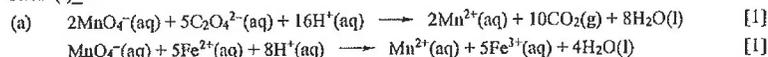
pH drops before the equivalent point because OH⁻(aq) ions are removed by H⁺(aq) ions. [1]



When it is close to the equivalence point, both [H⁺(aq)] and [OH⁻(aq)] are small. [½]

Addition of a drop of H₂SO₄(aq) can lead to a significant decrease in pH. [½]

AL11(I)_01



(b) $[\text{MnO}_4^- (\text{aq})] \text{ used} = \frac{0.0326 \times 25 \times 10^{-3}}{24.35 \times 10^{-3}} \times \frac{2}{5} = 0.0134 \text{ mol dm}^{-3}$ [1]

mole of Fe^{2+} in the solid sample = $0.0134 \times 31.85 \times 10^{-3} \times 5 = 2.13 \times 10^{-3}$ [1]

% by mass of $\text{Fe}^{2+} = \frac{2.13 \times 10^{-3} \times 55.8}{0.863} \times 100\% = 13.8\%$ [1]

Acceptable range: 13.6% – 13.9% [1]

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

1. $\text{KMnO}_4(\text{s})$ is a strong oxidizing agent. It readily reacts with reducing agents in the environment.

2. $\text{KMnO}_4(\text{s})$ cannot be obtained in high purity.

3. $\text{KMnO}_4(\text{aq})$ readily undergoes decomposition in the presence of light.

AL12(I)_07

(a) I_2 forms a very stable / water-insoluble complex with starch. Addition of starch right at the beginning will affect the accuracy of the titration. [1]

(b) $\text{S}_2\text{O}_3^{2-}(\text{aq})$ will hydrolyze under acidic conditions. [1]



AL12(I)_08

(a) Phenolphthalein / phenol red [1]

(b) mole of excess $\text{OH}^-(\text{aq}) = 2.50 \times 23.1 \times 10^{-3} = 5.78 \times 10^{-2}$ [½]

mole of $\text{OH}^-(\text{aq})$ originally used = $3.05 \times 25.0 \times 10^{-3} = 7.63 \times 10^{-2}$ [½]

mole of $\text{OH}^-(\text{aq})$ reacted with aspirin = $7.63 \times 10^{-2} - 5.78 \times 10^{-2} = 0.0185$ [½]

mass of aspirin = $0.0185 \times 180 = 3.33$ [½]

% by mass = $\frac{3.33}{2.25} \times 100\% = 148\%$ [1]

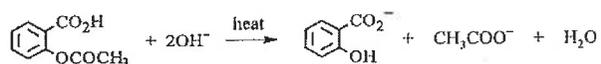
Reason: The ester group in aspirin undergoes alkaline hydrolysis. [½]

The amount of $\text{OH}^-(\text{aq})$ consumed is greater than the expected value. [½]

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

- Use a smaller amount of aspirin so that a less concentrated $\text{NaOH}(\text{aq})$ can be used.

- Heat the reaction mixture to ensure complete hydrolysis of the ester so that the calculation can be based on the reaction:



AL12(II)_01

(a) mole of $\text{Br}^- = \text{mole of AgBr}(\text{s}) \text{ formed} = \frac{0.816}{107.9 + 79.9} = 0.004345$ [1]

mole of MBr_2 formed = $\frac{0.004345}{2} = 0.00217$ [1]

formula mass of $\text{MBr}_2 = \frac{0.400}{0.00217} = 184.1$ [1]

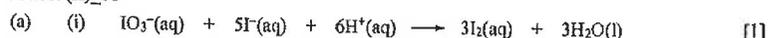
(b) Relative atomic mass of $\text{M} = 184.1 - 2 \times 79.9 = 24.3$ [1]

M is magnesium [1]

(c) No. $\text{AgF}(\text{s})$ is soluble in water. [1]

$\text{Ag}(\text{s})$ cannot be precipitated from $\text{MF}_2(\text{aq})$ by adding $\text{AgNO}_3(\text{aq})$. [1]

ASL13(II)_01



(ii) $\text{I}_2(\text{s})$ is volatile and cannot be weighed accurately. [1]

$\text{I}_2(\text{s})$ readily reacts with reducing agents in the surrounding.

(iii) mole of KI used = $\frac{2}{39.1 + 126.9} = 0.012$

$\text{I}^-(\text{aq})$ is in excess.

$[\text{I}_2(\text{aq})] \text{ prepared} = 0.01 \times 3 \times \frac{100}{25} = 0.012 \text{ mol dm}^{-3}$ [1]

(b) Add starch indicator. [1]

The solution turns blue when the end point is reached. [1]

(c) (i) moles of $\text{I}_2(\text{aq})$ used in the titration = $7.6 \times 10^{-3} \times 0.012$ [1]

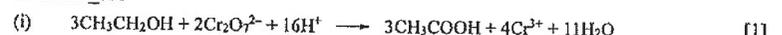
mass of ascorbic acid in 100 cm^3 of orange juice

$$= \frac{7.6 \times 10^{-3} \times 0.012 \times 100}{25.00} \times 176.0$$

$$= 0.0642 \text{ g}$$
 [1]

(ii) Apart from ascorbic acid, the orange juice does not contain any other substances that react with I_2 . [1]

DSE11SP_03b

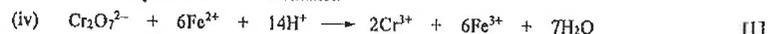


(ii) Large formula mass [1]

Stable in air [1]

(iii) Retain some portions and allow a longer period of time, say 2 days. [1]

Perform the titration again. If the titre is consistent with the previous result, there has been complete oxidation of ethanol. [1]



Mole of Fe^{2+} used in titration = $0.118 \times 12.23 \times 10^{-3}$ [1]

Mole of excess $\text{Cr}_2\text{O}_7^{2-}$

$$= \frac{1}{6} \times 0.118 \times 12.23 \times 10^{-3} = 2.405 \times 10^{-4}$$
 [1]

Mole of $\text{Cr}_2\text{O}_7^{2-}$ added = $0.156 \times 25 \times 10^{-3} = 3.9 \times 10^{-3}$
Mole of $\text{Cr}_2\text{O}_7^{2-}$ that react with $\text{CH}_3\text{CH}_2\text{OH}$
= $3.9 \times 10^{-3} - 2.405 \times 10^{-4} = 3.659 \times 10^{-3}$ [1]
Concentration of ethanol in the brand of spirit
= $\frac{3.659 \times 10^{-3} \times 10}{10 \times 10^{-3}} \times \frac{3}{2} = 5.49 \text{ mol dm}^{-3}$ [1]

DSE12PP_03b

- (i) Wash the precipitate thoroughly with deionized water. [1]
Dry the precipitate in an oven / ensure that the precipitate is dried before it is weighed. [1]
- (ii) $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
no. moles of Ba^{2+} present = $\frac{0.291}{(137.3 + 32.1 + 16 \times 4)} = 1.25 \times 10^{-3}$ [1]
mass of Ba in the sample = $1.25 \times 10^{-3} \times 137.3 = 0.171$ [1]
% by mass of Ba in the sample = $\frac{0.171}{0.305} = 56.1$ [1]
(acceptable range : 56.0 to 56.4)
- (c) Any TWO of the following: [2]
- The reaction must be significantly complete, i.e. the precipitate is practically insoluble.
- The product (precipitate) should have definite chemical composition.
- The rate of reaction must be fast enough to be practical.

DSE12_03c

- (i) (acidified) $\text{AgNO}_3(\text{aq})$ and $\text{NH}_3(\text{aq})$ [2]
(ii) Step 1: Add excess $\text{AgNO}_3(\text{aq})$ to the solution to form $\text{AgCl}(\text{s})$ and $\text{AgI}(\text{s})$. [1]
Step 2: Filter the mixture, wash with deionized water and dry the residue. [1]
Step 3: Determine / Weigh the total mass of $\text{AgCl}(\text{s})$ and $\text{AgI}(\text{s})$ collected. [1]
Step 4: Wash the solid residue with excess ammonia solution to dissolve / remove $\text{AgCl}(\text{s})$, filter and dry the residue, and determine the mass of $\text{AgI}(\text{s})$ remains. [1]
(iii) Subtracting the total mass of $\text{AgCl}(\text{s})$ and $\text{AgI}(\text{s})$ determined in Step 3 by the mass of $\text{AgI}(\text{s})$ determined in Step 4 to get the mass of $\text{AgCl}(\text{s})$. [1]
Number of mole of AgCl and AgI can be obtained by dividing their respective mass by the corresponding molar mass. Mole ratio of $\text{Cl}^-(\text{aq})$ to $\text{I}^-(\text{aq})$ can then be determined. [1]

DSE13_03b

- (i) Any ONE of the following: [1]
- A significant observable change can easily be detected with the complete consumption of the reagent in the conical flask, i.e. availability of suitable indicator

- The reaction must be significantly complete / it is not a reversible reaction
- The rate of reaction must be fast enough to be practical

- (ii) SO_2 easily escapes from solution / I_2 is volatile. [1]
(iii) From colorless to blue-black / blue / dark blue [1]
(iv) Mole of I_2 used = $0.00412 \times 10.50 \times 10^{-3} = 4.33 \times 10^{-5}$ [1]
Mole of SO_2 = no. of mole of $\text{I}_2 = 4.33 \times 10^{-5}$ [1]
Mass of $\text{SO}_2 = 4.33 \times 10^{-5} \times 64.1 = 2.77 \times 10^{-3} \text{ g} = 2.77 \text{ mg}$ [1]
 $[\text{SO}_2]$ in the wine sample = $\frac{2.77}{0.025} = 111 \text{ mg dm}^{-3}$ (Range: 110 – 112) [1]
(v) This method cannot be used as the intense red color of red wine may mask the color of iodine / iodine-starch complex which leads to a difficulty in the end-point detection. [1]
OR This method can be used if the color of red wine can be removed.

DSE14_03b

- (i) To ensure the reaction go to completion / To increase the reaction rate. [1]
(ii) (1) No more gas is given out / All solids are dissolved. [1]
(2) Brown precipitate formed. [1]
(iii) Mole of CaC_2O_4 formed in step 6 = $\frac{2.374}{128.1} = 0.01853$ [1]
Mass of CaCO_3 in the limestone sample = $0.01853 \times 100.1 = 1.855 \text{ g}$ [1]
% mass of $\text{CaCO}_3 = \frac{1.855}{2.025} = 91.60\%$ (Range: 91.3 – 91.9) [1]
(iv) Gravimetric analysis [1]

DSE15_03

- (i) (1) $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$ [1]
OR $(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{NH}_3 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
(2) $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$ [1]
OR $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
(ii) From red to orange [1]
(iii) Moles of KOH used in the titration = $0.100 \times 13.55 \times 10^{-3} = 1.355 \times 10^{-3}$ [1]
Moles of H^+ ions remained after Step 2 = $1.355 \times 10^{-3} \times 10 = 0.01355$ [1]
Moles of H^+ ions used in Step 2 = $1.00 \times 50 \times 10^{-3} = 0.05$ [1]
Moles of NH_3 liberated = $0.05 - 0.01355 = 0.03645$
Mass of N in the sample = $0.03645 \times 14 = 0.5103 \text{ g}$
% by mass of N in the sample = $\frac{0.5103}{3} \times 100 = 17.01\%$ [1]
(iv) The amount of nitrogen determined may come from other nitrogen-containing substances present in milk powder. [1]

DSE16_03a

Any ONE of the following answers:

- Sodium hydroxide (solid) is deliquescent / hygroscopic / can absorb H₂O / can dissolve in H₂O.
- Sodium hydroxide (solid) absorbs / reacts with carbon dioxide (gas from air). (accept any reasonable acidic gas e.g. SO₂ / NO₂ ...)

[1]

DSE16_03b

- (i) (1) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Fe}^{2+}(\text{aq}) + 14\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{Fe}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$ [1]
 (2) Moles of Fe²⁺ = $0.0642 \times 26.88 \times 10^{-3} = 0.0017257$ [1]
 $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] \times 25.00 \times 10^{-3} \times 6 = 0.0017257$
 $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})] = 0.0115 \text{ mol dm}^{-3}$ [1]
 (0.011505 mol dm⁻³ / 0.0120 mol dm⁻³ / wrong unit 0 mark)
- (ii) (1) (Blue filter allows blue light to pass through and the) orange Na₂Cr₂O₇(aq) solution absorbs blue light to a large extent. [1]
 (2) The absorbance is directly proportional to / ∝ the concentration of Cr₂O₇²⁻(aq). / linear relationship / shows a straight line [1]
 (3) Absorbance = 0.26,
 $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})]$ found from the graph is $7.0 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ [1]
 $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})]$ in sample B = $7.0 \times 10^{-4} \times (100) = 0.07 \text{ mol dm}^{-3}$ [1]
 Range : 0.0685 to 0.0705 mol dm⁻³)
- (iii) Colorimetry is more appropriate. / Volumetric analysis is less appropriate. [1]
 The low color intensity of the solution can still be determined by colorimetry. [1]

DSE17_03b

- (i) From (yellowish) green to pale pink. [1]
- (ii) (1) $(37.62 + 37.58 + 37.60) \div 3 = 37.60 \text{ cm}^3$ [1]
 [Not accept 37.6] Must show step and unit
 (2) Moles of Fe²⁺ ions formed in Step (1)
 $= 0.0282 \times 37.6 \times 10^{-3} \times 5 \times 10 = 0.0530$ [1]
 Moles of Fe³⁺ ions reacted in Step (1) = 0.0530 [1]
 [Accept 37.785 / 37.79 / 37.6 for 37.60, Range 0.0530 – 0.0533]
 Mole of HONH₂ reacted = $0.875 \div 33.0 = 0.0265$ [1]
 Mole ratio of HONH₂ : Fe³⁺ = 1 : 2 [1]
- (3) The oxidation number of iron changes from +3 to +2 and the oxidation number of N in HONH₂ is -1.
 Since the mole ratio of HONH₂ : Fe³⁺ = 1 : 2, [1]
 the oxidation number of N in this oxide = $-1 + 2 = +1$ [1]
- (iii) N₂O [1]

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DSE18_03b

- (i) Place the dissolved sample into a (250.0 cm³) volumetric flask. [1]
 (Deionised) water should be added to the mark of the volumetric flask (until the bottom of the meniscus reach the graduation mark) [1]
- (ii) $\text{ClO}_3^-(\text{aq}) + 6\text{I}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + 3\text{I}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$ [1]
- (iii) The solution turns from blue to colourless. [1]
- (iv) $\text{I}^-(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$
 moles of I₂(aq) = $0.112 \times 0.02788 \times \frac{1}{2} = 0.001561$ [1]
 moles of NaClO₃ in the sample = $\frac{0.001561}{3} \times \frac{250.0}{10.0} = 0.01301$ [1]
 % by mass of NaClO₃ = $\frac{0.01301 \times 106.5}{1.63} \times 100\%$ [1]
 = 85.0% [Range: 84 – 86]

DSE19_03b

- (b) (i) It is to prevent the formation of solid Ag₂CO₃ etc. 1

- (ii)  1

Correct labelling :

Burette, conical flask, KSCN(aq), acidified bacon sample with AgNO₃(aq) 1

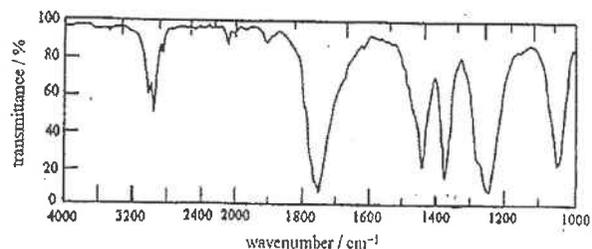
- (iii) No. of mole of KSCN(aq) = No. of mole of Ag⁺(aq) left in the mixture = No. of mole of Ag⁺(aq) reacted with KSCN(aq) = 0.1×0.00942
 No. of mole of AgCl formed
 $= 1.0 \times 0.0025 - 0.1 \times 0.00942 = 0.001558$
 Percentage by mass of sodium = $(0.001558 \times 23.0 \div 2.0) \times 100\%$
 = 1.79%

DSE20_03c

3. (c) (i) (1) orange to green 1
 $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$ 1
- (2) Driver B has a higher ethanol intake because the breath can also change the colour of the gel in position c while Driver A cannot. 1
 (A comparative sense and similar meaning)
- (3) (Exhale the) same amount / volume / strength of breath (into the tube). 1
- (ii) No. of mole of ethanol = $0.025 \times 4.38 \times 10^{-3} \times 3 = 0.0003285 \text{ mol}$ (0.00033 / 0.000329) 1*
 Mass of the ethanol = 0.0003285×46 (× 46) 1*
 $= 0.01511 \text{ g} = 15.11 \text{ mg}$
 The mass of ethanol in 100 cm³ of serum sample = $15.11 \text{ mg} \div 10 \times 100$ (÷10 × 100) 1*
 $= 151.1 \text{ mg}$
 (The mass is) 151.1 mg (which exceeds 55 mg. The driver would be found) guilty. 1
 (Range of answer: 150 – 152, max. 3 dec. places)

Instrumental Analysis
AL97(II)_06

Compound H, C₃H₆O₂, does not react with NaBH₄ and displays the following infra-red spectrum. Deduce all possible structures of H.



(4 marks)

AL98(I)_08a

Show how you would distinguish between propan-2-ol and propanone using spectroscopy

(1 mark)

AL98(II)_04

Sketch the expected mass spectrum for a gas sample having the composition: N₂ 78%, O₂ 21% and CO₂ 1%.

(You only need to consider the major isotope of each element)

(3 marks)

AL99(II)_01

Rubidium occurs naturally in two isotopic forms. The table below lists the mass and the relative abundance of each isotope.

Isotope	Mass / a.m.u.	Relative abundance
⁸⁵ Rb	84.939	72.15%
⁸⁷ Rb	86.937	27.85%

(a) Suggest an experimental method to detect the isotopes of rubidium and state how the relative abundance of each isotope can be obtained.

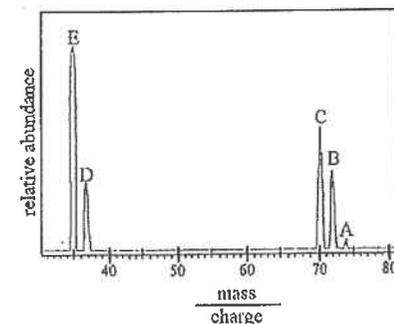
(2 marks)

(b) Calculate the relative atomic mass of rubidium.

(2 marks)

AL00(H)_01

Consider the mass spectrum of chlorine gas:



(A, B, C, D and E represent five different ionic species.)

(a) Explain why there are five peaks in the mass spectrum.

(3 marks)

(b) The ratio of relative abundance of D to E is 1 : 3.

(i) Calculate the relative atomic mass of chlorine.

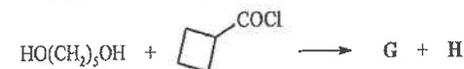
(2 marks)

(ii) Calculate the ratio of relative abundance of A to B to C.

(2 marks)

AL00(II)_05

A mixture of two organic products, G and H, was obtained in the reaction:



The mixture was separated by paper chromatography using a mixture of hexane and ether as solvent. The R_f values of G and H were found to be 0.84 and 0.55 respectively.

(a) Deduce the structures of G and H.

(4 marks)

(b) Suggest a chemical test to distinguish between G and H.

(2 marks)

(c) State how the use of infra-red spectroscopy can provide further proof for the structures of G and H.

(2 marks)

AL01(II)_01

Briefly describe the principle of mass spectrometry and its use to determine the relative atomic mass of a noble gas.

(8 marks)

AL01(II)_07

Study the following information:

Aromatic compound T and U have the same molecular formula $C_{10}H_{12}O$.

T gives positive result in iodoform test.

U reacts with hydrogen in the presence of a palladium catalyst to give compound V ($C_{10}H_{14}O$).

V can also be obtained from the reaction of T with $LiAlH_4$.

- (a) Deduce the structures of T, U and V. For each compound, give all possible stereoisomers. (7 marks)
- (b) Suggest how infra-red spectroscopy can be used to distinguish between T and U. (2 marks)

AL02(I)_05

Two acyclic structural isomeric compounds have the molecular formula $C_3H_6O_3$. Both are optically active and have infrared absorptions at 3400 and 1700 cm^{-1} . Neither possesses an alkoxy group.

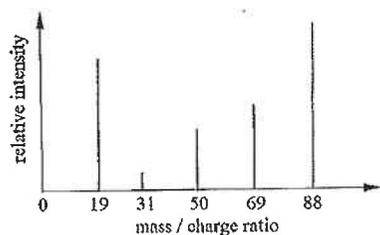
- (a) Draw the structure of each of the compounds. Label one of these structures 'A' and the other 'B'. (2 marks)
- (b) Suggest a chemical test, giving the expected observation, to distinguish between the compounds represented by 'A' and 'B'. (2 marks)
- (c) Give the structure of the major organic product formed when the two compounds are treated separately with excess $LiAlH_4$.

Product from the compound represented by 'A'	Product from the compound represented by 'B'

(2 marks)

AL02(II)_01b

Elements A and B form a compound with molecular formula AB_3 . A sample of the compound was injected into a mass spectrometer and the mass spectrum shown below was obtained.



- (i) A molecular ion AB_3^+ was formed in the mass spectrometer. Suggest how AB_3^+ was formed. (2 marks)

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- (ii) The peaks at mass/charge ratios 69 and 50 are due to cations formed from detaching one and two atoms of B from AB_3^+ respectively. Account for the presence of the peaks at mass/charge ratios 19 and 31. (2 marks)
- (iii) Suggest what compound AB_3 is. (1 mark)

AL03(II)_05

- (a) Hardening of vegetable oils can be done by hydrogenation. Explain. (2 marks)
- (b) The fumes from the two processes below were collected and analyzed using infra-red (IR) spectroscopy. The table below lists the wavenumbers of the major absorption peaks.

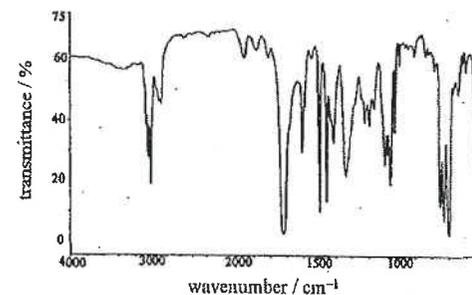
Process	Wavenumbers of major IR absorption peaks / cm^{-1}
Heating molten margarine	2950 and 1750
Frying potatoes with margarine	3100 (broad peak), 2959 and 1740

With the help of equation(s), suggest why the fumes from the two processes resulted in different IR absorptions.

(3 marks)

AL03(II)_07

Compound E ($C_{15}H_{14}O$) is a white solid with a melting point of $32\text{ }^\circ\text{C}$ and displays the following infra-red spectrum.



E gives a negative result when treated with Tollens' reagent but reacts readily with $LiAlH_4$ to give an achiral compound F. Drastic oxidation of F with potassium manganate(VII) gives an aromatic compound G ($C_7H_6O_2$) with pK_a value of 4.2 as the major product. Deduce the structure of E, F and G.

(6 marks)

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AL05(II)_05

Consider the isomeric compounds J and K below:



- (a) Name the type of isomerism involved. (1 mark)
- (b) Suggest, with explanation, how J and K can be distinguished from each other by
- A physical method (2 marks)
 - A chemical method, and (2 marks)
 - A spectroscopic method. (2 marks)

AL05(II)_06a

Formaldehyde (methanal) is one of the commonly found organic indoor air pollutants.

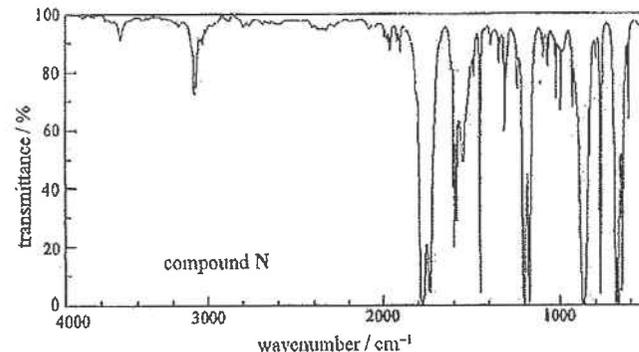
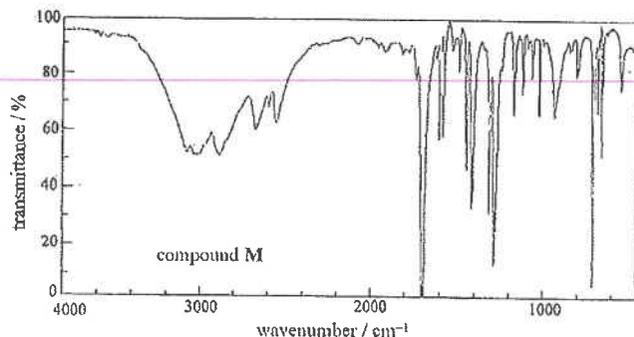
- Suggest a source of household formaldehyde. (1 mark)
- Some indoor purifiers remove formaldehyde by chemical means. Suggest one chemical for the removal of formaldehyde with the formation of less harmful products. (1 mark)
- Name one other organic indoor air pollutant and suggest its source. (2 marks)

AL05(II)_07

Compound L, with a relative molecular mass of 108, has the following composition by mass:

C 77.8%, H 7.4% and O 14.8%

L does not react with bromine, but undergoes oxidation with acidified $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ to give compound M. M reacts with PCl_5 to yield compound N. The infra-red spectra of M and N are shown below:



- Calculate the molecular formula of L. (3 marks)
- Based on the above information, deduce the structures of L, M and N. (5 marks)

AL06(II)_05

Deduce the structure of compound D on the basis of the information given below:

- Elemental analysis data show that D has the following composition by mass: C 40%, H 6.7% and O 53.3%. (3 marks)
- The relative molecular mass of D is estimated to be in the range of 172 to 182. (3 marks)
- The infra-red spectrum of D shows, apart from the absorption of C-H stretching near 2900 cm^{-1} , a strong and broad absorption around 3400 cm^{-1} , and no appreciable absorption around 1700 cm^{-1} . (3 marks)
- All carbon atoms of D have the same bonding environment. (3 marks)
- D is highly soluble in water, and the solution does not decolorize bromine water. (3 marks)

AL06(II)_06

Organic compounds in waste water can be degraded by oxidation with ozone. In a typical process, phenol is oxidized to give acyclic compound E ($\text{C}_6\text{H}_8\text{O}_4$). The infra-red spectrum of E shows a broad absorption band around 3300 cm^{-1} and a strong absorption at about 1700 cm^{-1} . Hydrogenation of E in the presence of 10% Pd on charcoal produces an acidic compound F ($\text{C}_6\text{H}_{10}\text{O}_4$).

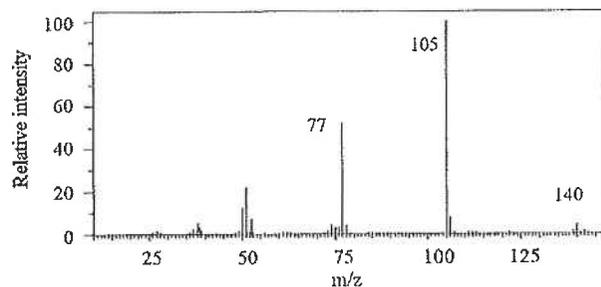
- Suggest one structure for E and one for F, and explain your answer. (5 marks)
- Suggest two advantages of using ozone to degrade organic compounds. (2 marks)

AL07(II)_07

Compound M has the following composition by mass:

C, 59.8%; H, 3.6%; Cl, 25.2%; O, 11.4%

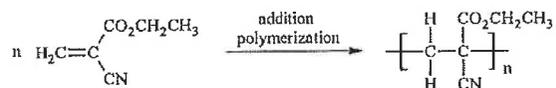
M displays the mass spectrum as shown below:



- Calculate the empirical formula of M. (2 marks)
- Deduce the structure of M. (3 marks)
- Suggest a chemical method to confirm the identity of a sample of M. (2 marks)

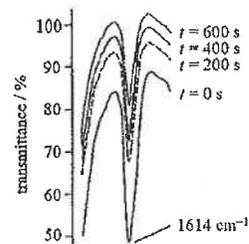
AL08(I)_08a

Super glue works as an adhesive by addition polymerization as shown below:



The progress of this polymerization was monitored by infra-red spectroscopy. Figure shows the change of transmittance with time (*t*) for the reaction system. Assign the functional group corresponding to the absorption at 1614 cm⁻¹. Account for the change of transmittance of this peak with time.

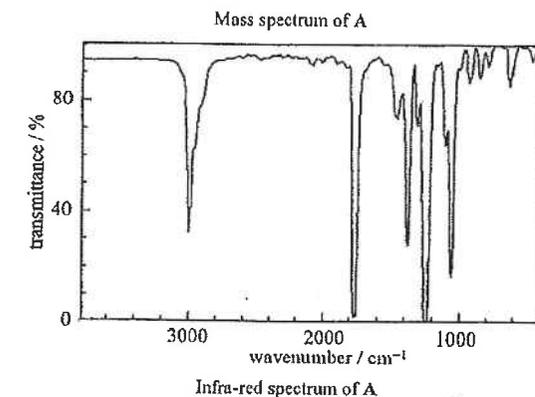
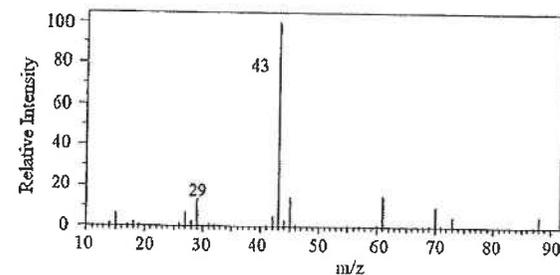
(2 marks)



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AL08(II)_06

Figures below respectively show the mass spectrum and infra-red spectrum of compound A (C₄H₈O₂). Based on the information in the figures, deduce ONE possible structure of A.

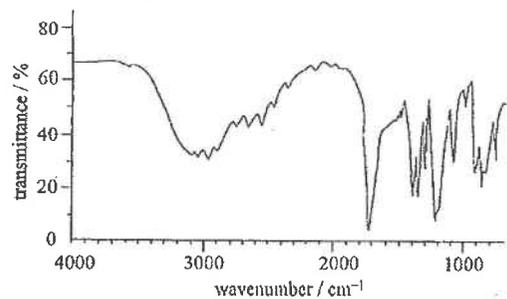


(6 marks)

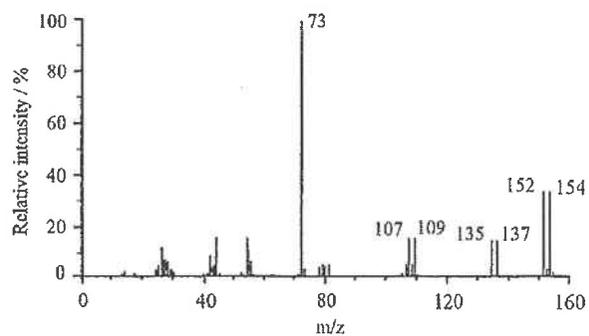
161

AL09(1D)_05

Below respectively show the infra-red spectrum and mass spectrum of compound P ($C_3H_5O_2Br$).
Based on the information in the figures, deduce ONE possible structure of P.



Infra-red spectrum of P



Mass spectrum of P

(7 marks)

AL10(1I)_03b

Mass spectrometry is often used in the determination of relative molecular mass, which is numerically equal to molar mass. Suggest TWO reasons why mass spectrometry is superior to the traditional method.

(2 marks)

AL10(1I)_05

Compound L has the following composition by mass:

C, 70.6%; H, 5.9%; O, 23.5%

Figures 5.1 and 5.2 respectively show the infra-red spectrum and mass spectrum of L.

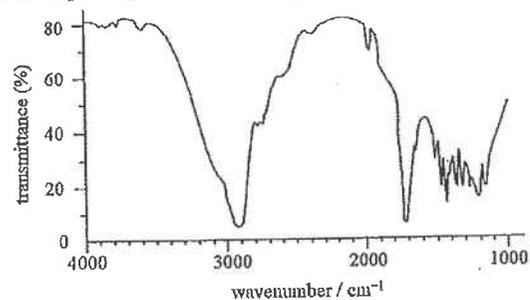


Figure 5.1 Infra-red spectrum of L

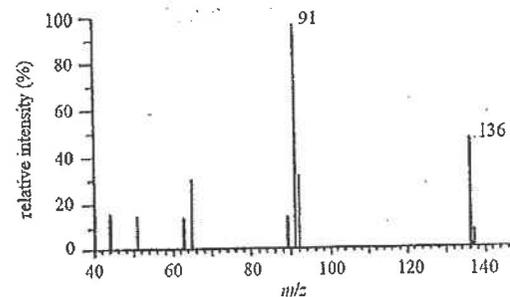


Figure 5.2 Mass spectrum of L

(a) Calculate the empirical formula of L.

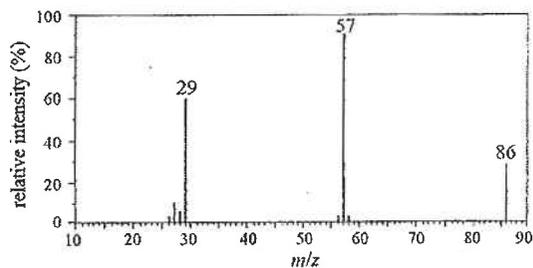
(2 marks)

(b) Deduce ONE possible structure of L.

(6 marks)

AL11(I)_10

Compound A contains carbon, hydrogen and oxygen only. It reacts with 2,4-dinitrophenylhydrazine to give a yellow precipitate, but shows negative results when treated with acidified $K_2Cr_2O_7(aq)$. The mass spectrum of A is shown below. Deduce ONE possible structure of A.

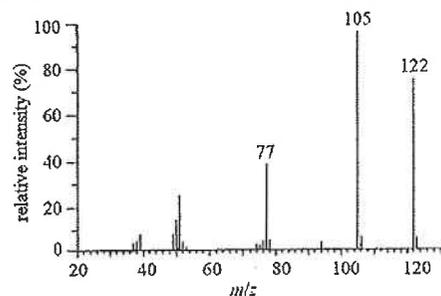


(5 marks)

AL12(I)_05

Based on the information given below, deduce the possible structures of compound F, G and J:

- (1) F ($C_9H_{10}O_2$) is optically active aromatic compound.
- (2) F reacts with acidified $K_2Cr_2O_7(aq)$ to give an optically inactive compound G. When treated with excess $NaHCO_3(aq)$, 1 mole of G gives 2 mole of $CO_2(g)$.
- (3) F reacts with hot acidified $KMnO_4(aq)$ to give another optically inactive compound J. J has the following mass spectrum.

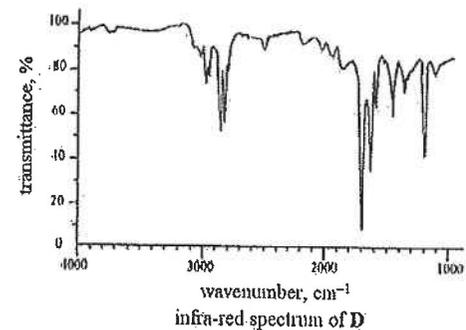
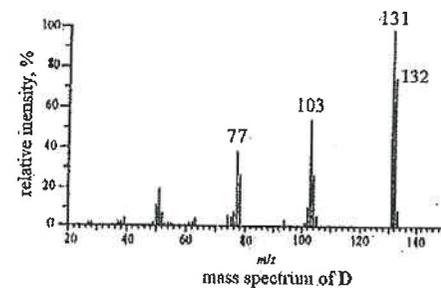


(7 marks)

AL13(I)_15

Form in information given below, deduce ONE possible structure for compound D.

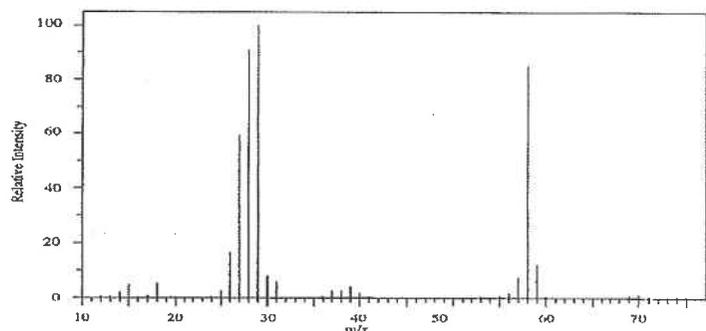
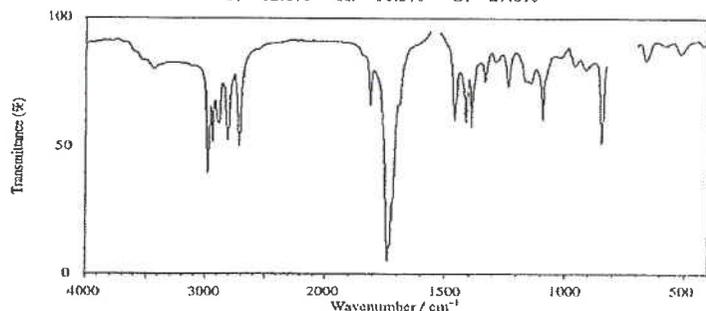
- (1) D has the following composition by mass:
C, 81.8% H, 6.1% O, 12.2%
- (2) D can turn acidified $K_2Cr_2O_7(aq)$ from orange to green.
- (3) D displays the following mass spectrum and infra-red spectrum.



DSE11SP_03a

Compound G, with relative molecular mass of 58, has the following composition by mass:

C: 62.1% H: 10.3% O: 27.6%



- (i) Deduce the molecular formula of compound G. (2 marks)
- (ii) From the given spectral information and the molecular formula obtained in (i), deduce the structural formula of compound G. (4 marks)
- (iii) Suggest an experiment, with detailed procedures, to support the structure of compound G you have deduced in (ii). (4 marks)

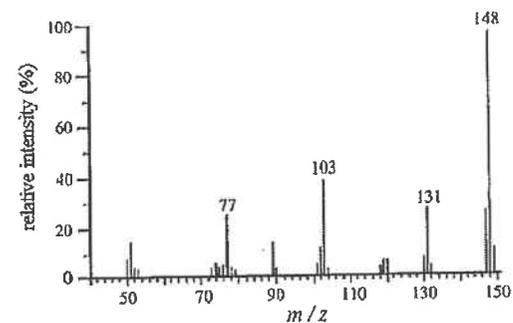
DSE12PP_03a

A colorless compound X ($C_9H_8O_2$) is obtainable from cinnamon. X has a melting point of $134\text{ }^\circ\text{C}$ and is insoluble in water.

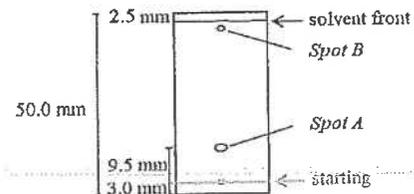
An experiment to extract X from an impure sample, which contains non-polar organic impurities, involves the following five steps:

Step 1:	Dissolve the sample in excess NaOH(aq).
Step 2:	Shake the solution from Step 1 with hexane and discard the organic layer.
Step 3:	Add HCl(aq) to the aqueous layer obtained until a white precipitate forms and the solution becomes acidic.
Step 4:	Collect the white precipitate by filtration.
Step 5:	Using ethanol as solvent, recrystallize the precipitate collected to obtain X.

- (i) From the above experimental steps, suggest ONE functional group present in X. (1 mark)
- (ii) Name the apparatus used in Step 2. (1 mark)
- (iii) Briefly explain the purpose of carrying out Steps 1, 2 and 3 respectively. (3 marks)
- (iv) X can decolorize Br_2 in CH_2Cl_2 . It displays the following mass spectrum. Deduce ONE possible structure of X.



- (v) Another sample of X is contaminated with a colorless organic compound. The sample is analyzed by thin-layer chromatography (TLC), and the result is shown below:



- (1) Suggest ONE method that can be used to make the two spots on the chromatographic plate become visible. (1 mark)
- (2) Given that Spot A corresponds to X, calculate the R_f of X. (1 mark)
- (3) Based on the TLC results, suggest ONE method to separate X from the contaminated sample. (1 mark)

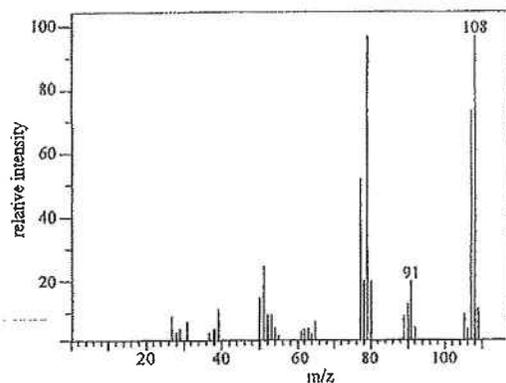
DSE12_03a

Compound X (molar mass < 118 g) contains a $-C_6H_5$ group. Two chemical tests are performed on X and the results are as follows:

Test (1) : X turns acidified potassium dichromate solution green.

Test (2) : X gives a negative result when tested with 2,4-dinitrophenylhydrazine.

- (i) With reference to the result of Test (1) only, suggest TWO functional groups that X may have. (2 marks)
- (ii) (1) What is the purpose of using 2,4-dinitrophenylhydrazine in Test (2)? (1 mark)
- (2) State the expected observation if X gives a positive result in Test (2). (1 mark)
- (iii) With reference to the results of both Test (1) and Test (2), suggest one functional group that may be present in X. (1 mark)
- (iv) The mass spectrum of X is shown below:



Suggest one chemical species corresponding to each of the signals at $m/z = 91$ and 108. (2 marks)

- (v) Draw a possible structure of X. (1 mark)

DSE12_03b

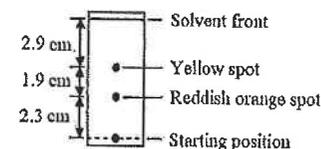
The dioxin levels in air are generally measured through instrumental analysis but not gravimetric analysis or volumetric analysis.

- (i) Suggest a source of dioxin in air. (1 mark)
- (ii) Explain why there is a need to measure the dioxin levels in air. (1 mark)
- (iii) Suggest an instrumental analytical method for measuring the dioxin levels in air, and state why this method, rather than methods based on gravimetric analysis or volumetric analysis, is to be used. (2 marks)

DSE13_03c

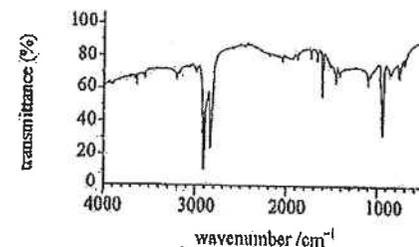
The main pigments in a certain brand of tomato paste are lycopene (reddish orange) and β -carotene (yellow). In order to isolate lycopene from the tomato paste, and experiment involving solvent extraction, thin-layer chromatography (TLC) and column chromatography was performed.

- (i) The result of TLC is shown below:

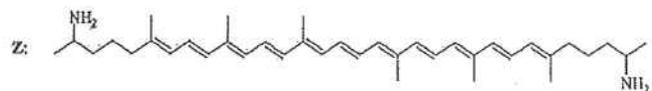
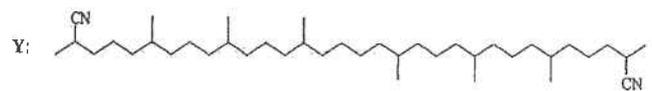
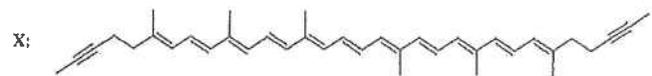
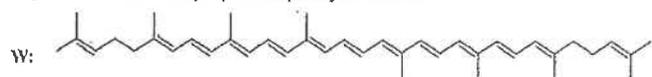


Calculate the R_f value for the lycopene spot.

- (ii) With reference to the result of TLC, explain whether the first-collected colored fraction in the column chromatography is lycopene or β -carotene, if the same stationary phase and mobile phase are used. (1 mark)
- (iii) Suggest an instrumental method that can be used to determine the concentration of lycopene in the collected lycopene fraction. State the physical property of the lycopene fraction that needs to be measured. (2 marks)
- (iv) The infra-red spectrum of lycopene is shown below:



By referring to the Characteristic Infra-red Absorption Wavenumber Ranges (Stretching modes) given in the table below, suggest which of the following structure (W, X, Y or Z) may be the structure of lycopene. Explain your answer.



(4 marks)

DSE14_03c

Under room temperature, T ($C_xH_yO_z$) is a colorless oily liquid and is immiscible with water. Moreover, T does not react with $NaHCO_3(aq)$.

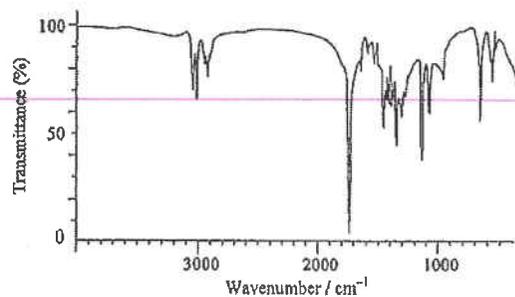
(i) A sample of T contains an organic acid as impurity. Outline the experimental steps for purifying the sample by using $NaHCO_3(aq)$ and pentane.

(2 marks)

(ii) With reference to the information given below, deduce the functional group(s) that T may have.

(I) T is NOT an ester, and it gives negative result with Tollen's reagent.

(II) T gives the following infra-red spectrum:



(2 marks)

(iii) The mass spectrum of T shows a parent peak at $m/z = 134$, and a strong peak at each of $m/z = 43$ and 91 . Suggest one chemical species corresponding to each of the signals at $m/z = 43$ and 134 .

(2 marks)

(iv) Draw one possible structure of T.

(1 mark)

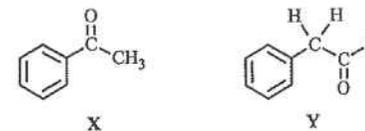
DSE15_03a

Suggest an instrumental method for determining the content of octane in a petrol sample.

(1 mark)

DSE15_03b

Compounds X and Y shown below are isomers with relative molecular mass 120.



(i) Each of X and Y can react with 2,4-dinitrophenylhydrazine solution to give a similar observation. State the observation.

(1 mark)

(ii) Suggest a chemical test to distinguish between X and Y.

(2 marks)

(iii) Illustrate how X and Y can be distinguished from their mass spectra.

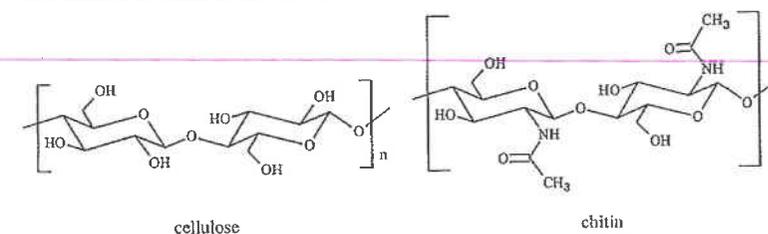
(2 marks)

(iv) With reference to the information given in the table below, suggest whether infra-red spectroscopy can be used to distinguish between X and Y.

(2 marks)

DSE16_03a

Both cellulose and chitin are natural polymers. Their structures are shown below:

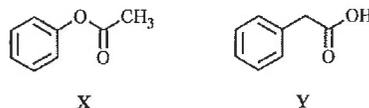


By referring to the data given in the table below, suggest one similarity and one difference between the infra-red spectra of cellulose and chitin.

(2 marks)

DSE16_03c

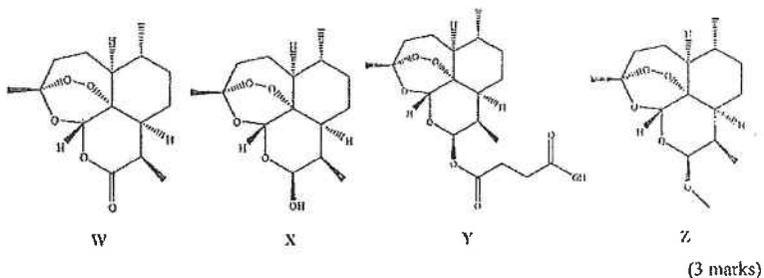
X and Y are isomeric compounds with their structures shown below:



- (i) Suggest, with explanation, how X and Y can be differentiated from their respective mass spectra. (2 marks)
- (ii) The melting point of X is 50 °C while that of Y is 77 °C. Both of them are insoluble in water but soluble in dichloromethane. When treated with dilute Na₂CO₃(aq), no reaction occurs for X but reaction occurs for Y to form a soluble salt.
- (1) You are provided with dilute Na₂CO₃(aq) and dilute H₂SO₄(aq). Outline an experimental procedure, based on solvent extraction, to separate solid Y from a solution of X and Y in dichloromethane. (4 marks)
- (2) Suggest how you can identify that the solid obtained in (1) is pure compound Y. (1 mark)

DSE17_03c

Artemisinin is an organic compound obtained from a certain plant. Artemisinin cannot react with NaHCO₃(aq). Its infra-red spectrum shows a strong absorption peak at around 1700 cm⁻¹. Suggest which one of W, X, Y and Z below would be a possible structure of artemisinin. Explain your answer.



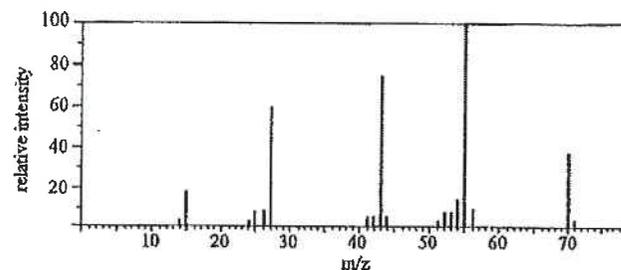
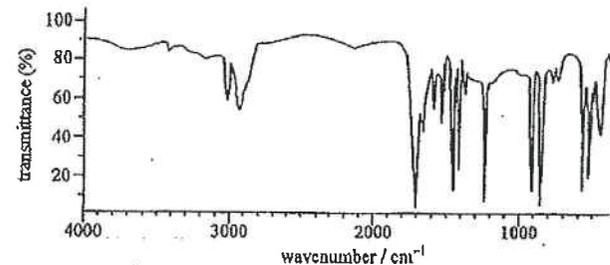
172

DSE18_03c

A liquid mixture consists of two organic compounds X and Y:

	X	Y
Molecular formula	C ₄ H ₆ O	C ₄ H ₈ O
Boiling point / °C	81.4	79.6

- (i) Explain why fractional distillation is NOT a suitable method to separate X from the mixture. (1 mark)
- (ii) X gives the following infra-red spectrum and mass spectrum:



- (1) By referring to the infra-red spectrum and the information given in the table below, deduce one functional group that may be present in X. (1 mark)
- (2) By referring to the mass spectrum, suggest one chemical species corresponding to each of the signals at m/z = 43 and 55. (2 marks)
- (3) According to (1) and (2) above, draw a possible structure of X. (2 marks)
- (iii) Compound Y shows a positive result in 2,4-dinitrophenylhydrazine test, and a negative result in Tollens' reagent test. Deduce what Y may be. (3 marks)

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DSE19_03cii

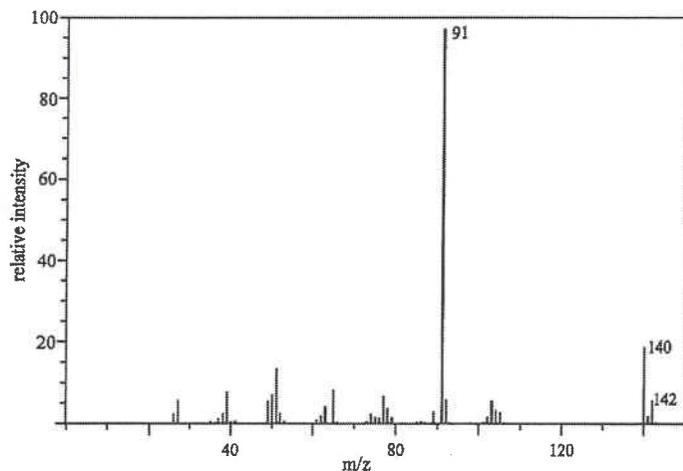
3. (c) Chlorine reacted with ethylbenzene (CC1=CC=CC=C1) under sunlight to give a mixture of different chlorinated compounds.

(i) Thin layer chromatography (TLC) was used to separate a small amount of the mixture.

- (1) Explain briefly why chromatography can be used to separate a mixture.
- (2) Based on the result in TLC, suggest a method to separate a large amount of the mixture.

(3 marks)

(ii) A monochlorinated compound was isolated from the mixture. It is known that chlorine has two isotopes, ^{35}Cl and ^{37}Cl . The mass spectrum of the compound is shown below:

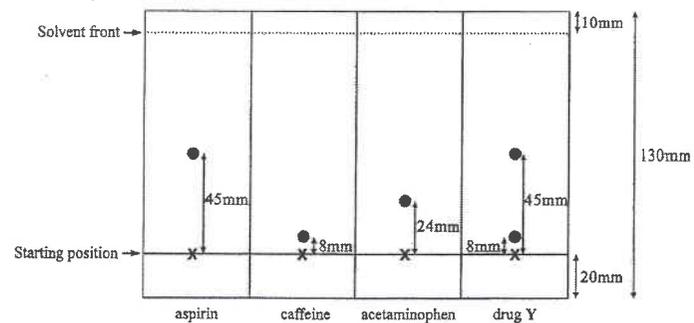


By referring to the labelled peaks, deduce a possible structure of the compound.

(3 marks)

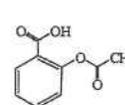
DSE20_03 iv

(b) The chromatograms from thin-layer chromatography (TLC) of aspirin, caffeine, acetaminophen and a drug Y are shown below.

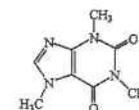


- (i) Draw a labelled diagram for the set-up in performing a TLC experiment. (2 marks)
- (ii) Calculate the R_f value for aspirin. (1 mark)
- (iii) Based on the chromatograms provided, suggest whether drug Y would contain aspirin, caffeine or acetaminophen. (1 mark)

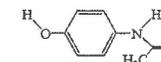
(iv) Consider the following structures:



aspirin



caffeine



acetaminophen

3. (b) (iv) (1) With reference to the table below, suggest how aspirin and caffeine can be distinguished from their infra-red spectra.

Characteristic Infra-red Absorption Wavenumber Ranges
(Stretching modes)

Bond	Compound type	Wavenumber range / cm^{-1}
C=C	Alkenes	1610 to 1680
C=O	Aldehydes, ketones, carboxylic acids and derivatives	1680 to 1800
C≡C	Alkynes	2070 to 2250
C≡N	Nitriles	2200 to 2280
O-H	Acids (hydrogen-bonded)	2500 to 3300
C-H	Alkanes, alkenes, arenes	2840 to 3095
O-H	Alcohols (hydrogen-bonded)	3230 to 3670
N-H	Amines	3350 to 3500

- (2) A pure sample may be aspirin, caffeine or acetaminophen. There is a major peak at $m/z = 43$ in the mass spectrum of the sample. Explain whether this information can confirm that the sample is aspirin, caffeine or acetaminophen.

(3 marks)

Marking Scheme

AL97(II)_06

IR peak at $\sim 1750 \text{ cm}^{-1}$ indicates the presence of a C=O, carbonyl group. [1]

No broad OH band at $2500 - 3400 \text{ cm}^{-1}$ implies that H is not a carboxylic acid.

No reaction with NaBH_4 implies H is not ketone or aldehyde / may be an ester.

Possible structures of H:



(deduce 1 mark for each extra structure).

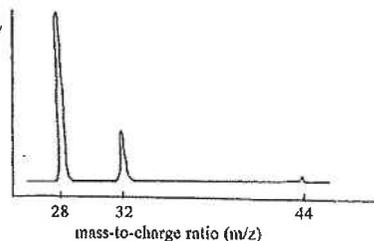
AL98(I)_08a

One of the following: [1]

- Infra-red spectroscopy, only propan-2-ol shows absorption (OH stretch) from $3230 - 3670 \text{ cm}^{-1}$.
- Infra-red spectroscopy, only propanone shows strong C=O stretching absorption at about $1680 - 1750 \text{ cm}^{-1}$.
- Mass spectroscopy, propan-2-ol has a m/z peak of 60 and propanone of 58.

AL98(II)_04

Relative abundance / Ion intensity .
Peak height



[3]

(½ marks for each axis; ½ marks for showing the correct position of each peak;

½ marks for showing the correct relative abundance)

AL99(II)_01

(a) Mass spectrometry [1]

The abundance of an isotope is proportional to the height of the peak (current intensity) of its cation. [1]

OR,
$$\frac{\text{Abundance of } ^{85}\text{Rb}}{\text{Abundance of } ^{87}\text{Rb}} = \frac{\text{height of peak at } m/z = 85}{\text{height of peak at } m/z = 87}$$

(b) Relative atomic mass of Rb [1]

$$= 84.939 \times 72.15\% + 86.937 \times 27.85\%$$
 [1]

$$= 85.495$$
 [1]

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AL00(II)_01

(a) Chlorine has two isotopes ^{35}Cl and ^{37}Cl . [1]

Bombardment of electron on chlorine produces atomic ion Cl^+ and molecular ion $[\text{Cl}-\text{Cl}]^+$. [1]

The five peaks correspond to the species: $^{35}\text{Cl}^+$, $^{37}\text{Cl}^+$, $[\text{Cl}-\text{Cl}]^+$, $[\text{Cl}-\text{Cl}]^+$ and $[\text{Cl}-\text{Cl}]^+$. [1]

(b) (i) relative atomic mass of $\text{Cl}_2 = \frac{35 \times 3 + 37 \times 1}{4} = 35.5$ [2]

(ii) Abundance of A $\propto \frac{1}{4} \times \frac{1}{4}$ [½]

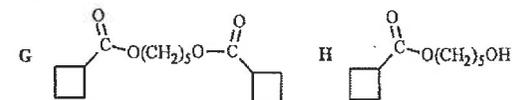
Abundance of B $\propto 2 \times \frac{1}{4} \times \frac{3}{4}$ [½]

Abundance of C $\propto \frac{3}{4} \times \frac{3}{4}$ [½]

Ratio of relative abundance of A : B : C = $\frac{1}{16} : \frac{6}{16} : \frac{9}{16} = 1 : 6 : 9$ [½]

AL00(II)_05

(a) [2]



G is less polar than H (or H has a polar OH group) and is therefore less tightly bound to the stationary phase and hence moves faster. [1]

(b) Reagent: $\text{PCl}_5 / \text{PCl}_3 / \text{SOCl}_2$ [1]

Only H will give misty fumes of HCl [1]

OR, Reagent: Na

Only H will react with Na to give gas bubbles (H_2).

(c) Compound H shows a IR absorption at $3200 - 3700 \text{ cm}^{-1}$ but G does not because [1]

H has an OH functionality whereas G does not. [1]

AL01(II)_01

The sample is vaporized in the mass spectrometer and is bombarded by fast moving electrons to give positive ions. [1]

The ions are accelerated by an electric field. [1]

The accelerated ions are then deflected by a magnetic field. [1]

The mass spectrometer is operated at low pressure to prevent ions from colliding with other particles. [1]

The lighter the positive ion, the greater is the deflection. [1]

By varying the strength of the deflecting magnetic field, ions of a particular mass / charge (m/e) ratio are brought to the ion detector. [1]

Determination of the relative atomic mass of a noble gas:

The current intensity produced by cations formed from an isotope is proportional to the [1]

175

relative abundance of the isotope.

$$\text{Relative atomic mass of the noble gas} = \sum(\text{isotopic mass} \times \text{relative abundance}) \quad [1]$$

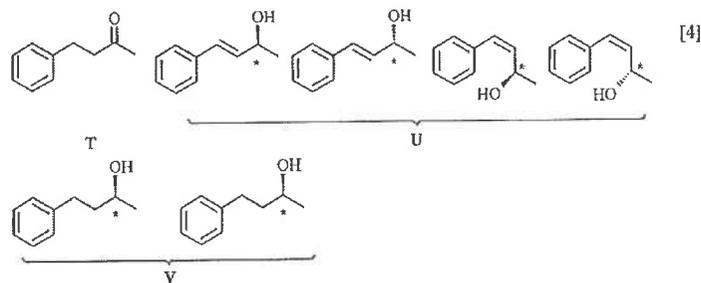
AL01 II_(7)

(a) T gives positive result in the iodoform test and has the structural characteristic [1]



U reacts with H_2 Pd \therefore U is an alkene / has a C=C group. [1/2]

T can be reduced by LiAlH_4 \therefore T is a ketone / has a C=O group [1/2]



T: 1 mark; U: 2 marks for 4 structures; V: 1 mark for 2 structures

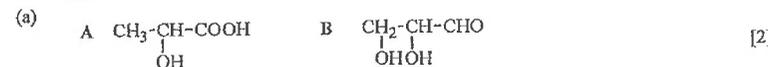
(b) T has a sharp absorption peak in the wavenumber range from 1680 to 1750 cm^{-1} but [1/2]

U has not. [1/2]

U has a broad absorption peak in the wavenumber range from 3230 to 3670 cm^{-1} but [1/2]

T has not. [1/2]

AL02(I)_05



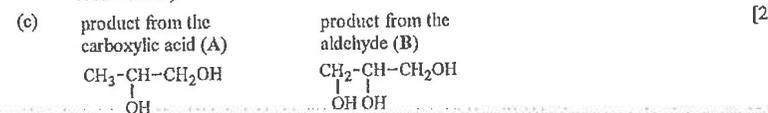
(b) Treat compounds with $\text{Na}_2\text{CO}_3(\text{aq})$ [1]

Only the carboxylic acid (A) will give $\text{CO}_2(\text{g})$ [1]

OR, Treat compounds with 2,4-dinitrophenylhydrazine / Fehling's reagent

Only the aldehyde (B) will give a yellow precipitate / red precipitate.

(Accept other test for the carbonyl group and the corresponding expected observations)



AL02(II)_01b

(i) In the ionization chamber, AB_3 molecules were bombarded by fast moving electrons. [1]
Knocking out an electron from $\text{AB}_3(\text{g})$ give $\text{AB}_3^+(\text{g})$. [1]

(ii) The peak at m/z ration = 31 is due to A^+ (P^+) ions. [1]

The peak at m/z ration = 19 is due to B^+ (R^+) ions. [1]

(iii) PF_3 [1]

AL03(II)_05

(a) Degree of unsaturation of oil decreases upon hydrogenation. [1/2]

Vegetable oil contains C=C bonds which are rigid. [1]

The C=C bonds prevent molecules of oil from packing close together. In hardened [1/2]

oils, interlocking of hydrocarbon chains restricts the relative motion of the fat [1/2]

molecules. \therefore Vegetable oils become hardened upon hydrogenation.

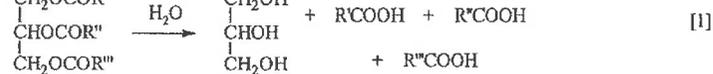
(b) The fumes from heating molten margarine consist mainly of triglycerides. The IR [1/2]

absorption wavenumbers at 2950 cm^{-1} and 1750 cm^{-1} are due to the stretching of [1/2]

C-H bond and C=O bond respectively.

Potatoes contain water which causes margarine to undergo hydrolysis to give free [1]

carboxylic acids and glycerine.



The IR absorption at is due to O-H bonds in glycerine and in carboxylic acids. [1/2]

AL03(II)_07

G ($\text{C}_7\text{H}_6\text{O}_2$) is an aromatic compound with pK_a value 4.2. It is benzoic acid. [1/2]

E has an IR absorption peak at 1720 cm^{-1} . It possesses a carbonyl group. [1/2]

E can be reduced by LiAlH_4 but cannot oxidized by Tollens' reagent

\therefore E is a ketone. [1/2]

F is formed from the reduction of a ketone. It is a secondary alcohol. [1/2]

Structure of E, F and G.



(3 marks for the three structure; 1 mark for optical inactive / achiral)

AL05(II)_05

(a) Functional group isomerism [1]

(b) (i) Compare their boiling points / melting points. [1]

J has a higher boiling point / melting points.

OR, J is a solid while K is liquid.

Intermolecular force between J molecules is hydrogen bond, while that between K molecules is van der Waals' force. [1]

(ii) Any ONE of the following: [2]

- Suspend compounds in a little water, and add NaOH(aq). Only J dissolves.
- Treat compounds with neutral FeCl₃(aq). Only J gives a purple solution. (Out of syllabus)
- Dissolve compounds in a little NaOH(aq), then add C₆H₅N₂⁺(aq). Only J gives a bright red precipitate / an azo dye.

(iii) Run IR spectrum of J and of K [1]

Only J gives a broad and strong absorption from 3230 to 3670 cm⁻¹ / stretching of O-H in alcohol. [1]

AL05(II)_06a

(i) Foam for insulation / furniture stuffing / carpet / plywood [1]

(ii) KMnO₄ on Al₂O₃ [1]

HCHO is oxidized to less harmful and less volatile product (HCOOH).

Pollutant	Source
Benzene / toluene	Paint / thinner / gasoline
Chlorinated hydrocarbons	Garments after dry cleaning
Chloroform	Chlorine-treated water

[2]

AL05(II)_07

(a) mole ratio of C : H : O = $\frac{77.8}{12} : \frac{7.4}{1} : \frac{14.8}{16} = 7 : 8 : 2$ [1]

Empirical formula: C₇H₈O [1]

Molecular formula: (C₇H₈O)_n

Relative molecular mass of L is 108

n = 1

∴ molecular formula: C₇H₈O [1]

(b) Each point 1 mark, maximum 5 marks: [5]

- L does not react with Br₂ ∴ L does not possess C=C bond.
- L has a double bond equivalence of 4. It is likely to be an aromatic compound. L is likely to be C₆H₅CH₂OH
- M has a broad IR absorption in the wavenumber range of 3300 – 2500 cm⁻¹ which is resulted from the stretching of O-H bond.
- M is obtained from the oxidation of L. M is likely to be benzoic acid C₆H₅COOH.
- The other absorption at 1700 cm⁻¹ is due to the stretching of C=O bond.
- N is also a carbonyl compound (IR) absorption at 1750 cm⁻¹. It is benzoyl chloride C₆H₅COCl. The absorption at 3000 cm⁻¹ is due to the stretching of C-H bond.

AL06(II)_05

mole ratio of C : H : O = $\frac{40.0}{12} : \frac{6.7}{1} : \frac{53.3}{16} = 3.3 : 6.7 : 3.33 = 1 : 2 : 1$ [1]

Empirical formula: CH₂O

Molecular formula: (C CH₂O)_n [1]

Relative molecular mass of D is 108

172 < (12 + 2 + 16)n < 182

n = 6

molecular formula of D is C₆H₁₂O₆ [1]

Infra-red spectrum:

✧ Strong and broad absorption near 3400 cm⁻¹. ∴ D has O-H groups. [1]

✧ No absorption around 1700 cm⁻¹. D does not possess carbonyl groups. [1]

✧ D does not decolorize bromine ∴ D does not have C=C bond. [1]

✧ All carbon atoms of D have the same bonding environment, i.e. they are in same hybridization state, bonded to the same groups, and have the same configuration. [1]

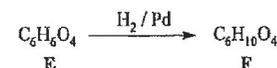


AL06(II)_06

(a) From IR spectrum

✧ E possesses a O-H group (broad absorption peak at 3300 cm⁻¹) [1]

✧ And carbonyl group (absorption peak at 1700 cm⁻¹) [1]



✧ E has two C=C bonds or one C≡C bond. [1]

✧ F is acidic. F has the structure HOOC(CH₂)₄COOH [1]

✧ E is an acyclic compound with formula C₆H₆O₄. It has the structure HOOCCH=CH-CH=CH-COOH [1]

(b) Upon reduction, ozone gives H₂O which is harmless. [1]

Ozone has short lifetime. The residual O₃ will not remain in the atmosphere for a long time. [1]

AL07(II)_07

(a) mole ratio of C : H : Cl : O = $\frac{59.8}{12} : \frac{3.6}{1} : \frac{25.2}{35.5} : \frac{11.4}{16} = 4.98 : 3.6 : 0.71 : 0.71$ [1]

mole ratio of C : H : Cl : O = 7 : 5 : 1 : 1

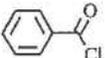
Empirical formula: C_7H_5ClO [1]

(b) The molecular-ion of M has $m/z = 140$ [½]

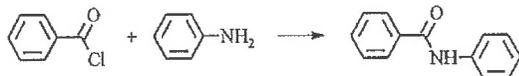
∴ molecular formula of M is C_7H_5ClO [½]

The peak at $m/z = 105$ is likely to be due to the stripping off of a Cl atom from the molecular-ion, e.g. $C_7H_5O^+$ [½]

The peak at $m/z = 77$ is due to $C_6H_5^+$ [½]

M is  [1]

(c) M can be identified by preparing a solid derivative of M, such as [1]



and compare the m.p. of the derivative with that of an authentic sample. [1]

OR,

◇ Add water to M. The white fume HCl will be given.

◇ Add $AgNO_3(aq)$. White precipitate will be given.

AL08(I)_08a

The absorption at 1614 cm^{-1} is due to the stretching of the C=C bond. [1]

As polymerization proceeds, the concentration of the monomers decreases. Thus, the intensity of C=C absorption reduces. [1]

AL08(II)_06

The IR spectrum of A shows a strong absorption at around 1750 cm^{-1} . A is likely to possess a carbonyl group. [1]

A does not have a broad absorption peak in the region of 2500 to 3500 cm^{-1} . A does not possess a hydroxyl group. [1]

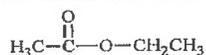
A can be an ester or an alkoxy carbonyl compound. [1]

In the mass spectrum, the peak at $m/z = 88$ is that of the molecular-ion. [½]

Peak at $m/z = 43$ is that of the $CH_3C=O^+$ ion. ∴ A is not an aldehyde. [1]

Peak at $m/z = 29$ is likely to be due to the $CH_3CH_2^+$ ion. ∴ A carries an ethyl group. [½]

A possible structure of A is $CH_3COOCH_2CH_3$ [1]



AL09(II)_05

The IR spectrum of P shows a broad absorption from around 2500 to 3300 cm^{-1} . P is likely to possess an OH group. [1]

P shows a strong absorption at 1710 cm^{-1} ($1680 - 1800\text{ cm}^{-1}$). It is likely to possess a carbonyl group. [1]

The peaks at $m/z = 152$ and 154 are due to the two molecular ions as Br has two isotopes with mass numbers 79 and 81, and they have almost the same relative abundance. [1]

The peaks at $m/z = 135$ and 137 are formed from the molecular ions by stripping off the OH group. [1]

The peaks at $m/z = 107$ and 109 are formed by further stripping off the C=O group. P is likely to be a carboxylic acid. [1]

The peaks at $m/z = 73$ is formed from the molecular ions by stripping off the Br atom. P is a bromopropanoic acid. [1]

Possible structure of P:

$BrCH_2CH_2COOH$ or $CH_3CHBrCOOH$ [1]

AL10(II)_03b

Any TWO of the following: [2]

- Relative molecular mass can be determined to very high accuracy.
- Only a very small amount of the compound is required.
- The time for the experiment is short.
- It can also be used to determine the relative molecular mass of non-volatile compounds.

AL10(II)_05

(a) mole ratio of C : H : O = $\frac{70.6}{12} : \frac{5.9}{1} : \frac{23.5}{16}$ [1]

= $5.88 : 5.9 : 1.47 = 4 : 4 : 1$

Empirical formula: C_4H_4O [1]

(b) Molecular formula: $(C_4H_4O)_n$

m/z of molecular ion is 136

$(12 \times 4 + 4 + 16 \times 1)n = 136$, $n = 2$

Molecular formula: $C_8H_8O_2$ [1]

In the IR spectrum, the broad peak in the wavenumber range of 2500 to 3300 cm^{-1} [1]

shows the presence of an -OH group.

The absorption at 1680 to 1800 cm^{-1} shows the presence of C=O group. [1]

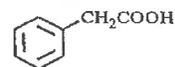
L is likely to have the structure of $C_7H_7(CO)(OH)$. It is an aromatic compound. [1]

The peak at $m/z = 91$ is likely to be due to the stable tropylium ion ($C_7H_7CH_2^+$). [1]

The tropylium ion is likely to be formed from L^+ by stripping off a -COOH group.

$(136 - 45 = 91)$

L is likely to be



[1]

AL11(I)_10

A gives yellow precipitate with 2,4-dinitrophenylhydrazine. ∴ it is an aldehyde or ketone. [½]

A does not react with acidified $K_2Cr_2O_7(aq)$. It is a ketone. [½]

The molecular ion at $m/z = 86$ suggests the molecular mass of A to be 86. [½]

$86 - 28$ (formula mass of $C=O$) = 58. A is likely to have the formula $(C_4H_{10})CO^+$ as the formula mass of C_4H_8 is 58. [½]

Molecular ions of ketone $(RCOR')^+$ tend to usually undergo fragmentation to give RCO^+ and $R'CO^+$. The peak at $m/z = 57$ is likely to be due to $C_2H_5CO^+$. [1]

The peak at $m/z = 29$ is likely to be due to $C_2H_5^+$ which is formed from $C_2H_5CO^+$ by stripping off the CO. [1]

A does not show other prominent m/z peak. It is likely to be $C_2H_5COC_2H_5$. [1]

AL12(I)_05

F has a double bond equivalence of 5

F is an aromatic compound. ∴ F has a benzene ring and a double bond.

Treating F with hot MnO_4^-/H^+ oxidized the alkyl side chain to carboxylic acid. [½]

J is an aromatic monocarboxylic acid.

From the mass spectrum, the molecular ion of J has $m/z = 122$. It is due to $[C_6H_5COOH]^+$. [½]

J can only be C_6H_5COOH [1]

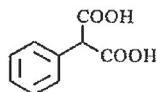
The peak at $m/z = 105$ ($122 - 17$) is due to $[C_6H_5CO]^+$. [½]

The peak at $m/z = 77$ ($105 - 28$) is due to $[C_6H_5]^+$ [½]

As J is benzoic acid, F can only be a mono-substituted aromatic compound.

G reacts with excess $NaHCO_3(aq)$ to give 2 mole of $CO_2(g)$. G is a dicarboxylic acid. [½]

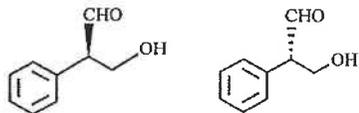
G is



[1]

$Cr_2O_7^{2-}/H^+$ can only oxidize $-CHO$ or $-CH_2OH$ to carboxylic acid. [½]

F is optically active. It can be [½]



[1]

AL13(I)_15

mole ratio of C : H : O = $\frac{81.8}{12} : \frac{6.1}{1} : \frac{12.1}{16} = 6.82 : 6.1 : 0.76 = 9 : 8 : 1$ [1]

Empirical formula: C_9H_8O [1]

D react with acidified $K_2Cr_2O_7(aq)$. It is either a primary alcohol, secondary alcohol or aldehyde. [½]

From the mass spectrum, the molecular ion of D has $m/z = 132$. It is due to $[C_9H_8O]^+$. [½]

Molecular formula of D is C_9H_8O . [½]

D has a double bond equivalence of 6

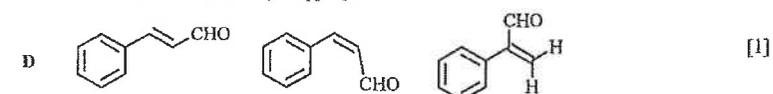
The peak at $m/z = 77$ is due to $[C_6H_5]^+$. ∴ D has a benzene ring. [1]

The absorption at $\sim 1680\text{ cm}^{-1}$ shows the presence of C=O group. [1]

D does not have a broad absorption peak in the region of 2500 to 3670 cm^{-1} . D does not possess $-OH$ / a hydroxyl group. [1]

D can be an aldehyde because the peak at $m/z = 103$ ($132 - 29 = 103$) is likely formed from $C_9H_8O^+$ by stripping off the $-CHO$. [1]

OR D can be an aldehyde because the peak at $m/z = 131$ ($132 - 1 = 131$) is likely formed from $C_9H_8O^+$ by stripping off the H.



[1]

DSE11SP_03a

(i) mole of carbon atom = $\frac{58 \times 0.621}{12} = 3$ [2]

mole of hydrogen atom = $\frac{58 \times 0.103}{1} = 6$

mole of oxygen atom = $\frac{58 \times 0.276}{16} = 1$

Molecular formula of G is C_3H_6O

(ii) From the IR spectrum, the presence of a sharp absorption peak at 1740 cm^{-1} indicates the presence of a carbonyl group. [1]

From the mass spectrum, the peaks at m/e 29 corresponds to $C_2H_5^+$ and [1]

the peak at m/e 58 corresponds to $CH_3CH_2CHO^+$. [1]

The structural formula of G should be CH_3CH_2CHO . [1]

(iii) Add 2,4-dinitrophenylhydrazine to G to prepare the corresponding 2,4-dinitrophenylhydrazone. [1]

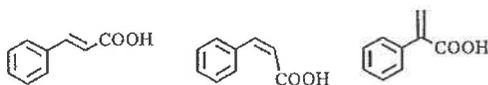
Recrystallize the 2,4-dinitrophenylhydrazone. [1]

Measure its melting point using a melting point apparatus. [1]

A sharp melting point, which is the same as that quoted in the literature, will support the deduction of G. [1]

DSE12PP_03a

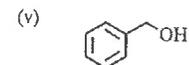
- (i) Carboxylic acid / carboxyl group (because X is soluble in NaOH(aq)) [1]
(Also accept phenol).
- (ii) Separating funnel [1]
- (iii) Step 1: Allow X to dissolve in NaOH(aq) to give (carboxylate) anions / a salt. [1]
Step 2: Allow the non-polar impurities to dissolve in hexane while the (carboxylate) anions / salt to stay in the aqueous layer. [1]
OR, Separate the non-polar impurities (in hexane) from the salt of X.
Step 3: Regenerate the (carboxylic) acid (which is insoluble in water) by adding acid. [1]
- (iv) X possesses a C=C bond because it decolorizes Br₂ in CH₂Cl₂. [1]
In the mass spectrum, the peak at m/z = 148 is due to the molecular ion. [1]
Any TWO of the following: [2]
The peak at m/z = 131 is due to the cation formed from the molecular ion by stripping off a -OH.
The peak at m/z = 103 is due to the cation formed from the molecular ion by stripping off a -CO₂H.
The peak at m/z = 77 shows that X carries a benzene ring (m/z for C₆H₅⁺ ion = 77).
Possible structures of X:



- (v) (1) Put the chromatographic plate into a jar that is saturated with iodine vapor. The spot will appear brown. [1]
OR, Irradiate the plate with UV. The stationary phase is fluorescent while the two spots are not. [1]
- (2) $R_f = \frac{\text{distance travelled by X}}{\text{distance travelled by solvent}} = \frac{9.5}{(50 - 3 - 2.5)} = 0.21$ [1]
- (3) Column chromatography (using the same moving phase and stationary phase) [1]

DSE12_03a

- (i) hydroxyl (group) / -OH / alcohol [1]
aldehyde (group) / -CHO / aldehyde [1]
- (ii) (1) Test for aldehyde (group) or ketone (group) / carbonyl (group) / aldehyde (group) and ketone (group). [1]
(2) 2,4-dinitrophenylhydrazine reacts with aldehyde or ketone to give yellow, orange or red precipitate. [1]
- (iii) hydroxyl (group) / -OH [1]
- (iv) m/z = 91 suggested the presence of C₇H₇⁺ / C₆H₅CH₂⁺. [1]
m/z = 108 suggested the presence of C₇H₈O⁺ / C₇H₇OH⁺ / C₆H₅CH₂OH⁺. [1]



[1]

DSE12_03b

- (i) Any ONE of the following: [1]
Combustion of materials containing chlorine / PVC
Incineration of materials containing chlorine
Emission from incinerators
Burning / combustion of plastic waste
- (ii) Dioxin is carcinogenic / can cause cancer. [1]
- (iii) Gas chromatography DSE12_03b phy-mass spectrometry / GCMS [1]
It can measure more accurately the low level of dioxin than using gravimetric analysis or volumetric analysis.

DSE13_03c

- (i) $\frac{2.3}{2.3 + 1.9 + 2.9} = \frac{2.3}{7.1} = 0.32$ [1]
(Accept also 0.324 and 0.3239 BUT NOT 0.3)
- (ii) β-Carotene [1]
Lycopene has a smaller R_f value / lycopene moves slower [1]
Lycopene takes a longer time to reach the bottom of the column.
- (iii) Method: colorimetry / use of colorimeter / use of spectrophotometer [1]
Measurement: absorbance / color intensity / light intensity / transmittance [1]
- (iv) Compound W is lycopene [1]
The absence of (absorption) peaks at around 2070 – 2250 cm⁻¹ suggesting it does not contain C=C groups / ruling out the possibility of compound X. [1]
The absence of (absorption) peaks at around 2220 – 2280 cm⁻¹ suggesting it does not contain C≡N groups / ruling out the possibility of compound Y. [1]
OR The presence of (absorption) peaks at around 1630 cm⁻¹ (1600 – 1680 cm⁻¹) (shows the presence of C=C / C–C double bonds) ruling out the possibility of compound Y.

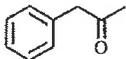
(Note: 2 marks for the absence of (absorption) peaks at around 2070 – 2280 cm⁻¹ suggesting it does not contain C=C and C≡N groups / ruling out (the possibility of compounds X and Y.)

The absence of sharp (absorption) peaks at around 3350 – 3500 cm⁻¹ suggesting it does not contain -NH₂ group / ruling out the possibility of compound Z. [1]

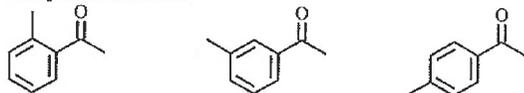
Compound W is a hydrocarbon which contains only C–H, C–C and C=C bonds. This agrees with the feature of the spectrum as there are small peaks at around 1630 cm⁻¹, showing the presence of C=C double bonds.

DSE14_03c

- (i) Dissolve the sample in pentane and shake the solution with $\text{NaHCO}_3(\text{aq})$ in a separating funnel. [1]
Collect the organic layer and carry out fractional distillation / distillation. [1]
[Only fractional distillation / distillation: 0 mark]
- (ii) The spectrum does not show strong absorption at about $3230 - 3670 \text{ cm}^{-1}$, ruling out the presence of a hydroxyl group (the possibility of being an alcohol) [1]
OR, The absence of absorption at $2070 - 2250 \text{ cm}^{-1}$ ruled out the presence of $\text{C}\equiv\text{C}$ group. [1]
OR, The absence of absorption at $1610 - 1680 \text{ cm}^{-1}$ ruled out the presence of $\text{C}=\text{C}$ group. [1]
The spectrum has a strong absorption at 1730 (1700 to 1750) cm^{-1} , which corresponds to $\text{C}=\text{O}$ stretching. The compound may contain an aldehyde group or a ketone group. [1]
- (iii) $m/z = 43$: $[\text{CH}_3\text{CO}]^+$ [1]
 $m/z = 134$ $[\text{C}_7\text{H}_7\text{COCH}_3]^+$ *OR* $[\text{C}_6\text{H}_5\text{C}_3\text{H}_5\text{O}]^+$ [1]
NOT accept: $[\text{C}_2\text{H}_3\text{O}]^+$ / $[\text{C}_9\text{H}_{10}\text{O}]^+$

(iv)  [1]

Other possible structures:



DSE15_03a

Chromatography / GC / GCMS / HPLC [1]

DSE15_03b

- (i) yellow / orange / red precipitate (solid/ppt) [1]
- (ii) Add acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$. [1]
Only Y turns the solution from orange to green. [1]
OR Only Y turns $\text{MnO}_4^-/\text{H}^+$ from purple to colorless. [1]
OR Only Y gives a silver mirror in Tollens' test. [1]
OR Only X gives a yellow precipitate with $\text{I}_2/\text{NaOH}(\text{aq})$. [1]
- (iii) A significant peak appears at m/z 105 ($\text{C}_6\text{H}_5\text{CO}^+$) / 43 (CH_3CO^+) / 15 (CH_3^+) in mass spectrum of X only. [1]
A significant peak appears at m/z 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$) or 29 (HCO^+) in mass spectrum of Y only. [1]
- (iv) Both compounds show a characteristic absorption in the wavenumber range (1680 to 1800 cm^{-1}) which is characteristic of carbonyl group ($>\text{C}=\text{O}$ bond). [1]
As the two compounds do not possess other different functional groups, they cannot be differentiated from each other using the given information. [1]

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DSE16_03a

Similarity: Both show an absorption peak at $3230 - 3670 \text{ (cm}^{-1}\text{)}$ ($\text{O}-\text{H}$ groups) [1]
Difference: Only chitin shows an absorption peak at $1680 - 1800 \text{ (cm}^{-1}\text{)}$ ($\text{C}=\text{O}$ groups) [1]
(comparison must be shown)

DSE16_03c

- (i) The mass spectra of X and Y are recorded respectively. [1]
In the mass spectrum of X, a significant peak at $m/z = 43$ appears for CH_3CO^+ ions which does not appear in the mass spectrum of Y. [1]
In the mass spectrum of Y, a significant peak at $m/z = 119$ appears for $\text{C}_6\text{H}_5\text{CH}_2\text{CO}^+$ ions which does not appear in the mass spectrum of X. [1]

OR

Mass spectrum of X	Mass spectrum of Y
CH_3^+ or m/z 15	
CH_3CO^+ or m/z 43	
$\text{C}_6\text{H}_5\text{O}^+$ or m/z 93	
$\text{C}_6\text{H}_5\text{OCO}^+$ or m/z 121	
	OH^+ or m/z 17
	COOH^+ or m/z 45
	$\text{C}_6\text{H}_5\text{CH}_2^+$ or C_7H_7^+ or m/z 91
	$\text{C}_6\text{H}_5\text{CH}_2\text{CO}^+$ or $\text{C}_7\text{H}_7\text{CO}^+$ or m/z 119

(any 2 answers each with comparisons: 1 mark each)

- (ii) (1) $\text{Na}_2\text{CO}_3(\text{aq})$ is added to the dichloromethane solution of X and Y. [1]
The mixture is shaken in a separating funnel. [1]
The mixture in the separating funnel is allowed to settle, and the aqueous layer was then separated from the organic layer. [1]
Dilute $\text{H}_2\text{SO}_4(\text{aq})$ is added to the aqueous layer / upper layer / lower aqueous layer / (until no more precipitate is formed.) / (the solution becomes acidic). [1]
Solid Y can be obtained by filtration. [1]
- (2) Measure the melting point of the solid obtained. [1]
If the melting point of the solid is 77°C / a sharp m.p. measured / a narrow melting point range, it may be pure compound Y. [1]
(mixed melting point technique \rightarrow sharp melting point / m.p. 77°C ;
OR compare the IR spectrum / mass spectrum / NMR spectrum of the solid obtained with that of authentic sample, if they are identical \rightarrow pure
OR run a TLC / paper chromatography for the sample; if only one spot is detected on the chromatogram \rightarrow pure)

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DSE19_03c

DSE17_03c

W

It has $>C=O$ / carbonyl group as it has a strong absorption (peak) at around 1700 cm^{-1} in its IR spectrum. [Y OR W; NOT X and Z] [1]

It has no $-COOH$ / carboxyl group as it does not react with $NaHCO_3(aq)$. [NOT Y] [1]
[NOT accept $NaHCO_3(s)$]

Accept: From the given information in IR spectrum, it has $>C=O$ group
From the given information on the reaction with $NaHCO_3$, it has no $-COOH$ group.

NOT accept: From the given information, it has $>C=O$ / no $COOH$ group (i.e. without further elaboration)]

DSE18_03c

(i) Boiling points of X and Y are too close. [1]

(ii) (1) Absorption peak at wavenumber about 1700 cm^{-1} corresponds to a $C=O$ group. [1]

OR, Absorption peak at wavenumber about 1650 cm^{-1} corresponds to a $C=C$ group.

[Range: $C=O$, $1680 - 1800$; $C=C$, $1610 - 1680$ one number: $C=O$: $1680 - 1720$; $C=C$: $1630 - 1670$]

(2) At $m/z = 43$: CH_3CO^+ / $C_2H_3O^+$ [CH_2CHO^+ not accepted] [1]

At $m/z = 55$: CH_2CHCO^+ / $C_3H_3O^+$ [1]

(3) $CH_2=CHCOCH_3$ [1]
[Must show $C=C$]

(iii) • positive result for 2,4-dinitrophenylhydrazine test: presence of carbonyl group [1]

• negative result for Tollens' reagent test: not an aldehyde [1]

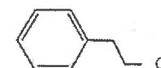
• [Note: If just have the conclusion: it is a ketone : 1 mark]

• Y may be $CH_3CH_2COCH_3$ / butanone. [1]

(c) (i) (1) • Different substances have different adsorptivity to the stationary phase. 1
• They have different solubility in mobile phase. 1

(2) column chromatography 1

(ii) The chemical species for the peak at $m/z = 91$ may be $C_6H_5CH_2^+$. 1
The chemical species for the peak at $m/z = 140$ may be $C_6H_5CH_2CH_2^{35}Cl^+$. 1
(or $m/z = 142$ may be $C_6H_5CH_2CH_2^{37}Cl^+$)
Possible structure :



(iii) (1) High levels of dioxins may cause cancer. 1

(2) Modern instrumentation is accurate and sensitive enough to measure very low levels of dioxins. 1

DSE20_03b

(b) (i) 2

(1 mark for labelling: solvent

1 mark for the drawing: pencil line above solvent, spot of mixture, TLC plate and a container)

(ii) $R_f = 45 / (130 - 10 - 20) = 0.45$ 1
(Only mark the answer.)

(iii) Aspirin and Caffeine 1

(iv) (1) IR spectrum of Aspirin shows (strong absorption) peak at 2500 cm^{-1} to 3300 cm^{-1} / corresponding to $O-H$ group of carboxylic acid while that of caffeine does not. 1
(A comparative sense)

(2) $m/z = 43$ corresponds to a CH_3CO^+ ion. 1
(Accept CH_3CO^+
Not accept CH_3CO^- , CH_3CO)

Both aspirin and acetaminophen have this fragment, only this information cannot help confirm which one of the three chemicals the sample is. 1

(iii) Pollutants, such as dioxins, can be formed in the manufacturing process of certain chlorine-containing products.

(1) Explain why there is a need to measure dioxin levels.

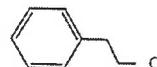
(2) Suggest why dioxin levels are generally measured using modern instrumentation.

(2 marks)

(c) (i) (1) • Different substances have different adsorptivity to the stationary phase. 1
 • They have different solubility in mobile phase. 1

(2) column chromatography 1

(ii) The chemical species for the peak at $m/z = 91$ may be $C_6H_5CH_2^+$. 1
 The chemical species for the peak at $m/z = 140$ may be $C_6H_5CH_2CH_2^{35}Cl^+$. 1
 (or $m/z = 142$ may be $C_6H_5CH_2CH_2^{37}Cl^+$)
 Possible structure :



(iii) (1) High levels of dioxins may cause cancer. 1

(2) Modern instrumentation is accurate and sensitive enough to measure very low levels of dioxins. 1