

EUNOIA JUNIOR COLLEGE JC2 Preliminary Examination 2023 General Certificate of Education Advanced Level Higher 2

Paper 2 Suggested Solutions with Marker's comments

- 1 (a) In the past two decades, scientists have observed a steady decrease in the pH of the oceans. This phenomenon is known as ocean acidification.
  - (i) Ocean acidification occurs when carbon dioxide dissolves and reacts with water in the ocean to form carbonic acid, H<sub>2</sub>CO<sub>3</sub>.

Write equations to illustrate how carbon dioxide decreases the pH of seawater.

 $CO_2(g) \rightarrow CO_2(aq)$ 

 $CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$ 

 $\begin{array}{l} H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq) \text{ or } H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \\ HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \end{array}$ 

(ii) In the past two centuries, the average pH of seawater has dropped from 8.2 to 8.1. Calculate the percentage increase in the concentration of H<sup>+</sup>(aq) ions in sea water.

percentage increase = 
$$\frac{10^{-8.1} - 10^{-8.2}}{10^{-8.2}} \times 100\% = \underline{25.9\%}$$
 [1]

(iii) The significant change in pH of seawater is unexpected as the oceans have a natural buffering system involving  $CO_3^{2-}(aq)$  and  $HCO_3^{-}(aq)$ .

Write an equation to show how the  $CO_3^{2-}(aq)/HCO_3^{-}(aq)$  buffer system helps resist the decrease in the pH of seawater when carbon dioxide dissolves.

 $CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^{-}(aq)$  [1]

# **Comments:**

- · Generally, well done except for a small group of students who were careless in (iii)
- Question analysis and references(where applicable) This is a simple application question that requires students to pick out information from the question and construct relevant equations.
- Common mistakes:
  - For (ii), not calculating percentage increase.
  - For (iii), Using  $\rightarrow$  instead of  $\rightleftharpoons$ .
  - Misinterpreting a decrease in pH as increase in OH<sup>-</sup> in the system instead of H<sup>+</sup>.

- Writing  $HCO_3^-$  +  $H^+ \rightarrow H_2CO_3$ . This is incorrect as the buffer system comprises of  $CO_3^{2-}$ , the conjugate base and  $HCO_3^-$ (aq), the acid. To resist a drop in pH, the conjugate base will remove acid ( $H^+$ ) to maintain relatively constant pH.

- (b) The main cause of ocean acidification is the rising carbon dioxide levels in the atmosphere, which is a result of the increase in the use of fossil fuels. To combat this, alternative fuels such as methanol are being explored.
  - (i) Define the term standard enthalpy change of combustion,  $\Delta H_c^{\ominus}$ .

It is the <u>energy released</u> when <u>1 mole of a substance</u> is <u>completely burnt</u> <u>in excess oxygen</u> under <u>standard conditions</u> (at 1 bar, at a specified temperature, usually 298 K). [1]

(ii) When 1.86 g of methanol, CH<sub>3</sub>OH, was combusted in a bomb calorimeter, a temperature rise of 5.1 K was measured.

In a separate experiment, 1.00 g of benzoic acid,  $C_6H_5CO_2H$ , produced a temperature rise of 3.2 K when combusted in the same bomb calorimeter under identical conditions.

Given that the enthalpy change of combustion of benzoic acid is -3226 kJ mol<sup>-1</sup>, calculate the enthalpy change of combustion of methanol.

amount of energy produced from combustion of benzoic acid sample

$$= -\left(-3226 \times \frac{1.00}{7 \times 12.0 + 6 \times 1.0 + 2 \times 16.0}\right)$$
  
= 26.44 kJ

amount of energy produced from combustion of methanol sample

$$=\frac{26.44}{3.2}\times5.1=42.14$$
 kJ

enthalpy change of combustion of methanol

$$= -42.14 \div \frac{1.86}{12.0 + 4 \times 1.0 + 16.0}$$
$$= -725 \text{ kJ mol}^{-1}$$

#### OR

Amount of energy produced from combustion of benzoic acid =  $C\Delta T$ where C is the heat capacity of the bomb calorimeter

$$26.44 \times 10^3 = C(3.2)$$
  
C = 8263.3 J K<sup>-1</sup>

Since the same bomb calorimeter is used, the heat capacity will be constant.

Amount of energy produced from combustion of methanol

= -8263.3 × 5.1

 $= -42.14 \times 10^3 \text{ J} = -42.14 \text{ kJ}$ 

Enthalpy change of combustion of methanol

 $= -42.14 \div \frac{1.86}{12.0 + 4 \times 1.0 + 16.0}$  $= -725 \text{ kJ mol}^{-1}$ 

[3]

# **Comments:**

• This part was not as well done as expected.

# • Question analysis

This part of the question involved simple handling of data given in the question. While it is not a difficult application question, students need to be clear of the concepts on calculation heat change from experimental data.

# Common mistakes:

- Using mass of methanol and benzoic acid as m in q = mc $\Delta$ T. m refers to the mass of solution that the temperature change is measured from. In this question, there is no mention of such mass. Students cannot use q = mc $\Delta$ T to calculate heat change.

- Some students tried to calculate m by using specific heat capacity of water, i.e.  $26.44 \times 10^3 = m(4.18)(3.2) \Rightarrow m = 1976.9$  g. Students should not assume that the

temperature change is measured via water medium.

- Some students tried to calculate c by  $26.44 \times 10^3 = (1)(c)(3.2) \Rightarrow c = 8263.3 \text{ J K}^{-1}$ . Then calculating heat released from combustion of methanol by q = (1.86)(8263.3)(5.1) This is incorrect as by substituting c, students are assuming that the specific heat capacity of benzoic acid and methanol are the same.

(c) Methanol can be synthesised through the reaction between carbon dioxide and hydrogen, as shown in equilibrium 1 below.

equilibrium 1  $CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(I) + H_2O(g)$   $\Delta H_1^{\ominus} = -49.5 \text{ kJ mol}^{-1}$ 

At the same time, a side reaction, as shown in equilibrium 2, can occur.

equilibrium 2  $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$   $\Delta H_2^{\ominus} = +41.2 \text{ kJ mol}^{-1}$ 

(i) Explain why the synthesis of methanol is usually conducted at low temperature and high pressure.

At low temperature, the position of equilibrium 1 lies to the right, favouring the forward exothermic reaction to produce some heat. This leads to higher yield of methanol. At the same time, at high pressure, the position of equilibrium 1 is also lying to the right, favouring the forward reaction to decrease the pressure by decreasing the number of gaseous molecules in the system. This also gives a higher yield of methanol. [2]

(ii) CO(g) is sometimes added to the reaction mixture at constant volume after synthesis has occurred to a certain extent. Suggest one advantage of doing so. The addition of CO(g) to the reactant mixture will shift the position of equilibrium 2 to the left to decrease the amount of CO(g) present. This limits the consumption of CO<sub>2</sub>(g) and H<sub>2</sub>(g) to form products other than methanol. OR This further shifts position of equilibrium 1 to the right [2] produce a higher yield of methanol. [Total: 12]

# **Comments:**

• Students have a good understanding of the concept tested in this part, however, greater attention needs to be given to how to accurately express the concept.

# • Question analysis

This part of the question is application of Haber Process (industrial production of ammonia).

# Common mistakes:

Part (i)

- Not making clear reference to the specific equilibrium in the answer.

- When explaining the favouring of the forward exothermic reaction, students should not state that the POE shifting is to increase the temperature. The correct phrase should be "to release some heat". Similarly, students should also mention that POE shifts to "decrease pressure".

- When explaining how POE shifts to the right due to the pressure factor, omitting the word "gaseous" i.e. "decreasing the number of molecules" is incorrect.

- Many students did not link back to the question of why the synthesis has to be done at a specific set of conditions. Similar to Haber Process, all these conditions are set to ensure a good yield of product can be obtained.

Part (ii)

- Many students did not refer to eqm 2 to explain how the system respond to the addition of CO(g).

- 2 Copper is a key metal needed in the production of electrical wirings that powers the modern world.
  - (a) Copper is first extracted from mineral ores such as cuprite (Cu<sub>2</sub>O) and tenorite (CuO).
    - (i) State the oxidation number and the electronic configuration of copper in Cu and CuO in Table 2.1.

copper species	oxidation number	electronic configuration
Cu	0	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>1</sup>
CuO	+2	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>9</sup>
		[2]

(ii) Explain why copper exists in different oxidation states such as in Cu<sub>2</sub>O and CuO.

Copper can exist in different oxidation states due to the small energy level

difference between the 3d and 4s orbitals. [1]

# Comments:

• (i) was generally well done. (ii) was a hit or miss.

# • Question analysis

- for (i), students need to recognise the oxidation state/ number of copper metal and copper(II) and work out the electronic configuration from there.

- for (ii), it is a straightforward understanding of how different oxidation states can occur for transition metals, in this case copper.

# Common mistakes:

# For **(i)**

- some forget that the electronic configuration should be written from the lowest energy to highest energy of filled orbitals. i.e. 3d before 4s, instead of 4s before 3d.

- some did not recall that a fully filled 3d subshell is more stable than a partially filled 3d subshell. Hence, writing the electronic config as  $3d^9 4s^2$  instead.

- some wrote the electron numbers as a sub-script. Do take note that it should be written as super-script.

For (ii)

- many simply restated the question and added it is a transition metal. This doesn't explain why.

- energy level difference between 3d and 4s electron was not accepted as it is the orbital/ subshell energy levels that matters.

(b) Samples of tenorite (CuO) was analysed for its isotopic composition of copper by means of mass spectrometry. The results of the analysis are given in the table below.

Table 2.2

mass number	16	63	65
% abundance	49	15	36

Using Table 2.2, calculate the  $A_r$  value for copper.

 $\frac{(63)(0.15) + (65)(0.36)}{(51/100)} = 64.4$ 

[1]

# **Comments:**

- This question proved challenging for most students.
- Question analysis

- In this case, one needs to focus on copper's % abundance only as you are calculating the  $A_r$  value for copper. As it is not 100% for copper, one will have to re-establish to 100% from a 51% of copper abundance in tenorite.

- Common mistakes:
   many added oxygen's % abundance into their calculation, which leads to a small A<sub>r</sub> that does not make sense.
- (c) After extraction from one of its mineral ores, the crude copper metal containing iron and silver metal impurities is further purified via electrolysis.
  - (i) Draw a labelled diagram of the electrolytic cell used to purify a piece of crude copper metal. Include details of the cathode, anode and electrolyte.



[1]

(ii) Using relevant data from the *Data Booklet*, explain what happens at the anode and the cathode during the purification process.

Anode:	Ag⁺.+. <i>e</i> ⁻ <del>,</del>	Ag	$E^{\leftrightarrow} = +0.80.V$
	$Cu^{2+} + 2e^{-} \rightleftharpoons$	Cu	$E^{\ominus}$ = +0.34 V
	$Fe^{2+} + 2e^{-} \Rightarrow$	Fe	$E^{\ominus} = -0.44 \text{ V}$

Since E (Fe2+/Fe) is the least positive, Fe is preferentially oxidised

first and goes into the solution (as Fet ions) first; followed by Cu. As

E<sup>e</sup>(Ag<sup>+</sup>/Ag) is the most positive; Ag impurities will not be oxidised and will

fall to the bottom as sludge:

Cathode: .Since E<sup>o</sup>(Cu<sup>2+</sup>/Cu) is more positive (than that of E<sup>o</sup>(Fe<sup>2+</sup>/Fe)), Cu<sup>2+</sup>

is preferentially reduced and deposited on the pure Cu rod. Fe<sup>2+</sup> ions remain

in the electrolyte and are not plated onto the cathode. [3]

# **Comments:**

• Those who revised this topic generally did well for the question. Those who did not, it was clear from the question attempt.

# • Question analysis and references(where applicable)

(i) requires one to know the setup for the purification of copper. This is important as it is clear in the learning objectives in the syllabus as an example of an electrolytic cell.
(ii) is a known question type, where one has to know how the purification of copper removes impurities, whether as sludge by-products or left as ions in the electrolyte. This was covered in tutorial under Qn:B9.

# Common mistakes:

For **(i)** 

- some did not realise that the way the electrical source is drawn is important. In other words, the long line and the short line represents the respective terminal which must face the correct electrode.

- some gave or attempted to give this as a galvanic cell setup instead of an electrolytic cell.

- some added acids to the electrolyte, which is not correct as the acid will react with the copper metal electrode which is undesirable.

# For (ii)

- some answers did not clearly use the correct information from the Data Booklet, i.e. the standard reduction electrode potential values, opting to use the reactivity series instead which does not explain the phenomenon.

- some answers which gave the values, did not clearly link the preference for oxidation and reduction. Much deep interpretation was done to see if the link was made.

- some answers decided to introduce impurities that did not exists in the setup (e.g. Zn) or omitted the impurities given entirely.

(iii) In a test run for the process, a current of 7.5 A was passed through the electrolytic cell. After some time, it was found that 250 g of pure copper was formed.

Calculate the time required for the reaction in minutes.

amount of copper produced = 250 / 63.5 = 3.9370 mol total charge needed, Q = nF = (2)(3.9370)(96500) = 759841 C time taken = Q/I = 379920 / 7.5 = 101312 s = <u>1690 min</u> [1]

(iv) The theoretical mass of copper formed should be 260 g. In addition, some bubbling was observed at the pure copper electrode.

Identify the gas evolved at the pure copper electrode and suggest a reason for the difference in mass of copper formed.

H <sub>2</sub> gas is evolved at the pu	ire copper	r electrode.
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 $\underline{H_2O}$  in the electrolyte is also reduced at the copper electrode, taking up some

amount of electrons is used. Hence less Cu<sup>2+</sup> is reduced. [2]

# **Comments:**

• Again, those who revised this topic generally did well for the question. Those who did not, it was poorly attempted, if at all.

# • Question analysis and references(where applicable)

- (iii) requires one to know the basic calculation required for electrolytic cells. This was practiced in tutorial under section B part 2.

- (iv) requires one to know what the setup for the purification of copper is like, and what is present in the electrolyte. Given that it is an aqueous solution, there is a high concentration of water that is present which may influence the electrolysis process.

# Common mistakes:

For (iii)

- some forgot that copper uses 2 mol of electrons for the reduction process.
- some forgot to convert time in seconds, to time in minutes.

- some used the  $A_r$  from (b). this is not correct as the copper used in this question after the first round of refinement to get the impure copper.

For (iv)

- many were not aware that the pure copper electrode refers to it being an *cathode* where reduction takes place. In other words, one must consider what might be reduced at the cathode aside from Cu<sup>2+</sup> ions. Based on this, one will need to refer to the Data Booklet to see the viability of the reduction of species present in the electrolyte.

- (d) A complex ion in the electrolyte is responsible for the light blue colour of the solution.
  - (i) Define the term "complex ion".

A complex ion consists of a central metal atom or ion surrounded by other

ions or molecules called ligands bonded to the central atom/ ion by dative

covalent bonds. [1]

(ii) Identify the complex ion responsible for the light blue colour.

[Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> [1]

A concentrated solution of HC*I* was accidently added into the electrolyte, which resulted in the formation of a new complex ion. This caused the electrolyte solution to turn from pale blue to yellow-green.

(iii) State the type of reaction that led to the change in colour.

Ligand exchange reaction	[1	1
	ι.	1

(iv) Suggest, with the aid of an ionic equation, an explanation for the observation.

$\left[\operatorname{Cu}(\operatorname{H}_{2}\operatorname{O})_{6}\right]^{2^{+}}(\operatorname{aq}) + 4\operatorname{C}l^{-}(\operatorname{aq}) \rightleftharpoons \left[\operatorname{Cu}\operatorname{C}l_{4}\right]^{2^{-}}(\operatorname{aq}) + 6\operatorname{H}_{2}\operatorname{O}(l)$
When concentrated HC1 is added, [Ct] increases, causing the position of
equilibrium to shift to the <b>right</b> to form [CuC4] <sup>2-</sup> complex.
The presence of both <u>blue <math>[Cu(H_2O)_6]^{2+}</math> and yellow <math>[CuC_4]^{2-}</math> causes the</u>
solution to appear yellow-green. [2]

[Total: 16]

## **Comments:**

• This part is largely well done or poorly attempted depending on the readiness of students in the topic of Transition Metals.

## • Question analysis and references(where applicable)

- (i) - (iii) are straight definitions and understanding of the complexes and the example of copper

- (iv) requires one to know the different copper complexes and how they form including their colours. This is expected of you based on the learning objective in the syllabus.

# • Common mistakes:

For (i) and (iii)

- some are not familiar with the definitions and the reaction that results in the different complexes being formed

For (ii)

- some did not give the complex ion formula, choosing to write it as (aq) instead.

- some were not familiar with the identity of the copper complexes.

For (iv)

- many attempted to answer this based on ligand exchange due to the nature of the ligand, where chlorine anion is a strong ligand. This is insufficient as this is really an equilibrium which leads to the ligand exchange. In fact, chlorine anion is a much weaker ligand than  $H_2O$ .

- many were not answering about the change in observation, i.e. the colour. Some were not familiar with the colour of the new complex ion form, which one should know.

- **3** Hydrochloric acid, HC*l* is a strong acid, while chloric(I) acid, HC*l*O is a weak acid.
  - (a) HCl and HClO can react with each other in a Bronsted-Lowry acid-base reaction.
    - (i) Write an equation for the reaction of HCl with HClO.

 $HCl + HClO \rightleftharpoons Cl + H_2ClO^+$ [1]

(ii) Identify the two different conjugate acid-base pairs in the reaction occurring in (a)(i).

base ...... HC IO conjugate acid H<sub>2</sub>C IO<sup>+</sup>

[1]

# Comments:

- The question was generally well done.
- Question analysis
  - (i) The reaction between HC*l* and HC*l*O is a Bronsted-Lowry acid-base reaction. A Bronsted-Lowry acid is a proton (H<sup>+</sup>) donor, while a Bronsted-Lowry base is a proton (H<sup>+</sup>) acceptor. The equation should thus reflect the stronger acid as the proton donor, while the other species is the proton acceptor.
  - (ii) Conjugate acid-base pairs differ by one proton only. Each pair given <u>should only</u> <u>differ by one H<sup>+</sup></u>, with the acid species having one H<sup>+</sup> more than the base species.

# Common mistakes:

- (i) Some gave a reaction between HCl and ClO<sup>-</sup> despite the question clearly stating the reaction of HCl with HClO. A number also thought that a proton from HCl and OH<sup>-</sup> from HClO would react to give water and chlorine, not realising that the reaction suggested would not be an acid-base reaction only as described in the question.
- (ii) A few did not realise that the species that they listed was not conjugate acidbase pairs. Some commonly seen incorrect acid-base pairs include: HCIO, H<sub>2</sub>O; HCIO, Ct.

(b) Two different solutions are prepared using HC/ and HC/O.

Solution X is made by mixing 50 cm<sup>3</sup> of 2.00  $\times$  10<sup>-3</sup> mol dm<sup>-3</sup> HC/(aq) with 50 cm<sup>3</sup> of 2.00  $\times$  10<sup>-3</sup> mol dm<sup>-3</sup> NaC/(aq). The resultant solution has a pH of 3.0.

Solution Y is made by mixing 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HC/O(aq) with 50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> NaC/O(aq). The resultant solution has a pH of 7.5.

(i) Use the information about Solution X to prove that HC*I*(aq) is a strong acid. Show your working.

 $[HCl] = \frac{2.00 \times 10^{-3} \times \frac{50}{1000}}{\frac{(50+50)}{1000}}$ = 1.00 × 10<sup>-3</sup> mol dm<sup>-3</sup> pH = 3 [H<sup>+</sup>] = 10<sup>-3</sup> = 1.00 × 10<sup>-3</sup> mol dm<sup>-3</sup> Since [HCl] = [H<sup>+</sup>] in a solution of pH 3, HCl(aq) is a strong acid. [2]

(ii) Write the expression for the acid dissociation constant,  $K_{a}$ , for chloric(I) acid, HC/O(aq).

 $K_{a} = \frac{[H^{+}][ClO^{-}]}{[HClO]}$ [1]

(iii) Use the information about Solution Y to calculate the  $K_a$  value for HC/O(aq).

Since Solution Y is a buffer solution,  $pH = pK_a + lg \frac{[(conjugate) base]}{[(conjugate) acid]}$   $7.5 = pK_a + lg \frac{0.05}{0.05}$   $K_a = 10^{-7.5}$   $= 3.16 \times 10^{-8} \text{ mol dm}^{-3}$ 

[1]

# **Comments:**

- (ii) was generally well done, while (iii) was poorly attempted. Many incorrect formulas were used for calculation in (iii).
- Question analysis
  - (i) How to tell if HCl is a strong acid? To do so, we will need to show that the [HCl] = [H<sup>+</sup>] in the solution.
  - (iii) Look carefully at the species present in Solution Y: it contains the weak acid and the salt of the weak acid (NaC*l*O) this is a buffer solution! Since two solutions are mixed, we will also need to determine the new concentration of each species in the solution.

## 14

#### • Common mistakes:

(i) - Many simply used the relationship  $[HCl] = [H^+]$  and simply went on to work in terms of  $[H^+]$  only, not realising that in doing so, they had already assumed that HCl was a strong acid instead of proving that it was one.

- Some incorrectly concluded that since " $pH = -lg[H^+]$ " that HC*l* was a strong acid, not realising that the equation doesn't indicate anything about the strength of the acid.

- A small minority attempted to use the  $K_a$  expression, not realising that  $K_a$  is generally for weak acids only. The [HC*l*] in solution would be close to zero (since it would be completely dissociated) rather than be close to the calculated concentration, thus making it impossible to determine the actual [HC*l*] left in solution, and hence difficult for  $K_a$  to be determined.

- Many wrote an incorrect expression  $\eta_{\text{HCI}} \equiv \eta_{\mu^{\star}}$  when it should have been

 $\eta_{HCl} = \eta_{H^+} \text{ or } HCl \equiv H^+$ .

(ii) - Some gave the incorrect expression of  $K_a = \frac{[H^+]^2}{[HClO]}$ , not realising that this does

not represent the acid dissociation constant.

It should be noted that  $[H^+]^2$  is only valid if the solution contains equal concentrations of H<sup>+</sup> and ClO. This simplification is made only for the purpose of calculations involving  $K_a$ .

(iii) - Majority thought that Solution Y contained a weak acid only and chose to use the equation  $[H^+] = \sqrt{K_a \times [acid]}$ , without realising that the presence of  $ClO^-$  added would mean that  $[H^+] \neq [ClO^-]$ .

- Some who recognised the presence of a buffer solution in Solution Y applied the Henderson-Hasselbalch equation incorrectly, either missing out the logarithm that needed to be applied to the ratio of [salt]/[acid], or using the wrong concentrations of salt and acid.

(c) Chloric(III) acid, HCIO<sub>2</sub> is much more acidic than chloric(I) acid, HCIO. This can be explained by the greater stability of the conjugate base of HCIO<sub>2</sub> due to the delocalisation of electrons over both oxygen and chlorine atoms.



With the aid of a suitable diagram, suggest how delocalisation of electrons occurs in the conjugate base of  $HCIO_2$ .

In  $ClO_2^-$ , an <u>unhybridised p orbital on each of the O and Cl atom</u>, that is

perpendicular to the plane of the ion overlaps side-way, giving a delocalised





[2]

## **Comments:**

• This question proved to be difficult for many.

# • Question analysis

The question requires an explanation of **how delocalisation can occur** i.e. why electrons can be "spread over" the various atoms.

#### Common mistakes:

- A large number of answers merely rehashed the information that was already given in the question stem i.e. "electrons are delocalised over both oxygen and chlorine atoms".
- Some attempted to describe the movement of electrons over the O-C*l*-O bond, or where the electrons would be, without any mention of how the delocalised  $\pi$  electron cloud would be formed.
- Those who realised the need to describe how the delocalised π electron cloud came about often omitted the mention of <u>sideway overlap</u> of p-orbitals with π electron cloud of the C*l*=O bond. Some wrongly described electrons overlapping, or drew diagrams that did not clearly show p-orbitals on the oxygen and chlorine atoms.
- A large number of answers incorrectly showed delocalisation of electrons in  $HClO_2$  when it should have been  $ClO_2$  instead.
- Many also did not realise that it was the lone pair of electrons on O<sup>-</sup> that delocalises with the 2 electrons already in the  $\pi$  electron cloud of the C*l*=O bond. Incorrect representation of the number of electrons in the p-orbitals of each atom were often seen.

(d) Esters can undergo hydrolysis in the presence of strong aqueous acids such as HC*I*(aq).

The aromatic ester **E** is an example of one such compound.



(i) Name the ester E.
<u>phenyl methanoate</u> [1]
(ii) To synthesise ester E, CH<sub>3</sub>OH must first be converted to HCO<sub>2</sub>H. State the reagents and conditions for the conversion of CH<sub>3</sub>OH to HCO<sub>2</sub>H. <u>K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(aq), H<sub>2</sub>SO<sub>4</sub>(aq), heat</u> [1]
(iii) Outline how ester E may be formed from HCO<sub>2</sub>H. <u>Add PCI<sub>5</sub> at room temperature to HCO<sub>2</sub>H to form HCOC*I*, then add phenol to form the ester.
</u>

# Comments:

• The part questions were badly done.

Majority had difficulty in naming the ester and giving the correct reagents and conditions to convert  $CH_3OH$  to  $HCO_2H$ .

In (iii), few were able to correctly suggest a suitable synthetic route to obtain the ester. Stronger answers also made clear mention of the use of NaOH to convert phenol into the stronger phenoxide nucleophile which would react more readily with methanoyl chloride.

# • Question analysis

- (i) The name of the ester consists of two components. The name of the alcohol precedes the acid. The name of the alcohol is changed from *-ol* to *-yl*, while the name of the acid would be changed from *-ic acid* to *-ate*.
- (ii) The conversion of CH<sub>3</sub>OH to HCO<sub>2</sub>H is an oxidation of a 1<sup>o</sup> alcohol to carboxylic acid. However, methanoic acid can also be further oxidised to carbon dioxide and water, so the chosen oxidising agent cannot be a strong oxidising agent.
- (iii) The synthesis of esters of phenol (Carboxylic acids and derivatives lecture notes pg 22) involves the use of acyl chloride with phenol at room temperature.

# • Common mistakes:

- (i) Common incorrect names include: benzyl methanoate, methyl benzoate.
  - Many who used "benzyl" did not realise that the benzyl alcohol refers to  $C_6H_5 \underline{CH_2}OH$ .
- (ii) Most answers mentioned the use of KMnO<sub>4</sub>, not realising that the strong oxidising agent would further oxidise methanoic acid readily to carbon dioxide and water.

- Some who recognised the need for a weaker oxidising agent incorrectly thought that the mixture should also be heated with immediate distillation, not realising that this would lead to the formation of methanal instead of the desired methanoic acid.

(iii) - Most incorrect answers mentioned heating of methanoic acid and phenol together with a conc acid catalyst, not realising that there would be no reaction between phenol and methanoic acid.

#### 18

(e) The  $K_a$  value for some weak acids are given in Table 3.1.

acid	formula	$K_{a}$ / mol dm <sup>-3</sup>
benzoic acid	CO <sub>2</sub> H	6.3 × 10⁻⁵
carbonic acid	H <sub>2</sub> CO <sub>3</sub>	$4.5 imes10^{-7}$
ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	$1.0  imes 10^{-16}$
ethanoic acid	CH <sub>3</sub> CO <sub>2</sub> H	1.8 × 10 <sup>−5</sup>
phenol	ОН	1.3 × 10 <sup>-10</sup>

(i) Explain the difference in  $K_a$  values between phenol and ethanol.

Acid strength: phenol > ethanol In the phenoxide ion of phenol,  $C_6H_5O^-$ , the p-orbital of O overlaps with the  $\pi$ electron cloud of the benzene ring so that the negative charge on O delocalises into the benzene ring. The dispersal of negative charge stabilises the phenoxide ion so that it is more stable than the alkoxide ion. In the ethoxide ion of ethanol,  $CH_3CH_2O^-$ , the <u>electron-donating alkyl group</u> intensifies the negative charge on O atom. The charge on  $CH_3CH_2O^-$  ion also remains <u>localised</u> on a single electronegative O. The ethoxide ion is, therefore, the <u>least stable</u> and hence ethanol is a weaker acid than phenol.

......[2]

(ii) Give the structural formula of the organic products that would be formed from each step in Table 3.2.

step	reaction	organic products formed	
1	heating ester F under reflux with an excess of NaOH(aq) $\downarrow 0 \qquad $	O <sup>-</sup> Na <sup>+</sup>	
2	bubbling CO <sub>2</sub> through the resultant mixture from step 1	O <sup>−</sup> Na <sup>+</sup> OH	
		[2]	



(iii) Using information from Table 3.1, explain the organic products formed in step 2.
CO<sub>2</sub> dissolves in water to give carbonic acid, H<sub>2</sub>CO<sub>3</sub>, which is a stronger acid than phenol but a weaker acid than ethanoic acid. Hence only sodium phenoxide reacts with H<sub>2</sub>CO<sub>3</sub> to give phenol. Sodium ethanoate have no reaction with H<sub>2</sub>CO<sub>3</sub>.

[Total: 16]

# **Comments:**

(i) was generally well attempted.
(ii) and (iii) was poorly attempted. Many made little or no attempts to (iii).

## • Question analysis

- (i) Explaining relative acidity of phenol and ethanol (Hydroxy Compounds page 27)
- (ii) Determine the products of hydrolysis of an ester. Since an alkaline medium is used, also consider possible acid-base reactions between the products of hydrolysis with OH<sup>-</sup> ions present.
- (iii) (with (ii) Step 2)  $CO_2$  when bubbled through the solution will form  $H_2CO_3$ . Since the question explicitly says to use information from the table, it is likely that the  $K_a$  of carbonic acid must be considered in deciding what happens to the products of hydrolysis from Step 1.

## Common mistakes:

(i) - Incorrect usage of terms such as 'resonance stabilised benzene ring' and 'negative charge deintensified' were observed.

It should be noted that the dispersal of negative charge does not equate to the negative charge being "deintensified" as the negative charge was not intensified in the first place.

- Some answers were vague and made no mention of the <u>negative charge on</u> <u>the O atom of the conjugate base</u>. Answers describing the "negative charge of the conjugate base is intensified/reduced" was commonly seen. Some incorrectly described the stabilisation of the molecule rather than the conjugate base ion.

(ii) - While most realised that the ester would undergo hydrolysis, many did not consider further acid-base reaction of the resulting carboxylic acid and phenol with sodium hydroxide present.

- For step 2, many did not understand the intention of the question and thought that both salts would be protonated.

(iii) - Many did not read the question carefully and did not use any information from Table 3.1 in their answers. While some knew to use the  $K_a$  values in their answers, the relative acidity of carbonic acid was often omitted in the comparison of relative acid strength of phenol, ethanoic acid and carbonic acid.

- 4 This question is mainly about the chemistry of unsaturated hydrocarbons.
  - (a) Alkynes are compounds containing a carbon-carbon triple bond and they undergo reactions similar to those of alkenes.

When gaseous but-2-yne,  $CH_3C\equiv CCH_3$ , is reduced with hydrogen gas using a modified palladium metal catalyst, it is possible to control the reduction such that only one of the stereoisomers of but-2-ene is formed.

(i) Draw the structural formula of *cis*-but-2-ene and *trans*-but-2-ene, indicating clearly which is the *cis*-isomer and the *trans*-isomer.



[1]

## Comments:

- Very well attempted only a few students failed to score a mark for this.
- Question analysis and references (where applicable) Straightforward question on drawing *cis* and *trans* isomer.
- Common mistakes:
- (1) Did not show trigonal planar shape around the alkene C atoms.
- (2) Drew 2-methylpropene instead.
- (3) Some drew CH<sub>3</sub> has <sub>3</sub>HC instead! (H<sub>3</sub>C is acceptable but not preferred)
  - (ii) Explain why *trans*-but-2-ene is thermodynamically more stable than *cis*-but-2-ene.

The methyl groups are on opposite sides of the C=C bond and thus there is

less steric repulsion / strain. [1]

#### Comments:

- Generally, decently attempted.
- Question analysis and references (where applicable) Need to consider what is different between cis and trans isomer which could affect their stability.
- Common mistakes: Many students attempted to explain in terms of closeness of packing or polarity and hence melting or boiling point. Many used the term "steric hindrance" though this was not penalised.

(iii) State the type of catalysis occurring in the reduction of but-2-yne and explain its mode of action.

Heterogeneous catalysis. The catalyst provides active sites / a surface

whereby the  $CO_2$  and  $H_2$  molecules may be physically **adsorbed**. This

increases the local / surface concentration of the two reactant gases and

weakens the covalent bonds within the reactants thus lowering the

activation energy for reaction to occur. The product molecules of CH<sub>3</sub>OH and

H<sub>2</sub>O break free from the catalyst surface and desorb from the surface.

......[3]

# **Comments:**

• Generally well-attempted and most were able to identify the type of catalyst.

# • Question analysis and references (where applicable)

"Mode of action" for heterogeneous catalyst means you need to describe the various stages of the catalytic process.

# Common mistakes:

- (1) A significant number of students had no idea what mode of action meant and thus just gave a generic explanation involving how catalyst can lower activation energy thus increasing rate of reaction.
- (2) Spelt "adsorb" as "absorb" which has a very different meaning!
- (3) Didn't specify clearly the increase in concentration was on the surface of the catalyst
- (4) Didn't explain why the E<sub>a</sub> would decrease.
- (5) Didn't mention the desorption process (some also thought it was "deadsorption" or "unadsorption").

(iv) Hence, suggest, with explanation, whether the *cis*- or the *trans*-isomer of but-2-ene is formed by reducing but-2-yne using the modified palladium metal catalyst.

Since the reactants adsorb onto the surface of the metal catalyst, the **<u>H atoms</u>** 

will add onto the same side of the C≡C bond via the catalyst surface to give

the <u>cis isomer</u>.

.....[1]

## **Comments:**

- Generally, very poorly attempted.
- Question analysis and references (where applicable) "Hence" suggests you need to look at the previous part(s) to help you explain thus you should try to reason using your (iii) answer.
- **Common mistakes:** Most students thought it was the trans-isomer as it was given to be more stable in (ii), rather than trying to link to their (iii) answer.
- (b) Benzene is an unsaturated hydrocarbon that can undergo reduction to cyclohexane. However, its reduction requires higher temperatures and pressures, and longer reaction times than the reduction of alkenes or alkynes. Explain why this is so.

The benzene ring is resonance stabilised due to the delocalisation of the 6  $\pi$ 

electrons thus it is very unfavourable for reduction of the ring to occur as it will

destroy the resonance stability of the ring.

The  $\pi$  bonds of alkenes and alkynes are weak and break more readily for them

to undergo reduction more easily. [1]

# Comments:

Generally, decently attempted.

# • Question analysis and references (where applicable)

Students needed to compare benzene vs. alkenes (and alkynes) in terms of their reactivity.

#### • Common mistakes:

- (1) Most recognised that benzene is resonance-stabilised but didn't explain why this was so.
- (2) Many tried to discuss about partial double bond character which sounds contradictory since alkenes and alkynes have stronger double and triple bonds.

(c) Pent-2-yne, CH<sub>3</sub>C≡CCH<sub>2</sub>CH<sub>3</sub>, can be oxidised by KMnO<sub>4</sub> under certain conditions to form an organic product, C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, which gives a yellow precipitate with aqueous alkaline iodine.

Suggest the structural formula of the organic product formed.



[1]

## Comments:

• Generally, decently attempted, which is pleasing to see as it is a novel reaction.

# Question analysis and references (where applicable)

Students had to realise from earlier info that alkenes and alkynes undergo similar reactions and thus predict that the alkyne should undergo oxidation to form possibly ketone and/or carboxylic acids just like alkenes.

Students should also learn to make use of the molecular formula given in questions to help deduce structures.

Common mistakes:

Ο

(1) - presumably, those who drew this just thought that the molecule looks nice and symmetrical because since the alkyne is between C2 and C3, logically the 2 extra O atoms should be on C2 and C3 as well.

(2) Drawing molecules whose molecular formula were not  $C_5H_8O_2$ . This is disturbing as it suggests poor reading skills or inability to count the atoms correctly.

(3) Drawing molecules which have alkenes or  $1^{\circ}/2^{\circ}$  alcohols or aldehydes, none of which makes sense as all of them can be oxidised by KMnO<sub>4</sub>.

(d) In some circumstances, organic compounds with halogen atoms will undergo an elimination reaction as shown in Fig. 4.1.



Fig. 4.1

(i) Suggest why it is much harder for 3-chlorohex-3-ene to undergo elimination compared to 3-chlorohexane.

The C-C1 bond of 3-chlorohex-3-ene is stronger due to the delocalisation

of a lone pair of electrons of the C1 atom into the C=C bond, thus the C-C1

bond has partial double bond character and thus making the bond harder

to break than that of 3-chlorohexane.

.....[1]

# Comments:

• Generally, poorly attempted.

# • Question analysis and references (where applicable)

Students had to compare the difference between the reactivity of a halogenoalkane vs. a halogenoalkene in a different context of elimination reaction instead of the usual nucleophilic substitution. but many didn't seem to recognise the halogenoalkene.

# • Common mistakes:

- (1) Out of those that did recognise the halogenoalkene, it was a pity that a significant number didn't discuss the delocalisation of the lone pair of electrons.
- (2) Some discussed the C=C bond is electron rich but that is not the main reason for explaining the reactivity between a halogenoalkane vs. a halogenoalkene.
- (3) Some claimed that it was difficult to form a C=C than a C=C bond which has no basis.

(ii) Given that the C atoms in a C≡C bond are sp hybridised, suggest why cyclohexyne is **not** formed.

The alkyne C atoms should ideally have a linear shape to minimize repulsion

but this is NOT possible in cyclohexyne as there would be too much

deviation from the ideal bond angle or too much ring strain / angle strain

making the compound too unstable to be formed. [1]

## Comments:

- Generally well-attempted.
- Question analysis and references(where applicable) Students were given the hybridisation thus they should try to think about the different aspects of hybridisation and how it relates to the question.
- Common mistakes:
- (1) Some claimed that it was because the alkyne C atoms have a different hybridisation to the other C atoms in cyclohexyne. However, cyclohexene does exist so this argument doesn't make sense.
- (2) Some answers seem to suggest that the student thinks that the skeletal formula of cyclohexyne implies that the alkyne C atoms have 5 bonds and thus it cannot exist.

(e) (i) With the aid of a labelled diagram, explain how the orbitals overlap to form the C≡C bond in ethyne, H–C≡C–H.



28

(ii) Propadiene is the simplest example of an allene, which are organic compounds with two adjacent carbon-carbon double bonds.



By considering the orientation of orbitals on C2, explain why propadiene is not a planar molecule.

The **p** orbitals involved in each  $\pi$  bond are perpendicular to each other, thus

the sp<sup>2</sup> orbitals of C1 and C3 are perpendicular to each other.

Hence, 2 of the H atoms lie on the same plane as the C atoms and 2 of the

<u>H atoms lie on a plane perpendicular to the plane of the C atoms</u>. [1]

# **Comments:**

• Generally, very poorly attempted.

# • Question analysis and references (where applicable)

This is an unusual and challenging question requiring students to think about the spatial arrangement of the orbitals involved in covalent bonds.

Nevertheless, hints were offered in the question. Students were asked to consider the orientation of orbitals on C2. Furthermore, **(e)(i)** was also meant to hint at how the orbitals are orientated by asking students to draw a diagram of the orbitals.

# • Common mistakes:

- (1) Many students seem to think that only molecules with a central atom with trigonal planar shape can be a planar molecule. Hence answers such as "Since the central atom has a linear shape / the molecule is linear, thus the molecule is not planar." Think about a common molecule such as CO<sub>2</sub> (O=C=O). It is linear but the molecule is planar!
- (2) Many students claimed that since the p orbitals are perpendicular to each other, hence the molecule is non-planar. However, ethyne (H–C≡C–H) has sp hybridised C atoms and the molecule is linear and planar!
- (3) The most disturbing mistakes were claims that C2 had a tetrahedral or bent shape despite the diagram showing linear shape and also you could deduce by observing the number of bond pairs and lone pairs around C2.

(f) Buta-1,3-diene can undergo electrophilic addition with liquid bromine in a 1 : 1 ratio to give two products as shown in Fig. 4.2.



Fig. 4.2

The formation of 1,4-dibromobut-2-ene is unexpected but can be rationalised due to the delocalisation of electrons to form an alternative carbocation.

Suggest the mechanism for the formation of 1,4-dibromobut-2-ene. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.



Alternative involving resonanced-stabilised allylic carbocation:



# Comments:

• Generally, decently attempted.

# • Question analysis and references (where applicable)

Question already stated the mechanism, reagents and mole ratio. Question also stated the delocalisation of electrons forms an alternative carbocation.

This suggests you should've used your knowledge of the electrophilic addition mechanism and started drawing the mechanism in the usual way rather than trying too hard and drawing arrows all over the place!

# • Common mistakes:

- (1) Clearly many students still struggle to grasp the concept of arrow-pushing and thus how to handle novel mechanisms (or in this case, just a slight variation of the usual E.A. mechanism) as students used the <u>wrong arrows</u> (half-arrows which are for radical mechanisms) or had <u>arrows that made no sense (e.g. arrows that did not</u> <u>start from a source of electrons)</u> especially in relation to the intermediates or products drawn. A reminder that <u>drawing arrows precisely is an important skill for</u> <u>mechanisms</u>!
- (2) Despite the questions stating "electrophilic addition with liquid bromine in a 1 : 1 ratio", students ignored one or more of the given information and made <u>mistakes such as</u> <u>drawing mechanisms that resembled FRS, using HBr rather than Br<sub>2</sub> and using 2 molecules of Br<sub>2</sub>.</u>
- (3) Many students made a basic mistake of forgetting to write the Br<sup>−</sup> in the first step or missing out the arrow from the Br–Br bond to the Br atom. Remember that <u>all</u> <u>equations (even in mechanisms) must be balanced</u> and that the <u>arrows should</u> <u>account for all bond breaking/forming</u>!
- (4) Some students broke up the  $Br_2$  to  $Br^+$  and  $Br^-$  but it wouldn't just dissociate like that to form ions!

**5** Glycinin is a water-soluble globular protein found in soy beans. Some amino acids found in glycinin are listed in Table 5.1.

amino acid	side chain, R	p <i>K</i> ₄ of side chain		
arginine	H NH      (CH <sub>2</sub> ) <sub>3</sub> NCNH <sub>2</sub>	12.5		
aspartic acid	—сн <sub>2</sub> —с́ он	3.9		
glutamic acid	—сн <sub>2</sub> сн <sub>2</sub> -с Он	4.3		
glycine	—н	-		
leucine	СН <sub>3</sub> —СН <sub>2</sub> С́Н СН <sub>3</sub>	_		
lysine	$-CH_2CH_2CH_2CH_2NH_2$	10.5		
*proline	CO <sub>2</sub> H	_		
valine	СН <sub>3</sub> —Сн СН <sub>3</sub>	_		

Table 5.1

\* The full structure of proline is shown as it is the only amino acid that possesses a secondary amine for its amino group.

Fig. 5.1 shows a polypeptide chain folding into a globular shape, due to side-chain interactions.



(a) With reference to Fig. 5.1 and Table 5.1, suggest another type of side-chain interaction found in a polypeptide chain of glycinin at pH 7.

Illustrate your answer with the side-chains of suitable pairs of amino acids on Fig. 5.2.

type of side chain interaction: ionic bonds between side chains with charged

groups  $(-NH_3^+ \text{ and } -CO_2^-)$ 





[2]





# • Question analysis and references(where applicable)

Refer to Nitrogen Lecture Notes pg 25-26 and Nitrogen Tutorial B4

- Depending on the nature of the side-chains as well as pH, there can be
- instantenous dipole-induced dipole between non polar groups
- ionic interactions between acidic and basic groups
- hydrogen bonding between polar groups (except cysteine which forms disulfide bonds)

Hence, using the  $pK_a$  and pH values given, you can deduce that the acidic groups are deprotonated while basic groups are protonated and show ionic interactions between relavants groups.

## Common mistakes:

Hydrogen bonding was the commonly given between the acidic and basic groups as students ignored the pH value given. E.c.f. is given with appropriate and correct hydrogen bonding drawn.



(b) Papain is an enzyme that breaks down proteins into smaller peptides and amino acids. It exhibits broad specificity, cleaving peptide bonds on the carboxyl side of glycine, leucine and basic amino acids.

A short segment of six amino acid sequence in glycinin is shown in Fig. 5.3.



Fig. 5.3

(i) With reference to Table 5.1 and your knowledge of the basicity of organic compounds, circle on Fig. 5.3 the peptide bonds that are cleaved by Papain. [2]

34

(ii) Suggest the reagent and condition needed to fully hydrolyse glycinin.

HCl(aq)/H<sub>2</sub>SO<sub>4</sub>(aq), heat or NaOH(aq), prolonged heat [1]

# Comments:Poorly done

# • Question analysis and references(where applicable)

This question requires students to first identify the amino acids that can be hydrolysed by papain, i.e. glycine, leucine and basic amino acids by using their respective side chains. Next, the bonds are cleaved on the **carboxyl side i.e right side**.

#### Common mistakes:

(ii) is a more common exam question yet many students were unable to state correctly the reagent used.

Wrong answers such as concentrated  $H_2SO_4(aq)$  were very common.

(c) Formaldehyde, HCHO, is a toxic chemical which was reported to be abused as a food preservative for food with short shelf life such as soy bean curds.

Formaldehyde content can be determined via the process below:

# A. Back titration

1. A 5 cm<sup>3</sup> sample containing HCHO, is reacted with excess of sodium bisulfite solution, NaHSO<sub>3</sub>. The mixture is left to stand for 30 minutes.

$$\begin{array}{c} O \\ \parallel \\ H \\ C \\ H \end{array} + NaHSO_3 \longrightarrow \begin{array}{c} OH \\ H \\ H \\ C \\ SO_3Na \\ A \end{array}$$

2. 20 cm<sup>3</sup> of 0.080 mol dm<sup>-3</sup> iodine solution,  $I_2$  is added to the reaction mixture in step 1 until the solution turns brown.

$$NaHSO_3 + I_2 + H_2O \rightarrow NaI + HI + H_2SO_4$$

3. The unreacted  $I_2$  from step 2 is then titrated with 0.100 mol dm<sup>-3</sup> of sodium thiosulfate solution, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

The titre volume,  $V_A$  is 25.30 cm<sup>3</sup>.

# B. Blank titration

The above steps are repeated using 5 cm<sup>3</sup> of deionised water instead of HCHO. The titre volume,  $V_{\rm B}$  is 22.00 cm<sup>3</sup>.

(i) The concentration of HCHO in the sample can be determined by considering the difference between  $V_A$  and  $V_B$ . Suggest why  $V_B$  is lower than  $V_A$ .

Since there is no HCHO present during the blank titration, all of the NaHSO3

......[1]

(ii) Determine the concentration of HCHO in the 5 cm<sup>3</sup> sample.

actual volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> =  $V_A - V_B$ = 25.30 - 22.00 = 3.30 cm<sup>3</sup>

Since  $2Na_2S_2O_3 \equiv NaHSO_3 \equiv HCHO$ 

amt of HCHO in 5 cm<sup>3</sup> sample =  $\frac{1}{2} \times \frac{3.30}{1000} \times 0.100 = 1.65 \times 10^{-4}$  mol

Hence, [HCHO] = 
$$\frac{1.65 \times 10^{-4}}{\frac{5.0}{1000}}$$
 =  $\frac{0.033 \text{ mol dm}^{-3}}{3}$  [3]

(iii) Suggest a chemical test to distinguish HCHO and compound A. You may assume  $-SO_3Na$  is inert.

2,4-DNPH		
For HCHO: orange ppt	formed.	
For A: no orange ppt alternative:		[2]
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (aq), H <sub>2</sub> SO <sub>4</sub> (aq) KMnO <sub>4</sub> (aq), H <sub>2</sub> SO <sub>4</sub> (aq):	: A change orange solution change to green HCHO decolourise purple $KMnO_4$ with $CO_2$ formed (white ppt with $Ca(OH)_2$ )	gas

#### 36

#### **Comments:**

This question is poorly done. Most students could answer (ii) but not (i).

## **Question analysis**

The information describes that reactions and stoichiometry relationship between reactants. Students have to be able to follow through each step and know clearly what the limiting reagents and excess reagents are.

A good strategy (as guided by the question) is to work from the last step (i.e titration results).

The hint given about difference between  $V_A$  and  $V_B$  relates to the amount of NaHSO<sub>3</sub> reacted in step 1 and allow students thus was able to solve (ii) quickly.

There was a number of students who used an alternative longer method, which marks was awarded accordingly.

Amt of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> used in B =  $\frac{22.0}{1000} \times 0.100 = 2.20 \times 10^{-3}$  mol Since I<sub>2</sub> = NaHSO<sub>3</sub> Amt of I<sub>2</sub> unreacted in step 2 = Amt of NaHSO<sub>3</sub> initially present in step 1 =  $\frac{1}{2} \times 2.20 \times 10^{-3} = 1.10 \times 10^{-3}$  mol

Initial amt of NaHSO<sub>3</sub> =  $\left(\frac{20}{1000} \times 0.080\right) - 1.10 \times 10^{-3} = 5.00 \times 10^{-4} \text{ mol}$ 

Amt of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> used in A =  $\frac{25.30}{1000} \times 0.100 = 2.53 \times 10^{-3}$  mol

Since  $I_2 \equiv NaHSO_3$ 

Amt of I<sub>2</sub> unreacted in step 2 = Amt of NaHSO<sub>3</sub> unreacted in step 1 =  $\frac{1}{2} \times 2.53 \times 10^{-3} = 1.265 \times 10^{-3}$  mol Amt of NaHSO<sub>3</sub> reacted = ( $\frac{20}{1000} \times 0.080$ ) - 1.265 × 10<sup>-3</sup> mol =  $3.35 \times 10^{-4}$  mol

Since NaHSO<sub>3</sub> = CH<sub>2</sub>O Amt of CH<sub>2</sub>O in 5 cm<sup>3</sup> sample =  $5.00 \times 10^{-4} - 3.35 \times 10^{-4}$  mol =  $1.65 \times 10^{-4}$  mol

Hence,  $[CH_2O] = (1.65 \times 10^{-4}) \div \frac{5.0}{1000} = 0.033 \text{ mol dm}^{-3}$ 

#### Common mistakes:

(i) Wrongly stating that water causes dilution which affects the concentration of NaHSO3. Wrongly relating acidity or strength of nuclephiles to stoichiometry.

(ii) Students were unable to make good use of the hint given about the difference between  $V_B$  and  $V_A$ . Instead they used an alternative method: While some students were able to obtain the NaHSO<sub>4</sub> reacted in step 1. They forgot that to use the initial NaHSO<sub>4</sub> which was in excess to determine the actual amount of NaHSO<sub>5</sub> used in step 1 during the back titration.

(d) Soy bean lipoxygenase is an iron-containing enzyme that oxidise unsaturated fatty acids in three stages as shown in Table 5.2.

The lipoxygenase is represented as LOX–Fe<sup>III</sup>–OH. The iron has a +3 oxidation state.







(i) In stage 1, the C-H bond undergoes *homolytic fission*. Explain the term *homolytic fission*.

Homolytic fission refer to cleavage of a bond in which the molecular fragments

between which the bond is broken retains one of the bonding electrons [1]

(ii) Use curly arrow notation to show the movement of electrons for stage 2 in Table 5.2.

(iii) Write the overall equation for the oxidation of fatty acid described in Table 5.2. Hence, determine the enthalpy change of reaction for the overall reaction



[2]

[Total: 15]

# Comments:

• (ii) and (iii) were poorly done

#### • Question analysis and references(where applicable)

This question required students to examine the mechanism provided. Based on the information, since there is an abstraction of H atom via a homolytic fission in step 1, then the reaction occurs via free radicals. Hence there will be homolytic bond breaking in subsequent steps as well.

(ii) Compare the bond broken and formed and show the correct half arrows.

(iii) Based on the overall reaction, compare the bonds broken and formed and use BE from data booklet accordingly.

#### Common mistakes:

(i) incomplete description of homolytic fission by merely stating "radicals are formed." Students have to clearly describe the equal distribution of a shared pair of electons or words to the effect.

(ii) Showing double arrows or a mixture of single and double arrows. Unclear starting/ending position of the arrows.

(iii) including the enzyme, which is the catalyst for the reaction in the overall equation.