TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

WORKED SOLUTIONS

CENTRE NUMBER | S | | | | |

INDEX NUMBER | | | | |

Chemistry **9729/02**

Paper 2 Structured Questions **25 August 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** the questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		/30
Paper 2	Q1	/9
	Q2	/14
	Q3	/10
	Q4	/8
	Q5	/20
	Q6	/14
	Total	/75
Paper 3		/80
TOTAL (%)		/100

This document consists of **23** printed pages and **1** blank page.

Answer **all** the questions in the space provided.

1 **(a)** Element **W** is from Period 5 of the Periodic Table. The first eight ionisation energies of element **W**, in kJ mol^{-1}, are

869 1800 2690 3610 5720 6670 12000 13800

(i) Identify element **W** and explain your answer. [2]

- ✓ Element W is Tellurium/ Te. Electronic configuration: $[Kr]4d^{10}5s^25p^4$.
- ✓ There is a large difference between the 6^{th} and 7^{th} ionisation energies of **W**.
- ✓ The 7^{th} electron is from an inner electronic shell.
- ✓ W has 6 valence electrons, hence it is from Group 16.

2 ticks – 1 mark

(ii) Explain the difference between the first ionisation energy of element **W** compared to the element to its left on the Periodic Table. [2]

- ✓ 1^{st} ionisation energy of Te involves the removal of paired 5p electrons
- ✓ which experiences inter-electronic repulsion.
- ✓ Less energy is needed to remove the electron from W/ Te than the valence electron/ unpaired 5p electron in Sb/ element to its left.
- ✓ IE of element W is lower.

2 ticks – 1 mark

(b) The chlorides of elements in Period 3 of the Periodic Table show different behaviours on addition to water.

(i) Describe and explain the reactions of aluminium chloride, $AlCl_3$, and phosphorus pentachloride, PCl_5, with excess water.

Write equations for any reactions that occur. [3]

$AlCl_3$ undergoes hydration and hydrolysis.

- ✓ Hydrolysis take place as Al^{3+} has a high charge density hence a high polarising power.
- ✓ Al^{3+} draws electrons from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule.
- ✓ $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$
- ✓ $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$
- ✓ PCl_5 undergoes hydrolysis in water due to the presence of energetically accessible vacant 3d orbitals in P for dative bonding with water molecules.
- ✓ $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

2 ticks – 1 mark

(ii) The reaction of PCl_5 with limited amount of water involves step-wise substitution of –Cl with –OH.

Write the overall balanced equation for the reaction of PCl_5 with limited amount of water. Hence, suggest a three-step reaction sequence for this reaction.

✓ Balanced equation: $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

✓ Step 1: $PCl_5 + H_2O \rightarrow PCl_4OH + HCl$

✓ Step 2: $PCl_4OH + H_2O \rightarrow PCl_3(OH)_2 + HCl$

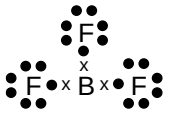
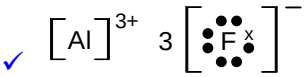
✓ Step 3: $PCl_3(OH)_2 \rightarrow POCl_3 + H_2O$

[Total: 9]

2 Boron trifluoride, BF_3, and aluminium fluoride, AlF_3, differ markedly in their physical properties.

compound	melting point / °C
BF_3	–127
AlF_3	1291

(a) **(i)** State the type of bonding present in each of these compounds and draw 'dot-and-cross' diagrams in the boxes below to illustrate this bonding.

✓  Type of bonding: ✓ covalent bonding	✓  Type of bonding: ✓ ionic bonding
BF_3	AlF_3

4 ticks – **[2]**

2 to 3 ticks – **[1]**

[2]

(ii) Outline the principles of the Valence Shell Electron Pair Repulsion theory.

Electron pairs in the valence shell of the central atom arrange themselves as far as possible to minimise repulsion and maximise stability. **[1]**

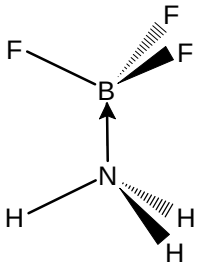
Strength of repulsion between electron pairs decreases in the order:

Lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion **[1]**

[2]

(iii) Boron trifluoride forms a compound with ammonia.

Use the Valence Shell Electron Pair Repulsion theory to predict and draw the likely shape of the product formed from this reaction.



[1]

Shape of product: tetrahedral around B *OR* N atom **[1]**
(Dative covalent bond must be clearly shown with an arrow from N to B atom.)

[2]

Cyclobutane is an example of a cyclic alkane. While itself has no commercial or biological significance, more complex derivatives of cyclobutane are important in biology and biotechnology.

Cyclobutane decomposes to ethene as shown by the following equation.

$$\square\,(g) \rightarrow 2CH_2{=}CH_2(g) \qquad \Delta H^{\ominus}_{decomp}$$

A student planned to determine $\Delta H^{\ominus}_{decomp}$ by using the standard enthalpy changes of combustion of cyclobutane and ethene, represented by $\Delta H^{\ominus}_{c}$(cyclobutane) and $\Delta H^{\ominus}_{c}$(ethene) respectively. Both substances are gases at 298 K.

$\Delta H^{\ominus}_{c}$(ethene) was previously determined to be –1411 kJ mol^{-1} in a flame calorimetric experiment.

To determine $\Delta H^{\ominus}_{c}$(cyclobutane), the student decided to conduct another flame calorimetric experiment under the same conditions.

There are two stages to this experiment.

Stage I : Calibration of calorimeter (i.e. copper can, water and other components in the calorimeter)

In the experiment, the calorimeter must first be calibrated by determining its heat capacity, ***C***, which is the amount of heat required to raise the temperature of the calorimeter by 1 K.

Stage II : Determination of $\Delta H^{\ominus}_{c}$(cyclobutane) using the calibrated calorimeter.

The student carried out the flame calorimetric experiment using the calorimeter. Part of his results is shown below.

Stage I, using ethene as the fuel,

- change in temperature of water = 33.8 °C
- mass of gaseous ethene burnt = 1.00 g

Stage II, using cyclobutane as the fuel,

- change in temperature of water = 32.9 °C
- mass of gaseous cyclobutane burnt = 1.00 g

(b) **(i)** Use the above information and experimental results to calculate the heat capacity, ***C***, of the calorimeter.

heat produced from combustion of ethene	=	heat gained by calorimeter
amount of ethene burnt × $\lvert\Delta H_c^{\ominus}$(ethene)$\rvert$	=	$C \times \lvert\Delta T\rvert$
$\frac{1.00}{28.0} \times 1411$	=	$C \times 33.8$
C	=	$1.4909 \approx$ **1.49** kJ K^{-1}

Working – **[1]**

Answer – **[1]**

[2]

(ii) Use your answer to **(b)(i)** to determine $\Delta H_c^{\ominus}$(cyclobutane).

heat produced from combustion of cyclobutane	=	heat gained by calorimeter
amount of cyclobutane burnt × $\lvert\Delta H_c^{\ominus}$(cyclobutane)$\rvert$	=	$C \times \lvert\Delta T\rvert$
$\frac{1.00}{56.0} \times \lvert\Delta H_c^{\ominus}$(cyclobutane)$\rvert$	=	1.4909×32.9
$\therefore \Delta H_c^{\ominus}$(cyclobutane)	=	$-2746.9 \approx$ **–2750 kJ mol^{-1}**

Working – **[1]**

Answer (with correct sign) – **[1]**

[2]

(iii) Hence, calculate the standard enthalpy change of decomposition of cyclobutane to ethene, $\Delta H_{decomp}^{\ominus}$.

$\Delta H_{decomp}^{\ominus}$ = $\Delta H_c^{\ominus}$(cyclobutane) – 2 $\Delta H_c^{\ominus}$(ethene)

= (–2746.9) – 2(–1411)

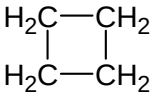
= **+75.1 kJ mol^{-1}**

Working + Answer – **[1]**

[1]

(c) **(i)** Use data from the *Data Booklet* and the $\Delta H^{\ominus}_{decomp}$ obtained in **(b)(iii)** to calculate the actual C–C bond energy in cyclobutane.

[You may assume that the difference between the C–H bond energy in cyclobutane and in ethene, and the difference between the C=C bond energy from the *Data Booklet* and in ethene are insignificant.]



(g) → $2CH_2=CH_2$(g) ΔH_{decomp} = +75.2 kJ mol^{-1}

bonds broken	bonds formed
4 C–C in cyclobutane 8 C–H	2 C=C 8 C–H

ΔH_{decomp} = 4 BE(C–C)$_{cyclobutane}$ – 2 BE(C=C)

75.1 = 4 BE(C–C)$_{cyclobutane}$ – 2(610)

BE(C–C)$_{cyclobutane}$ = $\frac{75.1 + 2(610)}{4}$

= 323.8 ≈ **324 kJ mol^{-1}**

Working – **[1]**

Answer – **[1]**

[2]

(ii) Suggest an explanation for the difference between the average C–C bond energy from the *Data Booklet* and the actual value calculated in **(c)(i)**.

From Data Booklet, BE(C–C)$_{average}$ = 350 kJ mol^{-1}

BE(C–C)$_{cyclobutane}$ < BE(C–C)$_{average}$

C–C bonds in cyclobutane experience **ring** *OR* **angle strain** and are thus **weaker** than the average C–C bond. **[1]**

[1]

[Total: 14]

3 **(a)** SO_2 gas is found in air near volcanoes. 213 cm^3 of SO_2 collected at r.t.p. near a volcano required 25.0 cm^3 of 0.120 mol dm^{-3} acidified potassium dichromate(VI) solution for complete reaction.

Calculate the final oxidation state of sulfur in the product mixture.

[R] $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$n_{Cr_2O_7^{2-}}$ = $\frac{25.0}{1000} \times 0.120$ = **3.00 x 10^{-3} mol**

n_e = 3.00 x 10^{-3} × 6 = 1.80 x 10^{-2} mol

n_{SO_2} = 213/ 24000 = 8.88 x 10^{-3} mol

$\frac{n_e}{n_{SO_2}} = \frac{1.80 \times 10^{-2}}{8.88 \times 10^{-3}}$ =2.03 ≈ 2 [1]

Initial O.N. of S: +4

Final O.N. of S = +4 + (+2) = +6 [1]

[2]

(b) The Contact process is an important industrial method of manufacturing sulfuric acid.

The key stage of the Contact process is the reaction between sulfur dioxide and oxygen:

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$ -------- Equation 1

Table 3.1 shows how the percentage of sulfur trioxide in the equilibrium mixtures varies with temperature as well as the volume of the reaction vessels.

Table 3.1

Temperature /°C	Percentage of sulfur trioxide in the equilibrium mixture for vessel		
	A	**B**	**C**
800	1.68	0.009	0.88
700	2.98	0.016	1.54
600	5.70	0.032	3.02
500	11.9	0.077	6.71

Using the data in Table 3.1,

(i) explain whether the forward reaction is exothermic or endothermic.

- ✓ **As temperature decreases, the percentage of SO_3 increased i.e. position of equilibrium shifted right.**
- ✓ **By Le Chaterlier's Principle, when temperature decreases, system responds by favouring the exothermic reaction to release heat.**
- ✓ **Therefore the forward reaction is exothermic.**

3 ticks = 2m; 2 ticks = 1m

[2]

(ii) explain and rank the three vessels in order of decreasing volume.

At the same temperature, as volume decreases, total pressure increases, position of equilibrium would shift right to decrease the number of moles of gas, hence decreasing pressure. [1]

Order of decreasing volume: B > C > A [1]

[2]

A mixture containing 2 moles of SO_2 and 1 mole of O_2 was heated in a closed 3.60 dm^3 flask at 500 °C and allowed to reach equilibrium. The flask was then rapidly cooled to liquefy SO_3.

After removing gaseous SO_2 and O_2, excess water was carefully added to the liquid SO_3, causing the following reaction to occur:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq) \quad \text{--------} \quad \text{Equation 2}$$

The resulting solution was made up to 250 cm^3 in a standard volumetric flask. 25.0 cm^3 of this solution was titrated with 5.00 mol dm^{-3} NaOH and required 38.50 cm^3 for complete neutralisation.

(iii) Calculate the equilibrium amount of SO_3 at 500 °C.

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Amount of H^+ in 25.0 cm^3 of solution = Amount of OH^-

= 5.00 x (38.5 / 1000)

= 0.1925 mol

Amount of SO_3, y = amount of H_2SO_4 = ½ x amount of H^+ in 250 cm^3 solution

= ½ x 0.1925 [1] x (250 / 25.0)

= 0.9625 mol [1]

[2]

(iv) Hence, calculate a value for the equilibrium constant, K_c, of equation 1.

	$2SO_2(g)$	**+**	**$O_2(g)$**	**$\rightleftharpoons$**	**$2SO_3(g)$**
Initial amount/ mol	**2**		**1**		**0**
Change in amount/ mol	**– y**		**– ½y**		**+ y**
Equilibrium amount/ mol	**2–y**		**1–½y**		**y**

Amount of SO_2 = 2 − y = 2 − 0.9625 = 1.0375 = 1.04 mol

Amount of O_2 = 1 − (y/2) = 1 – (0.9625 / 2) = 0.51875 = 0.519 mol **[1]**

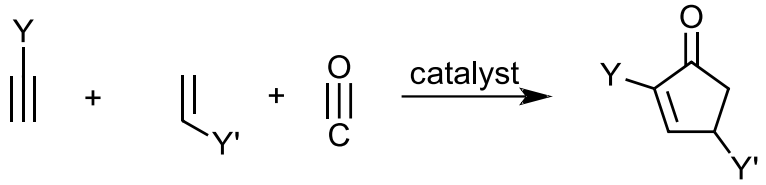
Amount of SO_3 = y = 0.9625 = 0.963 mol

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{0.9625}{3.60}\right)^2}{\left(\frac{1.0375}{3.60}\right)^2\left(\frac{0.51875}{3.60}\right)} = 5.97 \text{ mol}^{-1} \text{ dm}^3$$ **[1]**

[2]

[Total: 10]

4 **(a)** The Pauson-Khand reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown in Fig. 4.1.



where Y and Y' can be C*l* or H.

Fig. 4.1

An organic compound **A** was produced from the Pauson-Khand reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% C*l* and 4.3% H. The relative molecular mass of **A** is 116.5.
Upon heating with ethanolic $AgNO_3$, **A** gave a white precipitate.

(i) Determine the molecular formula of **A** and draw its structural formula. [2]

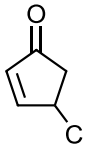
	C	O	C*l*	H
% by mass	51.5	13.7	30.5	4.3
Relative amount / mol	4.29	0.856	0.859	4.3
Simplest ratio	5	1	1	5

Empirical formula of **A**: C_5H_5OCl

Let molecular formula of **A** be $(C_5H_5OCl)_n$

$\therefore n(12.0 \times 5 + 1.0 \times 5 + 16.0 + 35.5) = 116.5$

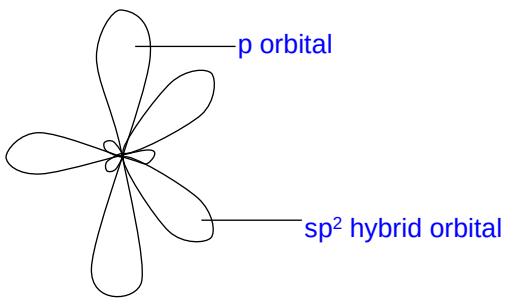
$n = 1$



Molecular formula of **A** = C_5H_5OCl **[1]** **[1]**

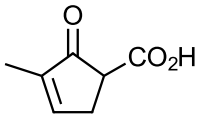
Note: white ppt of AgCl is formed, implies chloroalkane present, so Cl cannot be on the alkene (stronger C-Cl bond due to partial double bond character, similar to chlorobenzene)

(ii) Draw a diagram to show the orbitals of the carbonyl carbon in compound **A**. State the type of hybridisation involved. [1]



sp² hybridisation

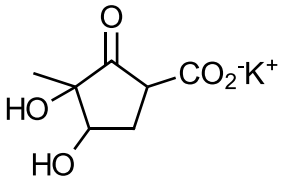
(b) Another possible product of the Pauson-Khand reaction is shown below:



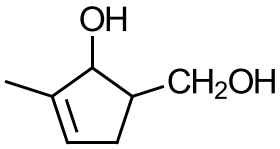
B

Draw the organic product formed when **B** reacts with each of the following.

(i) cold $KMnO_4$(aq) in KOH(aq)



(ii) $LiAlH_4$



[2]

(c) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas **Z**, filling the flask. The results, measured at 26 °C and 1.00 x 10^5 Pa are shown.

Mass of flask containing air	= 47.930 g
Mass of flask containing **Z**	= 47.989 g
Density of air	= 0.00118 g cm^{-3}

Calculate the relative molecular mass of **Z**. [3]

Mass of air = 100 x 0.00118 = 0.118 g
Mass of flask = 47.930 – 0.118 = 47.812 g
Mass of Z = 47.989 – 47.812 = 0.177 g [1]

$$pV = nRT = \frac{m}{M_r}RT$$

$$M_r = \frac{m}{pV}RT = \frac{0.177 \times 8.31 \times 299}{1 \times 10^5 \times 100 \times 10^{-6}}$$ [1] correct *working*

$$= 44.0$$ [1] correct answer

[Total:8]

5 **(a)** The 'bromine clock' involves a reaction between bromide ions and bromate(V) ions in acid solution:

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The reaction can be monitored by adding phenol and a constant volume of methyl red to all the experiments.

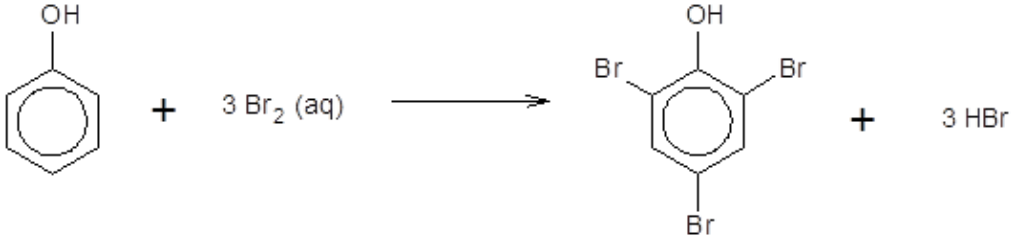
Phenol reacts immediately with the bromine as it is produced. Once all the phenol added has reacted, the bromine that is subsequently produced will oxidise the methyl red causing the disappearance of the red colour in the reaction mixture.

A series of experiments were carried out to investigate the order of reaction with respect to $[BrO_3^-]$ and the results obtained are shown in Table 5.1.

Table 5.1

Expt	Volume of BrO_3^- / cm^3	Volume of Br^- / cm^3	Volume of H^+ / cm^3	Volume of phenol / cm^3	Volume of deionised water / cm^3	Time taken for the colour of methyl red to disappear /s
1	5.0	5.0	10.0	1.0	11.0	82
2	10.0	5.0	10.0	1.0	6.0	42
3	10.0	5.0	10.0	2.0	5.0	x

(i) Write an equation for the reaction between phenol and bromine water.



[1]

(ii) Deduce the order of reaction with respect to $[BrO_3^-]$. Explain your reasoning.

Expt	Volume of BrO_3^- / cm^3	Time taken for the colour of methyl red to disappear /s	Relative rate / $cm^3\ s^{-1}$
1	5.0	82	1/82 = 0.0122
2	10.0	42	1/42 = 0.0238

Comparing expts 1 and 2 where the $[Br^-]$ and $[H^+]$ are constant, the rate is doubled when $[BrO_3^-]$ is doubled. Thus, the reaction is first order w.r.t $[BrO_3^-]$.

[1]

(iii) Using your answer in **(a)(ii)**, calculate the value of x.

The volume and amount of phenol will affect the amount of bromine that it would react with. Hence, the time taken for the colour of methyl red to disappear would also be different.

rate $\propto \frac{Vol\ of\ phenol}{time}$

Comparing expt 1 and 3,

$\frac{\frac{1}{82}}{\frac{2}{x}} = (\frac{5}{10})$

x = 82 s [1]

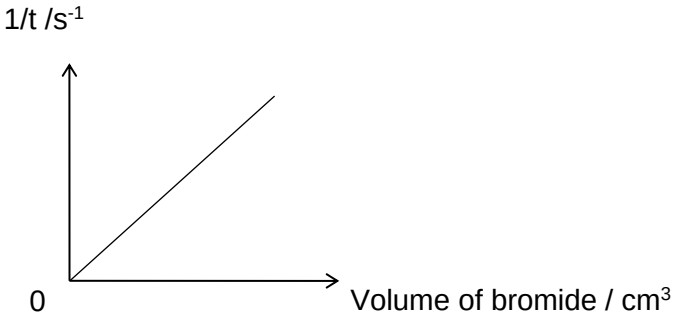
Alternative answer:

Comparing expt 2 and 3

$\frac{\frac{1}{42}}{\frac{2}{x}} = (\frac{10}{10})$

x = 84 s

(iv) Another series of experiments were conducted with varying volumes of bromide ions and large excess of BrO_3^- and H^+. The total volume of the mixture was kept constant. The results obtained were used to plot a graph of 1/t against the volume of bromide.



Deduce the order with respect to $[Br^-]$, explain your reasoning.

The order of reaction with respect to $[Br^-]$ is 1 as the graph shows a line passing through origin i.e. rate of reaction is directly proportional to $[Br^-]$. [1]

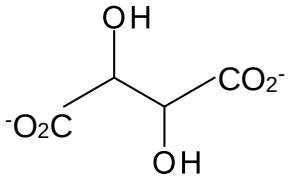
(v) Given that the unit of the rate constant is $mol^{-3}\ dm^9\ s^{-1}$, deduce the order with respect to $[H^+]$.

rate = k $[Br^-][BrO_3^-][H^+]^y$

(mol dm^{-3} s^{-1}) = (mol^{-3} dm^9 s^{-1})(mol dm^{-3})(mol dm^{-3})(mol dm^{-3})^y

y = 2 [1]

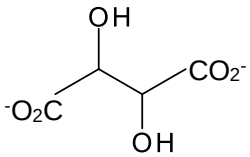
(b) The reaction between $S_2O_8^{2-}$ and tartrate ions is catalysed by iron(III) ions and the overall equation is as shown.



$$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

Tartrate ions

Write equations to illustrate how iron(III) ions catalyses the reaction.



$6Fe^{3+}$ + $+ 2H_2O \rightarrow 6Fe^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$ [1]

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ [1]

(c) Methyl red is a pH indicator. It is red when the pH is less than 4.4 and yellow when the pH is above 6.2.

In microbiology, methyl red is used to identify bacteria that produces acids from the metabolism of glucose. The type of acid produced depends on the specific enzymatic pathways present in the bacteria.

All the bacteria initially metabolise glucose to pyruvic acid, CH_3COCO_2H. After which, some bacteria use the mixed acid pathway to metabolise pyruvic acid while other bacteria use the butanediol fermentation pathway. The products formed and the colour of methyl red are shown in Table 5.2.

Table 5.2

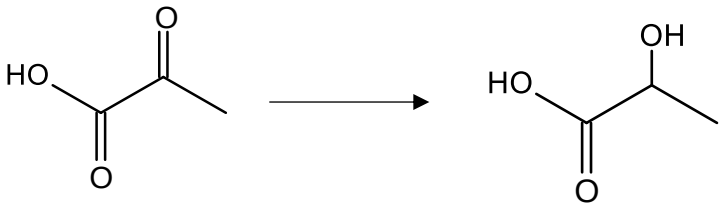
Metabolism pathway	Products formed per mole of glucose	Colour of methyl red
Mixed acid pathway	4 mol of acids (mainly lactic acid, $CH_3CH(OH)CO_2H$, and ethanoic acid), 1 mol of ethanol, 1 mol of CO_2 1 mol of H_2	Red
Butanediol fermentation pathway	1 mol of acid	Yellow

(i) Explain the colours of methyl red shown in Table 5.2.

For the mixed acid metabolism pathway, the larger amount of acids produced lower the pH to below 4.4 resulting in methyl red turning red.

For the butanediol fermentation pathway, less acid is produced so the pH is not lowered to less than 6.2 / is more than 6.2 (and less than 7) hence it appeared as yellow. [1]

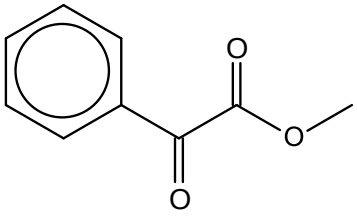
(ii) State the reagent and condition to obtain lactic acid from pyruvic acid.



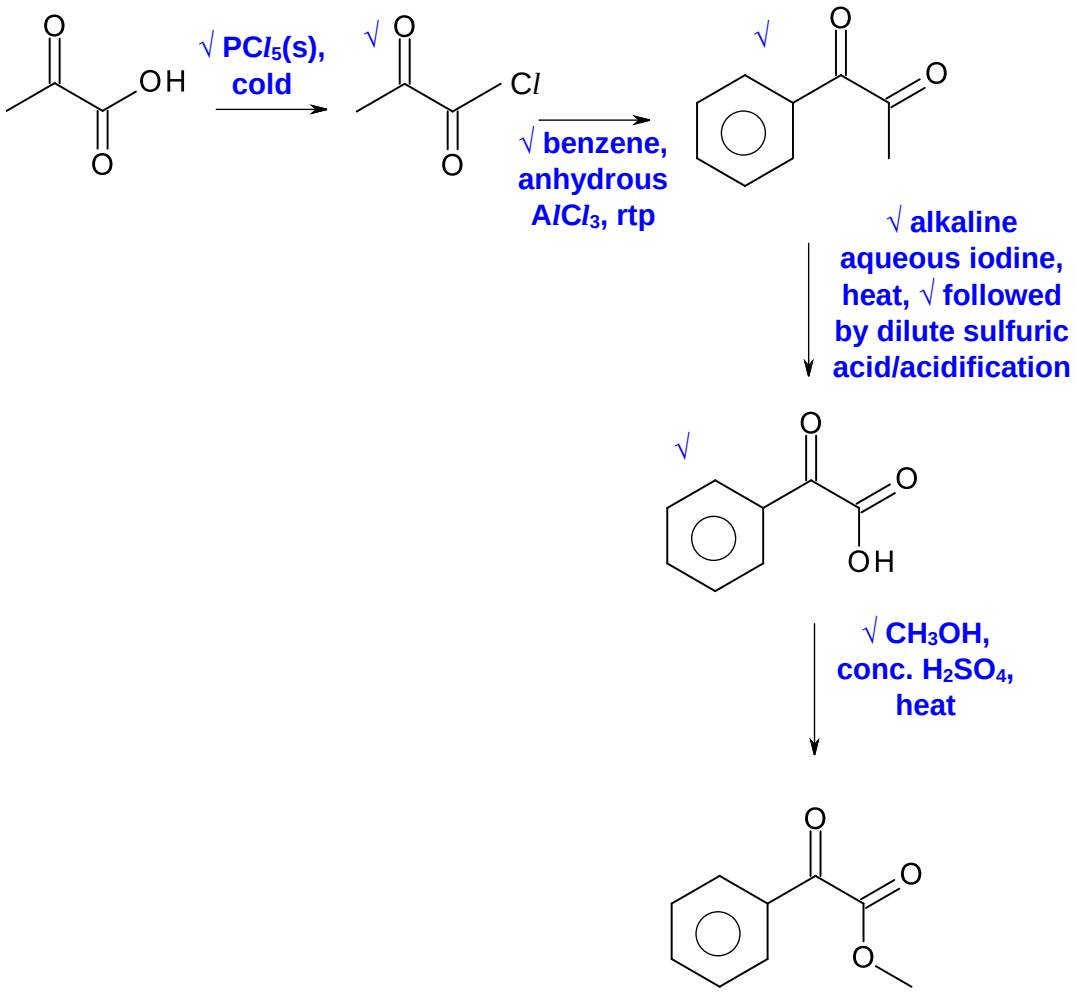
pyruvic acid lactic acid

$NaBH_4$ in alcohol, rtp **[1]**

(iii) Suggest the reagents and conditions, including the structures of the intermediates, for the synthesis of compound **Y** from pyruvic acid.



compound **Y**



(steps 2 and 3 can be swapped)

(d) Table 5.3 shows the pK_a values of some compounds, including phenol.

Table 5.3

Compound	pK_a
Phenol	10.0
Phenylmethanol, $C_6H_5CH_2OH$	15.4
Phenylmethanethiol, $C_6H_5CH_2SH$	9.93

(i) Suggest how the acidities of phenol and phenylmethanol compare with each other.

The lower the pK_a, the stronger the acid. Hence, the acid strength is

$C_6H_5OH > C_6H_5CH_2OH$

The more stable the anion formed, the stronger the acid.

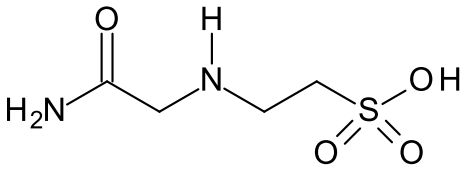
C_6H_5OH is the stronger acid because the lone pair of electrons on the oxygen atom of $C_6H_5O^-$ ion is delocalised into the benzene ring. This disperses the negative charge on the oxygen atom, stabilising the $C_6H_5O^-$ ion. [1]

The electron-donating $C_6H_5CH_2$- group intensifies the negative charge on the $C_6H_5CH_2O^-$ ion, destabilising the anion. The negative charge is also localised on the O atom of the $C_6H_5CH_2O^-$. Therefore, $C_6H_5CH_2OH$ is the weaker acid and has the less tendency to dissociate to give H^+ than C_6H_5OH [1]

(ii) Suggest a reason why the pK_a for $C_6H_5CH_2SH$ is much lower than that for $C_6H_5CH_2OH$.

$C_6H_5CH_2SH$ is a much stronger acid than $C_6H_5CH_2OH$ because the size of S atom is larger than O atom, which leads to less effective atomic orbital overlap and weaker S – H bond. Hence, $C_6H_5CH_2SH$ dissociates more readily to give H^+. [1]

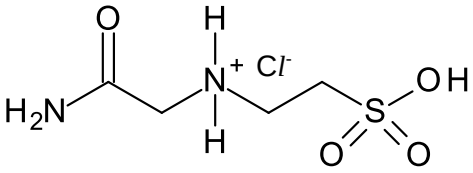
(e) ACES, $C_4H_{10}N_2O_4S$, is another compound containing sulfur.



ACES

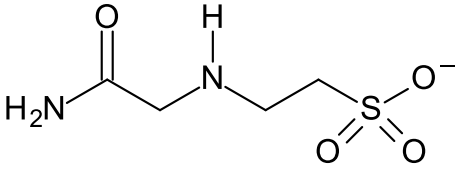
ACES has a pK_a value of 6.88.

(i) Draw the structure of the product formed when dilute hydrochloric acid is added to ACES at room temperature.



[1]

(ii) Draw the structure of the conjugate base of ACES.



[1]

(iii) The pH of a solution of ACES is 2.2.

Calculate the ratio of [conjugate base of ACES] to [ACES].

$K_a = \frac{[C_4H_9N_2O_4S^-][H^+]}{[C_4H_{10}N_2O_4S]}$

$10^{-6.88} = \frac{[C_4H_9N_2O_4S^-]10^{-2.2}}{[C_4H_{10}N_2O_4S]}$

$\frac{[C_4H_9N_2O_4S^-]}{[C_4H_{10}N_2O_4S]} = 2.09 \times 10^{-5}$ [1]

Alternative method: use buffer equation.

(iv) 0.0200 mol of the conjugate base of ACES is dissolved in 100 cm^3 of deionised water. 50 cm^3 of 0.300 mol dm^{-3} of hydrochloric acid was added to the solution.

Given that the conjugate base reacts with hydrochloric acid in a 1:1 stoichiometry, calculate the pH of the solution.

	$C_4H_9N_2O_4S^-$	+ HCl	→ $C_4H_{10}N_2O_4S$	+ $NaCl$
Initial no. of moles /mol	0.0200	$\frac{50}{1000}$ x 0.3	0	0
Final no. of moles / mol	0.020 – 0.015 = 0.005	0	0.015	

correct calculation of the amount of salt and acid [1]

$pH = pK_a + \log \frac{[C_4H_9N_2O_4S^-]}{[C_4H_{10}N_2O_4S]}$

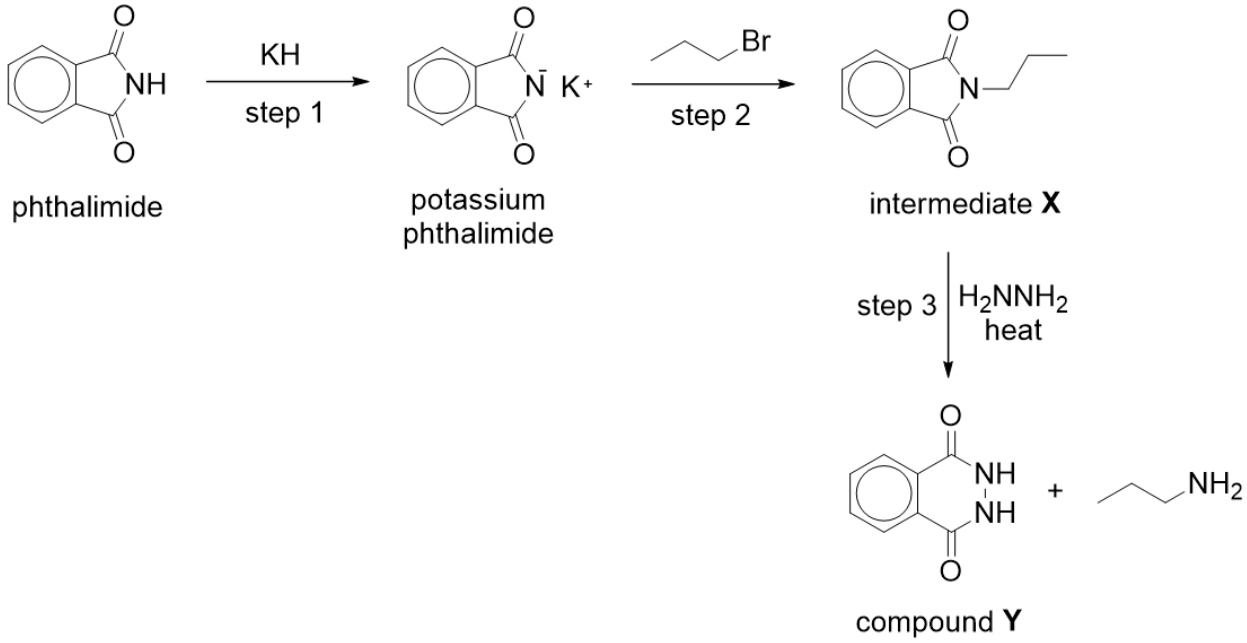
$= 6.88 + \log \frac{(0.005)/\frac{150}{1000}}{(0.015)/\frac{150}{1000}}$

$= 6.40$ [1]

[Total: 20]

6 The Gabriel synthesis is a 3-step approach to synthesis amines. Phthalimide is used as the main reactant, which has a nitrogen atom flanked by two carbonyl groups.

Propylamine is obtained from the Gabriel synthesis method as shown in Fig. 6.1.



phthalimide — potassium phthalimide — intermediate **X**

compound **Y**

Fig. 6.1

(a) **(i)** State the role of phthalimide in the above reaction in step 1. [1]

• Bronsted acid

(ii) With reference to the product formed in step 1, explain why phthalimide is able to function as the role identified in **(a)(i)**. [1]

Phthalimide can function as an acid as after deprotonation, the lone pair of electrons on the nitrogen atom can be delocalised over the 2 C=O groups, resulting in resonance stabilised anion. Hence, phthalimide can dissociate H^+ in water easily.

(b) Step 2 of Gabriel synthesis is a nucleophilic substitution reaction.

With reference to the structures of relevant reactants, explain why potassium phthalimide does not react with 2-bromo-2-methylpropane at all. [2]

✓ For S_N2 reaction, the nucleophile approach is blocked by the bulky alkyl groups behind the C-Br bond.

✓ For S_N1 reaction, the bulky benzene ring in potassium phthalimide makes it difficult for it to approach the carbocation.

Hence, there is • high steric hindrance around both potassium phthalimide and 2-bromo-2-methylpropane, hence it is difficult for the nucleophile to react with 2-bromo-2-methylpropane.

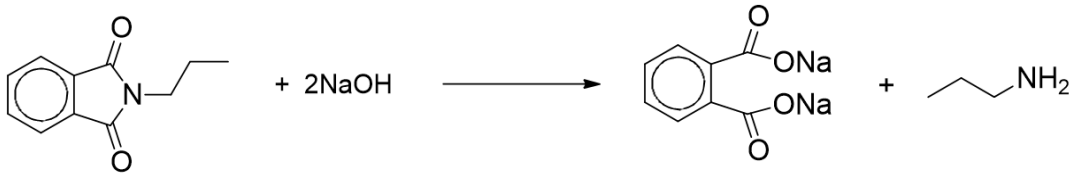
Every 2 ✓ = 1 mark

(c) Suggest another reagent and condition used to liberate the free amine from intermediate **X** in the last step.

Construct a balanced equation for this reaction, showing the structures of all reactants and products. [2]

• Dilute NaOH / KOH, heat.

•



(d) A sample contains both propylamine and compound **Y** after the Gabriel synthesis shown in Fig. 6.1. A student decides to purify propylamine from the impure sample and starts by adding an equal volume of dilute hydrochloric acid, with stirring, to the sample.

Some physical data for various compounds are given in Table 6.1.

Table 6.1

	propylamine	water	compound **Y**
Density / g cm^{-3}	0.719	1.0	1.3
Boiling point / °C	47.8	100.0	523.5

(i) With reference to structure and bonding, explain the purpose of the addition of dilute hydrochloric acid in the purification process. [3]

Propylamine reacts with hydrochloric acid to form a ✓ salt, which has ionic bonds between the cations and anions. ✓ Water is a polar solvent with hydrogen bonds between the solvent molecules. The ✓ formation of ion-dipole interactions between the ions and water molecules releases ✓ sufficient energy to overcome both the ionic bonds in the salt and hydrogen bond between water molecules. Hence the ✓ salt of propylamine will be more soluble in aqueous medium and hence ✓ extracted out as a separate layer from organic compound Y.

Every 2 ✓ = 1 mark

(ii) Starting with the mixture from **(d)(i)**, plan an experiment to purify propylamine from the impure mixture. [3]

Your plan should include details of:

• how propylamine is obtained in its anhydrous liquid form; and

• suitable apparatus used.

Pour the mixture from (d)(i) into a ✓ separatory funnel. ✓ Stopper and shake the separatory funnel, occasionally opening the tap to prevent pressure build-up.

✓ Collect the upper aqueous layer (containing salt of propylamine) from the separatory funnel into a conical flask. ✓ Add dilute NaOH, with stirring, until the solution is just made alkaline by occasionally testing with red litmus paper. Transfer the mixture to a round bottom flask and add boiling chips.

✓ Connect the round bottom flask to a distillation setup with a thermometer. Propylamine will be the first distillate to be collected when the thermometer reads 47.8 °C.

DO NOT WRITE IN THIS MARGIN

✓ **Add anhydrous $MgSO_4$ / Na_2SO_4 / $CaCl_2$ / $CaSO_4$, with stirring, to dry the distillate. Filter the suspension into a dry conical flask to obtain anhydrous propylamine.**

Every 2 ✓ = 1 mark

(e) A student made the following statement in his journal

"Using a 2:1 mole ratio of bromomethane and potassium phthalimide in the Gabriel synthesis method will produce a dimethylamine."

Comment on the validity of the student's statement. [2]

The student's statement is • incorrect / invalid / wrong.

The • lone pair of electrons on the nitrogen atom on intermediate X is delocalised over the 2 neighbouring C=O groups, hence it is no longer available to act as nucleophile to attack the electron deficient C of a second equivalent of bromomethane. Bromomethane and potassium phthalimide will only react in a 1:1 mole ratio.

[Total: 14]