Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE
NAME

CENTRE
NUMBER

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CHEMISTRY (PRINCIPAL) **9791/03**

Paper 3 Part B Written **May/June 2015**

2 hours 15 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not include appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or
part question.

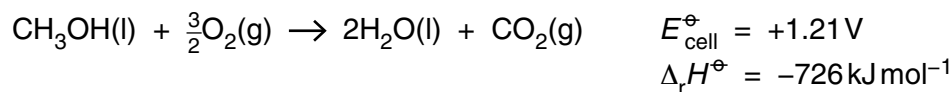| **For Examiner's Use**	
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3	
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6	
Total	

This document consists of **19** printed pages and **1** blank page.

CAMBRIDGE
International Examinations

[Turn over

1 The direct methanol fuel cell, DMFC, is a fuel cell that uses methanol.

The overall reaction that takes place in this fuel cell is shown.

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) \rightarrow 2H_2O(l) + CO_2(g) \qquad E^{\ominus}_{cell} = +1.21V$$
$$\Delta_r H^{\ominus} = -726 \, kJ \, mol^{-1}$$

(a) The half-equation for one electrode reaction in the DMFC is shown.

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E^{\ominus} = +1.23V$$
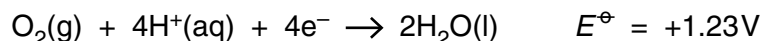
(i) State and explain, with reference to the redox process occurring, at which electrode in the DMFC this reaction occurs.

....

....

....[2]

(ii) Assuming that a platinum electrode is used and that this electrode is on the right-hand side of a conventional cell diagram, draw the **half-cell** diagram for this electrode.

....[2]

(iii) Calculate the standard electrode potential, $E^{\ominus}$, at the other electrode in the DMFC. Include a sign in your answer.

$E^{\ominus}$ = ... V [1]

(iv) Write the half-equation for the reaction that occurs at the other electrode in the DMFC.

....[1]

(b) (i) Use the appropriate equation in the *Data Booklet* to calculate the cell free energy change, $\Delta G^{\ominus}$, in $kJ \, mol^{-1}$, for the overall reaction occurring in the DMFC.

$\Delta G^{\ominus}$ = ... $kJ \, mol^{-1}$ [2]

(ii) Comment on the significance of your answer to **(b)(i)** in terms of the feasibility of the overall reaction.

....

....[1]

(iii) Use the appropriate equation in the *Data Booklet* to calculate the standard entropy change of reaction, $\Delta S^{\ominus}$, for the overall reaction occurring in the DMFC. Give the units of your answer.

$\Delta S^{\ominus}$ = ...

units ....

[3]

(iv) Use the appropriate equation in the *Data Booklet* to calculate the temperature, T, at which $\Delta G^{\ominus}$, for the overall reaction occurring in the DMFC, is zero.

Explain the significance of this temperature.

Assume that $\Delta_r H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature.

T = ... K

....

....

[2]

[Total: 14]

2 (a) The atomic radii of five elements across Period 4 are shown.

Period 4 element	K	Ca	Ga	Ge	As
atomic radius / nm	0.203	0.174	0.125	0.122	0.121

(i) Explain why these values decrease across the period.

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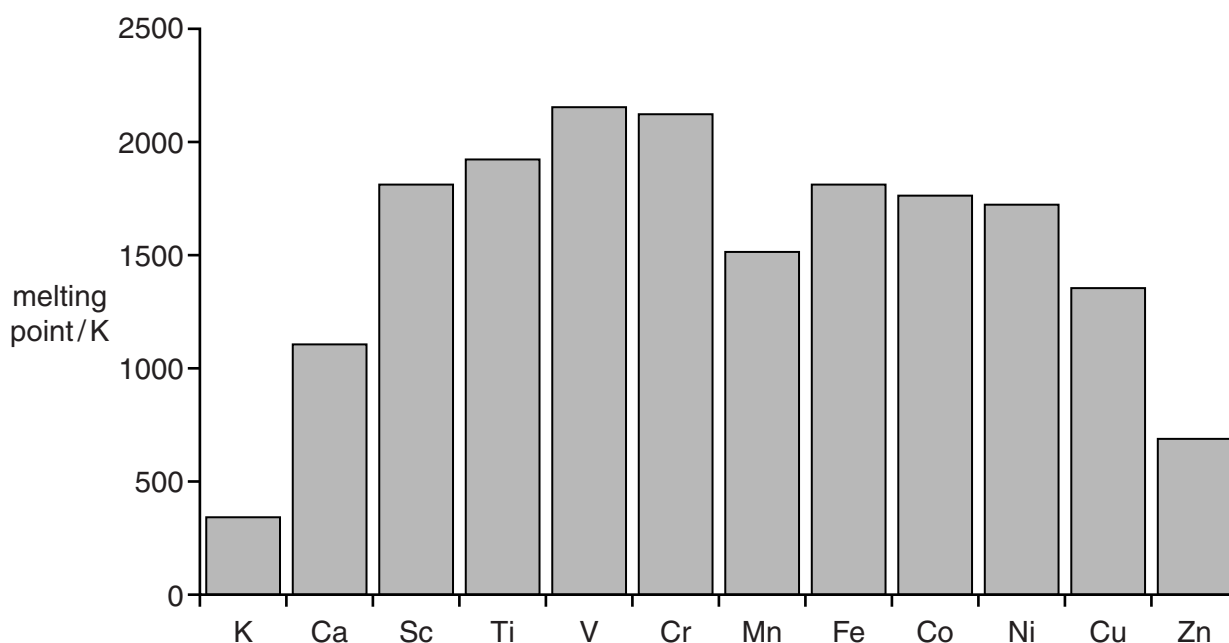...[2]

(ii) State how the pattern of atomic radii across the first transition series compares with the trend shown above.

....

....[1]

(b) The bar chart shows the melting points of the elements in Period 4 from potassium, K, to zinc, Zn.

(i) The melting points of the transition elements are, in general, higher than those of potassium and calcium, due to the stronger metallic bonding.

Explain why the metallic bonding is stronger in the transition elements.

....

....[1]

5

   (ii) Suggest why nickel has a lower melting point than vanadium.

   ....

   ....[1]

(c) The diagram shows the relative energies of each of the 3d orbitals of an isolated transition metal ion and of a transition metal ion within an octahedral complex.

increasing energy

$3d_{xy}$ $\quad$ $3d_{xz}$ $\quad$ $3d_{yz}$ $\quad$ $3d_{z^2}$ $\quad$ $3d_{x^2-y^2}$

isolated transition metal ion

transition metal ion in an octahedral complex
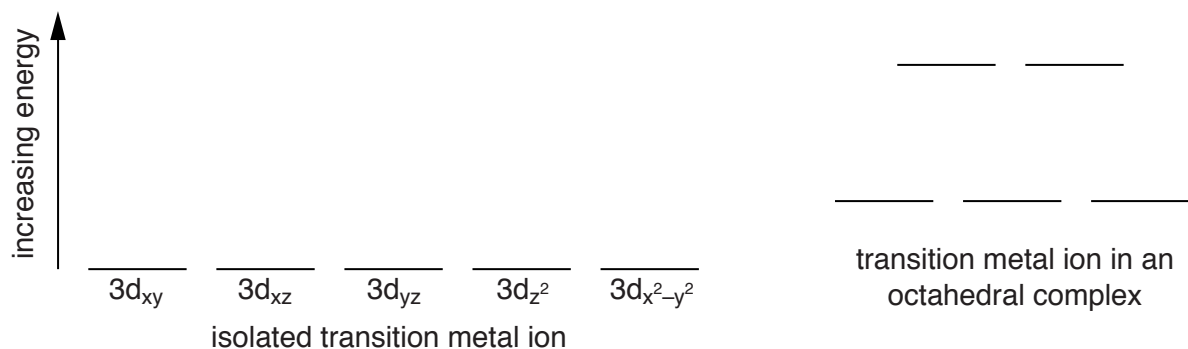
   (i) Complete the diagram by labelling the orbitals on the right of the diagram. [1]

   (ii) With reference to the orientation of the atomic orbitals explain why the orbitals are split as shown in the diagram.
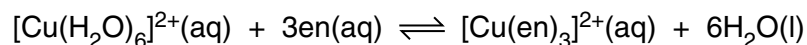
   ....

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   ....[3]

   (iii) Use the diagram to explain why the complexes of some transition metal ions are coloured.

   ....

   ....

   ....

   ....

   ....[3]

(d) The ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, is commonly abbreviated to 'en' in complexes and reacts with hexaaquacopper(II) ions as shown.

$$[Cu(H_2O)_6]^{2+}(aq) \; + \; 3en(aq) \; \rightleftharpoons \; [Cu(en)_3]^{2+}(aq) \; + \; 6H_2O(l)$$

The equilibrium constant for this reaction has a value of approximately 5×10^{18} at 298 K.

(i) State, and explain in terms of entropy change, the significance of the value of the equilibrium constant.

....

....

....

....[2]

(ii) State the type of isomerism shown by the $[Cu(en)_3]^{2+}$ ion.

....[1]

(iii) Explain why this complex ion exhibits this type of isomerism.

....

....[1]

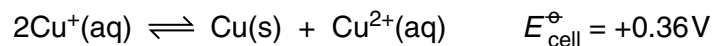**(iv)** Draw diagrams of the three-dimensional structures of the isomers of $[Cu(en)_3]^{2+}$.

[2]

[Total: 18]

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3 Copper(I) salts in aqueous solution are unstable as shown by the equation.

$$2Cu^+(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq) \qquad E^{\ominus}_{cell} = +0.36\,V$$

(a) Describe the essential components of, and conditions in, the cell that are necessary for this $E^{\ominus}_{cell}$ to be recorded.

....

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....

....[4]

(b) With reference to the equation, explain the meaning of the term *disproportionation*.

....

....[1]

(c) (i) Give the expression for the equilibrium constant, K_c, for this equilibrium.

$K_c =$

[1]

(ii) Combining equations from the *Data Booklet* gives the following relationship.

$$\ln K = \frac{nFE^{\ominus}_{cell}}{RT}$$

Calculate the value of the equilibrium constant, K_c, at 298 K for the equilibrium shown.

$K_c =$ ....[2]

(iii) Calculate the concentration of $Cu^+(aq)$ that would be present under standard conditions in a solution containing $1.00\,mol\,dm^{-3}$ $Cu^{2+}(aq)$ in contact with solid copper.
Give your answer to **three** significant figures.

$[Cu^+(aq)]$ = ... $mol\,dm^{-3}$ [2]

(d) The solubility product, K_{sp}, for copper(I) bromide, CuBr, has a value of 3.20×10^{-8} at $298\,K$.

Give the expression for the solubility product K_{sp} for copper(I) bromide, CuBr.
Use the expression to calculate the minimum concentration of bromide ions needed to precipitate CuBr from a solution containing a $Cu^+(aq)$ concentration of $5.72 \times 10^{-7}\,mol\,dm^{-3}$.

K_{sp} =

$[Br^-(aq)]$ = ... $mol\,dm^{-3}$ [2]

[Total: 12]

4 The concept of functional group level can be used to help explain many organic interconversions.

(a) Acyl chlorides, esters and amides all belong to the same functional group level.

(i) What is the **name** of this functional group level?

....[1]

(ii) Propanoyl chloride, CH_3CH_2COCl, can be synthesised from carbon dioxide and the Grignard reagent CH_3CH_2MgBr, in three steps.

Write a balanced equation for each step and state what happens to the functional group level in each step.
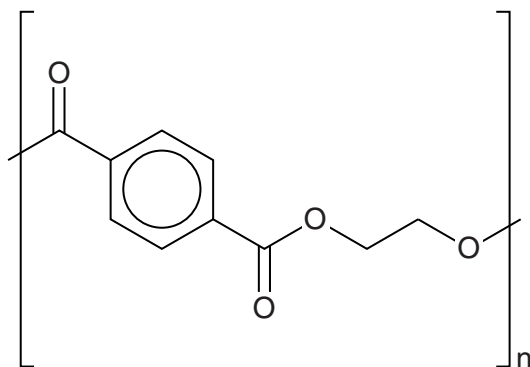
step 1 ....

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step 2 ....

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step 3 ....

....[4]
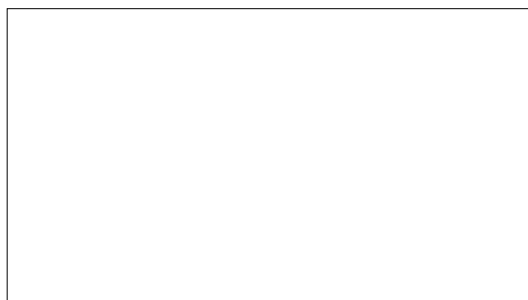
(b) Mylar is a polymer film used in thermal blankets for space travel. The functional groups in Mylar react in very similar ways to the same functional groups in simple molecules. The structure of Mylar is shown.

(i) Other than the benzene ring, name the functional group present in Mylar.

....[1]

(ii) Give the structural formulae of the two monomers from which Mylar could be made.

[2]

(iii) What type of reaction occurs when Mylar reacts with aqueous alkali?

....[1]

(iv) Give the structures of the products of the reaction of Mylar with aqueous alkali.

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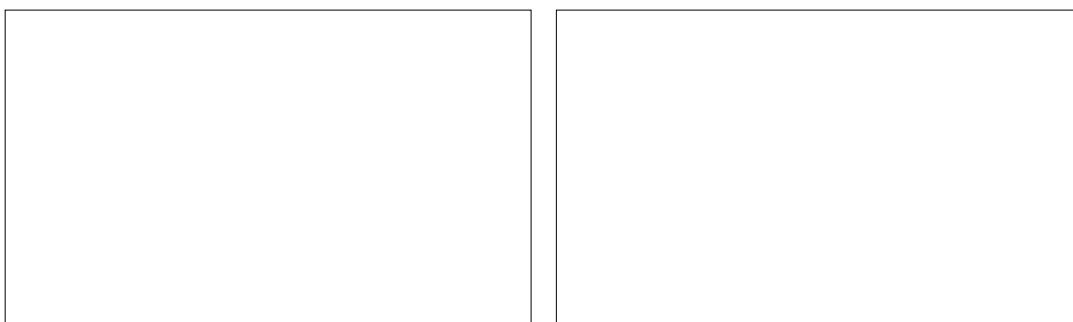<tr><td>

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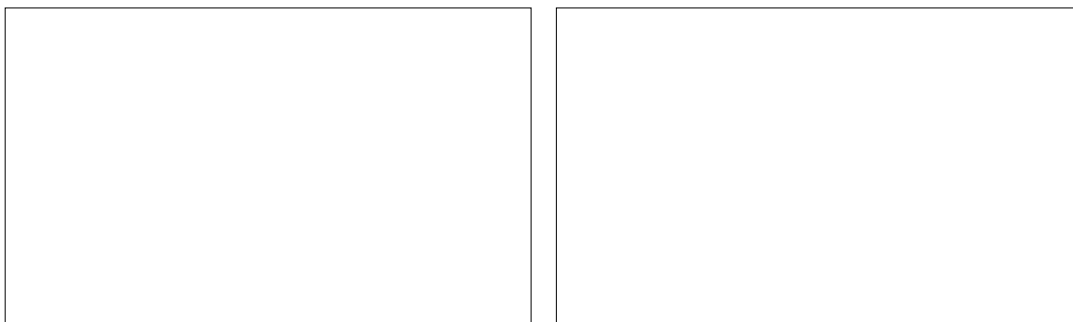
[2]

(v) What type of reaction occurs when Mylar reacts with LiAlH$_4$?

....[1]

(vi) Give the structures of the products of the reaction of Mylar with LiAlH$_4$.

<table>
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[2]

(c) The benzene ring in Mylar could be brominated under suitable conditions.

(i) Give the name of the mechanism of bromination of a benzene ring.

....[1]

(ii) Suggest the nature of the catalyst needed for this bromination reaction.

....[1]

(iii) State and explain how the ease of bromination of the benzene ring in Mylar would compare with the ease of bromination of benzene.

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....

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....[3]

[Total: 19]

5 Chirality is an important feature of many molecules involved in biochemical systems.

(a) In aqueous acid, one molecule of sucrose is hydrolysed into one molecule of glucose and one molecule of fructose. The enantiomer of glucose formed rotates polarised light clockwise whilst the enantiomer of fructose rotates polarised light anticlockwise. A series of measurements of the angle of rotation, α, was made during a study of this reaction.

time, t/min	0	4	12	18	24	42	48	61	86	95	∞
rotation, α_t/°	78.0	65.1	44.6	32.4	22.5	2.3	−2.0	−9.0	−15.8	−17.3	−20.0

(i) Suggest why the rotation, α_t, reduces and eventually switches from clockwise to anti-clockwise.

....

....[1]

(ii) The rate equation for this hydrolysis is of the form

$$\text{rate} = k[\text{sucrose}]^a[H_2O]^b[H^+]^c$$

and the conditions of this reaction are chosen such that the water and acid are in large excess, so that their concentrations can be assumed to be constant. Hence

$$\text{rate} = k'\,[\text{sucrose}]^a$$

A graph was plotted of $\ln\left[\dfrac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}\right]$ vs time,

where the term $\alpha_t - \alpha_\infty$ is proportional to the concentration of sucrose at each time, t, and the term $\alpha_0 - \alpha_\infty$ is proportional to the initial concentration of the sucrose.
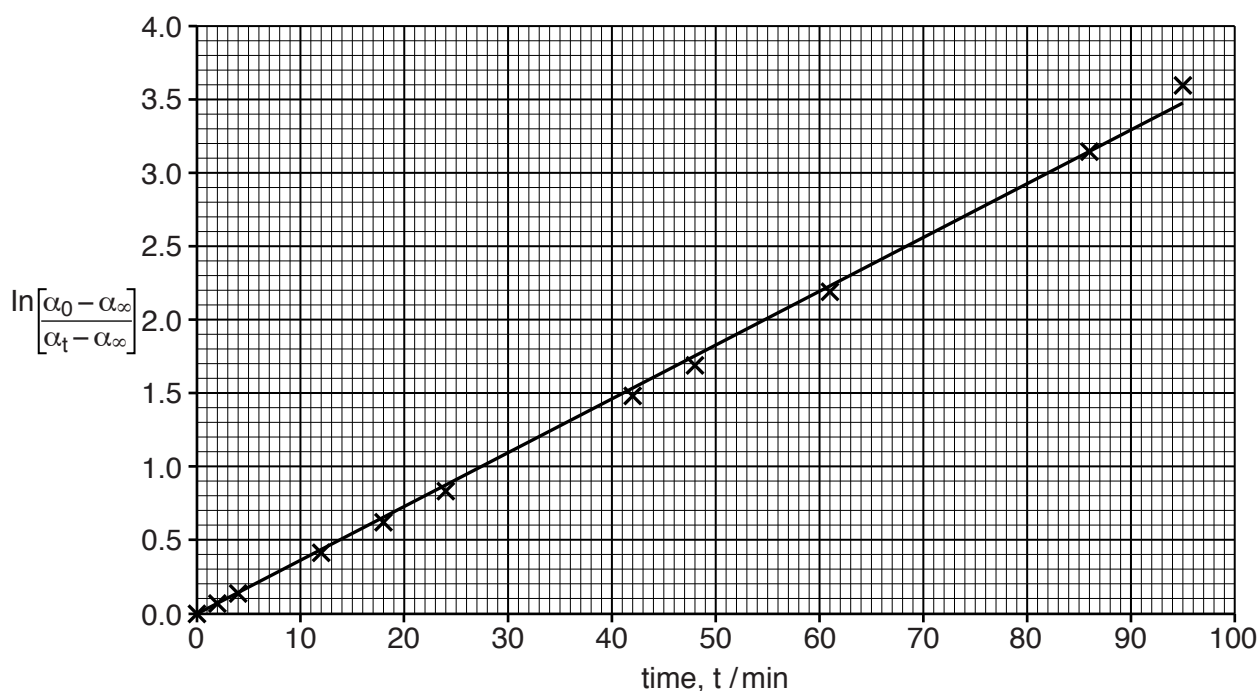
Using the appropriate equation in the *Data Booklet*, state and explain what conclusion can be drawn from the shape of this graph.

....[Turn........

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....

....[3]

(iii) Use the graph to calculate the value of the effective rate constant, k'. Show your working, including suitable annotations on the graph. Give the units of k'.

k' = ... [3]

value   units

(b) Fumarase catalyses the reversible hydration of *trans*-butenedioate, $^-OOCCH=CHCOO^-$, to form (S)-2-hydroxybutanedioate, $^-OOCCH_2CH(OH)COO^-$.

Like many enzymes fumarase is both stereospecific (only catalysing the reaction of one stereoisomer) and stereoselective (only forming a single stereoisomer).

(i) State the feature of fumarase that gives it its stereospecific and stereoselective properties.

....

....[1]

(ii) Write an equation for the hydration of butenedioate.

....[1]

(iii) Draw the two stereoisomers of butenedioate, labelling them clearly to show which is which.
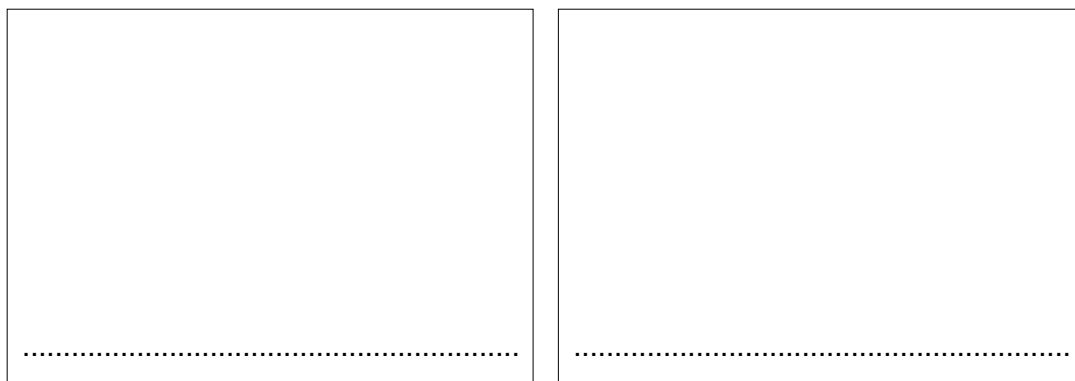
....   [2]

(iv) Draw three-dimensional structures of the two stereoisomers of 2-hydroxybutanedioate labelling them and explaining clearly which is which.

....	....

explanation ....

....

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....[4]

(v) The hydration of *trans*-butenedioate can also be catalysed by aqueous acid, $H^+(aq)$.

State and explain the optical characteristics of the product of this reaction when catalysed by aqueous acid.
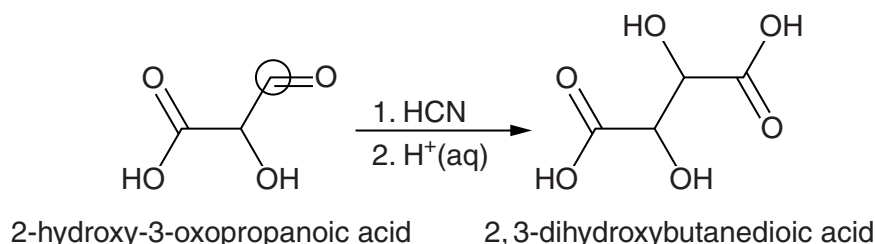
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....[2]

(c) (2*R*,3*R*)-2,3-dihydroxybutanedioic acid is one of the main acids found in wine and occurs naturally in many plants.

Reacting an equimolar mixture of (*R*)- and (*S*)- 2-hydroxy-3-oxopropanoic acid with hydrogen cyanide, followed by acid hydrolysis, produces 2,3-dihydroxybutanedioic acid.

2-hydroxy-3-oxopropanoic acid   2,3-dihydroxybutanedioic acid

(i) Explain why the *R* and *S* configurations are equally likely to be produced at carbon-3 (circled) during the reaction of 2-hydroxy-3-oxopropanoic acid with hydrogen cyanide.

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....

....[2]

(ii) As 2,3-dihydroxybutanedioic acid contains two chiral centres it might be expected that four optical isomers would be produced (2*R*,3*S*; 2*R*,3*R*; 2*S*,3*S*; and 2*S*,3*R*), but only three different molecules are actually formed.

Identify which pair of molecules are superimposable.

What feature of the molecules makes them superimposable?

What term is given to this form of the product?

....

....

....

....

....[3]

[Total: 22]

6 ^{1}H NMR and IR are important analytical tools in organic chemistry.

(a) Six of the structural isomers with molecular formula $C_4H_8O_2$ are carboxylic acids or esters.

The ^{1}H NMR and IR spectra for two of these isomers, **P** and **Q**, are shown.

Draw a displayed formula for each of **P** and **Q** and explain clearly the interpretation of the key features of each spectrum in terms of the structures of these isomers.

(i) Isomer **P**
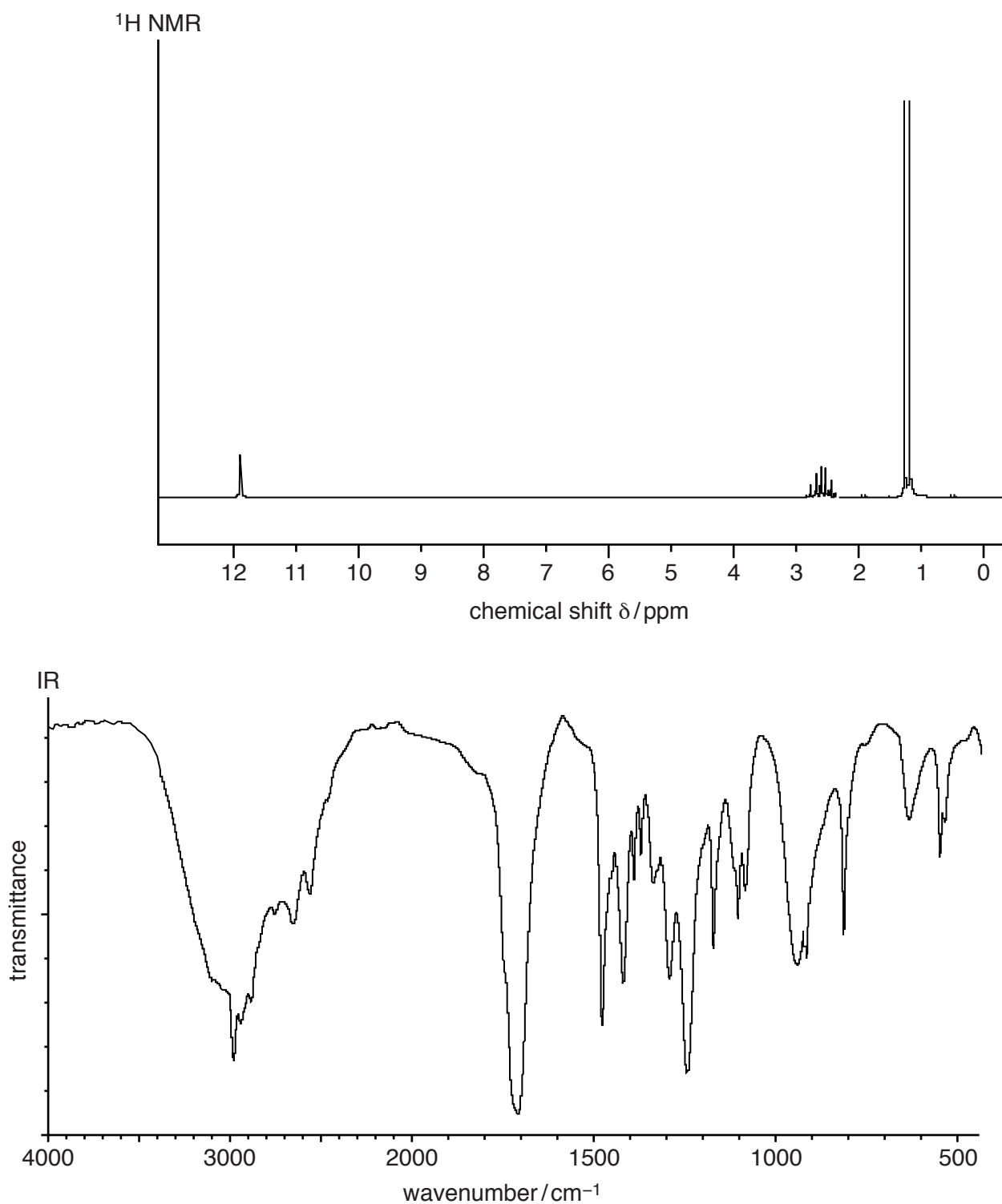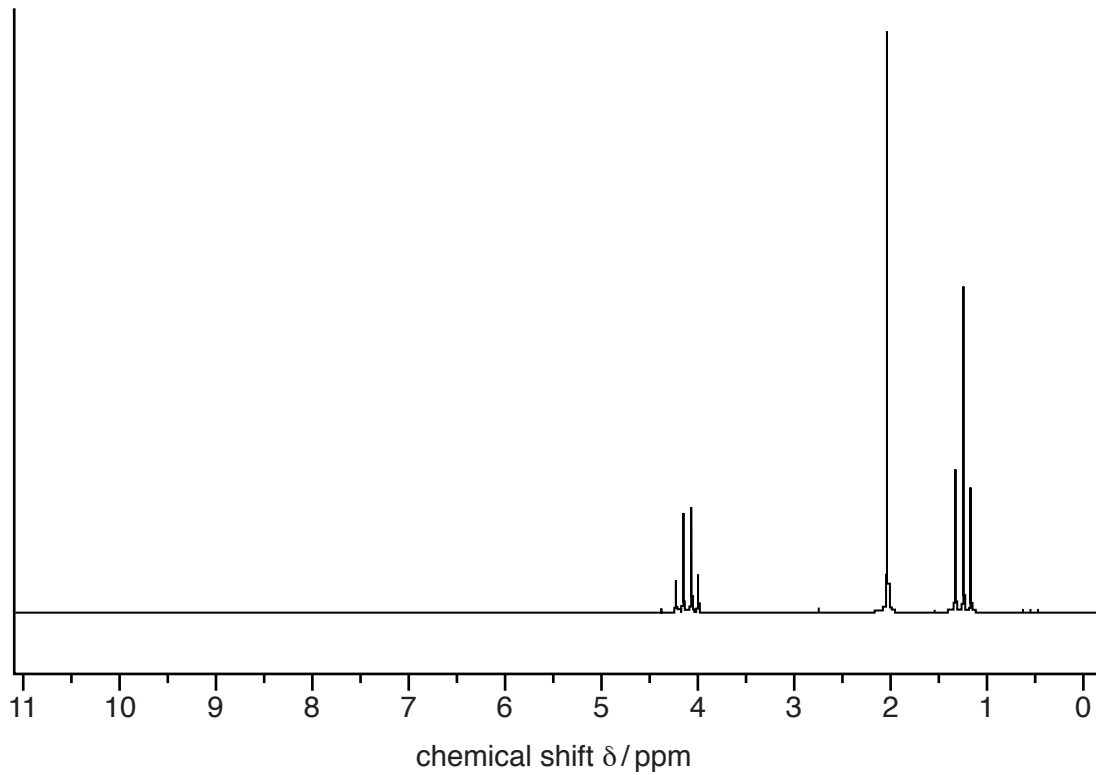
Displayed formula of **P**
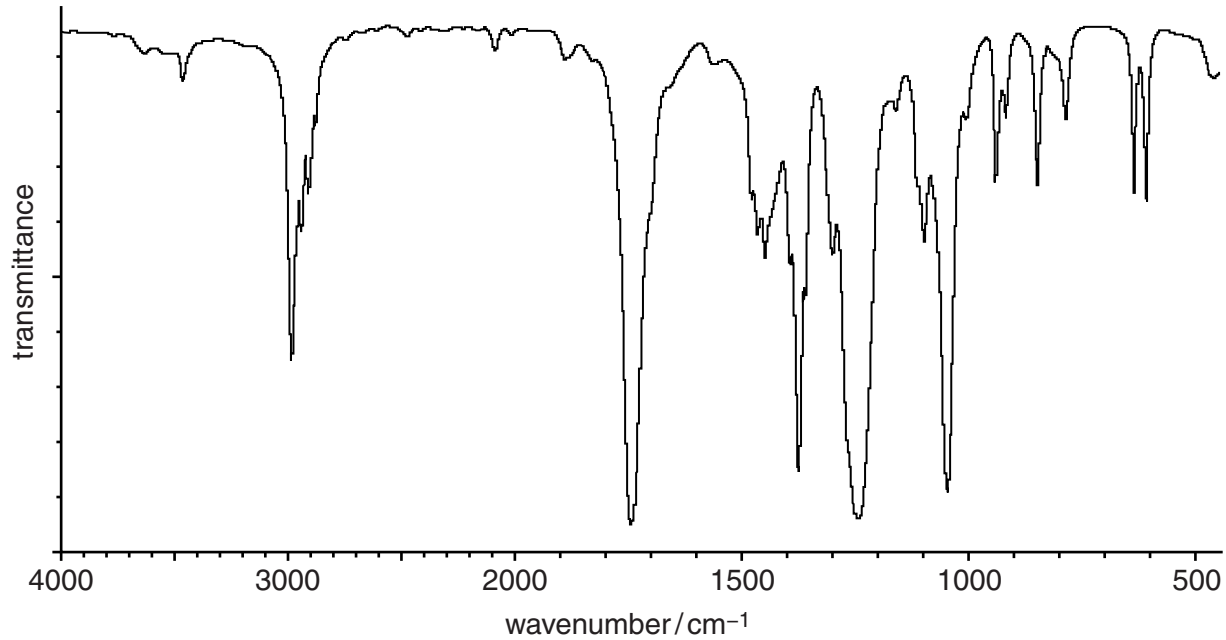

Explanation ....

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[4]

                                                                         [Turn over

18

(ii) Isomer **Q**

^{1}H NMR

chemical shift δ / ppm

IR

wavenumber / cm^{-1}

Displayed formula of **Q**

Explanation ....

....

....

....

....

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[4]

 [Turn over

(b) ^{1}H NMR depends on the fact that a proton has spin.

(i) Explain, briefly, the basis of ^{1}H NMR. Include reference to the feature of a ^{1}H nucleus that makes it suitable for this technique, the energetic basis of the signal and how the signal is detected.

....

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....[3]

(ii) Identify the molecule used as the normal reference standard for ^{1}H NMR.

....[1]

(iii) The positions of different signals in a ^{1}H NMR spectrum are measured on the delta chemical shift scale.

Explain why protons in different chemical environments give signals at different positions on this scale.

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....[3]

[Total: 15]