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Pearson Edexcel
International
Advanced Level

Centre Number

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Candidate Number

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Chemistry

Advanced

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

Wednesday 27 January 2016 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

WCH05/01

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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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 elements is both a d-block element and a transition element?

- A Calcium
 B Copper
 C Scandium
 D Zinc

(Total for Question 1 = 1 mark)

2 The following complexes have different shapes.

- A $[\text{Ag}(\text{NH}_3)_2]^+$
B $[\text{CrCl}_4]^-$
C $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$
D $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(a) Which complex is square-planar?

(1)

- A
 B
 C
 D

(b) Which complex has geometric isomers?

(1)

- A
 B
 C
 D

(Total for Question 2 = 2 marks)

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- 3 This question is about water, and equimolar aqueous solutions of ammonia, butylamine and phenylamine.

The order of **increasing** pH is

- A phenylamine, butylamine, ammonia, water.
- B water, ammonia, butylamine, phenylamine.
- C water, phenylamine, ammonia, butylamine.
- D ammonia, phenylamine, butylamine, water.

(Total for Question 3 = 1 mark)

- 4 What are the colours of the complex ions formed by copper(II) ions with butylamine and chloride ions?

	$[\text{Cu}(\text{C}_4\text{H}_9\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+}$	$[\text{CuCl}_4]^{2-}$
<input type="checkbox"/> A	blue	yellow
<input type="checkbox"/> B	blue	green
<input type="checkbox"/> C	yellow	blue
<input type="checkbox"/> D	yellow	green

(Total for Question 4 = 1 mark)

- 5 Iron(III) ions form a more stable complex with EDTA than with water. What is the **best** explanation for this?

- A Iron(III) ions form stronger bonds with EDTA than with water.
- B Iron(III) ions form more bonds with EDTA than with water.
- C ΔS_{system} is positive for the formation of the EDTA complex from $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
- D $\Delta H_{\text{reaction}}$ is positive for the formation of the EDTA complex from $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

(Total for Question 5 = 1 mark)



6 What is the relationship between the equilibrium constant, K , and $E_{\text{cell}}^{\ominus}$ for a reaction?

- A K is directly proportional to $\ln E_{\text{cell}}^{\ominus}$
- B K is directly proportional to $E_{\text{cell}}^{\ominus}$
- C $\ln K$ is inversely proportional to $E_{\text{cell}}^{\ominus}$
- D $\ln K$ is directly proportional to $E_{\text{cell}}^{\ominus}$

(Total for Question 6 = 1 mark)

7 What is the order of **increasing** reducing power of the ions Cr^{2+} , Fe^{2+} and V^{2+} ?
Use items 20, 54 and 26 on pages 14 and 15 of your Data Booklet.

- A $\text{V}^{2+}, \text{Cr}^{2+}, \text{Fe}^{2+}$.
- B $\text{Cr}^{2+}, \text{V}^{2+}, \text{Fe}^{2+}$.
- C $\text{Fe}^{2+}, \text{V}^{2+}, \text{Cr}^{2+}$.
- D $\text{Fe}^{2+}, \text{Cr}^{2+}, \text{V}^{2+}$.

(Total for Question 7 = 1 mark)

8 Which of the following **cannot** disproportionate?

- A I_2
- B Cu^+
- C H_2O_2
- D MnO_4^-

(Total for Question 8 = 1 mark)

9 Dichromate(VI) ions, $\text{Cr}_2\text{O}_7^{2-}$ in dilute sulfuric acid, react with ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, on warming to form chromium(III) ions and ethanal, CH_3CHO . The half equation for this oxidation of ethanol is



What is the mole ratio of dichromate(VI) ions to ethanol in this redox reaction?

- A 3:1
- B 2:3
- C 3:2
- D 1:3

(Total for Question 9 = 1 mark)

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10 These are four successive ionization energies (in kJ mol^{-1}) of four different elements. Which could be those of a transition element?

- A 658 1310 2653 4175 9573
- B 578 1817 2745 11578 14831
- C 738 1451 7733 10541 13629
- D 496 4563 6913 9544 13352

(Total for Question 10 = 1 mark)

11 Hydrated chromium(III) chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, exists in several isomeric forms with varying numbers of chloro and water ligands.

A solution containing 0.10 mol of one of these isomers reacts with excess silver nitrate. 0.20 mol of silver chloride, AgCl , is precipitated immediately. The formula of the complex ion in this isomer is

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

(Total for Question 11 = 1 mark)

12 A solution is prepared for use in the standard half cell $\text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq})|\text{Pt}$.

What is the mole ratio of the solids iron(II) sulfate, FeSO_4 , and iron(III) sulfate, $\text{Fe}_2(\text{SO}_4)_3$, which should be dissolved to make the solution for this cell?

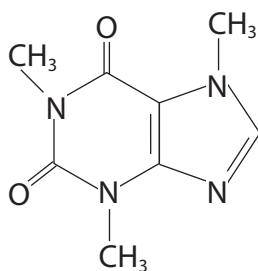
- A 2:1
- B 1:1
- C 1:2
- D 3:2

(Total for Question 12 = 1 mark)

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



13 The structure of caffeine, $C_8H_{10}O_2N_4$, is



Which functional group is **not** present?

- A ketone
- B alkene
- C amide
- D amine

(Total for Question 13 = 1 mark)

14 The overall reaction between ethanoyl chloride and ethylamine to form N-ethyl ethanamide is best classified as

- A free radical substitution.
- B nucleophilic substitution.
- C free radical addition.
- D nucleophilic addition.

(Total for Question 14 = 1 mark)

15 Four isomers with the formula $C_4H_9NH_2$ are

- A 1-aminobutane, $CH_3CH_2CH_2CH_2NH_2$
- B 2-aminobutane, $CH_3CH_2CH(NH_2)CH_3$
- C 1-amino-2-methylpropane, $(CH_3)_2CHCH_2NH_2$
- D 2-amino-2-methylpropane, $(CH_3)_3CNH_2$

(a) Which isomer is chiral?

(1)

- A
- B
- C
- D



(b) Which isomer gives a **low** resolution proton nmr spectrum with the fewest peaks?

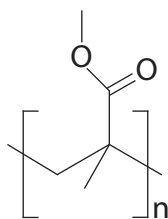
(1)

- A
- B
- C
- D

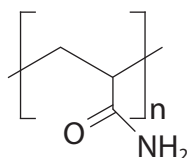
(Total for Question 15 = 2 marks)

16 The formulae of four synthetic polymers, **W**, **X**, **Y** and **Z**, are given below.

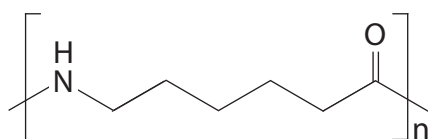
W Poly(methyl-2-methylpropenoate)



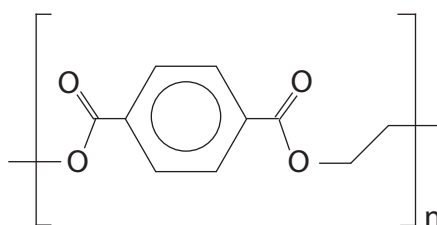
X Poly(propenamide)



Y Poly(amide 6)



Z Poly(ethylene terephthalate)



Which polymers are made by condensation polymerization reactions?

- A **W** and **Z**
- B **X** and **Y**
- C **Y** and **Z**
- D **W** and **X**

(Total for Question 16 = 1 mark)



17 All naturally occurring amino acids exist as crystalline solids.
The **best** explanation for this is that amino acids

- A have large numbers of electrons.
- B form hydrogen bonds.
- C form ionic bonds.
- D are symmetrical so the molecules can pack closely in the lattice.

(Total for Question 17 = 1 mark)

18 When recrystallization is used to purify a solid, which of the following statements is true?

- A Soluble impurities are removed by filtering the hot solution.
- B Insoluble impurities are removed by filtering the hot solution.
- C All impurities must be insoluble in the solvent used.
- D All impurities must be soluble in the solvent used.

(Total for Question 18 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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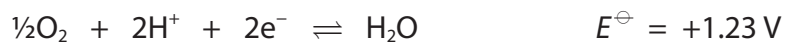


SECTION B

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

- 19 Methanol fuel cells have significant advantages over hydrogen fuel cells.

The half equations for the methanol fuel cell are



- (a) Use your knowledge of the hydrogen electrode to draw a labelled diagram of the half cell that could be used to measure the oxygen electrode potential.

Include the conditions needed for the standard electrode potential to be measured.

(3)

- (b) Write the overall equation for the methanol fuel cell reaction.
State symbols are not required.

(1)



(c) Calculate the emf of this methanol cell.

(1)

* (d) Suggest **one** advantage and **one** disadvantage of a methanol fuel cell compared to a hydrogen fuel cell.

(2)

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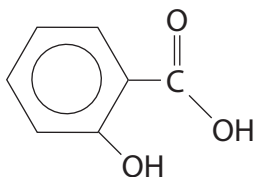
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(Total for Question 19 = 7 marks)



- 20 This question is about the naturally occurring substance, 2-hydroxybenzoic acid, which can be extracted from the bark of willow trees.



- (a) Give the molecular formula of 2-hydroxybenzoic acid.

(1)

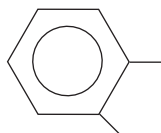
- (b) The presence of the carboxylic acid group in 2-hydroxybenzoic acid is shown by the fact that it neutralizes sodium carbonate solution.

Write the equation for this neutralization. State symbols are not required.

(2)

- (c) The 2-hydroxybenzoic acid forms a hydrogen bond within the molecule.

- (i) Complete the formula below to show this hydrogen bonding by displaying all the remaining atoms and bonds.



(1)

- *(ii) Will the melting temperature of 4-hydroxybenzoic acid be higher or lower than that of 2-hydroxybenzoic acid? Justify your answer.

(2)

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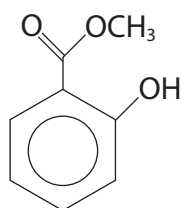
(d) Phenol and 2-hydroxybenzoic acid react with excess bromine water in a similar way.

Suggest the structural formula and name of the organic product formed when excess bromine water reacts with 2-hydroxybenzoic acid.

(2)

Name

(e) The main chemical present in oil of wintergreen is methyl 2-hydroxybenzoate which is a liquid at room temperature.



(i) Give the chemicals and conditions needed to prepare methyl 2-hydroxybenzoate from 2-hydroxybenzoic acid in a **single** step reaction.

(2)

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* (ii) Because methyl 2-hydroxybenzoate is sparingly soluble in water, it is extracted from the reaction mixture using ethyl ethanoate.

Explain why methyl 2-hydroxybenzoate is sparingly soluble in water.

(3)

(iii) The solution of methyl 2-hydroxybenzoate in ethyl ethanoate is washed and then dried.

Suggest the chemicals needed for these steps.

Justify your suggestions.

(3)

(iv) State how methyl 2-hydroxybenzoate is separated from ethyl ethanoate.

(1)

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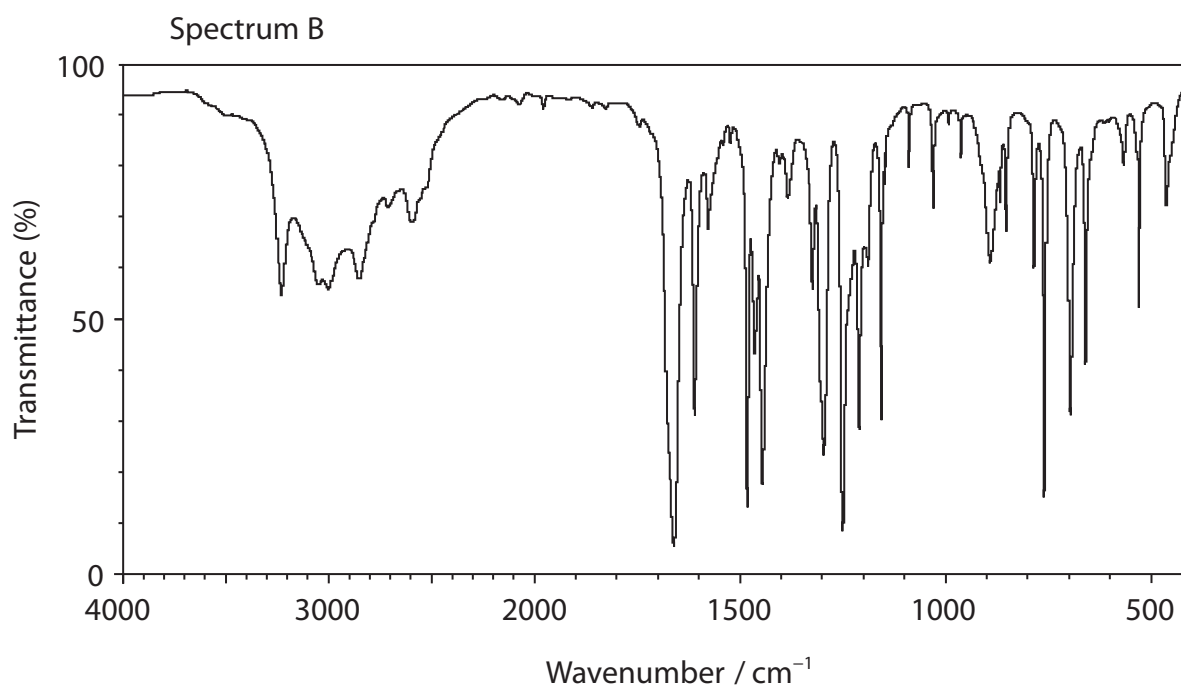
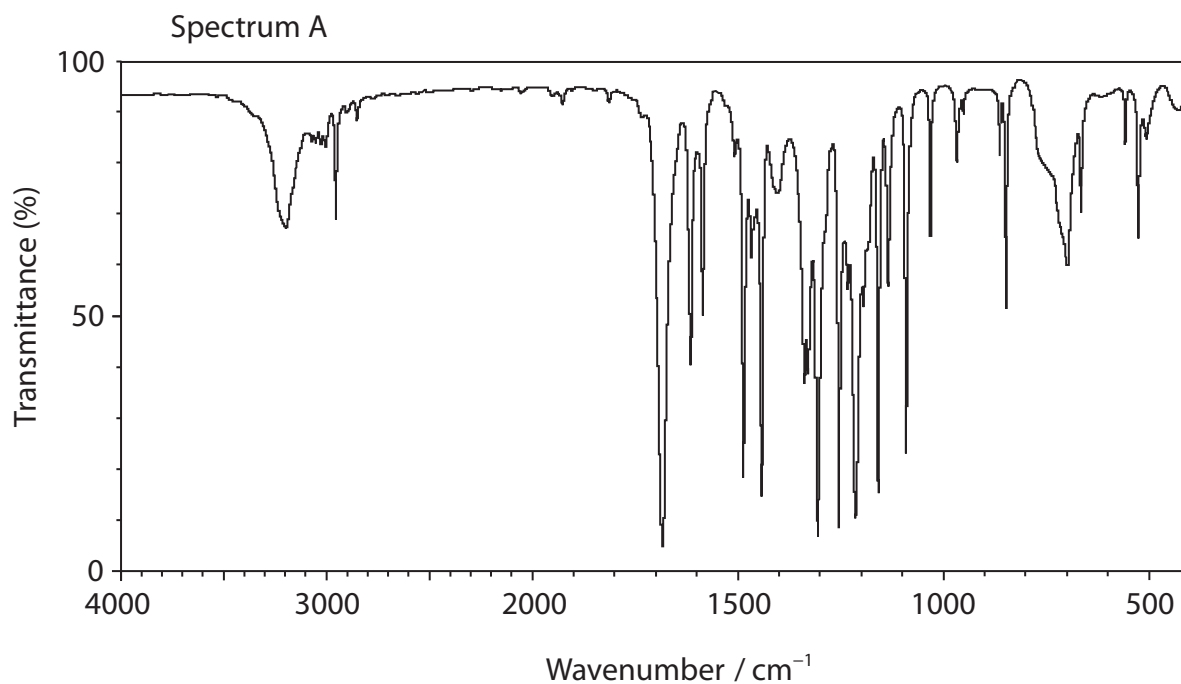


- (v) The identity of methyl 2-hydroxybenzoate can be confirmed by infrared spectroscopy.

Which of the infrared spectra below is given by methyl 2-hydroxybenzoate and which by 2-hydroxybenzoic acid?

Justify your answer by identifying the bond responsible for a distinguishing absorption. Give the wavenumber range for this absorption.

(2)



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- (vi) Calculate the **volume** of methyl 2-hydroxybenzoate produced from 9.00 g of 2-hydroxybenzoic acid, assuming the yield for this reaction is 60%, and the other reagents are present in excess.

DATA

Molar mass of 2-hydroxybenzoic acid = 138 g mol^{-1}

Molar mass of methyl 2-hydroxybenzoate = 152 g mol^{-1}

Density of methyl 2-hydroxybenzoate = 1.174 g cm^{-3}

(3)

(Total for Question 20 = 22 marks)



21 This question is about the element chromium and some of its compounds.

(a) (i) Complete the electronic configuration of the chromium atom, using the s, p, d notation.

(1)

[Ar]

*(ii) State how this electronic configuration of the chromium atom is unusual compared with most other transition metals.

Give **two** reasons why chromium has this electronic configuration.

(2)

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- (b) (i) A solution containing chromium(II) ions can be produced in the laboratory by reducing a solution of potassium dichromate(VI) using zinc in 50% hydrochloric acid. This reaction takes place in two steps. Dichromate(VI) ions are reduced to chromium(III) ions and the chromium(III) ions are then reduced to chromium(II) ions.

Use the relevant standard reduction potentials from page 17 or standard electrode potentials on pages 14 and 16 of the Data Booklet to calculate $E_{\text{cell}}^{\ominus}$ for each step.

Use your $E_{\text{cell}}^{\ominus}$ values to explain why both steps are spontaneous.

(3)

- (ii) State the colour changes you would expect to see during this reaction.

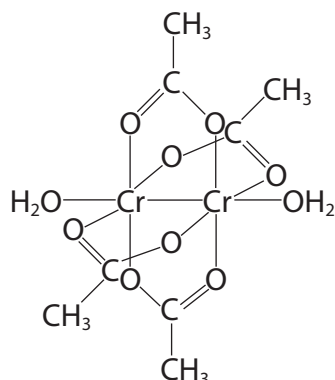
(1)

- (iii) A student suggests that the hydrogen produced by the reaction of the zinc with hydrochloric acid in this experiment is a serious risk. Evaluate the student's suggestion.

(1)



- (c) Chromium(II) ions in aqueous solution are quickly oxidized by the oxygen in air. One method of stabilising chromium(II) ions is by adding a solution of sodium ethanoate, forming a complex, $[\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2]$. This complex may be represented by the structure below.



- (i) What type of ligand is the ethanoate ion in this complex? (1)

- (ii) State the type of bonding which occurs between the ligands and the chromium(II) ions. (1)

- (iii) Suggest **two** unusual features in the structure and bonding of this complex. (2)

- (iv) This complex is red. Explain why the colour of chromium(II) ethanoate is different from that of $\text{Cr}(\text{H}_2\text{O})_6^{2+}(\text{aq})$. (2)



(v) Predict the number and relative areas of the peaks in the **low** resolution proton nmr spectrum of $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$.

Justify your answers.

(2)

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(d) An experiment is carried out to check the oxidation number of chromium in chromium(II) ethanoate $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$.

1.00 g (2.66×10^{-3} mol) of chromium(II) ethanoate is dissolved in 25 cm^3 of 1.00 mol dm^{-3} sulfuric acid.

The solution is diluted with distilled water until the volume is 250 cm^3 .

25.0 cm^3 portions of the diluted solution are titrated with $0.00750 \text{ mol dm}^{-3}$ potassium manganate(VII).

Calculate the volume of potassium manganate(VII) needed to oxidize the chromium(II) ions present in each 25.0 cm^3 portion to the +6 oxidation state. The manganese is reduced to the +2 oxidation state.

Comment on your answer and suggest how the experiment could be improved to give a more suitable titre.

(5)

Comment

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(Total for Question 21 = 21 marks)

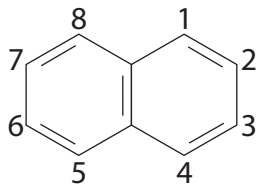
TOTAL FOR SECTION B = 50 MARKS



SECTION C

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

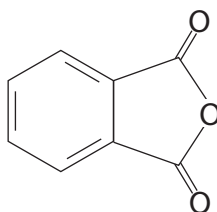
- 22 Naphthalene is a white solid traditionally used in mothballs and is extracted from coal tar. It is an arene which can be represented by the formula below.



Although it is an aromatic compound, naphthalene has carbon to carbon bonds of different lengths.

Like benzene, naphthalene undergoes electrophilic substitution. Substitution usually occurs at one of the carbons 1, 4, 5 or 8 and naphthalene reacts under milder conditions than benzene.

Oxidation of naphthalene, using oxygen gas with vanadium(V) oxide catalyst at about 650 K, produces phthalic anhydride:



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(a) State which physical method would be used to determine the lengths of the carbon to carbon bonds in naphthalene.

(1)

(b) Use your knowledge of benzene to draw an alternative way of representing the structure of naphthalene. Explain what this structure represents and how it arises.

(3)



(c) Naphthalene is nitrated using a mixture of concentrated nitric and sulfuric acids. Write a mechanism for this reaction. Include one or more equations to show how the electrophile is formed.

(4)

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(d) 1.28 g of naphthalene is completely burned in oxygen.

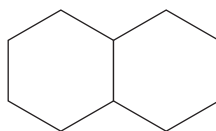
Write the equation for the combustion of naphthalene. State symbols are not required.

Calculate the volume of carbon dioxide produced, measured at room temperature and pressure.

1 mol of a gas occupies 24.0 dm^3 at room temperature and pressure.

(3)

(e) Suggest the reagent and appropriate conditions for the synthesis of decalin from naphthalene.

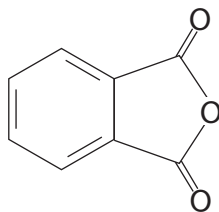


Decalin

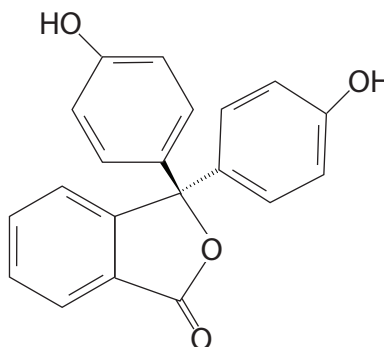
(2)



- (f) When phenol is heated with phthalic anhydride in the presence of the catalyst concentrated sulfuric acid, the indicator phenolphthalein is formed.



Phthalic anhydride



Phenolphthalein

- (i) When phenol reacts with phthalic anhydride to form phenolphthalein, state the inorganic product of the reaction.

(1)

- (ii) When phenolphthalein is colourless it can be represented as H_2In .

At very low pH, H_3In^+ is formed which is orange.

Between pH 9 and 12, In^{2-} is formed which has the familiar pink colour.

By referring to the structure of phenolphthalein given above, suggest how these two ions are formed.

(2)

H_3In^+

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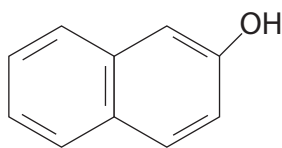
In^{2-}

.....

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(g) Coal tar also contains 2-naphthol.



2-naphthol and phenol react with phenylamine in a similar way to form dyes.

Suggest a synthesis of a chemical dye starting with 2-naphthol and phenylamine.

You should include chemicals and conditions for your reactions.

Suggest the structural formula of your dye.

(4)

(Total for Question 22 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS



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