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Chemistry

Advanced

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

Wednesday 22 June 2016 – Morning

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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3/6/6/3/5/5/e2


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 gives the oxidation states of manganese in the ions shown?

| | MnO_4^{2-} | MnO_3^- |
|----------------------------|---------------------|------------------|
| <input type="checkbox"/> A | +7 | +6 |
| <input type="checkbox"/> B | +6 | +5 |
| <input type="checkbox"/> C | +7 | +5 |
| <input type="checkbox"/> D | +6 | +6 |

(Total for Question 1 = 1 mark)

- 2 Which of the following gives the electrodes and electrolyte that are used in an alkaline hydrogen fuel cell?

| | Electrodes | Electrolyte |
|----------------------------|------------|------------------------------|
| <input type="checkbox"/> A | graphite | potassium hydroxide solution |
| <input type="checkbox"/> B | graphite | water with a little salt |
| <input type="checkbox"/> C | platinum | potassium hydroxide solution |
| <input type="checkbox"/> D | platinum | water with a little salt |

(Total for Question 2 = 1 mark)

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3 Which of the following **cannot** be used to detect alcohol in a breathalyser test?

- A Fractional distillation
- B Fuel cell
- C Infrared spectroscopy
- D Reduction of dichromate(VI) ions

(Total for Question 3 = 1 mark)

4 A titration using potassium manganate(VII) in dilute sulfuric acid can be used to determine the percentage of

- A aspirin in aspirin tablets.
- B chlorine in bleach.
- C copper in an alloy.
- D iron(II) sulfate in iron tablets.

(Total for Question 4 = 1 mark)

5 Which of the following gives the electronic configurations for a chromium atom and a chromium(II) ion?

| | Cr | Cr ²⁺ |
|----------------------------|-------------------------------------|-------------------------------------|
| <input type="checkbox"/> A | [Ar]3d ⁴ 4s ² | [Ar]3d ⁴ |
| <input type="checkbox"/> B | [Ar]3d ⁵ 4s ¹ | [Ar]3d ⁴ |
| <input type="checkbox"/> C | [Ar]3d ⁴ 4s ² | [Ar]3d ² 4s ² |
| <input type="checkbox"/> D | [Ar]3d ⁵ 4s ¹ | [Ar]3d ³ 4s ¹ |

(Total for Question 5 = 1 mark)



- 6 Aqueous sodium hydroxide and aqueous ammonia are added to separate solutions of the same metal ion. The observations are shown in the table below.

| Reagent added | A few drops | Excess |
|----------------------|-------------------|---|
| NaOH(aq) | green precipitate | green precipitate remains |
| NH ₃ (aq) | green precipitate | green precipitate dissolves to form a blue solution |

The metal ion is

- A Cr³⁺(aq).
 B Fe²⁺(aq).
 C Fe³⁺(aq).
 D Ni²⁺(aq).

(Total for Question 6 = 1 mark)

- 7 The reaction between cerium(IV) ions and thallium(I) ions is very slow.



Which of these ions could catalyse this reaction?

- A Al³⁺
 B Fe³⁺
 C Na⁺
 D Zn²⁺

(Total for Question 7 = 1 mark)

- 8 Which of these hydroxides is amphoteric?

- A Cu(OH)₂
 B Mg(OH)₂
 C Ni(OH)₂
 D Zn(OH)₂

(Total for Question 8 = 1 mark)

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- 9 During a titration between acidified manganate(VII) ions and sulfate(IV) ions, the manganate(VII) ions are reduced to manganese(II) ions and the sulfate(IV) ions are oxidized to sulfate(VI) ions.

The mole ratio of manganate(VII) ions to sulfate(IV) ions in this reaction is

- A 5:2
 B 7:4
 C 2:5
 D 4:7

(Total for Question 9 = 1 mark)

- 10 The total number of compounds with the structural formula $C_6H_3CH_3(NO_2)_2$, which contain a benzene ring, is

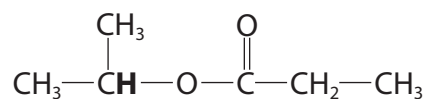
- A four.
 B five.
 C six.
 D seven.

(Total for Question 10 = 1 mark)

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11 This question is about the ester shown below.



(a) The number of peaks seen in the **low** resolution proton nmr spectrum of this ester is (1)

- A two.
- B three.
- C four.
- D five.

(b) The peak in the **high** resolution proton nmr spectrum corresponding to the proton in **bold** on the structure above will (1)

- A not be split.
- B be split into three peaks.
- C be split into four peaks.
- D be split into seven peaks.

(Total for Question 11 = 2 marks)

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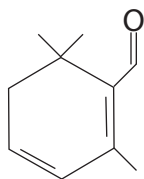
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12 Safranal is one of the substances that contributes to the aroma of saffron.



Separate samples of safranal were tested with bromine water, 2,4-dinitrophenylhydrazine and Fehling's solution.

What are the final observations when safranal is tested with each of those reagents?

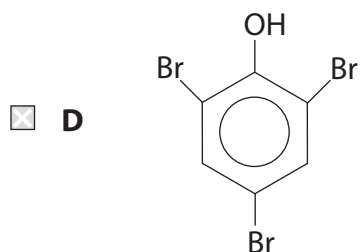
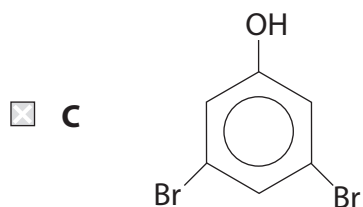
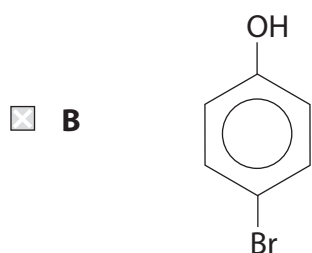
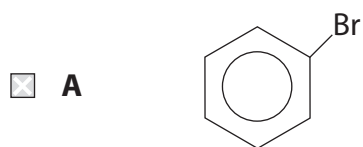
| | Bromine water | 2,4-dinitrophenylhydrazine | Fehling's solution |
|----------------------------|---------------------|----------------------------|--------------------|
| <input type="checkbox"/> A | orange solution | orange solution | red precipitate |
| <input type="checkbox"/> B | colourless solution | orange precipitate | red precipitate |
| <input type="checkbox"/> C | orange solution | orange solution | blue solution |
| <input type="checkbox"/> D | colourless solution | orange precipitate | blue solution |

(Total for Question 12 = 1 mark)

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13 The structure of the organic product of the reaction between phenol and excess bromine water is



(Total for Question 13 = 1 mark)

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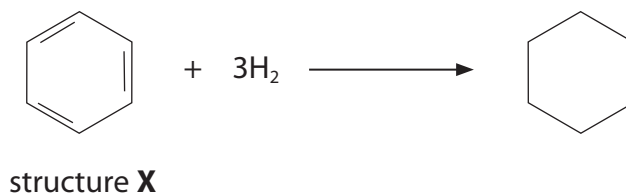
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- 14 If it is assumed that the structure of benzene has three localised double bonds (structure **X**), the calculated standard enthalpy change of hydrogenation is -360 kJ mol^{-1} .



The actual standard enthalpy change of hydrogenation of benzene is -208 kJ mol^{-1} .

From these data, it can be deduced that the

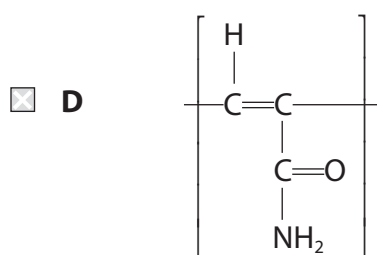
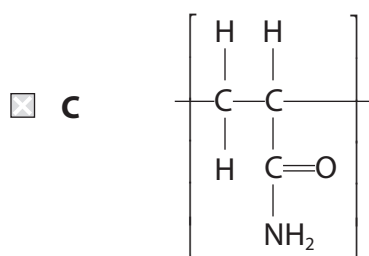
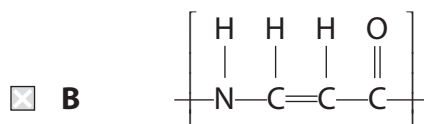
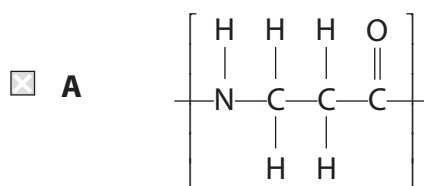
- A** actual benzene structure is kinetically more stable than structure **X** as it requires a high activation energy to react.
- B** actual benzene structure is thermodynamically more stable than structure **X** as it has a lower enthalpy content.
- C** structure **X** is kinetically unstable as it undergoes addition reactions at room temperature.
- D** structure **X** is thermodynamically more stable than the actual benzene structure as the standard enthalpy change of hydrogenation is more exothermic.

(Total for Question 14 = 1 mark)

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



15 The repeat unit for poly(propenamide) is



(Total for Question 15 = 1 mark)

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16 The structures of three amino acids are shown in the table.

| Amino acid | Structure |
|------------|--|
| cysteine | $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ |
| glycine | $\text{H}_2\text{NCH}_2\text{COOH}$ |
| threonine | $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$ |

The tripeptide glycine-cysteine-threonine is

- A $\text{H}_2\text{NCH}_2\text{CONHCH}(\text{CH}(\text{OH})\text{CH}_3)\text{CONHCH}(\text{CH}_2\text{SH})\text{COOH}$
- B $\text{H}_2\text{NCH}_2\text{CONHCH}(\text{CH}_2\text{SH})\text{CONHCH}(\text{CH}(\text{OH})\text{CH}_3)\text{COOH}$
- C $\text{H}_2\text{NCH}(\text{CH}(\text{OH})\text{CH}_3)\text{CONHCH}(\text{CH}_3\text{SH})\text{CONHCH}_2\text{COOH}$
- D $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CONHCH}_2\text{CONHCH}(\text{CH}(\text{OH})\text{CH}_3)\text{COOH}$

(Total for Question 16 = 1 mark)

17 The amino acid alanine, $\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$, exists as a solid at room temperature.

The most important reason for this is that it

- A exists as a zwitterion.
- B forms hydrogen bonds.
- C is amphoteric.
- D has strong London forces.

(Total for Question 17 = 1 mark)

18 Complete combustion of a hydrocarbon produced 0.66 g of carbon dioxide and 0.225 g of water.

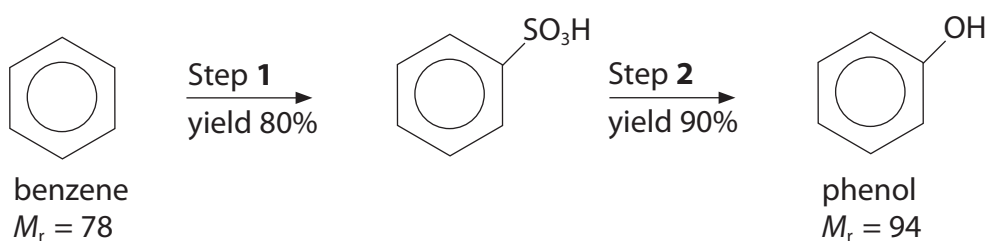
Which of the following molecular formulae is consistent with these data?

- A C_3H_6 .
- B C_3H_8 .
- C C_6H_6 .
- D C_6H_{10} .

(Total for Question 18 = 1 mark)



19 Phenol can be produced from benzene as shown in the reaction sequence below.



The mass of phenol, to 2 decimal places, produced from 3.90 g of benzene is

- A 3.38 g.
- B 3.76 g.
- C 4.23 g.
- D 4.70 g.

(Total for Question 19 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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P 4 6 6 6 1 A 0 1 3 3 2

SECTION B

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

20 Vanadium exists in different oxidation states which can be interconverted using suitable oxidising and reducing agents.

(a) Use relevant standard electrode potential values, on page 14 of the Data Booklet, to complete the table below in which two E^\ominus values are missing.

(1)

| Half-equation | E^\ominus / V |
|--|-----------------|
| $V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$ | |
| $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ | |
| $VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$ | +0.34 |
| $I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ | +0.54 |
| $VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ | +1.00 |

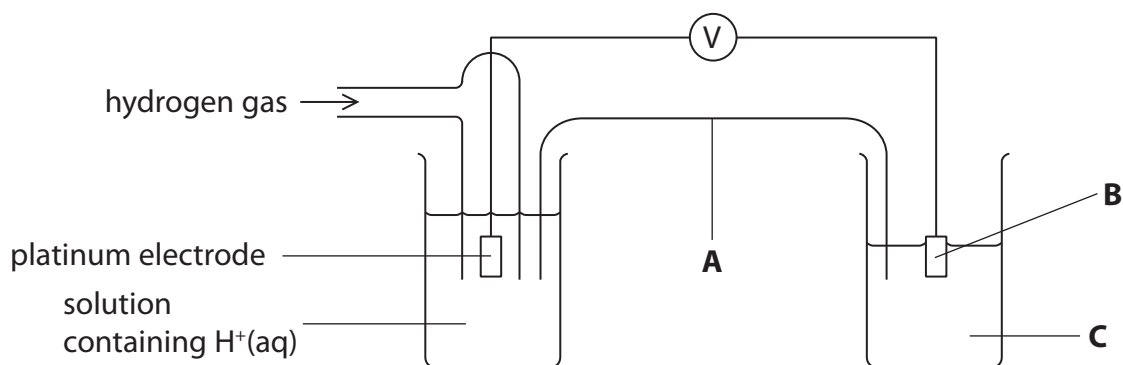
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(b) The standard electrode potential of $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ is measured using the apparatus below.



(i) Identify, by name or formula, the substances needed in the salt bridge and the right-hand half-cell to measure the standard electrode potential.

(3)

A Salt bridge containing a solution of

.....

B Electrode made of

.....

C Solution containing

.....

(ii) State the **three** standard conditions needed for this measurement.

(2)

1

2

3

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* (c) A solution containing iodide ions, I^- , was added to an acidified solution containing vanadium(V) ions, VO_2^+ .

Predict the oxidation state of the vanadium ions left at the end of the reaction. Justify your prediction by calculating the E_{cell} for any relevant reaction(s).

Write the ionic equation for any reaction(s) occurring. State symbols are not required.

(5)

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(Total for Question 20 = 11 marks)

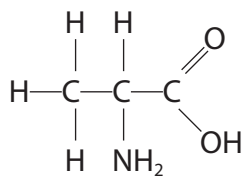
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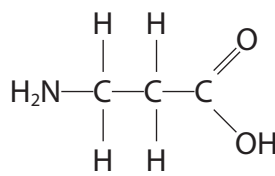
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21 (a) The structures of 2-aminopropanoic acid and 3-aminopropanoic acid are shown.



2-aminopropanoic acid



3-aminopropanoic acid

(i) Explain how the **low** resolution proton nmr spectra of these two amino acids differ. (2)

.....

.....

.....

.....

(ii) Explain whether or not 3-aminopropanoic acid is chiral. (1)

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.....

(iii) Write ionic equations for the reaction of 3-aminopropanoic acid with (2)

H⁺ ions

OH⁻ ions

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(iv) Draw two repeat units of the polymer formed when 3-aminopropanoic acid polymerizes.

(1)

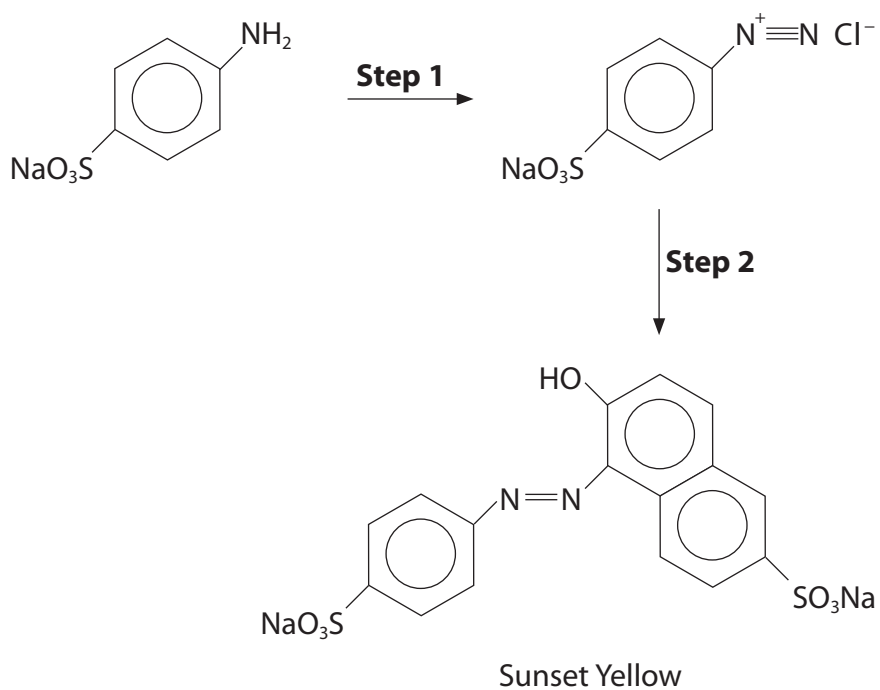
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(b) The food colouring E110 is also known as Sunset Yellow.

It can be synthesised as shown below.



(i) Give the reagents and condition for **Step 1**.

(2)



(ii) Draw the structure of the reagent needed for **Step 2**. (1)

(iii) Explain why Sunset Yellow can exist as geometric isomers. (1)

* (iv) Describe the essential steps of the method that you would use to prepare a pure, dry sample of the solid Sunset Yellow from an impure sample of the food colouring. You may assume that ethanol is a suitable solvent for this method. (4)

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(v) Suggest how you could check that a sample of Sunset Yellow is pure.

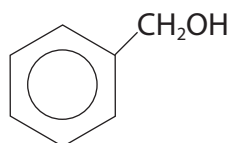
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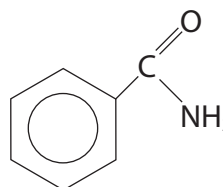
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(c) Explain how a chemist could use phenylmethanol to synthesise a sample of benzamide in three steps.



phenylmethanol



benzamide

Include the reagents for the steps in the synthesis and draw the structures of **all** the intermediates.

(5)

(Total for Question 21 = 20 marks)



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22 Copper and zinc are both in the d-block of the Periodic Table. Copper forms compounds that contain Cu^+ and Cu^{2+} ions but zinc only forms compounds that contain Zn^{2+} ions.

(a) Complete the electronic configurations of the Cu^{2+} ions and Zn^{2+} ions and hence explain why copper is classified as a transition metal but zinc is not.

(2)

Cu^{2+} [Ar]

Zn^{2+} [Ar]

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.....

(b) Some photochromic glasses contain silver(I) and copper(I) chlorides.

Explain, with the aid of an equation, why these photochromic glasses go darker in sunlight.

(2)

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(c) Copper forms a complex ion with the formula $[\text{CuCl}_4]^{2-}$. This has the same shape as $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Draw the shape of the $[\text{CuCl}_4]^{2-}$ ion and state the type of bonding between the ligands and the metal ion.

(2)

Shape

Bonding.....

(d) The $[\text{CuCl}_2]^-$ ion is formed by boiling a solution of copper(II) chloride with copper turnings and concentrated hydrochloric acid.

(i) Write an equation for this reaction. State symbols are not required.

(1)

(ii) State the meaning of the term **disproportionation** and explain whether or not this reaction to form the $[\text{CuCl}_2]^-$ ion is a disproportionation reaction.

(2)

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(iii) Explain why the $[\text{CuCl}_2]^-$ ions are colourless.

(2)

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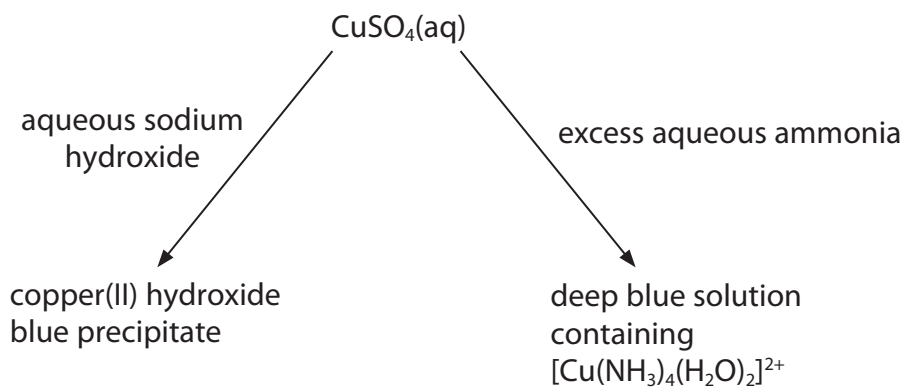
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(e) Copper(II) sulfate solution reacts with aqueous sodium hydroxide and with aqueous ammonia.



(i) Write the **ionic** equation for the reaction of copper(II) sulfate solution with aqueous sodium hydroxide. Include state symbols.

(1)

(ii) State the type of reaction occurring overall when excess aqueous ammonia is added to copper(II) sulfate solution.

(1)

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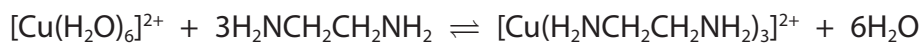
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- (f) 1,2-diaminoethane is a bidentate ligand. It reacts with copper(II) ions in aqueous solution.



- (i) State what is meant by the term **bidentate**. (1)

- (ii) Explain, in terms of entropy, why the reaction takes place. (2)

(Total for Question 22 = 16 marks)

TOTAL FOR SECTION B = 47 MARKS



SECTION C

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

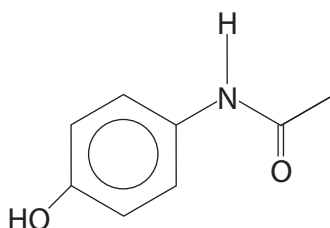
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Analgesics

Analgesics are taken to relieve the symptoms of pain.

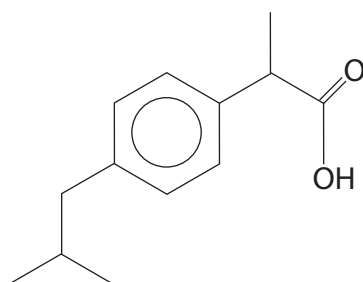
Paracetamol

This has been synthesised in a three-step process since the 1950s.



Ibuprofen

This was first synthesised in the 1960s from propanoic acid. That process involved six steps and produced more waste than the required drug.



It is now manufactured in a three-step process.

Some data about these two analgesics are given in the table below.

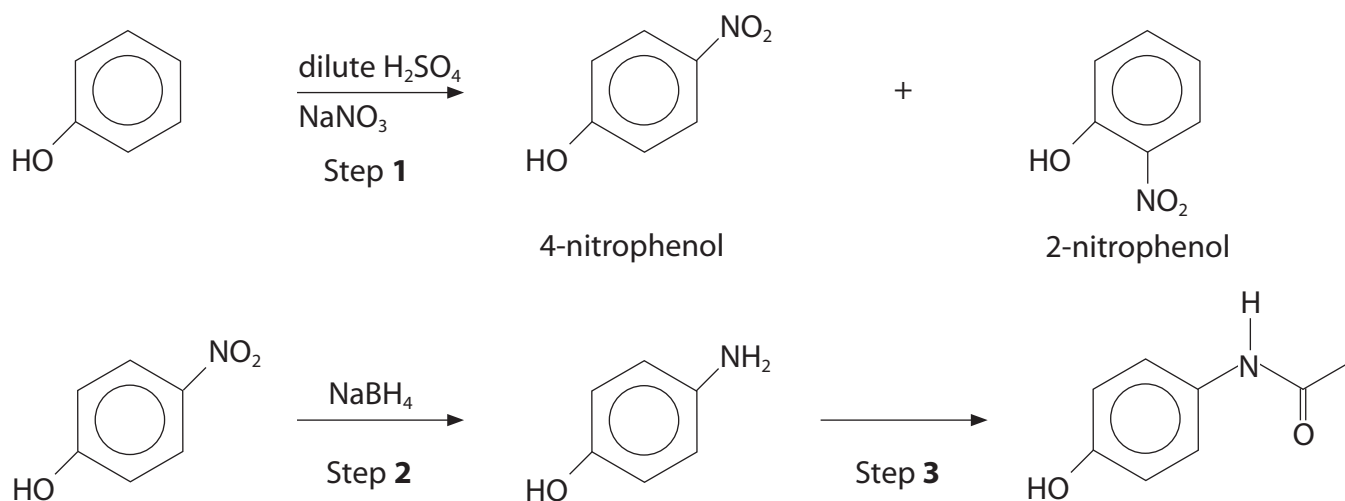
| Analgesic | Molecular formula | Molar mass / g mol ⁻¹ |
|-------------|--|----------------------------------|
| paracetamol | C ₈ H ₉ NO ₂ | 151 |
| ibuprofen | C ₁₃ H ₁₈ O ₂ | 206 |



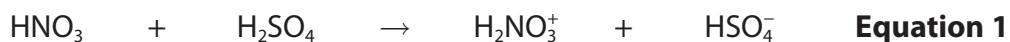
(a) **Name** the functional group in paracetamol, other than the phenol group.

(1)

(b) Paracetamol is made from phenol in a three-step process.



(i) In a typical nitration of an arene, the electrophile is formed as shown below.



.....



Identify the acid-base conjugate pairs in **Equation 1**. Write your answers on the dotted lines under the equation.

(1)



(ii) Give a mechanism for the nitration of phenol by NO_2^+ to form 4-nitrophenol.

(3)

(iii) Explain why phenol is nitrated much more readily than benzene.

(2)

(iv) State the type of reaction taking place in Step 2.

(1)

(v) Suggest a reagent for Step 3.

(1)

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(vi) 2-nitrophenol has a melting temperature of 46 °C and 4-nitrophenol has a melting temperature of 114 °C.

Suggest, in terms of intermolecular forces, why these two compounds have different melting temperatures.

(2)

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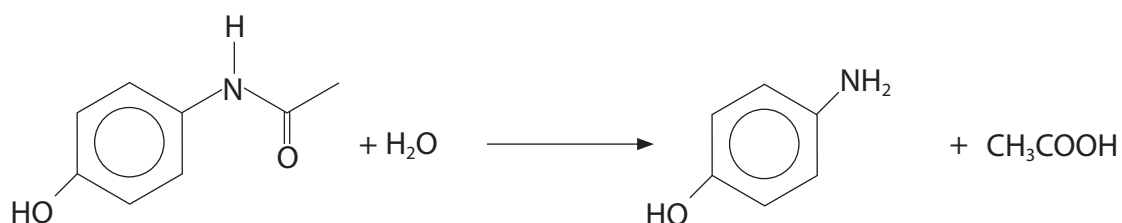
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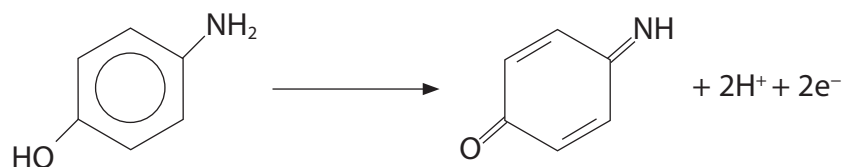
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(c) Paracetamol can be hydrolysed to form 4-aminophenol and ethanoic acid.



The amount of 4-aminophenol produced can be determined using a redox titration. The half-equation for the oxidation of 4-aminophenol is given below.



The oxidizing agent is ammonium cerium(IV) sulfate and ferroin indicator is used to detect the end-point of the titration. During the reaction, the Ce^{4+} ions are reduced to Ce^{3+} ions.

(i) Write the overall equation for the reaction between Ce^{4+} ions and 4-aminophenol.

(1)



- (ii) In an experiment, 0.500 g of a tablet containing paracetamol was hydrolysed and the solution was made up to 100 cm³.

20.0 cm³ portions of the resulting solution were titrated with 0.100 mol dm⁻³ ammonium cerium(IV) sulfate solution.

The mean titre was 12.60 cm³.

Calculate the percentage, by mass, of paracetamol in the tablet.

(5)

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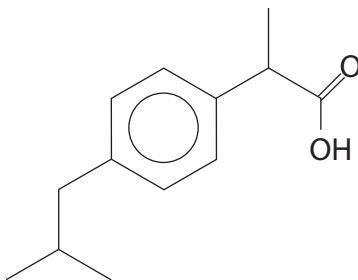
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(d) (i) Identify the chiral carbon atom in ibuprofen with an asterisk (*).

(1)



(ii) Suggest a problem in the manufacture of a single isomer of a chiral drug and describe a way that the pharmaceutical industry might overcome this problem.

(2)

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(e) Ibuprofen was originally made in a six-step process but is now made in a three-step process.

Suggest a specific environmental reason why the manufacturing process was changed.

(1)

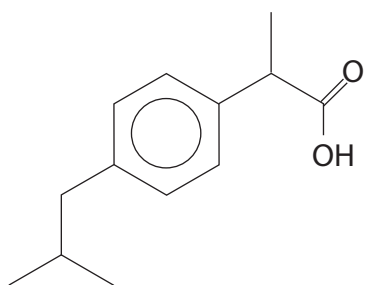
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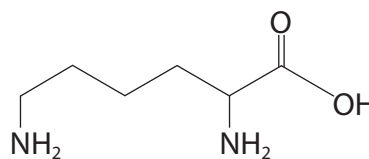
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- (f) Ibuprofen is not very soluble in water. It can be made into an ionic, soluble salt by reacting it with lysine.



Ibuprofen



Lysine

Draw the structures of **both** the cation and the anion in the soluble salt formed when ibuprofen reacts with lysine.

(2)

(Total for Question 23 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS

TOTAL FOR PAPER = 90 MARKS



The Periodic Table of Elements

| | | | | | | | | | | | | | | | | | | | | | | | |
|--------------------------------------|--|--|--|--------------------------------------|---------------------------------------|---------------------------------------|------------------------------------|---------------------------------------|---|--|---|--------------------------------------|------------------------------------|--|--------------------------------------|---------------------------------------|-------------------------------------|-------------------------------------|----------------------------------|---------------------------------------|------------------------------------|--|---------------------------------------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 0 (8) | | | | | | | | | | | | | | | | |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | | | | | | | | | | | | | | | | |
| 6.9 Li lithium 3 | 9.0 Be beryllium 4 | 11 Na sodium 11 | 12 Mg magnesium 12 | 13 B boron 5 | 14 C carbon 6 | 15 N nitrogen 7 | 16 O oxygen 8 | 17 F fluorine 9 | 18 Ne neon 10 | | | | | | | | | | | | | | |
| 19 K potassium 19 | 20 Ca calcium 20 | 21 Sc scandium 21 | 22 Ti titanium 22 | 23 V vanadium 23 | 24 Cr chromium 24 | 25 Mn manganese 25 | 26 Fe iron 26 | 27 Co cobalt 27 | 28 Ni nickel 28 | 29 Cu copper 29 | 30 Zn zinc 30 | 31 Ga gallium 31 | 32 Ge germanium 32 | 33 As arsenic 33 | 34 Se selenium 34 | 35 Br bromine 35 | 36 Kr krypton 36 | | | | | | |
| 37 Rb rubidium 37 | 38 Sr strontium 38 | 39 Y yttrium 39 | 40 Zr zirconium 40 | 41 Nb niobium 41 | 42 Mo molybdenum 42 | 43 Tc technetium [98] | 44 Ru ruthenium 44 | 45 Rh rhodium 45 | 46 Pd palladium 46 | 47 Ag silver 47 | 48 Cd cadmium 48 | 49 In indium 49 | 50 Sn tin 50 | 51 Sb antimony 51 | 52 Te tellurium 52 | 53 I iodine 53 | 54 Xe xenon 54 | | | | | | |
| 55 Cs caesium 55 | 56 Ba barium 56 | 57 La* lanthanum 57 | 72 Hf hafnium 72 | 73 Ta tantalum 73 | 74 W tungsten 74 | 75 Re rhenium 75 | 76 Os osmium 76 | 77 Ir iridium 77 | 78 Pt platinum 78 | 79 Au gold 79 | 80 Hg mercury 80 | 81 Tl thallium 81 | 82 Pb lead 82 | 83 Bi bismuth 83 | 84 Po polonium 84 | 85 At astatine 85 | 86 Rn radon 86 | | | | | | |
| [223] Fr francium 87 | [226] Ra radium 88 | [227] Ac* actinium 89 | 104 Rf rutherfordium 104 | 105 Db dubnium 105 | 106 Sg seaborgium 106 | 107 Bh bohrium 107 | 108 Hs hassium 108 | 109 Mt meitnerium 109 | 110 Ds darmstadtium 110 | 111 Rg roentgenium 111 | Elements with atomic numbers 112-116 have been reported but not fully authenticated | | | | | | | | | | | | |
| 132.9 Cs caesium 55 | 137.3 Ba barium 56 | 138.9 La* lanthanum 57 | 178.5 Hf hafnium 72 | 180.9 Ta tantalum 73 | 183.8 W tungsten 74 | 186.2 Re rhenium 75 | 190.2 Os osmium 76 | 192.2 Ir iridium 77 | 195.1 Pt platinum 78 | 197.0 Au gold 79 | 200.6 Hg mercury 80 | 204.4 Tl thallium 81 | 207.2 Pb lead 82 | 209.0 Bi bismuth 83 | [209] Po polonium 84 | [210] At astatine 85 | [222] Rn radon 86 | | | | | | |
| 140 Ce cerium 58 | 141 Pr praseodymium 59 | 144 Nd neodymium 60 | 147 Pm promethium 61 | 150 Sm samarium 62 | 152 Eu europium 63 | 157 Gd gadolinium 64 | 158 Tb terbium 65 | 162 Dy dysprosium 66 | 165 Ho holmium 67 | 167 Er erbium 68 | 173 Yb ytterbium 70 | 175 Lu lutetium 71 | 232 Th thorium 90 | 231 Pa protactinium 91 | 238 U uranium 92 | 237 Np neptunium 93 | 242 Pu plutonium 94 | 243 Am americium 95 | 247 Cm curium 96 | 251 Cf californium 98 | 254 Fm fermium 100 | 256 Md mendelevium 101 | 257 Lr lawrencium 103 |
| 173 Yb ytterbium 70 | 169 Tm thulium 69 | 167 Er erbium 68 | 165 Ho holmium 67 | 163 Dy dysprosium 66 | 159 Tb terbium 65 | 157 Gd gadolinium 64 | 158 Tb terbium 65 | 162 Dy dysprosium 66 | 165 Ho holmium 67 | 167 Er erbium 68 | 173 Yb ytterbium 70 | 175 Lu lutetium 71 | 253 Fm fermium 100 | 256 Md mendelevium 101 | 254 No nobelium 102 | 257 Lr lawrencium 103 | | | | | | | |

1.0
H
hydrogen
1

Key
relative atomic mass
atomic symbol
name
atomic (proton) number

* Lanthanide series
* Actinide series



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