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Chemistry

Advanced

**Unit 5: General Principles of Chemistry II – Transition
Metals and Organic Nitrogen Chemistry
(including synoptic assessment)**

Monday 15 June 2015 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

6CH05/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
– *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
– *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
– *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ►

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P 4 5 0 7 3 R A 0 1 2 8

PEARSON

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☐. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☐.

1 Which of the following is a redox reaction?

- ☐ A $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
- ☐ B $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$
- ☐ C $4\text{OH}^- + 4\text{MnO}_4^- \rightarrow 4\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + \text{O}_2$
- ☐ D $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightarrow [\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3] + 3\text{H}_2\text{O}$

(Total for Question 1 = 1 mark)

2 The oxidation state of nickel is **not** +2 in

- ☐ A $[\text{Ni}(\text{CO})_4]$
- ☐ B $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH})_2]$
- ☐ C $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- ☐ D $[\text{Ni}(\text{CN})_4]^{2-}$

(Total for Question 2 = 1 mark)

3 Which of the statements about a standard hydrogen electrode, for which $E^\ominus = 0 \text{ V}$, is correct?

- ☐ A A suitable solution for use in the electrode is hydrochloric acid with a concentration of 0.1 mol dm^{-3} .
- ☐ B The pressure of the hydrogen has no effect on the value of $E^\ominus$.
- ☐ C The metal used in the electrode is platinum.
- ☐ D The temperature is 273 K .

(Total for Question 3 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.



4 The table below gives the standard electrode potentials of three half cells.

System	$E^{\ominus} / \text{V}$
$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$	0.00
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Ag}^{2+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}^+(\text{aq})$	+1.98

From these data it may be deduced that, under standard conditions,

- ☐ A Ag is a stronger reducing agent than H_2 .
- ☐ B Ag^{2+} ions are stronger oxidizing agents than H^+ ions.
- ☐ C Ag^+ ions will disproportionate.
- ☐ D Ag^+ ions will react with H^+ ions.

(Total for Question 4 = 1 mark)

5 The value of E_{cell} indicates whether the cell reaction is thermodynamically feasible. Which of the following is a correct statement about E_{cell} ?

- ☐ A E_{cell} is directly proportional to the equilibrium constant.
- ☐ B E_{cell} is directly proportional to the entropy change of the system, ΔS_{system} .
- ☐ C E_{cell} is directly proportional to the total entropy change, ΔS_{total} .
- ☐ D The value of $\ln E_{\text{cell}}$ is directly proportional to the total entropy change, ΔS_{total} .

(Total for Question 5 = 1 mark)

6 In a methanol fuel cell, the following half-reaction occurs



The half-reaction occurring in the other half of the fuel cell is

- ☐ A $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{OH}^-(\text{aq})$
- ☐ B $2\text{H}^+(\text{aq}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}(\text{l})$
- ☐ C $2\text{OH}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{O}_2(\text{g}) + 2\text{e}^-$
- ☐ D $\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}^+(\text{aq}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^-$

(Total for Question 6 = 1 mark)



7 Which of the following statements about fuel cells is **not** true?

- ☐ A Reactants must constantly be fed into the cell when it is in use.
- ☐ B Fuel cells are 100% efficient.
- ☐ C Fuel cells convert chemical energy directly into electrical energy.
- ☐ D Fuel cells produce electricity more efficiently than a diesel generator.

(Total for Question 7 = 1 mark)

8 Copper(II) ions combine with three molecules of 1,2-diaminoethane, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, to form a complex ion.

A bond angle, $\text{N} - \text{Cu} - \text{N}$, in this complex is

- ☐ A 120°
- ☐ B 109.5°
- ☐ C 107°
- ☐ D 90°

(Total for Question 8 = 1 mark)

9 Which of the following does **not** have a central metal ion having six bonds and an oxidation state of +2?

- ☐ A $[\text{Cu}(\text{C}_2\text{O}_4)_3]^{4-}$
- ☐ B $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$
- ☐ C $[\text{Fe}(\text{CN})_6]^{3-}$
- ☐ D $[\text{Zn}(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$

(Total for Question 9 = 1 mark)

10 The reaction



is an example of

- ☐ A oxidation.
- ☐ B reduction.
- ☐ C ligand exchange.
- ☐ D acid-base behaviour.

(Total for Question 10 = 1 mark)



- 11 Hydrated crystals of a compound have the formula $\text{CrCl}_3(\text{H}_2\text{O})_6$.
A solution containing one mole of the compound reacts with two moles of silver nitrate to form two moles of silver chloride.
The complex chromium ion in the compound is most likely to be

- ☐ A $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]^{3+}$
☐ B $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
☐ C $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$
☐ D $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

(Total for Question 11 = 1 mark)

- 12 A **heterogeneous** catalyst is often preferred to a **homogenous** catalyst for an industrial process because

- ☐ A it is easily separated from the products.
☐ B it has empty d-orbitals.
☐ C it has more than one oxidation state.
☐ D it cannot be poisoned.

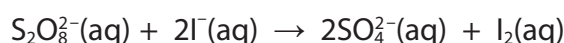
(Total for Question 12 = 1 mark)

- 13 In the reaction of benzene with chloromethane, aluminium chloride is added because it reacts with

- ☐ A benzene to produce an electrophile.
☐ B benzene to produce a nucleophile.
☐ C chloromethane to produce a nucleophile.
☐ D chloromethane to produce an electrophile.

(Total for Question 13 = 1 mark)

- 14 The reaction below can be catalysed by either Fe^{2+} ions or Fe^{3+} ions.



This is because

- ☐ A both reactants can react with Fe^{2+} ions.
☐ B both reactants can react with Fe^{3+} ions.
☐ C $\text{S}_2\text{O}_8^{2-}$ ions can be oxidized by Fe^{3+} ions and I^- ions can be reduced by Fe^{2+} ions.
☐ D $\text{S}_2\text{O}_8^{2-}$ ions can be reduced by Fe^{2+} ions and I^- ions can be oxidized by Fe^{3+} ions.

(Total for Question 14 = 1 mark)



15 The enthalpy changes of the reactions below are similar. The equilibrium constants for the two reactions are K_1 and K_2 respectively.



The value of K_1 is greater than K_2 because

- ☐ **A** ΔS_{system} is much more positive in Reaction 1.
- ☐ **B** $\Delta S_{\text{surroundings}}$ is much more positive in Reaction 1.
- ☐ **C** the EDTA^{4-} is more highly charged than Cl^{-} .
- ☐ **D** a lower concentration of EDTA^{4-} is needed than Cl^{-} .

(Total for Question 15 = 1 mark)

16 Which of the following reacts with benzene under suitable conditions to form $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$?

- ☐ **A** $\text{C}_6\text{H}_5\text{CHO}$
- ☐ **B** $\text{C}_6\text{H}_5\text{COOH}$
- ☐ **C** $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
- ☐ **D** $\text{C}_6\text{H}_5\text{COCl}$

(Total for Question 16 = 1 mark)

17 Benzene is converted to benzenesulfonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, by reaction with

- ☐ **A** sulfuric(IV) acid, H_2SO_3 .
- ☐ **B** sulfuric(VI) acid, H_2SO_4 .
- ☐ **C** sulfur dioxide dissolved in sulfuric(IV) acid.
- ☐ **D** sulfur trioxide dissolved in sulfuric(VI) acid.

(Total for Question 17 = 1 mark)

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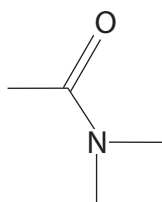


18 Benzene reacts with chlorine to produce 1,2,3,4,5,6-hexachlorocyclohexane, $C_6H_6Cl_6$, by

- ☐ A free radical addition.
- ☐ B free radical substitution.
- ☐ C electrophilic addition.
- ☐ D electrophilic substitution.

(Total for Question 18 = 1 mark)

19 The skeletal formula of an organic compound is shown below.

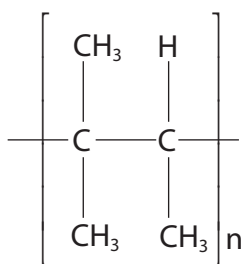


This compound is

- ☐ A an amino acid.
- ☐ B an amide.
- ☐ C a primary amine.
- ☐ D a secondary amine.

(Total for Question 19 = 1 mark)

20



Which is the IUPAC name for the monomer which reacts to make the polymer shown above?

- ☐ A 2-methylbut-1-ene
- ☐ B 2-methylbut-2-ene
- ☐ C 1,2-dimethylpropene
- ☐ D 1,1,2-trimethylethene

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS



SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

- 21** (a) The table below shows the first and second ionization energies of nickel, copper and zinc.

Element	1st ionization energy / kJ mol^{-1}	2nd ionization energy / kJ mol^{-1}
Ni	737	1753
Cu	746	1958
Zn	906	1733

- (i) Complete the electronic configurations for an atom of nickel and an atom of copper. (2)

Ni: $1s^2 2s^2 2p^6$

Cu: $1s^2 2s^2 2p^6$

- *(ii) The values for the first ionization energies of copper and nickel are similar, but the values of the second ionization energies are significantly different.

Explain how these data give evidence for the electronic configuration of a copper atom.

(2)

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(iii) Suggest why you might expect the **third** ionization energies of the three elements to increase from nickel to zinc.

(1)

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(b) (i) $\text{Cu}^+(\text{aq})$ ions are not stable in solution and undergo a disproportionation reaction. Suggest an equation for this reaction, including state symbols.

(1)

(ii) Suggest in what way the **appearance** of CuI is similar to that of ZnI_2 . Give a reason for this similarity.

(2)

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(c) Explain why zinc is **not** classified as a transition element.

(1)

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(Total for Question 21 = 9 marks)



22 This question is about vanadium and its ions.

(a) Consider the data below.

Electrode system	Standard electrode potential $E^{\ominus} / \text{V}$
$\text{V}^{2+}(\text{aq}) \text{V}(\text{s})$	-1.18
$\text{V}^{3+}(\text{aq}), \text{V}^{2+}(\text{aq}) \text{Pt}$	-0.26

- (i) Draw a labelled diagram showing how to set up a cell, using the two electrode systems in the table above, in order to measure $E_{\text{cell}}^{\ominus}$. Include standard conditions in your labelling.

(3)

- (ii) Write an equation for the reaction in this cell. State symbols are not required.

(2)

- (b) (i) Complete the table below with the missing standard electrode potentials. Use the table starting on page 14 of your Data Booklet.

(1)

Electrode system	Standard electrode potential $E^{\ominus} / \text{V}$
$[\text{VO}^{2+}(\text{aq}) + 2\text{H}^{+}(\text{aq})], [\text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})] \text{Pt}$	
$[\text{VO}_2^{+}(\text{aq}) + 2\text{H}^{+}(\text{aq})], [\text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})] \text{Pt}$	
$\text{I}_2(\text{aq}), 2\text{I}^{-}(\text{aq}) \text{Pt}$	+0.54
$[2\text{H}^{+}(\text{aq}) + \text{O}_2(\text{g})], [\text{H}_2\text{O}_2(\text{aq})] \text{Pt}$	+0.68



(ii) The colours of the different oxidation states of vanadium are shown below.

Oxidation state	Colour
+5	yellow
+4	blue
+3	green
+2	violet

For each of the following experiments, **A** and **B**, calculate the $E^\ominus$ value for the proposed reaction. Use your answers to predict whether or not a reaction occurs in each case.

Give the formula of the vanadium product formed where a reaction occurs and give **one** observation you would make in each experiment.

(6)

Experiment A: Hydrogen peroxide is added to an aqueous solution containing VO_2^+ ions.

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Experiment B: An aqueous solution of potassium iodide is added to an aqueous solution containing VO^{2+} ions.

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- (c) An experiment was carried out to determine the percentage purity of a sample of ammonium vanadate(V), NH_4VO_3 .

An impure sample of ammonium vanadate(V) with mass 0.150 g was dissolved in dilute sulfuric acid. This produced a solution containing VO_2^+ ions. Excess zinc powder was added to the solution, and this reduced the VO_2^+ ions to V^{2+} ions.

The solution containing V^{2+} ions was titrated with potassium manganate(VII) of concentration $0.0200 \text{ mol dm}^{-3}$. The manganate(VII) ions oxidized the V^{2+} back to VO_2^+ . The volume of potassium manganate(VII) required was 35.50 cm^3 .

- (i) The manganate(VII) ions react as shown:



Show, by writing the appropriate half equation or otherwise, that 5 mol V^{2+} react with 3 mol MnO_4^- .

(1)

- (ii) Calculate the number of moles of manganate(VII) ions used in the titration.

(1)



- (iii) Calculate the number of moles of VO_2^+ in the original solution, and hence the percentage purity of the sample of NH_4VO_3 . Give your answer to **three** significant figures.

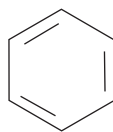
Molar mass of $\text{NH}_4\text{VO}_3 = 116.9 \text{ g mol}^{-1}$.

(3)

(Total for Question 22 = 17 marks)



- 23** Benzene is sometimes represented as Structure **X**, shown below, called a Kekulé structure after the chemist who suggested it.



Structure **X**

- (a) What structural feature of benzene shows that Structure **X** is not an accurate representation?

(1)

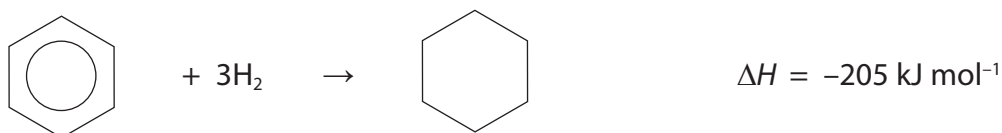
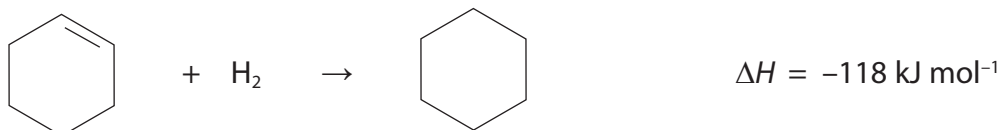
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- (b) The enthalpy changes for the formation of cyclohexane from cyclohexene and from the actual structure of benzene are given below.



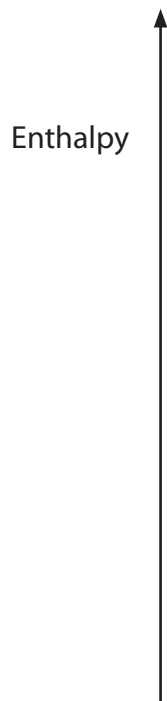
- (i) Use the necessary data to estimate the enthalpy change for the theoretical conversion of Structure **X** to cyclohexane.

(1)



- (ii) On the enthalpy level diagram below, draw labelled horizontal lines to show the relative enthalpies of the actual structure of benzene, Structure **X** and cyclohexane. Add an arrow to show the enthalpy change from Structure **X** to benzene and calculate the value of this enthalpy change in kJ mol^{-1} . Write this value next to your arrow.

(2)



- *(iii) Explain the difference in the arrangement of the electrons between benzene and Structure **X**.

(2)

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(c) Benzene reacts with bromine in the presence of a catalyst of iron(III) bromide.

Write a mechanism for the reaction of benzene with bromine to form bromobenzene. Include an equation to show the involvement of the catalyst.

(4)



(d) (i) State **two** observations which would be made when phenol reacts with bromine water.

(2)

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(ii) Write the equation for this reaction showing the structure of the organic product.

(2)

*(iii) Explain why phenol can react with either bromine or with bromine water without a catalyst.

(2)

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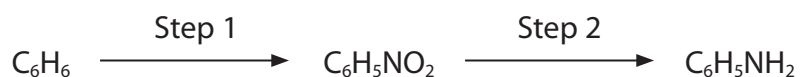
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(Total for Question 23 = 16 marks)



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24 Benzene can be converted to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, in two steps.



(a) (i) Name the **two** reagents needed in Step 1.

(1)

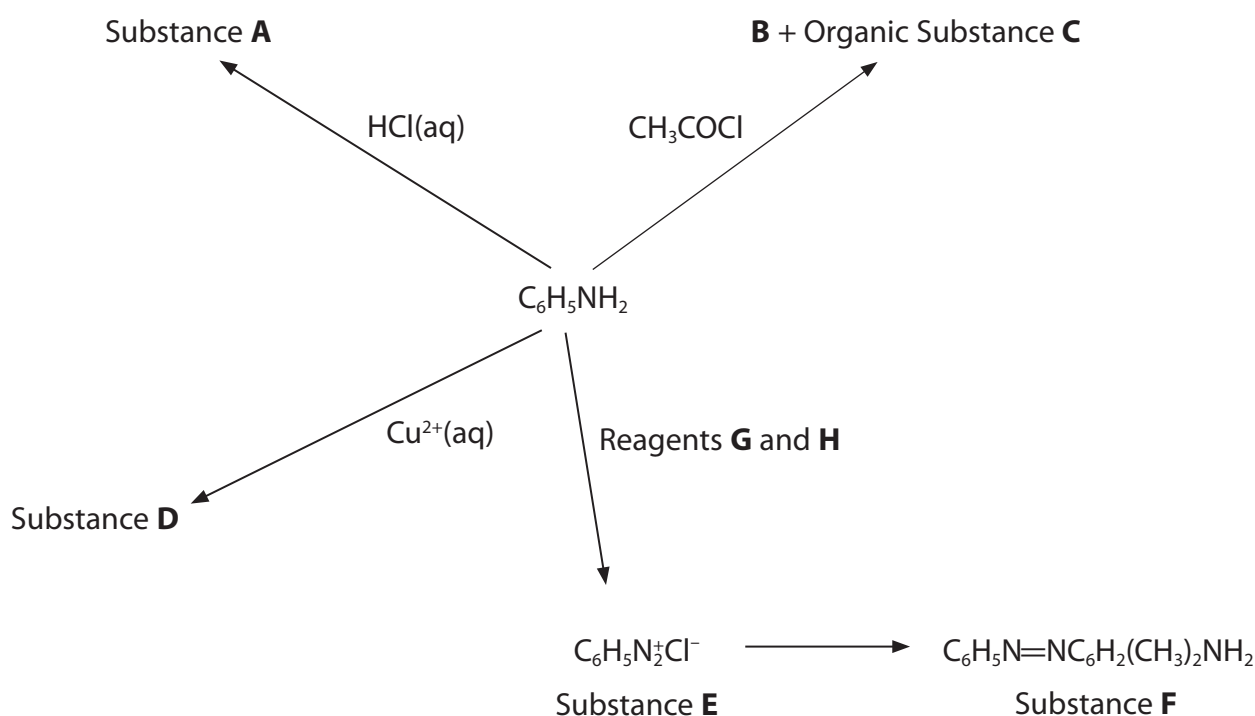
(ii) Suggest why the temperature should not be allowed to go above 55°C in Step 1.

(1)

(iii) Identify the **two** reagents used to carry out the reduction in Step 2.

(1)

(b) Some reactions of phenylamine are shown below.



(i) Give the formula of Substance **A**.

(1)

(ii) Draw the displayed formula of the organic Substance **C**.

You need not display the benzene ring.

(1)

(iii) Substances **D** and **F** are both brightly coloured but for different reasons.
Classify Substances **D** and **F**.

(2)

Substance **D**

Substance **F**

(iv) Name Substance **E**.

(1)

(v) What **two** Substances, **G** and **H**, are required in the conversion of phenylamine to Substance **E**?

(1)

(vi) Suggest the structural formula of the substance which reacts with Substance **E** to form Substance **F**.

(1)

(Total for Question 24 = 10 marks)

TOTAL FOR SECTION B = 52 MARKS



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SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

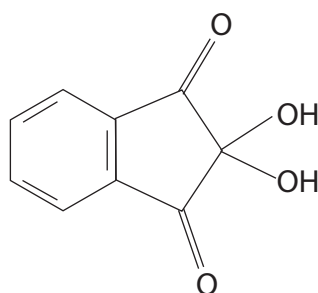
25 Read the passage below carefully and answer the questions which follow.

The general formula of most naturally occurring amino acids can be written $\text{RCH}(\text{NH}_2)\text{COOH}$, though in some amino acids, such as proline, the nitrogen atom is part of a five-membered ring. Amino acids are water soluble, though the extent of their solubility varies. All but one of the naturally occurring amino acids show optical activity.

The formula of the R group for some naturally occurring amino acids is shown below.

Amino acid	Formula of R group
serine	$-\text{CH}_2\text{OH}$
lysine	$-(\text{CH}_2)_4\text{NH}_2$
phenylalanine	$-\text{CH}_2\text{C}_6\text{H}_5$
leucine	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$
iso-leucine	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
alanine	$-\text{CH}_3$

Mixtures of amino acids can be separated by electrophoresis. This method depends on amino acids moving different distances through paper or gel when an electric field is applied. They can also be separated by chromatography. Ninhydrin, shown below, is the chemical which is used to locate the position of the amino acids on chromatograms.



Ninhydrin detects ammonia and primary and secondary amines. When it reacts with primary amines, a deep blue or purple colour is produced in a complex series of reactions. With proline, a yellow compound forms.

Ninhydrin is widely used to detect fingerprints. Sweat secretions from ridges on the finger contain dipeptides and proteins. These are left on porous surfaces such as paper, and react with ninhydrin.

When ninhydrin reacts with amino acids, carbon dioxide is released from the carboxylic acid group. Archaeologists have used this reaction to release the carbon from proteins in ancient bones, and, by comparing the proportions of carbon and nitrogen in the remains, they have obtained evidence for the diets of these animals.



(a) (i) At a pH of 5.68, serine exists as a zwitterion. Draw the formula of serine at this pH. (1)

*(ii) At pH 5.68, serine and lysine can be separated by electrophoresis. By considering the structures of the amino acids at this pH, suggest why this separation occurs. (2)

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*(b) Serine is very soluble in water, whilst phenylalanine is much less soluble. Explain the difference, disregarding any effect of zwitterion formation. (2)

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(c) The naturally occurring amino acid which does not show optical activity is not shown in the table. Give the formula of the R group for this acid. (1)



(d) The optical activity of equimolar solutions of naturally occurring samples of leucine and iso-leucine can be measured in an experiment using plane-polarized light.

(i) What measurement is made to show the optical activity of amino acids?

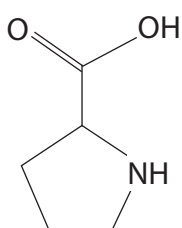
(1)

(ii) By considering the structures of iso-leucine and leucine, explain why iso-leucine has more stereoisomers than leucine.

Amino acid	Formula of R group
leucine	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$
iso-leucine	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

(1)

(e) The amino acid proline, shown below, does not contain a primary amine group, but it can still form peptide bonds.

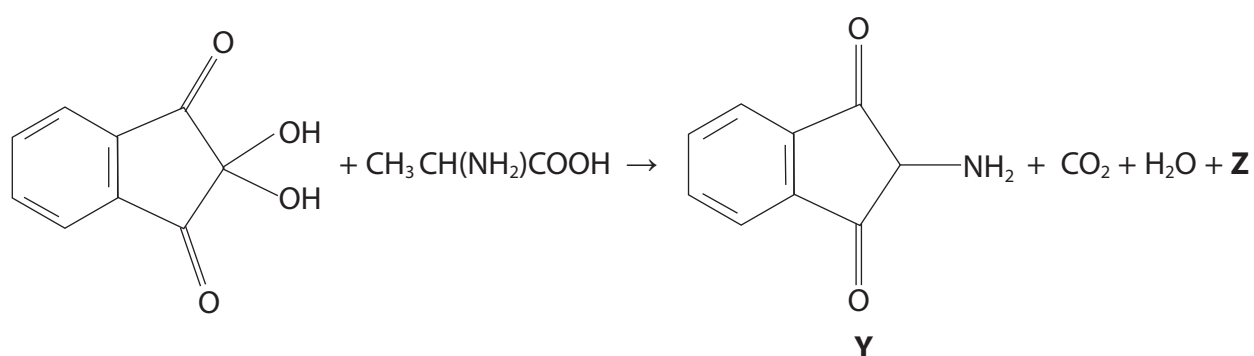


Draw the structure of the dipeptide formed when the carboxylic acid group of alanine reacts with proline. Circle the peptide group on your drawing.

(2)

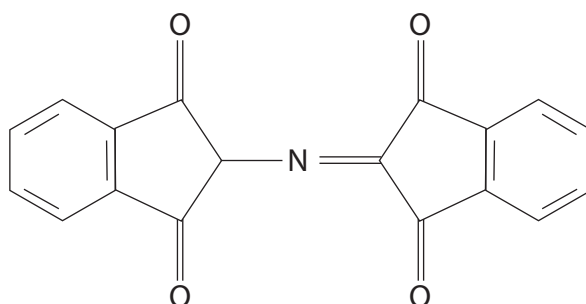


- (f) The first steps of the reaction of ninhydrin with alanine can be summarised in the equation shown below.



- (i) By balancing the equation, suggest the structural formula of the product **Z**. (1)

- (ii) In the final stage, **Y** reacts with another molecule of ninhydrin to form a dye, **Q**, shown below.



What is the molecular formula of **Q**? (1)

- (iii) On combustion, 1.000 g of **Q** produces 2.614 g carbon dioxide, 0.2673 g water and 0.04620 g nitrogen.

Use these data to calculate the percentage composition by mass of **Q**, and hence its empirical formula. Show whether your answer is consistent with the molecular formula of **Q**.

(4)

- (iv) Evidence for the structure of **Q** is obtained from data in its mass spectrum, and the number of peaks in its low resolution nmr spectrum.

Suggest **one** piece of evidence from **each** type of spectroscopy which would support the structure shown in (f)(ii). Give data where appropriate.

(2)

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(Total for Question 25 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS

TOTAL FOR PAPER = 90 MARKS



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