



Oxford Cambridge and RSA

Tuesday 13 October 2020 – Morning

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Time allowed: 2 hours 15 minutes

You must have:

- a clean copy of the Advance Notice Article (inside this document)
- the Data Sheet for Chemistry B

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

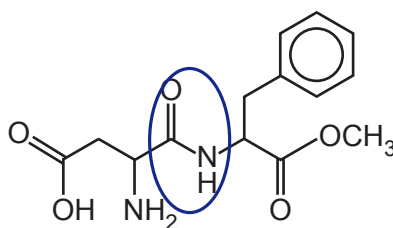
- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **24** pages.

ADVICE

- Read each question carefully before you start your answer.

Answer **all** the questions.

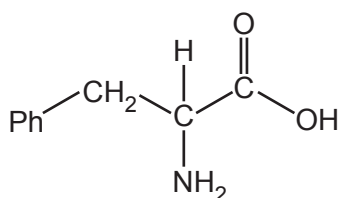
- 1 Aspartame is a dipeptide that is used as an artificial sweetener. The structure of aspartame is shown in **Fig. 1.1**.



aspartame

Fig. 1.1

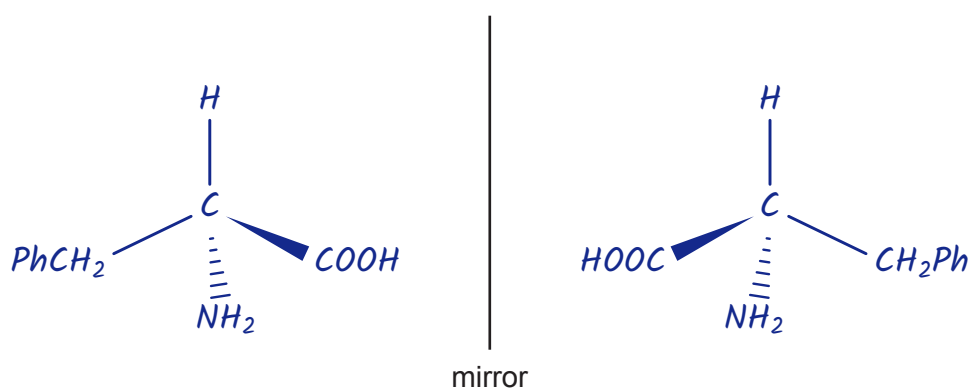
- (a) Circle a secondary amide group on the structure of aspartame in **Fig. 1.1**. [1]
- (b) Aspartame is hydrolysed by boiling with acid. One of the products is phenylalanine which is shown in **Fig. 1.2**. 'Ph' represents a benzene ring.



phenylalanine

Fig. 1.2

- (i) Phenylalanine has a chiral centre. Draw the three dimensional formulae to show the enantiomers of phenylalanine.



[2]

- (ii) Phenylalanine in solution exists mainly as a zwitterion. Complete the diagram in **Fig. 1.3** to show the structure of this zwitterion.

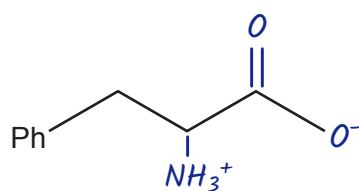


Fig. 1.3

[1]

- (iii) A student says that acid hydrolysis of aspartame will only produce phenylalanine and one other amino acid.

Comment on the accuracy of this statement, giving the structures of any compounds you include in your answer.

The statement is not accurate. As well as phenylalanine, aspartic acid, $H_2NCH(COOH)CH_2COOH$, is formed from hydrolysis of the amide (peptide) bond. The ester group ($COOCH_3$) is also hydrolysed, so methanol, CH_3OH , is produced as well. So three products form, not only two amino acids.

[3]

- (c) Aspartame tastes sweet. One theory is that the sweetness is caused by hydrogen bonds forming between sweetener molecules and sweetness receptors in the body.

On the structure of aspartame in **Fig. 1.4** circle **all** the atoms that could hydrogen bond with a receptor.

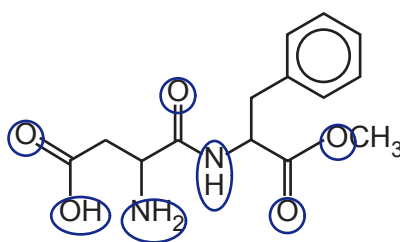


Fig. 1.4

[1]

- (d) The enzyme pepsin catalyses the hydrolysis of protein chains. Some students read that pepsin breaks the peptide bonds adjacent to aromatic amino-acids, for example phenylalanine. This is because the active site is specific to benzene rings.

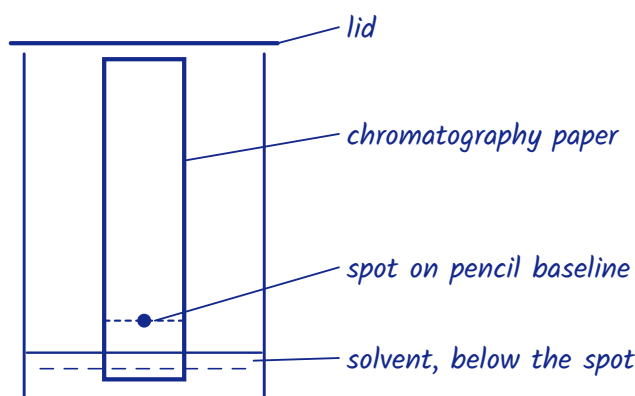
Suggest the type of bonds that form between a benzene ring and the active site.

Instantaneous dipole-induced dipole (id-id / London) bonds

[1]

- (e) The students mix excess aspartame and pepsin in aqueous solution at room temperature. After 30 minutes they place a spot of the mixture on some chromatography paper.
- (i) Describe the rest of their method, including how they could tell whether hydrolysis has occurred.

You may include a diagram in your answer.



Place the paper in a tank containing a small amount of solvent, with the solvent level below the spot (baseline), and cover with a lid.

Allow the solvent to rise up the paper until it is near the top, then remove the paper and mark the solvent front.

Dry the paper and spray it with ninhydrin (a locating agent) and warm it, or view under UV light, to show the spots.

If more than one spot is seen, hydrolysis has occurred (the spots match spots from pure phenylalanine and aspartic acid run on the same paper).

One spot (aspartame only) means no hydrolysis.

[4]

- (ii) Other students boil the mixture of aspartame and pepsin to attempt to speed up the hydrolysis reaction.

State and explain whether or not this would work.

No. Boiling denatures the enzyme: its tertiary structure and active site are broken down, so no reaction is catalysed. [1]

- (iii) Another student says that using a higher concentration of aspartame at room temperature will speed up the hydrolysis reaction.

Comment on this statement.

The statement is wrong: there is no difference to the rate. Aspartame is already in excess, so all the active sites of pepsin are occupied; the reaction is zero order with respect to aspartame (substrate) at high concentration. [2]

- 2 Some students use a method based on an electrochemical cell to measure the concentration of silver ions in solution.

They set up a cell as shown in **Fig. 2.1**.

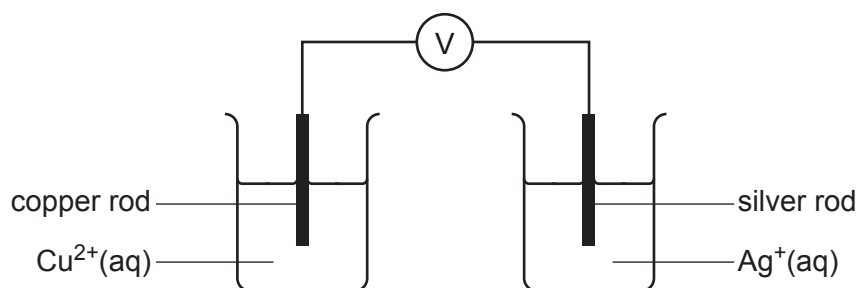


Fig. 2.1

- (a) (i) There is something missing from the diagram.

State what it is and describe what it is made of.

A salt bridge made of filter paper soaked in potassium nitrate solution...... [2]

- (ii) State **two** conditions necessary for the cell to measure electrode potentials under **standard** conditions.

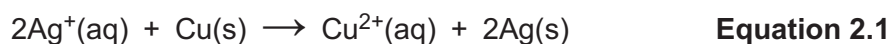
1 *Temperature of 298 K (25 °C)*.....
 2 *Concentrations of ions in solution of 1 mol dm⁻³*..... [2]

- (b) **Table 2.1** shows the electrode potential data for the cell in **Fig. 2.1**.

Half-equation	E°/V
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80

Table 2.1

Equation 2.1 shows the reaction that occurs when the standard cell delivers a current.



- (i) Identify the oxidising agent in **equation 2.1**.

Silver ions, Ag⁺(aq)..... [1]

- (ii) State and explain which way electrons flow in the wire when the standard cell is delivering a current.

From Cu to Ag, because the Cu electrode potential is less positive (Cu is oxidised and loses electrons, Ag⁺ gains them). [1]

- (c) Silver bromide, AgBr, is usually described as 'insoluble' but a small amount can dissolve in water.

The students have a saturated solution of AgBr. This contains as much AgBr as will dissolve. They place this saturated solution in the right-hand beaker of the cell in **Fig. 2.1**.

They measure the cell potential against a standard copper electrode. Their result is 0.09 V (with the same electrode polarity as in the standard cell in **(b)**).

The students are told that the relationship between their measured cell potential, E_{cell} , and the concentration of silver ions is given by:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} + 0.06 \log[\text{Ag}^+]$$

Calculate the silver ion concentration in the saturated solution of AgBr.

$$E^{\ominus}_{\text{cell}} = 0.80 - 0.34 = 0.46 \text{ V}$$

$$0.06 \log[\text{Ag}^+] = E_{\text{cell}} - E^{\ominus}_{\text{cell}} = 0.09 - 0.46 = -0.37$$

$$\log[\text{Ag}^+] = -0.37 / 0.06 = -6.17$$

$$[\text{Ag}^+] = 10^{-6.17} = 6.8 \times 10^{-7} \text{ mol dm}^{-3}$$

$$[\text{Ag}^+] = 6.8 \times 10^{-7} \text{ mol dm}^{-3} \text{ [4]}$$

- (d) Some other students make another cell, using two different half cells as shown in **Table 2.2**.

Half-reaction	$E^{\ominus}/\text{V}$
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$2\text{IO}_3^{-}(\text{aq}) + 12\text{H}^{+}(\text{aq}) + 10\text{e}^{-} \rightleftharpoons \text{I}_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$	+1.19

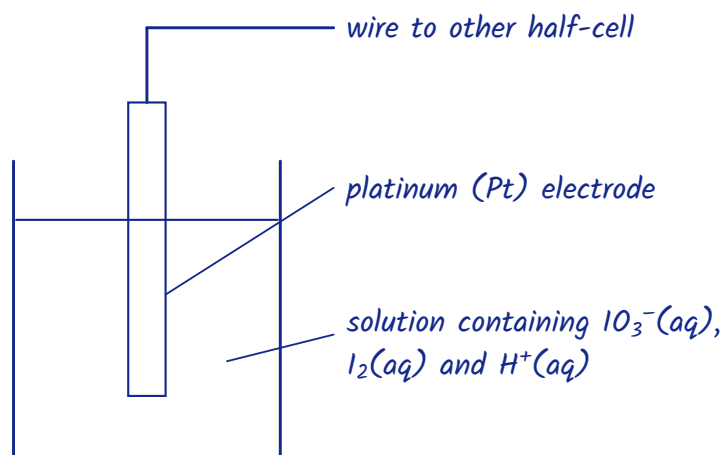
Table 2.2

- (i) Write an equation for the reaction that occurs when the cell delivers a current.



[2]

- (ii) Draw a labelled diagram to show how the IO_3^-/I_2 electrode is made up. You do **not** need to give concentrations.



[2]

- (iii) The students are told that in a standard IO_3^-/I_2 electrode $[\text{IO}_3^-]^2 = [\text{I}_2]$.

They plan to prepare 40 cm^3 of the solution for the electrode by mixing 20 cm^3 of 0.08 mol dm^{-3} $\text{I}_2(\text{aq})$ with 20 cm^3 of $\text{IO}_3^-(\text{aq})$.

Calculate the concentration of IO_3^- needed so that $[\text{IO}_3^-]^2 = [\text{I}_2]$.

$$[\text{I}_2] \text{ in } 40\text{ cm}^3 \text{ mixture} = 0.08 \times 20/40 = 0.04\text{ mol dm}^{-3}$$

$$[\text{IO}_3^-] \text{ in mixture} = \sqrt{0.04} = 0.2\text{ mol dm}^{-3}$$

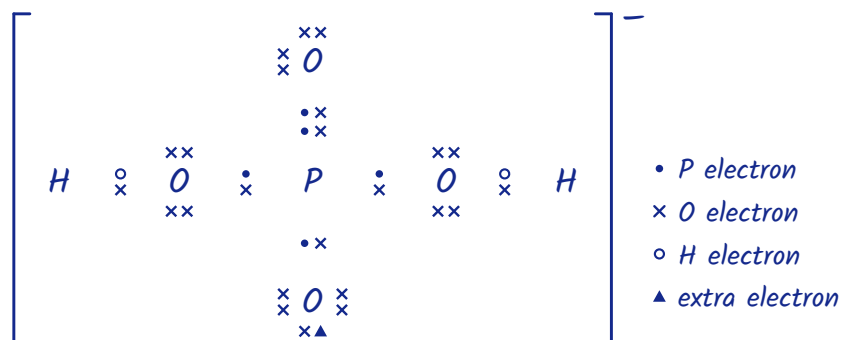
$$\text{before mixing (diluted } \times 2\text{): } [\text{IO}_3^-] = 0.2 \times 40/20 = 0.4\text{ mol dm}^{-3}$$

$$[\text{IO}_3^-] = \dots\dots\dots 0.4 \dots\dots\dots \text{ mol dm}^{-3} \quad [3]$$

- 3 'Monopotassium phosphate', KH_2PO_4 , is added to fertilisers. KH_2PO_4 acts as a buffer and supplies phosphorus.

(a) The H_2PO_4^- ion has two OH groups.

Draw a 'dot-and-cross' diagram for this ion.



[2]

- (b) KH_2PO_4 when used in fertilisers is said to be equivalent to 52% P_2O_5 and 34% K_2O by mass.

Show that the mole ratio of potassium to phosphorus in 52% P_2O_5 and 34% K_2O is the same as in KH_2PO_4 .

$$\text{Mr}(\text{P}_2\text{O}_5) = 142; \quad \text{Mr}(\text{K}_2\text{O}) = 94.2 \quad (\text{in } 100 \text{ g})$$

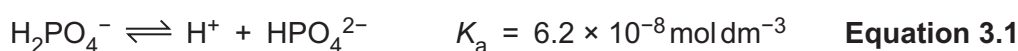
$$\text{mol P} = 2 \times 52/142 = 0.73 \text{ mol}$$

$$\text{mol K} = 2 \times 34/94.2 = 0.72 \text{ mol}$$

$$\text{K} : \text{P} = 0.72 : 0.73 \approx 1 : 1, \text{ the same as in } \text{KH}_2\text{PO}_4 \text{ (1 K : 1 P)}$$

[2]

- (c) In a solution of KH_2PO_4 , the equilibrium in **equation 3.1** occurs:



- (i) Identify the base in this reaction and explain your choice.

...HPO₄²⁻, because it accepts a proton (H⁺) in the reverse reaction...

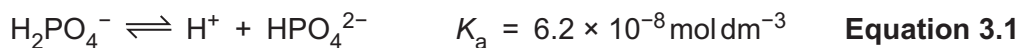
..... [1]

- (ii) Calculate the $\text{p}K_a$ for the equilibrium in **equation 3.1**.

$$\text{p}K_a = -\log(6.2 \times 10^{-8})$$

$$\text{p}K_a = \dots\dots\dots 7.21 \dots\dots\dots [1]$$

Equation 3.1 is repeated again.



(iii) Calculate the pH of a $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ solution of KH_2PO_4 .

$$[\text{H}^+] = \sqrt{K_a \times [\text{H}_2\text{PO}_4^-]} = \sqrt{6.2 \times 10^{-8} \times 1.0 \times 10^{-3}}$$

$$[\text{H}^+] = 7.87 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(7.87 \times 10^{-6})$$

$$\text{pH} = \dots\dots\dots 5.10 \dots\dots\dots [2]$$

(d) The acidity of KH_2PO_4 reduces the loss of ammonia from ammonium ions (NH_4^+) in a fertiliser.

Explain how this happens when the fertiliser is in solution.

In solution: $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$

The H^+ ions (acid) from KH_2PO_4 move the position of this equilibrium to the

left, so less NH_3 forms and less ammonia is lost.

..... [2]

(e) A mixture of HPO_4^{2-} and H_2PO_4^- ions in solution makes a 'phosphate buffer'.

Calculate the mass of KH_2PO_4 that must be added to 1.0 dm^3 of a 0.10 mol dm^{-3} solution of HPO_4^{2-} to make a solution with a pH of 6.50.

The volume of the solution does not change when the solid is added.

$$[\text{H}^+] = 10^{-6.50} = 3.16 \times 10^{-7} \text{ mol dm}^{-3}$$

$$K_a = [\text{H}^+][\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$$

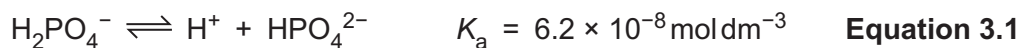
$$[\text{H}_2\text{PO}_4^-] = [\text{H}^+][\text{HPO}_4^{2-}] / K_a$$

$$= 3.16 \times 10^{-7} \times 0.10 / 6.2 \times 10^{-8} = 0.51 \text{ mol dm}^{-3}$$

$$\text{Mr}(\text{KH}_2\text{PO}_4) = 136.1; \quad \text{mass} = 0.51 \times 136.1 = 69 \text{ g}$$

$$\text{mass of } \text{KH}_2\text{PO}_4 = \dots\dots\dots 69 \dots\dots\dots \text{ g [4]}$$

Equation 3.1 is repeated again.



- (f) (i) A student says that a solution of HPO_4^{2-} alone will act as a buffer when acid is added. The student says that this is because the position of equilibrium in **equation 3.1** moves to the left to remove H^+ ions.

Discuss the student's statements.

*The student is right that the equilibrium moves to the left to remove the added H^+ .
But $[\text{H}^+]$ (pH) is only restored to almost unchanged if $[\text{H}_2\text{PO}_4^-]$ is also large, so HPO_4^{2-} alone is not a good buffer.* [2]

- (ii) A student is doing calculations involving solutions of hydrochloric acid.

The student says that the concentration of hydrogen ions can be taken as the concentration of the acid.

Discuss this statement.

The student is correct: HCl is a strong acid, so it fully dissociates (ionises) in solution. [1]

- (iii) Calculate the **change** in pH when 1 drop (0.05 cm^3) of $0.01 \text{ mol dm}^{-3} \text{ HCl}$ is added to 1.0 dm^3 of water at pH 7.0.

$$[\text{H}^+] = 0.05 \times 0.01 / 1000 = 5 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{new pH} = -\log(5 \times 10^{-7}) = 6.3$$

$$\text{pH change} = 7.0 - 6.3 = 0.7$$

pH change = *0.7* [2]

- 4 'Fumaric acid' is used as an acidity regulator in food. 'Maleic acid' is a stereoisomer of fumaric acid. The structure of the two acids are shown in **Fig. 4.1**.

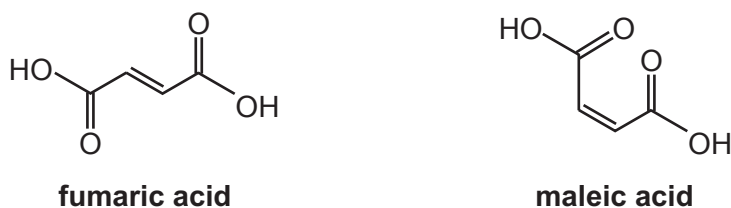


Fig. 4.1

- (a) (i) Describe chemical tests that can be carried out in a laboratory to identify the two functional groups in both acids.

C=C: add bromine water; it is decolourised (orange to colourless).
COOH: add sodium carbonate; it fizzes and the gas (CO₂) turns
limewater cloudy.

[2]

- (ii) A solution has 2.32 g dm⁻³ of maleic acid.

Calculate the volume (in cm³) of 2.0 mol dm⁻³ NaOH(aq) that would completely neutralise 250 cm³ of the solution.

$$Mr(C_4H_4O_4) = 116; \text{ conc} = 2.32/116 = 0.020 \text{ mol dm}^{-3}$$

$$\text{mol acid in } 250 \text{ cm}^3 = 0.020 \times 250/1000 = 0.0050 \text{ mol}$$

$$\text{diprotic, so mol NaOH} = 2 \times 0.0050 = 0.010 \text{ mol}$$

$$\text{vol NaOH} = 0.010/2.0 \times 1000 = 5.0 \text{ cm}^3$$

volume = 5.0 cm³ [3]

- (b) (i) Give the **empirical** formula of both acids.

CHO [1]

- (ii) Give the systematic name for **maleic acid**.

(Z)-butenedioic acid [2]

- (c) Explain why maleic acid and fumaric acid are different compounds.

The COOH groups are arranged differently in space across the C=C (same side in maleic, opposite sides in fumaric). There is no free rotation about C=C, so the groups are fixed in position. [2]

- (d) The mass spectra of maleic and fumaric acid both have a peak at 71. Suggest a reason for this.

Both lose a COOH group ($116 - 45 = 71$), giving the fragment $[CHCHCOOH]^+$, $C_3H_3O_2^+$. [1]

- (e) Fumaric acid is made from maleic acid by an acid-catalysed isomerisation reaction.

A student suggests the mechanism shown in **Fig. 4.2** for the reaction.

- (i) Draw 'curly arrows' on **Fig. 4.2** to complete the mechanism.

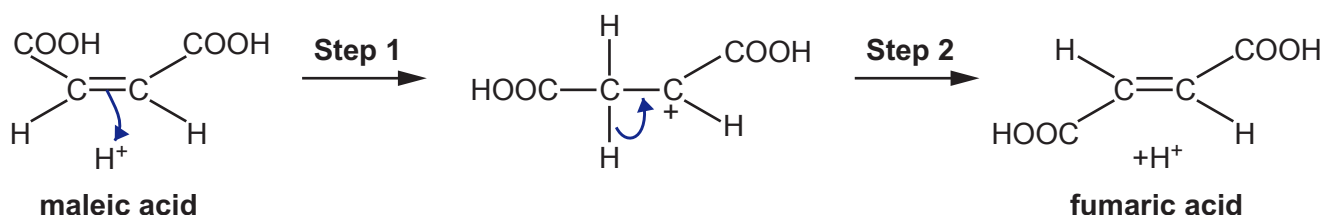


Fig. 4.2

[2]

- (ii) Name the **type** of reaction that is occurring in **step 2**.

(Electrophilic) elimination [1]

- (iii) The student then reads that if $^2H^+$ ions are used for the isomerisation, then there isn't any ^2H found in the fumaric acid formed.

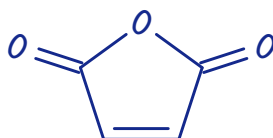
Does this support the student's mechanism in **Fig. 4.2**?

Explain your answer.

No. In the carbocation either of the two H atoms on the left-hand carbon (one of them ^2H) could be lost in step 2. So some ^2H would be incorporated into the fumaric acid formed. [2]

- (f) Maleic acid can be made from 'maleic anhydride', $C_4H_2O_3$.

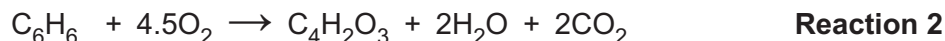
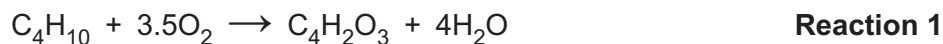
Suggest a skeletal formula for maleic anhydride.



[1]

Turn over

(g) Maleic anhydride can be made industrially by oxidising butane or benzene.



(i) Use calculated atom economies to suggest, with a reason, which reaction is used more.

$$M_r \text{C}_4\text{H}_2\text{O}_3 = 98$$

$$\text{Reaction 1: } 98 / (58 + 3.5 \times 32) \times 100 = 98/170 \times 100 = 58\%$$

$$\text{Reaction 2: } 98 / (78 + 4.5 \times 32) \times 100 = 98/222 \times 100 = 44\%$$

..Reaction 1 (from butane) is used more, as it has the higher atom economy, so it produces less waste..... [2]

(ii) Suggest another reason why the reaction selected in (g)(i) is preferred.

..Benzene is toxic (carcinogenic) and butane is cheaper and more available;.... reaction 1 also produces no CO₂..... [1]

(iii) Calculate the maximum mass of maleic anhydride, C₄H₂O₃, (in kg) that could be made from 15 m³ of butane (measured at RTP).

Give your answer to an **appropriate** number of significant figures.

$$\text{mol butane} = 15\,000 \text{ dm}^3 / 24.0 \text{ dm}^3 \text{ mol}^{-1} = 625 \text{ mol}$$

$$1 : 1 \text{ ratio, so mol C}_4\text{H}_2\text{O}_3 = 625 \text{ mol}$$

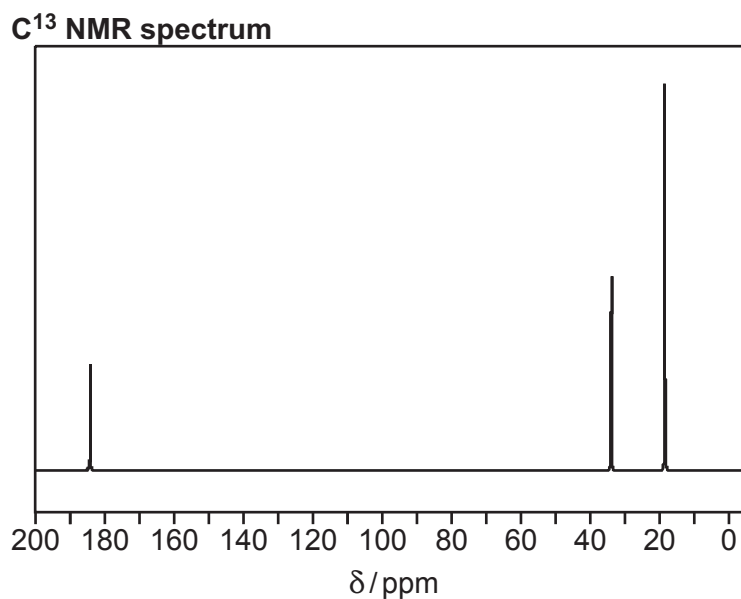
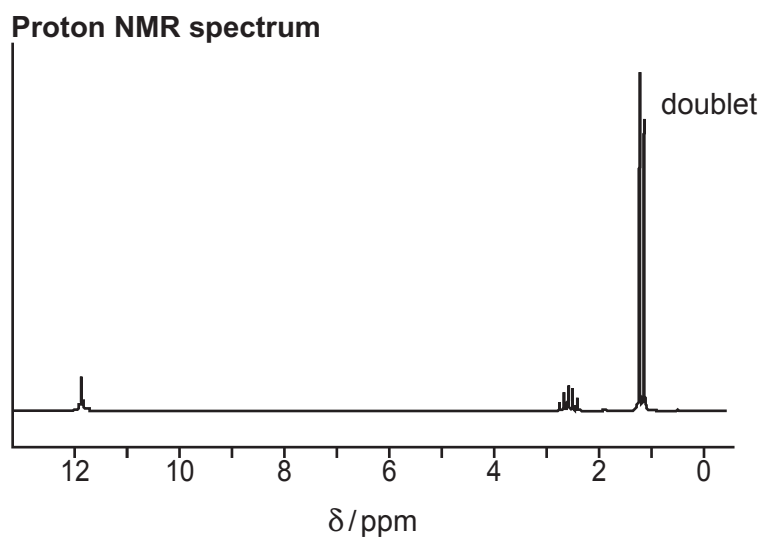
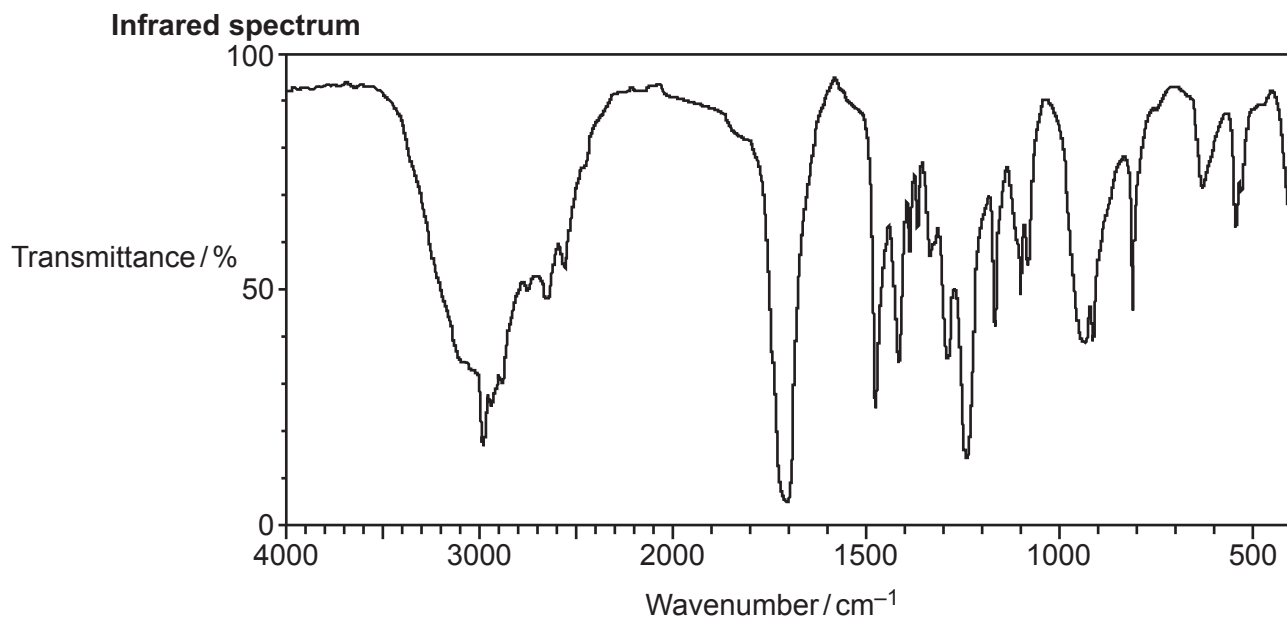
$$\text{mass} = 625 \times 98 = 61\,250 \text{ g} = 61 \text{ kg (2 s.f.)}$$

mass of maleic anhydride = ...61..... kg [2]

15
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PLEASE DO NOT WRITE ON THIS PAGE

(h)* Compound **A** has spectra as shown below.



You may do working on this page but it will not be marked

Compound **A** has four carbon atoms in its molecule.

Identify compound **A**, giving evidence from each spectrum.

[6]

IR: the strong, sharp absorption at about 1700 cm^{-1} is a $\text{C}=\text{O}$ bond, and the very broad absorption from about 2500 to 3300 cm^{-1} is an $\text{O}-\text{H}$ in a carboxylic acid. So **A** contains a COOH group.

Proton NMR: there are three peaks, so three different H environments. The peak at about 11.8 ppm is the H of the COOH group. The large doublet at about 1.2 ppm is from H atoms on CH_3 carbons bonded to a carbon with one H ($\text{C}-\text{H}$), and is split into a doublet by that one H . The small peak (multiplet) at about 2.5 ppm is the single H on a carbon attached to carbons with many H atoms (two CH_3 groups), next to $\text{C}=\text{O}$. The peak sizes ($6 : 1 : 1$) fit this.

$\text{C}-13$ NMR: there are only three peaks, so three C environments, but **A** has four carbons, so two carbons are in the same environment (two equivalent CH_3 groups, peak at about 19 ppm). The peak at about 183 ppm is the $\text{C}=\text{O}$ carbon of COOH and the peak at about 34 ppm is the CH carbon ($\text{C}-\text{C}$ bonds only).

Additional answer space if required

So compound **A** is 2-methylpropanoic acid, $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$.

- 5 This question refers to the Advance Notice Article 'Platinum metal complexes in medicine' that is included inside this document.

(a) Cisplatin is a neutral molecule.

(i) Explain why the oxidation state of the platinum in cisplatin is +2.

The two chloride ligands are each -1 and the two NH₃ ligands are neutral, so Pt is +2. [1]

(ii) Suggest the electronic configuration of the outermost sub-shell in a Pt²⁺ ion.

5d⁸ [1]

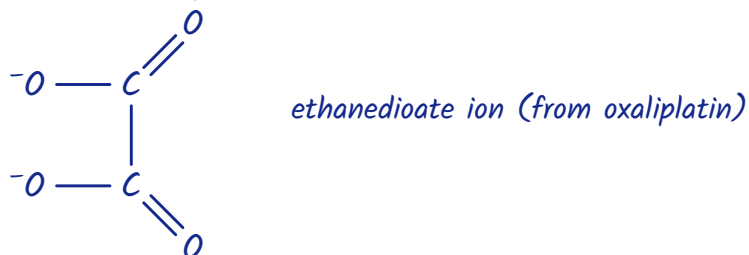
(iii) Is platinum a transition metal?

Give a reason.

Yes, it forms an ion (Pt²⁺) with an incomplete d sub-shell. [1]

(b) Some ligands are described as bidentate.

Give the **full** structural formula of a bidentate ligand from a compound in the article.



[2]

- (c) **Fig. 5.1** is a diagram from page 3 of the article. It shows a possible way in which a compound derived from cisplatin is thought to attach to a base in DNA. Two bonds have been labelled **B** and **C**.

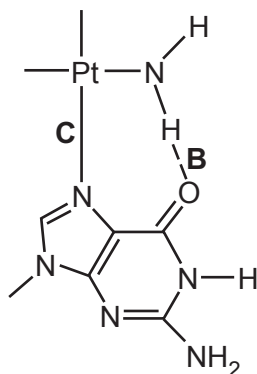


Fig. 5.1

- (i) What is the name of the base in **Fig. 5.1**? Use the Data Sheet to help you.

guanine [1]

- (ii) What is the name of the type of bond at **B** in **Fig. 5.1**?

hydrogen bond [1]

- (iii) Name the type of bond at **C** in **Fig. 5.1** and describe how it is formed.

A dative covalent (co-ordinate) bond

A lone pair of electrons on the nitrogen atom is donated to the Pt, so

both electrons in the bond come from N.

..... [2]

- (d) Satraplatin was designed to be taken by mouth as it is soluble.

- (i) Name the shape of a satraplatin molecule around the Pt atom.

octahedral [1]

- (ii) Give the co-ordination number of Pt in satraplatin.

6 [1]

- (iii) Suggest, in terms of intermolecular bonds, why satraplatin is soluble whereas cisplatin is not.

Satraplatin has two ethanoate ligands with C=O groups (four extra O

atoms) as well as the NH₃ group that cisplatin also has.

These O atoms form more H-bonds with water molecules than cisplatin

can.

Forming these H-bonds more than compensates for breaking H-bonds in

water (and the 'insoluble' ring), so satraplatin dissolves. [3]

- (e)* Give the **disadvantages** of using cisplatin as an anti-cancer drug and give examples of how newer platinum-based drugs attempt to overcome these disadvantages. [6]

Disadvantages of cisplatin: it is toxic, damaging the kidneys, the gastrointestinal tract and the nervous system. This is because it targets all cells indiscriminately, healthy and tumorous. It is also difficult to administer, as it can only be given by intravenous injection.

Cancer cells can also become resistant to cisplatin: its entry into the cell can be slowed or prevented, its exit from the cell can be accelerated so it is removed before it acts on the DNA, or the cancer cells evolve improved methods of DNA repair, so apoptosis is not triggered.

Newer drugs: carboplatin (second generation) has a bidentate dicarboxylate ligand in place of the two Cl ligands and is much less toxic, although less active. Oxaliplatin also has improved side-effects. Third generation drugs have a different structure so they stay active in cisplatin-resistant cells: satraplatin, Pt(IV) with ethanoate ligands, is soluble so it can be taken by mouth, and it remains active in resistant cells. Picoplatin has a bulky nitrogen ligand (steric bulk) which helps it overcome resistance.

Additional answer space if required

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END OF QUESTION PAPER

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