

# Gold Paper A Level only

## Model Answers 1

Level	A Level
Subject	Chemistry
Exam Board	OCR
Paper	A Level only
Booklet	Model Answers 1

**Time allowed:** 96 minutes

**Score:** /71

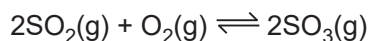
**Percentage:** /100

### Grade Boundaries:

A*	A	B	C	D	E
>85%	73%	60%	47%	34%	21%

## Question 1

The reversible reaction of sulfur dioxide and oxygen to form sulfur trioxide is shown below.



An equilibrium mixture contains 2.4 mol  $\text{SO}_2$ , 1.2 mol  $\text{O}_2$  and 0.4 mol  $\text{SO}_3$ .  
The total pressure is 250 atm.

What is the partial pressure of  $\text{SO}_3$ ?

- A. 15 atm
- B. 25 atm**
- C. 100 atm
- D. 200 atm

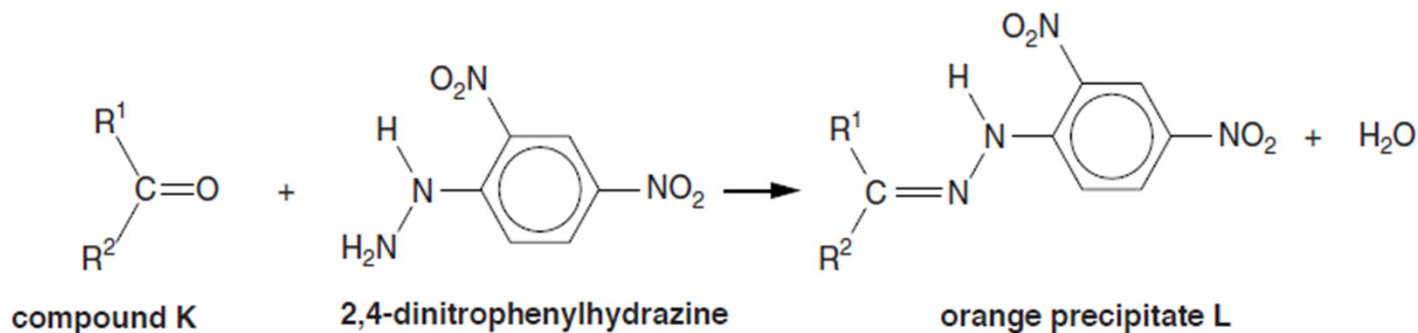
[1]

Step	Working out
1. Calculate the <b>mole fraction</b> of $\text{SO}_3$ .	$x(\text{SO}_3) = \frac{0.4}{4} = 0.1$
2. Use the answer from step 1 to calculate the partial pressure of $\text{SO}_3$ .	$p(\text{SO}_3) = 0.1 \times 250 = 25 \text{ atm}$

- A, C and D are thus incorrect.

## Question 2

A student reacts compound **K** with 2,4-dinitrophenylhydrazine. An orange precipitate, **L**, was



The student purifies the orange precipitate, **L**, and sends the sample for analysis using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy.

- (a) Describe a use for NMR spectroscopy in medicine. [1]

NMR spectroscopy can be used in **magnetic resonance imaging (MRI)** to provide scanning of internal structures.

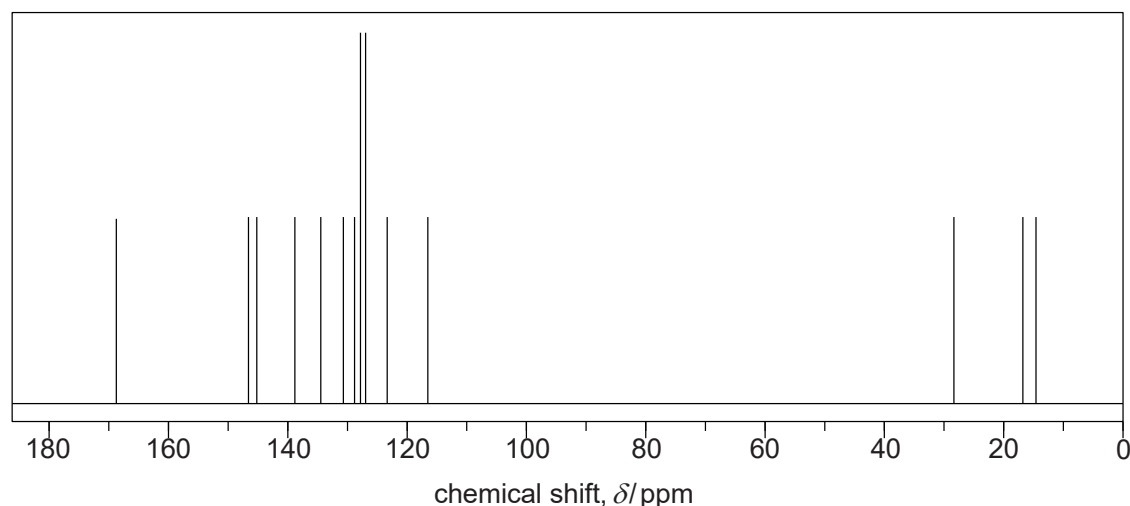
- (b) (i) State the region of the electromagnetic spectrum used in  $^1\text{H}$  NMR spectroscopy. [1]

**Radio waves**

- (ii) Explain why  $\text{CDCl}_3$  is used as a solvent in  $^1\text{H}$  NMR spectroscopy. [1]

As  $\text{CDCl}_3$  does **not contain any hydrogen atoms**. This is to prevent  $^1\text{H}$  nuclei from the solvent from interfering with the NMR spectrum

- (c) The  $^{13}\text{C}$  NMR spectrum of **L** is shown below.

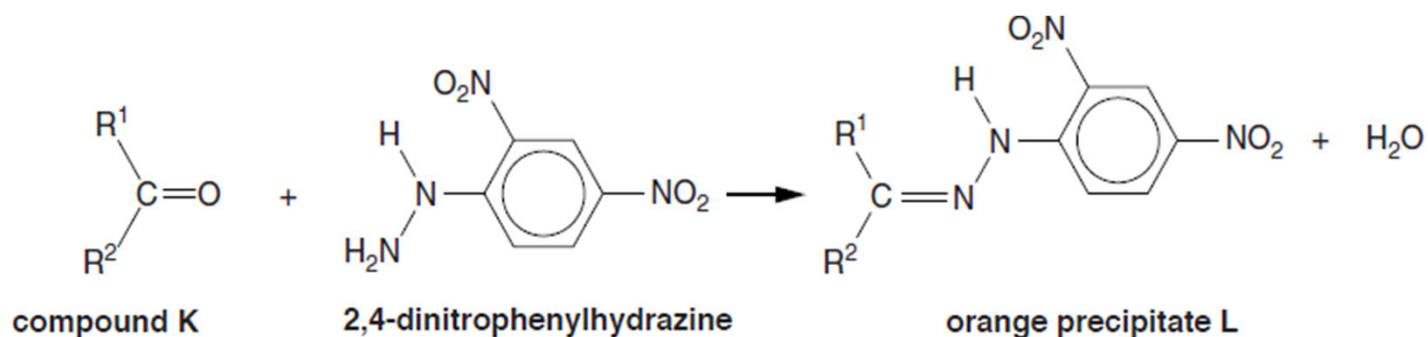


How many different carbon environments (types of carbon) are present in a molecule of compound **L**? [1]

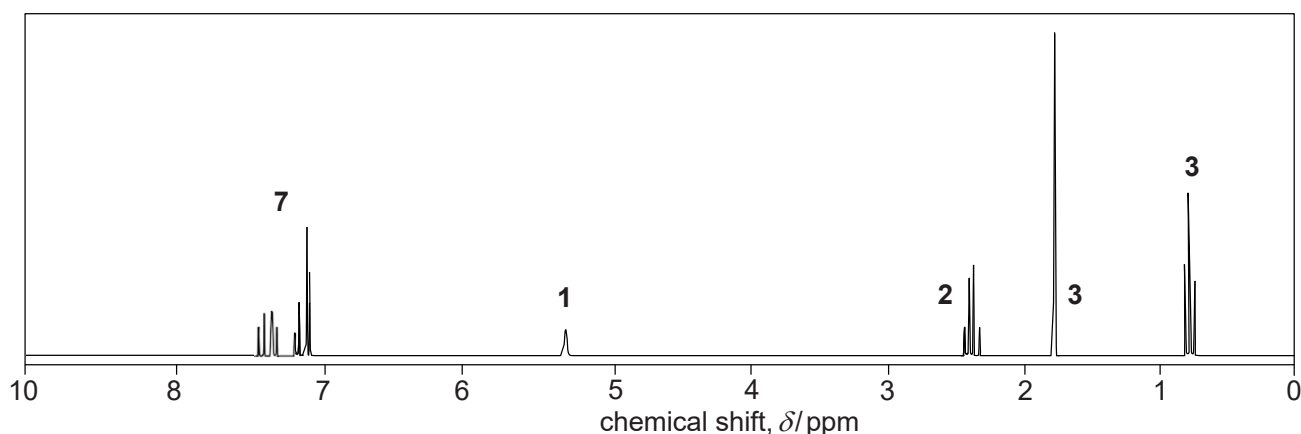
Number of carbon environments are dictated by the number of peaks

Counting on the C spectrum gives 14 peaks

(d) The reaction of **K** to form **L** is repeated below.



The <sup>1</sup>H NMR spectrum of **L** is shown below.



Use your answer to (c) and the data given to identify R<sup>1</sup>, R<sup>2</sup> and the structure of compound **L**.

Explain how you used the chemical shifts and splitting patterns in the <sup>1</sup>H NMR spectrum and any evidence from the <sup>13</sup>C NMR spectrum.



In the <sup>1</sup>H NMR spectrum, HC=C=N– would have a peak in the range  $\delta = 1.6\text{--}2.2$  ppm.

In your answer, you should use appropriate technical terms, spelled correctly.

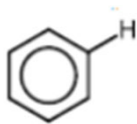
[7]

2,4-dinitrophenylhydrazine (2,4-DNPH) is more commonly known as Brady's reagent. It is used to test for carbonyls (aldehyde or ketones) as it forms an orange precipitate if the C=O group is present.

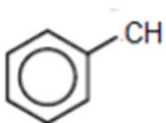
### NMR analysis

1. Multiplet between  $\delta$  7.1 and 7.5 ppm and a relative peak area of 7

indicates the presence of:



2. Peak at  $\delta$  5.2/5.3 with a relative peak area of 1 indicates a N-H
3. Peak at  $\delta$  2.3/2.4 with a relative peak area of 2 indicates the presence of  $\text{C}_6\text{H}_5\text{CH}_2$

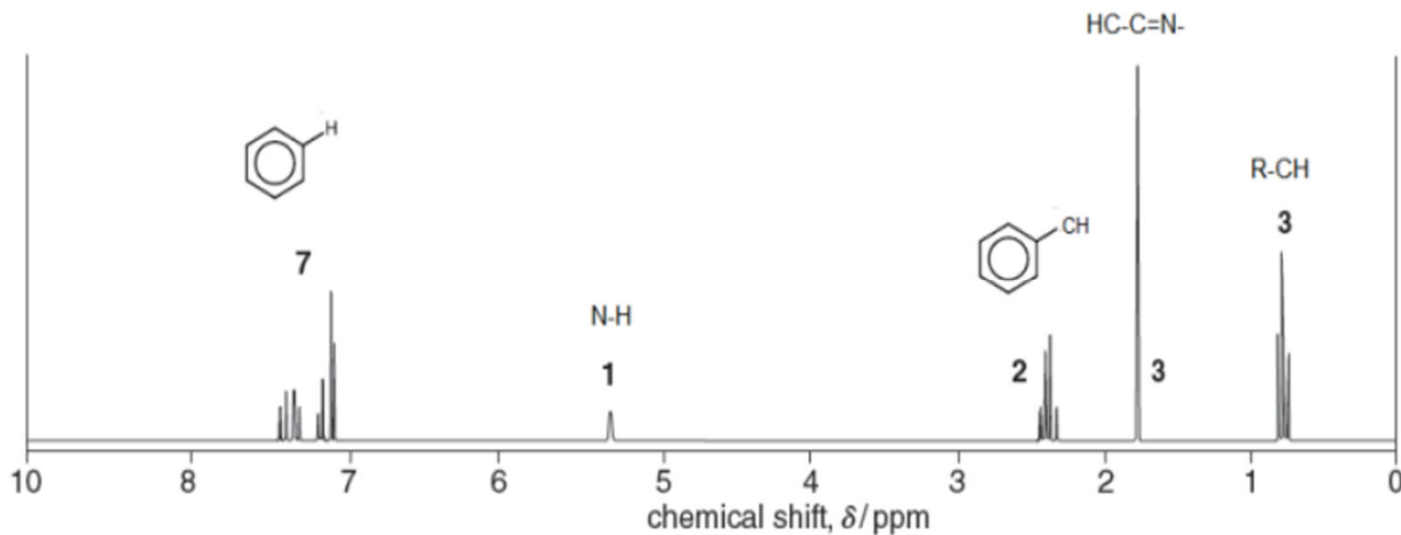


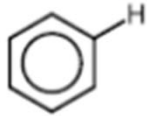
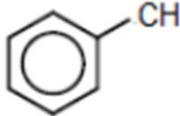
4.  $\delta$  0.7/0.8 indicates R-CH or R-CH<sub>3</sub>.
5. Triplet at  $\delta$  0.7 shows a C with 2 adjacent Hs and quartet at  $\delta$  2.3

shows C with 3 adjacent Hs, therefore we can conclude it is **CH<sub>2</sub>CH<sub>3</sub>**

Also mentioned in the question that at  $\delta$  1.7/1.8 is by a HC-C=N-,

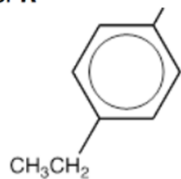
Collecting all the information,



Chemical shift/ppm	Relative peak area	Splitting pattern	Type of proton
7.1 – 7.5	7	Multiplet	
5.3	1	Singlet	N-H
2.3/2.4	2	Quartet	
1.7/1.8	3	Singlet	HC-C=N-
0.7/0.8	3	triplet	R-CH/R-CH <sub>3</sub>

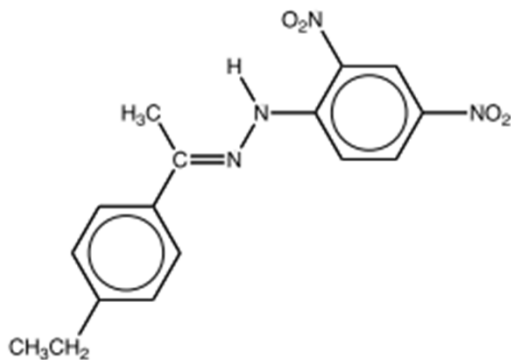
The groups are:

R<sup>1</sup> or R<sup>2</sup> =



Distributed 1,4 due to the 14 carbon environments found in the C NMR spectrum

R<sup>1</sup> or R<sup>2</sup> = -CH<sub>3</sub>



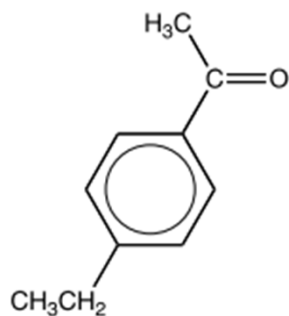
The structure of compound L is:

(Note: 1. that either orientation of R1 and R2 will be accepted)

(e) Draw the structure of compound **K**.

[1]

Carbonyl compound **K** is therefore,



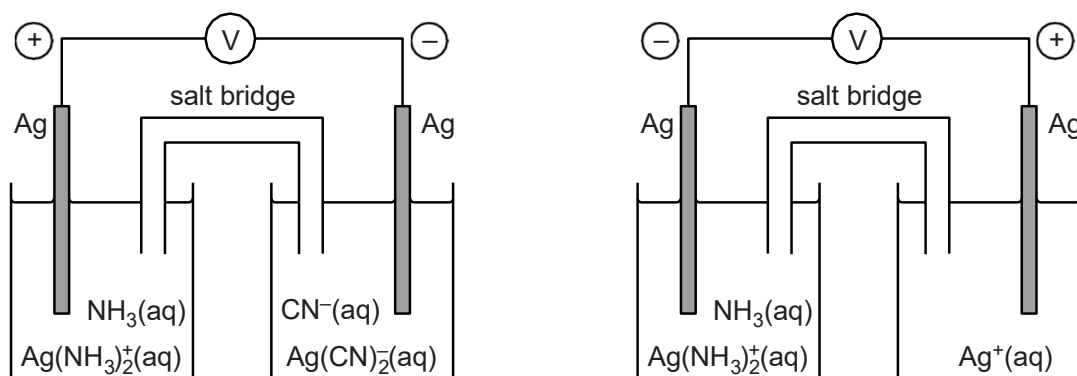
[Total 12 Marks]

Three redox systems, **C**, **D** and **E** are shown in Table 6.1.

<b>C</b>	$\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{NH}_3(\text{aq})$
<b>D</b>	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$
<b>E</b>	$\text{Ag}(\text{CN})_2^-(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{CN}^-(\text{aq})$

**Table 6.1**

The two cells below were set up in an experiment to compare the standard electrode potentials of redox systems **C**, **D** and **E**. The signs on each electrode are shown.



(a) List the three redox systems in order by adding the labels **C**, **D** and **E** to the table below. [1]

$E^\ominus$	redox system
Most negative	<b>E</b>
↑	<b>C</b>
Least negative	<b>D</b>

Order can be deduced from the two cell diagrams provided.

Redox system **E** has more negative potential than **C** because it is the negative electrode.

Redox system **C** has more negative potential than **D** for the same reason.



- (b) A standard cell is set up between redox system **D** in **Table 6.1** and a standard hydrogen half-cell. The standard cell potential of redox system **D** is +0.34V.

The cell delivers a current for a length of time.

The pH of the solution in the standard hydrogen half-cell decreases.

- (i) What is the pH of the solution in a standard hydrogen half-cell? [1]

In the standard hydrogen electrode, the concentration of  $H^+$  ions is  $1 \text{ mol dm}^{-3}$  (standard conditions).

Therefore  $\text{pH} = -\log[H^+]$

$$\text{pH} = -\log(1) = 0$$

- (ii) Explain, in terms of electrode potentials and equilibrium, why the pH of the solution in the hydrogen half-cell decreases as this cell delivers current. [2]

pH decreases =  $[H^+]$  increase

If the cell potential for electrode system D and the standard hydrogen electrode is + 0.34 V, the hydrogen electrode is more negative, and will be electron releasing ( $H_2$  is oxidised).

As the cell delivers current, the standard hydrogen electrode equilibrium,



shifts to increase  $[H^+]$  and more electrons are produced. The reaction taking place in the standard hydrogen electrode is:



- (iii) Write the equation for the overall cell reaction that takes place in this cell. [1]

Write the two half equations:



Multiply all the species in redox system D so that the electrons will cancel on both side:



Combine both equations and cancel the electrons:  $\text{H}_2 + 2\text{Ag}^+ \rightarrow 2\text{H}^+ + 2\text{Ag}$

- (c) The  $\text{CN}^-$  ion is the conjugate base of a very toxic weak acid.

In aqueous solutions of  $\text{CN}^-$  ions, an acid–base equilibrium is set up.

- (i) Complete the equation for this equilibrium and label the conjugate acid–base pairs.

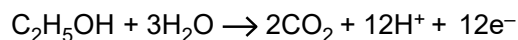


- (ii) Explain, in terms of equilibrium, why acidic conditions should **not** be used with cells containing  $\text{CN}^-(\text{aq})$  ions. [1]

When in acidic conditions, **equilibrium shifts to the right** since  $\text{H}^+$  would react with  $\text{CN}^-$  to form **HCN**.

- (d) Direct-ethanol fuel cells (DEFCs) are being developed in which the fuel is ethanol rather than hydrogen.

The half-equation for the reaction at the ethanol electrode of the DEFC is shown below:



- (i) State **one** important difference between a fuel cell and a modern storage cell. [1]

Any one from:

- Fuel cells react with **oxygen** to give **electrical energy**.
- For example:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
- Fuel cell requires constant supply of fuel and oxygen
- Fuel cells operate continuously as long as they have fuel and oxygen

- (ii) Suggest **one** advantage of using ethanol, rather than hydrogen, in a fuel cell for vehicles. [1]

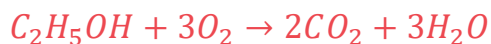
Any one from:

- Ethanol is a liquid OR is less volatile
- Ethanol is **easier to transport/** store
- Hydrogen is explosive

- (iii) The overall reaction in a DEFC is the same as for the complete combustion of ethanol.

Write the equation for the overall reaction in a DEFC. [1]

The overall reaction is the combustion of ethanol with oxygen, producing carbon dioxide and water;



- (iv) Deduce the half-equation for the reaction at the oxygen electrode in a DEFC. [1]

Half-equation at the ethanol electrode – oxidation:



Half-equation at the oxygen electrode – reduction



- (v) Using oxidation numbers, show that oxidation and reduction take place in a DEFC.

Oxidation: C oxidation number changed from -2 in  $C_2H_5OH$  to +4 in  $CO_2$  [2]

Reduction: O oxidation number changed from 0 in  $O_2$  to -2 in  $H_2O$

**[Total: 13 Marks]**

## Question 4

Ethanoic acid,  $\text{CH}_3\text{COOH}$ , is a weak Brønsted–Lowry acid.

- (a) An acid–base equilibrium is set up when ethanoic acid is added to water.

Write the equation for the equilibrium that would be set up and label the two conjugate acid–base pairs.

[2]



Acid 1      Base 2                  Acid 2    Base 1

Acid 1 becomes conjugate base 1 by proton loss:  $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$

Base 2 becomes conjugate acid 1 by proton gain:  $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$

- (b) An aqueous solution of  $\text{CH}_3\text{COOH}$  has a pH of 3.060.  
This solution contains both hydrogen ions and hydroxide ions.

- (i) How can an aqueous solution of an acid contain hydroxide ions?

[1]

Water dissociates/ionises

OR



OR



Water dissociates only a very tiny amount ( $1 \times 10^{-7} \text{ mol dm}^{-3}$  of pure water) but it does dissociate and produce  $\text{OH}^-$  and  $\text{H}^+$  ions.

- (ii) Calculate the concentration of hydroxide ions in this solution of ethanoic acid. [2]

$$[\text{H}^+] = 10^{-3.06} = 8.71 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$$

$$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}} = 1.15 \times 10^{-11} \text{ (mol dm}^{-3}\text{)} \checkmark$$

**ALLOW** answer to two or more significant figures

2SF:  $1.1 \times 10^{-11}$ ; 4SF:  $1.148 \times 10^{-11}$ ;

calculator  $1.148153621 \times 10^{-11}$

Step	Working out
1.Substitute values into $\text{pH} = -\log[\text{H}^+]$	$3.060 = -\log[\text{H}^+]$
2.Rearrange and solve for $[\text{H}^+]$	$[\text{H}^+] = 3.060 / -\log$ $[\text{H}^+] = 10^{-3.060}$ $[\text{H}^+] = 8.71 \times 10^{-4}$
3.Use the equation for the ionic product of water to calculate $[\text{OH}^-]$	$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$ $[\text{OH}^-] = 1. \times 10^{-14} / 8.71 \times 10^{-4}$ $[\text{OH}^-] = 1.15 \times 10^{-11} \text{ mol dm}^{-3}$

- (c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate. The resulting solution is able to act as a buffer solution.

- (i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate. [1]



Equations should be double checked to make sure they are balanced.

- (ii) Explain why this buffer solution has formed. [1]

Solution contains  $\text{CH}_3\text{COOH}$  AND  $\text{CH}_3\text{COO}^-$

Both of these together act as a buffer as they resist small changes to the pH. A suitable mixture for a buffer is one which contains an acid and alkali strong enough to react with  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , but weak enough not to react with one other.

- (iii) Explain how this buffer solution controls pH when either an acid or an alkali is added.



*In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.* [5]



This is the overall reaction

In the case of an alkali being added:

$\text{CH}_3\text{COOH}$  reacts with added alkali

**OR**  $\text{CH}_3\text{COOH} + \text{OH}^-$

**OR** added alkali reacts with  $\text{H}^+$

**OR**  $\text{H}^+ + \text{OH}^-$

In the case of there being an alkali added, the buffer solution neutralises it by reacting with the  $\text{OH}^-$  ions and the equilibrium shifts to the **right** to replace those used up.

In the case of an acid being added:

Equilibrium right **OR** Equilibrium  $\text{CH}_3\text{COO}^-$  **(QWC)**

$\text{CH}_3\text{COO}^-$

reacts with added acid

Equilibrium left **OR** Equilibrium  $\text{CH}_3\text{COOH}$  **(QWC)**

In the case of there being an acid added, the buffer solution neutralises it by reacting with the  $\text{H}^+$  ions and the equilibrium shifts to the **left**.

(d) A biochemist plans to make up a buffer solution with a pH of 5.000.

The biochemist adds solid sodium ethanoate,  $\text{CH}_3\text{COONa}$ , to  $400\text{ cm}^3$  of  $0.200\text{ mol dm}^{-3}$  ethanoic acid.

$K_a$  for ethanoic acid =  $1.75 \times 10^{-5}\text{ mol dm}^{-3}$

Calculate the mass of sodium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

Assume that the volume of the solution remains constant at  $400\text{ cm}^3$  on dissolving the sodium ethanoate. [5]

First calculate the concentration of  $\text{H}^+$  ions needed to achieve a pH of 5.000 using the formula

$$[\text{H}^+] = 1 \times 10^{-\text{pH}}$$

$$[\text{H}^+] = 10^{-5}\text{ (mol dm}^{-3}\text{)}$$

$$[\text{CH}_3\text{COO}^-] = \frac{1.75 \times 10^{-5}}{10^{-5}} \checkmark \times 0.200 = 0.350\text{ mol dm}^{-3} \checkmark$$

Use the  $[\text{H}^+]$  and  $K_a$  for ethanoic acid to calculate  $[\text{CH}_3\text{COO}^-]$  in  $0.200\text{ mol dm}^{-3}$



$$\begin{aligned} n(\text{CH}_3\text{COONa}/\text{CH}_3\text{COO}^-) \text{ in } 400 \text{ cm}^3 \\ = 0.350 \times \frac{400}{1000} = 0.14(0) \text{ (mol) } \checkmark \end{aligned}$$

The amount of moles in the 400cm<sup>3</sup> is calculated

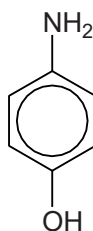
$$\text{Mass CH}_3\text{COONa} = 0.140 \times 82.0 = 11.48 \text{ OR } 11.5 \text{ (g)}$$

Moles are then converted into g,  $M_r\text{CH}_3\text{COONa} = 82 \text{ g mol}^{-1}$

**[Total: 17 Marks ]**

## Question 5

4-Aminophenol is an organic compound that can behave as an acid and a base.



**4-aminophenol**

(a) State how 4-aminophenol can behave as a base.

[1]

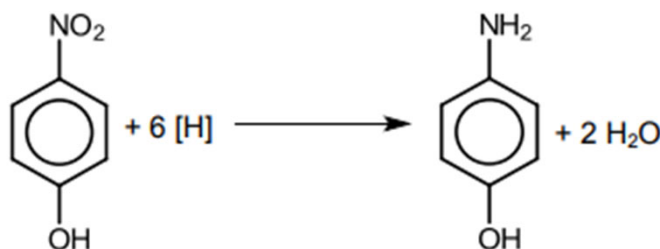
Due to the presence of the lone pair of electrons on the nitrogen in the amine group, 4-aminophenol can accept a proton ( $\text{H}^+$ ), acting as base

(b) 4-Aminophenol is produced by the reduction of 4-nitrophenol.

Write an equation to show the production of 4-aminophenol from 4-nitrophenol. Use  $[\text{H}]$  to represent the reducing agent.

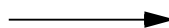
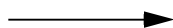
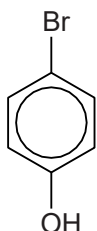
[1]

In the reduction reaction to produce 4-aminophenol, the O atoms in the nitro group of 4-nitrophenol are removed and replaced by H atoms. The O atoms react with H atoms to produce water molecules:



(c) 4-Nitrophenol can be produced from 4-bromophenol.

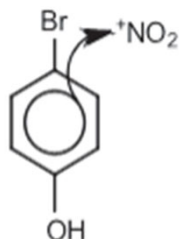
- Complete the mechanism for this reaction.
- Use  $^+\text{NO}_2$  as the electrophile. Include any intermediate and the products.
- In the mechanism for this reaction,  $\text{NO}_2$  substitutes for Br on the ring.



[4]

This is an electrophilic substitution reaction, with  $\text{NO}_2^+$  (the electrophile) replacing the Br atom on the ring.

A curly arrow from the electron rich benzene ring to the  $\text{NO}_2^+$  electrophile is the first step,

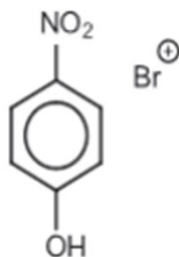


An intermediate carbocation is formed, as shown by the + in the broken ring.

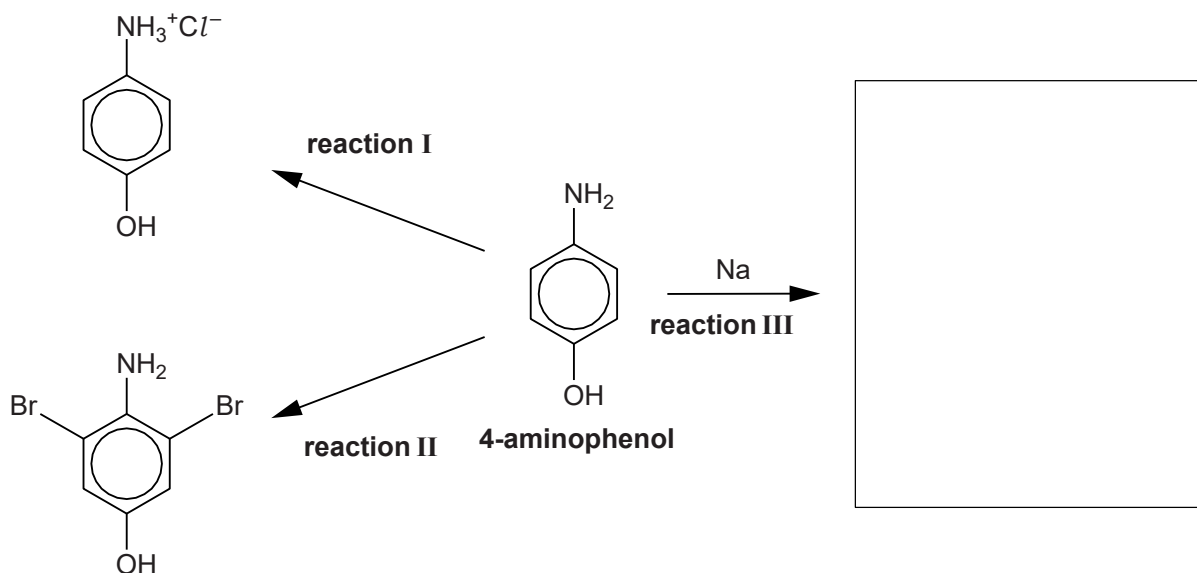
Ensure that the broken ring covers over half of the benzene structure. The curly arrow shows the pair of electrons which formed the C-Br bond move to the benzene ring to reform its structure,



Products are formed, namely 4-nitrophenol and  $\text{Br}^+$



(d) The flowchart below shows some reactions of 4-aminophenol.



(i) Identify the reagent in **reaction I** [1]

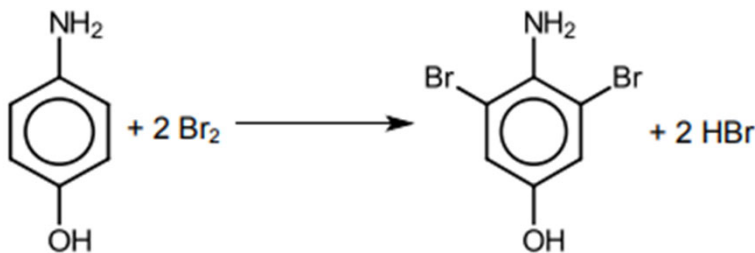
Reaction 1 from 4-aminophenol requires **hydrochloric acid**

(ii) Name the organic product of **reaction II**. [1]

Using 4-aminophenol as the base, bromine atoms are located on carbon atoms number 3 and 5. Naming functional groups alphabetically, the name of the compound formed is **4-amino-3,5-dibromophenol**

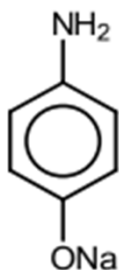
(iii) Write the equation for **reaction II**. [1]

Two H atoms on the ring are replaced with Br atoms,



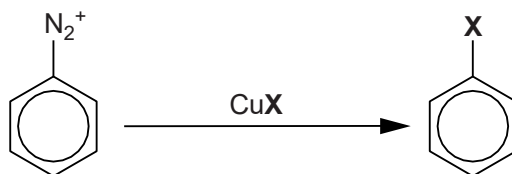
- (iv) In the box on the flowchart, draw the structure of the organic compound formed by **reaction III**. [1]

The hydroxyl group on phenol is **more acidic** than in straight chained alcohols, hence it **readily donates** protons, reacting with metallic sodium to give off hydrogen gas and forming sodium phenoxide:

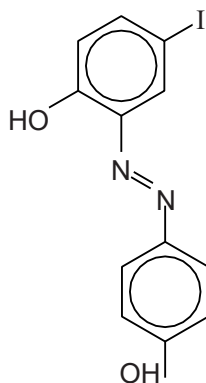


- (e) The Sandmeyer reaction can be used to replace a diazonium group,  $\text{N}_2^+$ , with a halogen atom, **X**, on an aromatic ring.

The reagent used for the reaction is a copper(I) halide,  $\text{CuX}$ .



Compound **C**, shown below, can be synthesised using **only** 4-aminophenol and other standard laboratory reagents. The flowchart on the next page shows this synthesis.



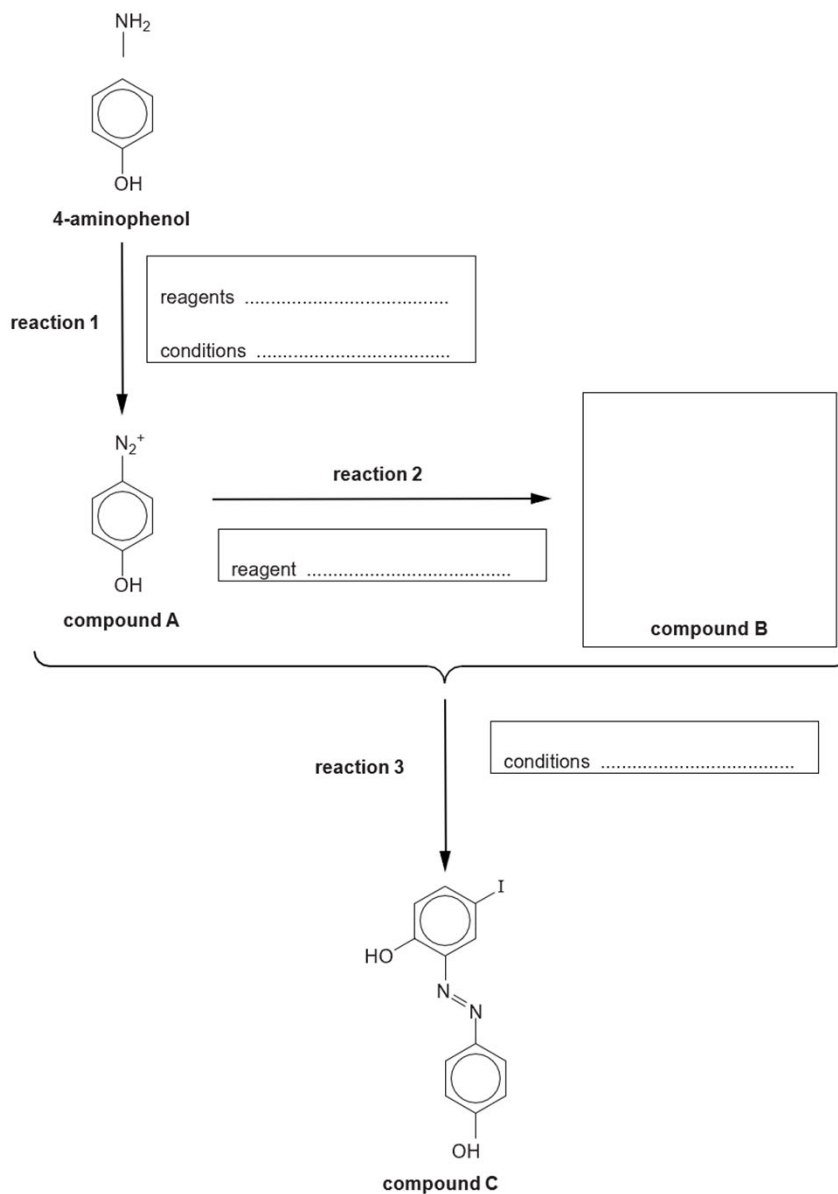
**compound C**

- (i) State a possible use for compound **C**. [1]

Compound **C** is an azo compound. Used primarily in dyestuffs, pigments and food colourings

- (ii) On the flowchart on the next page:
- state the reagents and conditions used for **reaction 1**
  - suggest the structure of compound **B**
  - suggest the reagent used for **reaction 2**
  - state the conditions used for **reaction 3**.

[5]



Reaction 1 requires  $\text{NaNO}_2$  and  $\text{HCl}$  to produce a diazonium ion below  $10^\circ\text{C}$ .

Since the final product has an iodine atom attached, reaction 2 requires  $\text{CuI}$ .

Compound B is therefore,



To form compound C, the azo compound, alkaline conditions are required to turn phenol into phenoxide ( $\text{O}^-$ ) and link the two benzene groups by the  $\text{N}=\text{N}$  bridge in this coupling reaction.

[Total 16 Marks]

## Question 6

A chemist isolated compound **L** from the leaves of a common garden herb. He analysed the compound using a number of techniques.

- (a) Compound **L** contains C, H and O only. Elemental analysis shows that **L** has the percentage composition by mass: C, 73.15%; H, 7.37%.

The mass spectrum of **L** has a molecular ion peak at  $m/z = 164$ .

Show that the molecular formula of **L** is  $C_{10}H_{12}O_2$ .

[2]

$$\text{Percentage of O} = 100 - (73.15 + 7.37) = 19.48\%$$

$$\text{Ratio of C:H:O} = \frac{73.15}{12} : \frac{7.37}{1} : \frac{19.48}{16} = 6.1 : 7.37 : 1.22$$

Simplest ratio would be 5:6:1

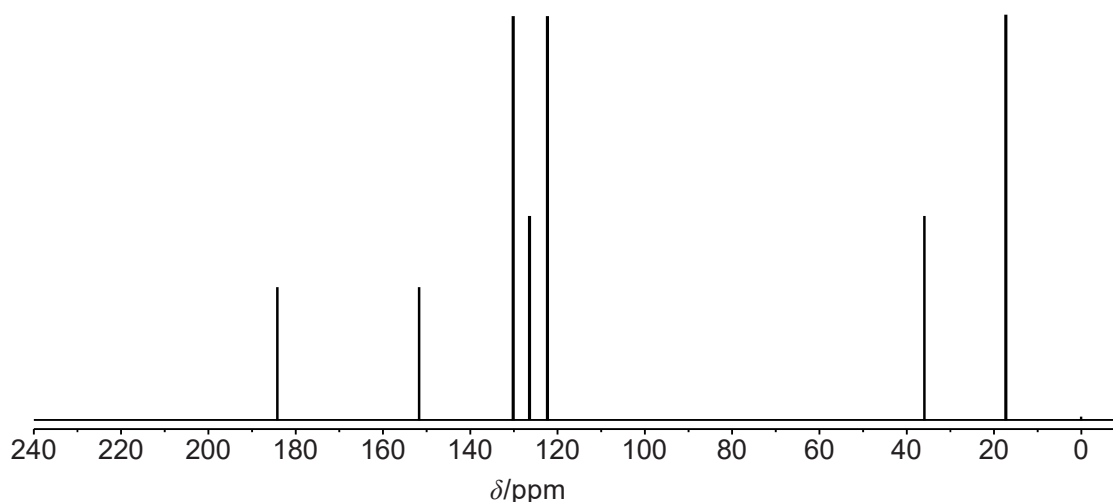
Hence the empirical formula is  $C_5H_6O$ ,  $M_r = 82$

If the  $M_r$  of **L** is 164 (from molecular ion peak in the mass spectrum),  $164 \div$

$82 = 2$ , therefore the empirical formula is multiplied by two to give the

molecular formula of  $C_{10}H_{12}O_2$

- (b) The  $^{13}\text{C}$  NMR spectrum of compound **L** is shown below.



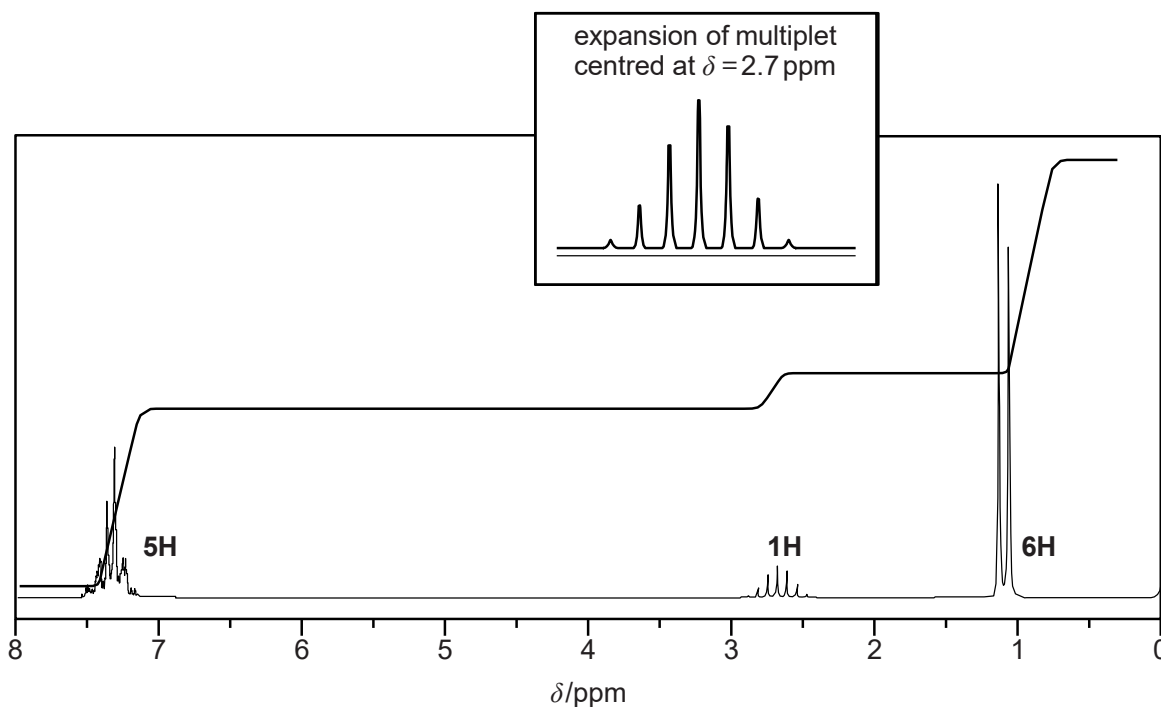
How many different carbon environments (types of carbon) are present in a molecule of compound **L**?

[1]

Seven peaks, hence 7 different carbon environments



- (c) The  $^1\text{H}$  NMR spectrum of compound **L**,  $\text{C}_{10}\text{H}_{12}\text{O}_2$ , is shown below. One of the signals has been enlarged to help its analysis.



- (i) A signal at  $\delta = 0$  ppm results from tetramethylsilane (TMS). TMS had been added to the sample of compound **L** before the NMR spectrum was run.

State why TMS was added.

[1]

TMS is the **standard** for chemical shift measurements

- (ii) The  $^1\text{H}$  NMR spectrum includes an integration trace.

What information can be deduced about compound **L** from the integration trace? [1]

The integration trace provides **information about the relative number of protons in each environment.**

Hence we could deduce **three proton environments with protons in the ratio 5:1:6**

- (iii) Using the information given in parts (a), (b) and (c) of this question, determine the structure of compound L.

Show all your reasoning.



In your answer, you should use appropriate technical terms, spelled correctly.

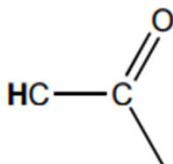
[7]

Via the  $^{13}\text{C}$  NMR,

- The peak at 185 ppm suggests an **ester** group
- The peaks at 120 ppm and 160 ppm suggest a **benzene** ring
- The peaks at 18 ppm and 36 ppm suggest a **C-C**

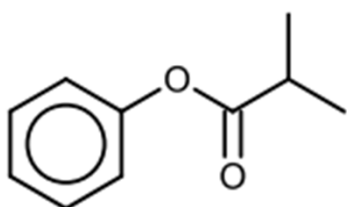
Via the  $^1\text{H}$  analysis,

- The doublet at 1.2 shows R-CH and 6 protons in this environment, hence **2 methyl groups**
- The peak splitting into 7 at 2.7 ppm indicates the structure,



- The doublet suggests that **2 methyl groups are attached to a CH**
- The peak at 7.3 ppm indicates a benzene ring and 5 protons

Hence compound L would most likely be,



[Total 12 Marks ]