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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)

Tuesday 17 June 2014 – 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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P 4 2 9 7 9 A 0 1 3 2

**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 In which of the following compounds is there an element with the same oxidation number as that of chromium in  $\text{K}_2\text{Cr}_2\text{O}_7$ ?

- ☐ A  $\text{Cl}_2\text{O}_7$   
☐ B  $\text{Na}_3\text{Fe}(\text{CN})_6$   
☐ C  $\text{K}_2\text{MnO}_4$   
☐ D  $\text{CaTiF}_6$

(Total for Question 1 = 1 mark)

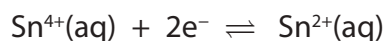
- 2 Chlorine exists in oxidation states from  $-1$  to  $+7$ . For which of the following compounds is a reaction resulting in the disproportionation of chlorine **impossible**?

- ☐ A  $\text{NaClO}$   
☐ B  $\text{NaClO}_2$   
☐ C  $\text{NaClO}_3$   
☐ D  $\text{NaClO}_4$

(Total for Question 2 = 1 mark)

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



**3** The standard reduction potential of the system

is  $E^{\ominus} = +0.15 \text{ V}$ .

- (a) What are the components of the half-cell required to measure the standard reduction potential of this system?

(1)

|                                   | Ion(s) in the solution                | Metal electrode |
|-----------------------------------|---------------------------------------|-----------------|
| <input type="checkbox"/> <b>A</b> | $\text{Sn}^{2+}$                      | tin             |
| <input type="checkbox"/> <b>B</b> | $\text{Sn}^{4+}$                      | tin             |
| <input type="checkbox"/> <b>C</b> | $\text{Sn}^{2+}$ and $\text{Sn}^{4+}$ | tin             |
| <input type="checkbox"/> <b>D</b> | $\text{Sn}^{2+}$ and $\text{Sn}^{4+}$ | platinum        |

- (b) A standard  $[\text{Sn}^{4+}(\text{aq})]$ ,  $[\text{Sn}^{2+}(\text{aq})]$  half cell is connected to a standard hydrogen electrode. At the hydrogen electrode

(1)

- ☐ **A** hydrogen gas is oxidized to hydrogen ions.  
☐ **B** hydrogen ions are oxidized to hydrogen gas.  
☐ **C** hydrogen gas is reduced to hydrogen ions.  
☐ **D** hydrogen ions are reduced to hydrogen gas.

(Total for Question 3 = 2 marks)

**4** In an ethanol / oxygen fuel cell, the ethanol is

- ☐ **A** oxidized at the positive electrode.  
☐ **B** oxidized at the negative electrode.  
☐ **C** reduced at the positive electrode.  
☐ **D** reduced at the negative electrode.

(Total for Question 4 = 1 mark)



5 The electronic configuration of the element chromium is

- ☐ A [Ar] 

|   |   |   |   |  |
|---|---|---|---|--|
| ↑ | ↑ | ↑ | ↑ |  |
|---|---|---|---|--|

|    |
|----|
| ↑↓ |
|----|
- ☐ B [Ar] 

|   |   |   |   |   |
|---|---|---|---|---|
| ↑ | ↑ | ↑ | ↑ | ↑ |
|---|---|---|---|---|

|   |
|---|
| ↑ |
|---|
- ☐ C [Ar] 

|    |    |  |  |  |
|----|----|--|--|--|
| ↑↓ | ↑↓ |  |  |  |
|----|----|--|--|--|

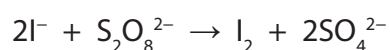
|    |
|----|
| ↑↓ |
|----|
- ☐ D [Ar] 

|    |    |   |  |  |
|----|----|---|--|--|
| ↑↓ | ↑↓ | ↑ |  |  |
|----|----|---|--|--|

|   |
|---|
| ↑ |
|---|

(Total for Question 5 = 1 mark)

6 Iodide ions are oxidized by peroxodisulfate ions in aqueous solution:



This reaction is catalysed by  $\text{Fe}^{3+}$  ions. The mechanism is most likely to involve

- ☐ A  $\text{I}^-$  reducing  $\text{Fe}^{3+}$  to an intermediate which is then oxidized by  $\text{S}_2\text{O}_8^{2-}$ .
- ☐ B  $\text{I}^-$  oxidizing  $\text{Fe}^{3+}$  to an intermediate which is then reduced by  $\text{S}_2\text{O}_8^{2-}$ .
- ☐ C  $\text{S}_2\text{O}_8^{2-}$  oxidizing  $\text{Fe}^{3+}$  to an intermediate which is then reduced by  $\text{I}^-$ .
- ☐ D  $\text{S}_2\text{O}_8^{2-}$  reducing  $\text{Fe}^{3+}$  to an intermediate which is then oxidized by  $\text{I}^-$ .

(Total for Question 6 = 1 mark)

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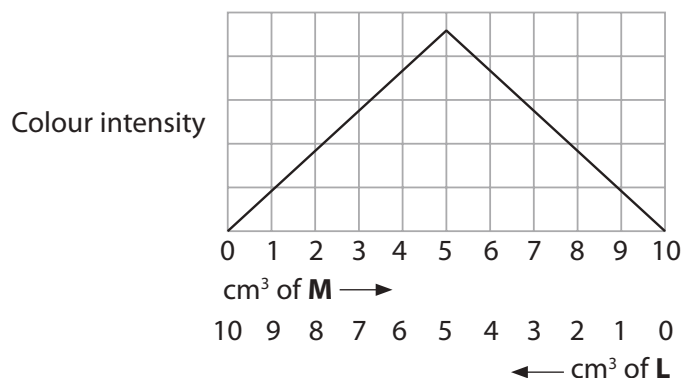


- 7 A transition metal ion, **M**, reacts with a complexing agent, **L**, to form a coloured complex with the formula **ML<sub>2</sub>**.

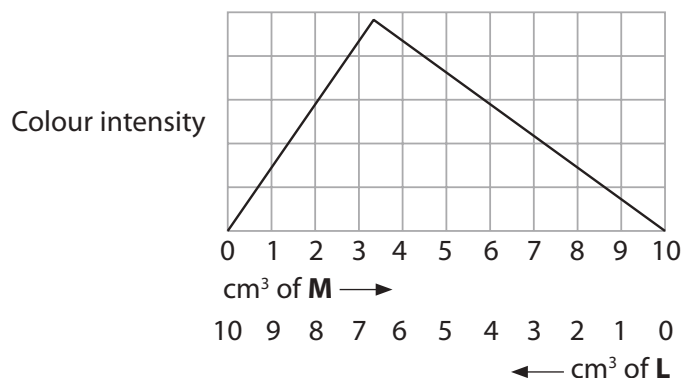
Portions of a  $0.05 \text{ mol dm}^{-3}$  solution of **M** were mixed with portions of a  $0.05 \text{ mol dm}^{-3}$  solution of **L**, so that the total volume of the resulting mixture was always  $10 \text{ cm}^3$ . The colour intensities of the complex in these mixtures were measured using a colorimeter.

What would the graph of the results look like?

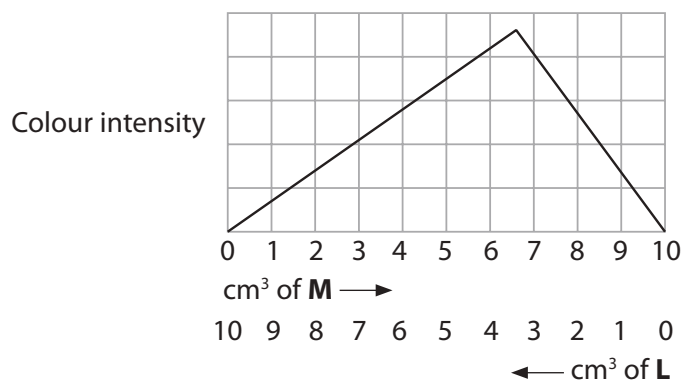
☒ A



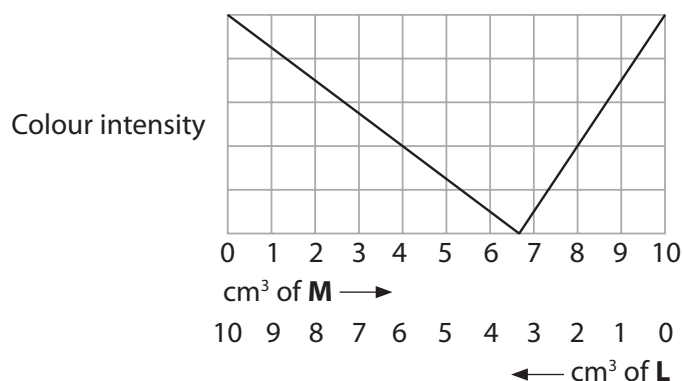
☒ B



☒ C



☒ D



(Total for Question 7 = 1 mark)



8 When concentrated hydrochloric acid is added to an aqueous solution of copper(II) sulfate, the blue solution changes to green then yellow. The change in colour is due to

- ☐ A the formation of chlorine in the solution.
- ☐ B the gradual replacement of the sulfate ion ligands by chloride ions.
- ☐ C the gradual replacement of the water ligands by chloride ions.
- ☐ D the reduction of the copper(II) ions to copper(I) ions.

(Total for Question 8 = 1 mark)

9 Dilute hydrochloric acid and dilute aqueous sodium hydroxide are added in excess to separate samples of chromium(III) hydroxide. What would be observed?

|                            | Addition of HCl(aq) | Addition of NaOH(aq) |
|----------------------------|---------------------|----------------------|
| <input type="checkbox"/> A | green solution      | green solution       |
| <input type="checkbox"/> B | green solution      | green solid          |
| <input type="checkbox"/> C | green solid         | green solution       |
| <input type="checkbox"/> D | green solid         | green solid          |

(Total for Question 9 = 1 mark)

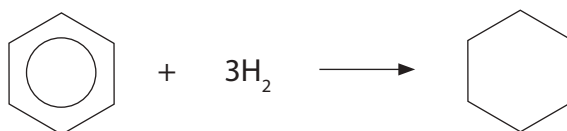
10 The reaction between hydrogen and benzene is normally very slow but it speeds up in the presence of finely divided nickel. The nickel

- ☐ A acts as a homogeneous catalyst by acting as an electron pair acceptor in the formation of an electrophile.
- ☐ B acts as a homogeneous catalyst by acting as an electron pair donor in the formation of an electrophile.
- ☐ C acts as a heterogeneous catalyst by providing active sites on which the reaction occurs.
- ☐ D reacts with the hydrogen to form nickel(II) hydride which then reacts with the benzene.

(Total for Question 10 = 1 mark)



11 When the enthalpy change for the hydrogenation of benzene to cyclohexane



is compared to the calculated enthalpy change for the hydrogenation of the theoretical compound cyclohexa-1,3,5-triene to cyclohexane, benzene is calculated to have a stabilization energy of  $150 \text{ kJ mol}^{-1}$ . This means that

- ☐ A the enthalpy change for the hydrogenation of benzene is  $+150 \text{ kJ mol}^{-1}$ .
- ☐ B the enthalpy change for the hydrogenation of benzene is  $-150 \text{ kJ mol}^{-1}$ .
- ☐ C the enthalpy change for the conversion of benzene to cyclohexa-1,3,5-triene is  $+150 \text{ kJ mol}^{-1}$ .
- ☐ D the enthalpy change for the conversion of benzene to cyclohexa-1,3,5-triene is  $-150 \text{ kJ mol}^{-1}$ .

(Total for Question 11 = 1 mark)

12 Nitrobenzene is prepared by heating benzene and a mixture of concentrated nitric and sulfuric acids under reflux at  $55^\circ\text{C}$ . If the temperature rises above  $55^\circ\text{C}$ , the yield of nitrobenzene is reduced. This is because, at temperatures above  $55^\circ\text{C}$ , the

- ☐ A benzene evaporates.
- ☐ B nitrating mixture decomposes.
- ☐ C nitrobenzene reacts to form benzenesulfonic acid.
- ☐ D nitrobenzene reacts to form dinitrobenzene.

(Total for Question 12 = 1 mark)

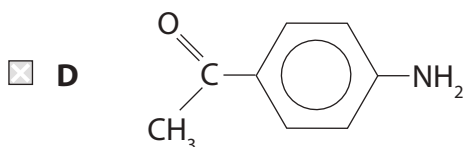
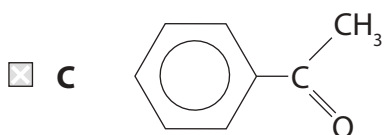
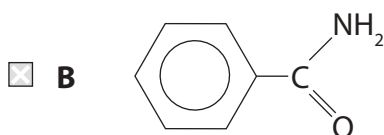
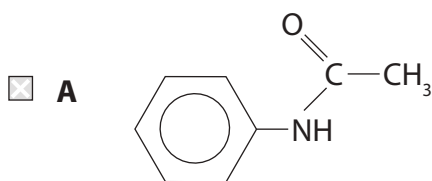
13 Dilute sulfuric acid was added to a sample of phenylamine until the reaction was just complete. The resulting mixture was poured onto a watch-glass and allowed to stand in a warm place for about 24 hours. At the end of this time, the watch-glass contained

- ☐ A no residue.
- ☐ B a liquid inorganic residue.
- ☐ C a liquid organic residue.
- ☐ D a white solid.

(Total for Question 13 = 1 mark)



14 When ethanoyl chloride is added to phenylamine at room temperature, the main organic product of the reaction is



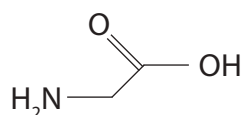
(Total for Question 14 = 1 mark)

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15 Glycine (2-aminoethanoic acid) is the simplest amino acid. The structure of glycine is



Which of the following is **not** true about glycine?

- ☐ A Glycine is a white crystalline solid at room temperature.
- ☐ B A glycine molecule is non-superimposable on its mirror image.
- ☐ C Glycine reacts with ninhydrin to form a purple compound.
- ☐ D Glycine molecules form condensation polymers with other amino acids.

(Total for Question 15 = 1 mark)

16 The mass spectrum of a compound, **Z**, has a peak at  $m/e = 43$ . Which of the following could **not** be **Z**?

- ☐ A  $\text{CH}_3\text{COCH}_2\text{CH}_3$
- ☐ B  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
- ☐ C  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$
- ☐ D  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

(Total for Question 16 = 1 mark)

17 The low resolution proton nmr spectrum of a compound contains only two peaks. The compound could be

- ☐ A butan-1-ol
- ☐ B butan-2-ol
- ☐ C 2-methylpropan-1-ol
- ☐ D 2-methylpropan-2-ol

(Total for Question 17 = 1 mark)



18 A compound, **G**, has the following properties:

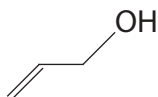
**G** reacts with phosphorus(V) chloride to form hydrogen chloride.

**G** reacts by addition with hydrogen in the presence of a nickel catalyst.

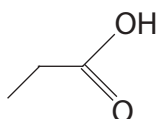
**G** reacts with sodium hydroxide to form an ionic solid.

Compound **G** could be

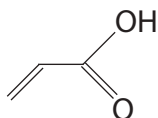
☐ **A**



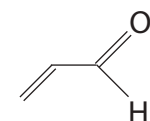
☐ **B**



☐ **C**



☐ **D**



(Total for Question 18 = 1 mark)

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



**19** In the first stage of the synthesis of methyl 3-nitrobenzoate, methyl benzoate,  $\text{C}_6\text{H}_5\text{COOCH}_3$ , is prepared by the reaction of benzoic acid with methanol in the presence of concentrated sulfuric acid. When the reaction is complete, the sulfuric acid is neutralized by the addition of aqueous sodium carbonate. The simplest way of obtaining the impure methyl benzoate from this mixture will be

- ☐ **A** refluxing.
- ☐ **B** solvent extraction.
- ☐ **C** filtration.
- ☐ **D** recrystallization.

(Total for Question 19 = 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.

20 The table below shows some ions of vanadium that are stable in aqueous solution.

| Ion              | Oxidation number of vanadium | Colour in aqueous solution |
|------------------|------------------------------|----------------------------|
| $V(H_2O)_6^{2+}$ |                              | violet                     |
| $V(H_2O)_6^{3+}$ |                              | green                      |
| $VO^{2+}$        |                              | blue                       |
| $VO_2^+$         | +5                           | yellow                     |

(a) (i) Complete the table above by adding the missing oxidation numbers.

(1)

(ii) Complete the electronic configuration of the element vanadium and hence explain the highest oxidation number shown by vanadium.

(2)

Electronic configuration of the element vanadium:

[Ar] .....

Explanation of the highest oxidation number

.....  
.....  
.....



\*(iii) Explain why  $V(H_2O)_6^{3+}$  is coloured.

(4)

(iv) Suggest why the +5 oxidation state of vanadium exists as  $VO_2^+$  in aqueous solution, rather than  $V(H_2O)_6^{5+}$ .

(2)

(v) If  $V(H_2O)_6^{5+}$  did exist in aqueous solution, would it be coloured? Explain your answer.

(1)



- (b) (i) Sulfur dioxide dissolves in water to form sulfuric(IV) acid,  $\text{H}_2\text{SO}_3$ .

Determine the feasibility of using sulfur dioxide dissolved in water to reduce  $\text{VO}^{2+}(\text{aq})$  to  $\text{V}^{3+}(\text{aq})$ . Quote the relevant half equations and standard electrode potentials from page 15 of the Data Booklet and write the overall equation for the reaction.

(3)

- (ii) Write an ionic equation for the disproportionation of vanadium in oxidation state +3 to vanadium in oxidation states +2 and +4.

(1)

- (iii) Calculate the  $E_{\text{cell}}$  for this disproportionation and hence determine its feasibility.

(2)

(Total for Question 20 = 16 marks)



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- 21** Limestone is an important industrial raw material. The chemically important component of limestone is calcium carbonate and the proportion of this compound determines the quality of the material.

One method of determining the proportion of calcium carbonate in limestone involves dissolving the limestone in acid and precipitating the calcium ions as calcium ethanedioate. The precipitate is filtered and then re-dissolved in dilute sulfuric acid. The concentration of ethanedioate ions is determined by titration with a solution of potassium manganate(VII) of known concentration.

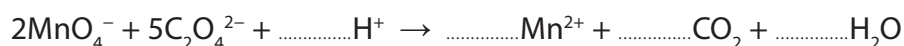
In one such determination, 1.77 g of limestone produced 250 cm<sup>3</sup> of calcium ethanedioate solution and 25.0 cm<sup>3</sup> samples of this solution were titrated at about 70 °C with potassium manganate(VII) solution of concentration 0.0205 mol dm<sup>-3</sup>. The mean titre was 24.55 cm<sup>3</sup>.

- (a) (i) State the appearance of the titration mixture at the end-point.

(1)

- (ii) Complete the ionic equation for this titration.

(1)



- \*(iii) Calculate the percentage by mass of calcium carbonate in the limestone.  
Show your working and give your final answer to **three** significant figures.

(5)



- (b) (i) Before the calcium ethanedioate is re-dissolved, it is washed in deionized or distilled water. Explain why this step is necessary and the effect its omission would have on the titration.

(2)

.....

.....

.....

.....

.....

- (ii) The table below summarises the tolerances on the measuring apparatus used in this experiment.

Complete the table by calculating the percentage error for each piece of apparatus to **two** significant figures.

(2)

| Apparatus        | Value                 | Maximum total error on the stated value | Percentage error on the stated value |
|------------------|-----------------------|---|--------------------------------------|
| Balance          | 1.77 g                | $\pm 0.01$ g                            |                                      |
| Volumetric flask | 250 cm <sup>3</sup>   | $\pm 0.12$ cm <sup>3</sup>              |                                      |
| Pipette          | 25 cm <sup>3</sup>    | $\pm 0.06$ cm <sup>3</sup>              |                                      |
| Burette          | 24.55 cm <sup>3</sup> | $\pm 0.10$ cm <sup>3</sup>              |                                      |



- (iii) Using the method in (a), it was found that 2.00 g of a **different** sample of limestone contained 0.015 mol of calcium carbonate.

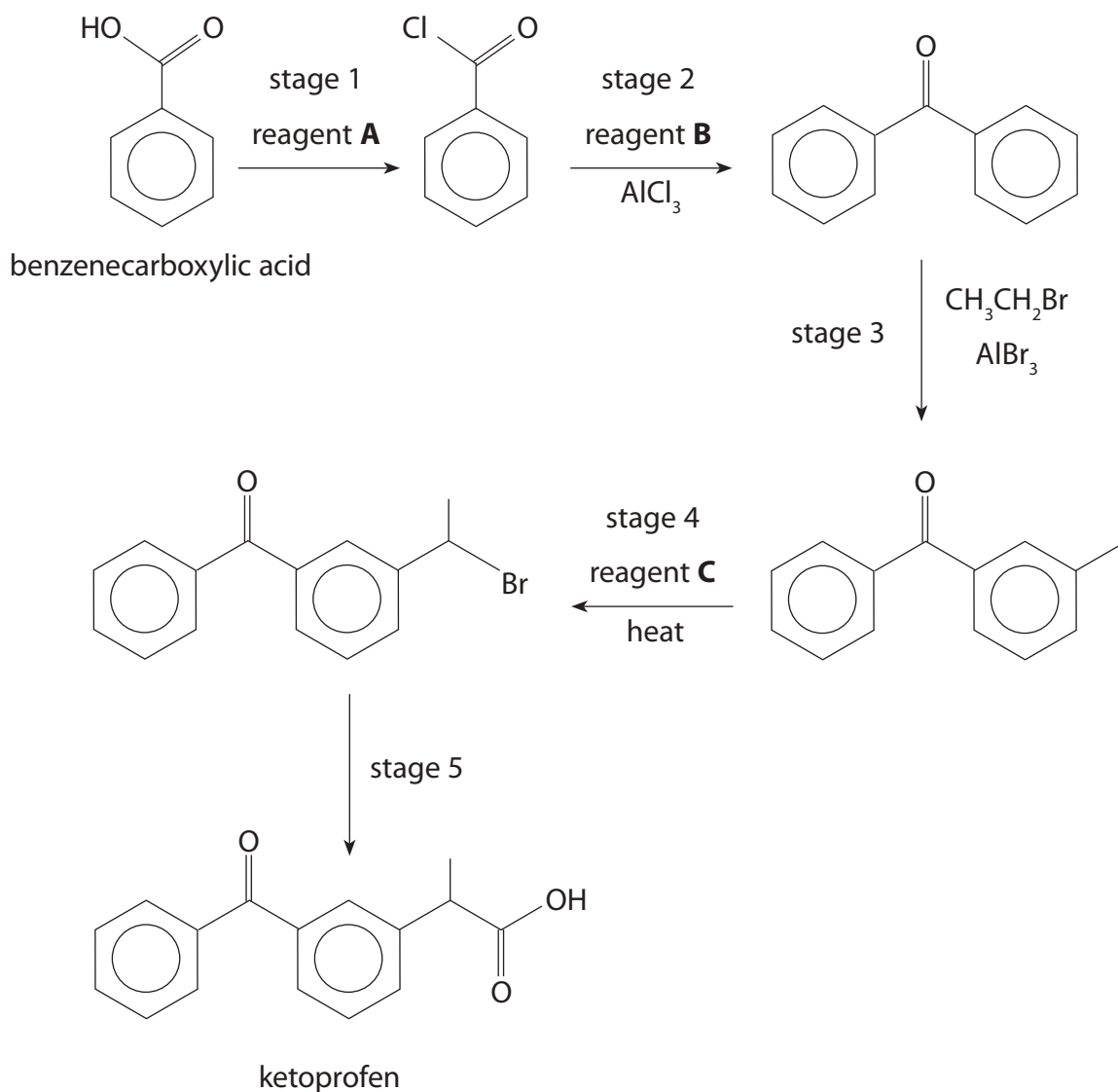
Use the data from (b)(ii), and the fact that the solubility of calcium ethanedioate in water is  $0.0067 \text{ g dm}^{-3}$ , to calculate whether the fact that some calcium ethanedioate remains in solution has a significant effect on the accuracy of this **second** calcium carbonate determination. Assume that the combined volume of the filtrate and the washings is approximately  $500 \text{ cm}^3$ .

(3)

(Total for Question 21 = 14 marks)



**22** Ketoprofen is an analgesic used in the treatment of arthritis-related inflammatory pains. A synthesis of ketoprofen from benzenecarboxylic acid is shown below.



(a) Identify reagents **A**, **B** and **C** by name or formula.

(3)

**A** .....

**B** .....

**C** .....



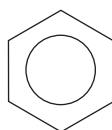
(b) Stage 3 is an electrophilic substitution.

- (i) Write an equation for the formation of the electrophile and explain the role of the  $\text{AlBr}_3$  in this process.

(2)

- (ii) Complete the mechanism for the electrophilic substitution in stage 3. You need only show the benzene ring on the right of the structure. This is given below.

(3)



- (c) The first step of stage 5 of the synthesis is the addition of a carbon atom to the chain. One way of achieving this is to replace the bromine atom with a nitrile group in a nucleophilic substitution.
- (i) Suggest the name or formula of a reagent that could be used in this nucleophilic substitution. Suggest a suitable solvent in which to carry out the reaction.

(2)

- (ii) The second step of stage 5 is the conversion of the nitrile into ketoprofen. State the reagent or reagents required.

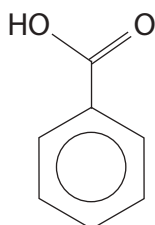
(1)



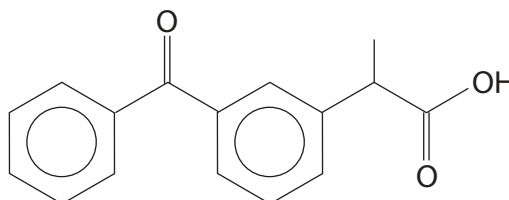
(d) Benzenecarboxylic acid and ketoprofen have different infrared spectra.

- (i) In the diagram below, insert in the boxes the wavenumber **ranges** for the infrared absorptions due to C=O groups in benzenecarboxylic acid and ketoprofen.

(3)



benzenecarboxylic  
acid



ketoprofen

- (ii) Explain how these absorptions can be used to distinguish between the two compounds.

(1)

.....

.....

.....

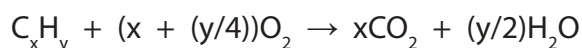
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(Total for Question 22 = 15 marks)



- 23** 10 cm<sup>3</sup> of a gaseous hydrocarbon, C<sub>x</sub>H<sub>y</sub>, was mixed with excess oxygen and ignited. The total gas volume was measured at room temperature and pressure before and after combustion, and it was found that it had contracted by 20 cm<sup>3</sup>. On shaking the remaining gases with excess potassium hydroxide solution, the total gas volume contracted by a further 40 cm<sup>3</sup>.

The equation for the complete combustion of C<sub>x</sub>H<sub>y</sub> is



- (a) Explain why the volume of gas contracts after combustion.

(1)

- (b) Explain why the volume of gas contracts after shaking with excess potassium hydroxide.

(1)

- (c) Calculate the molecular formula of C<sub>x</sub>H<sub>y</sub>.

(3)

(Total for Question 23 = 5 marks)

TOTAL FOR SECTION B = 50 MARKS





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P 4 2 9 7 9 A 0 2 5 3 2

## SECTION C

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

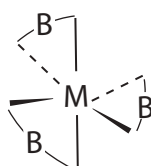
24

**Stereoisomerism**

Stereoisomerism occurs when species have the same formula and their atoms are bonded in the same sequence, but the spatial orientation of the atoms is different. Stereoisomers that are non-superimposable mirror images are optical isomers, or enantiomers. These have identical chemical and physical properties, apart from their effect on plane-polarized light. Optical isomerism arises most simply when a tetrahedral atom has four different groups bonded to it, but the presence of such a system does not necessarily result in an optical isomer.

Stereoisomers that are not enantiomers are called diastereoisomers. Complex optically active species can be diastereoisomers, but a more familiar example is found with geometric isomers. In organic chemistry, geometric isomerism may arise when there is an energetic barrier to free rotation. Restricted rotation occurs with double bonds, because a  $\pi$  bond is formed by the *lateral* overlap of p orbitals, and also with cyclic compounds. Diastereoisomers have different physical properties and can be separated by conventional techniques.

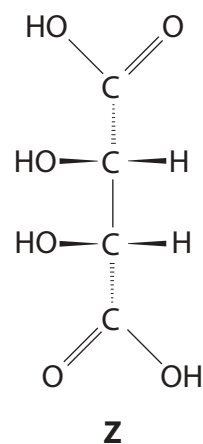
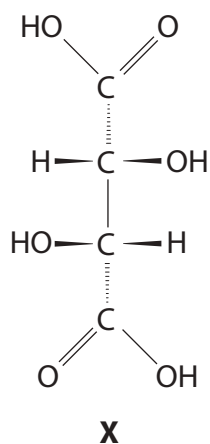
Stereoisomerism is not confined to organic chemistry. Inorganic compounds may also show stereoisomerism and it is a particular feature of transition metal complexes. The simplest geometric isomers in transition metal complexes occur in square planar complexes  $ML_2N_2$  and octahedral complexes  $ML_4N_2$ , where M is the metal ion and L and N are ligands. Geometric isomerism also occurs with octahedral complexes of the type  $ML_3N_3$ . The most important optical isomers of transition metals are octahedral complexes of the type  $MB_3$  where B is a bidentate ligand; the structure of an enantiomer of  $MB_3$  is shown below. The stability of complexes with polydentate ligands makes them easier to prepare.



Because many biochemical reactions are stereospecific, stereoisomerism is of great importance in the pharmaceutical industry. Wherever possible, the industry aims to synthesize specific isomers.



- (a) 2,3-dihydroxybutanedioic acid (tartaric acid) exists in three isomeric structures, **X**, **Y** and **Z**, two of which are shown below.



Isomer **X** occurs in many plants including grapes, bananas and tamarinds.

- (i) Circle the chiral centres of isomer **X** on the diagram.

(1)

- (ii) Draw the structure of isomer **Y**, which is an enantiomer of **X**.

(1)



(iii) How can plane-polarized light be used to distinguish the enantiomers **X** and **Y**?

(2)

(iv) Suggest, with a reason, whether or not nuclear magnetic resonance could be used to distinguish between the enantiomers **X** and **Y**.

(1)

(v) An important use of **X** is in the preparation of other chiral molecules. One example is the substitution of the alcohol groups by bromine atoms.

State and explain what may be deduced about the mechanism of this reaction if the product is also chiral.

(2)



(vi) Isomer **Z** is a diastereoisomer. Suggest why it is not an optical isomer, even though it has two asymmetric carbon atoms.

(1)

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(b) (i) Suggest why the lateral overlap that forms a  $\pi$  bond results in a barrier to free rotation about a carbon-carbon double bond.

(2)

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(ii) Draw the geometric isomers of 1,2-dichlorocyclohexane.

(1)



(c) Cisplatin,  $[\text{PtCl}_2(\text{NH}_3)_2]$ , is an example of a stereospecific anti-cancer drug.

(i) Draw the structure of cisplatin and its geometric isomer.

(1)

(ii) Explain the term 'stereospecific drug'.

(1)

\*(iii) Suggest **three** reasons why the pharmaceutical industry prefers to use stereospecific synthetic routes.

(3)



(d) The ethanedioate ion,  $\text{C}_2\text{O}_4^{2-}$ , is an example of a bidentate ligand.

(i) Explain the term 'bidentate ligand'.

(1)

(ii) Explain why the complexes formed with bidentate ligands are generally more stable than those with monodentate ligands.

(1)

(iii) The complex,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , exists as two enantiomers. Use the information in the passage to draw the two enantiomers.

(2)

(Total for Question 24 = 20 marks)

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



# The Periodic Table of Elements

[illegible]