Cambridge Pre-U

UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
Cambridge International Level 3 Pre-U Certificate
Principal Subject

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

0132856355

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2011**

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 in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
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	
1	
2	
3	
4	
5	
6	
Total	

This document consists of **16** printed pages.

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UNIVERSITY of CAMBRIDGE International Examinations

[Turn over

For Examiner's Use

1 At 298 K the nitrogen and oxygen in air do not react together at a significant rate. However, a car engine produces about 4 g per mile of nitrogen monoxide because the reaction shown in equation 1.1 occurs much more quickly at the high temperatures that exist in the engine.

equation 1.1 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(a) **(i)** State Le Chatelier's principle.

....

....

.... [1]

(ii) Give the expression for K_p for the reaction shown in equation 1.1.

[2]

(iii) At 298 K the value of K_p for the reaction in equation 1.1 is 5.0×10^{-31} while at 1500 K its value is 1.0×10^{-5}.
Use this information to explain whether the formation of nitrogen monoxide is endothermic or exothermic.

....

....

....

.... [2]

(iv) State and explain the effect of an increase in pressure on the position of the equilibrium shown in equation 1.1.

....

....

....

.... [2]

(b) **(i)** Sketch two Boltzmann distribution curves on the axes below to represent the distributions of molecular energies in a sample of gas at two temperatures, $\mathbf{T_1}$ and $\mathbf{T_2}$, where $\mathbf{T_2}$ is significantly higher than $\mathbf{T_1}$. Label the curves clearly to show which one represents which temperature and add titles to the axes.

For Examiner's Use

[4]

(ii) Use the curves to explain why the reaction shown in equation 1.1 occurs so much more quickly in the car engine than at 298 K.

....

....

....

....

....

....

....

.... [3]

[Total: 14]

2 **(a)** Write an expression that represents the relationship defined by Charles's law.

.... [1]

(b) The graph in Fig. 2.1 shows the variation of pV with increasing pressure for an ideal gas and four 'real' gases at 273 K.

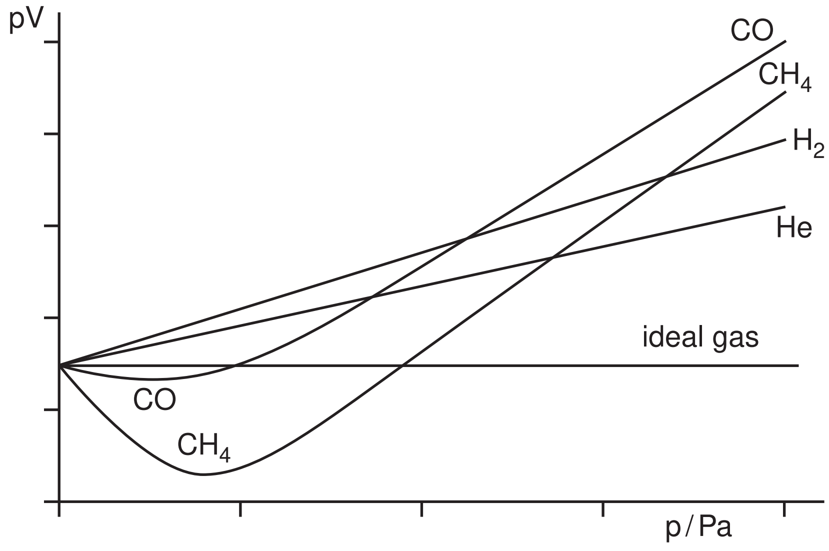


Fig. 2.1

(i) State the two properties of real gases that explain the deviations from ideal behaviour that are shown in Fig. 2.1.

1 ....

....

2 ....

.... [2]

(ii) Calculate the volume, in dm^3, of one mole of an ideal gas at 10^5 Pa and 273 K.

.... dm^3 [2]

(iii) Explain the positive deviation from ideal behaviour that is shown by all four real gases at high pressures.

....

....

.... [2]

(iv) Explain why the positive deviations at high pressures are in the order shown above, i.e. $CO > CH_4 > H_2 > He$.

For Examiner's Use

....

.... [1]

(c) At lower temperatures, the negative deviation from ideal behaviour shown by CH_4 becomes greater. Explain why this is so.

....

.... [2]

[Total: 10]

3 Fig. 3.1 is a diagram of a hydrogen/oxygen fuel cell.

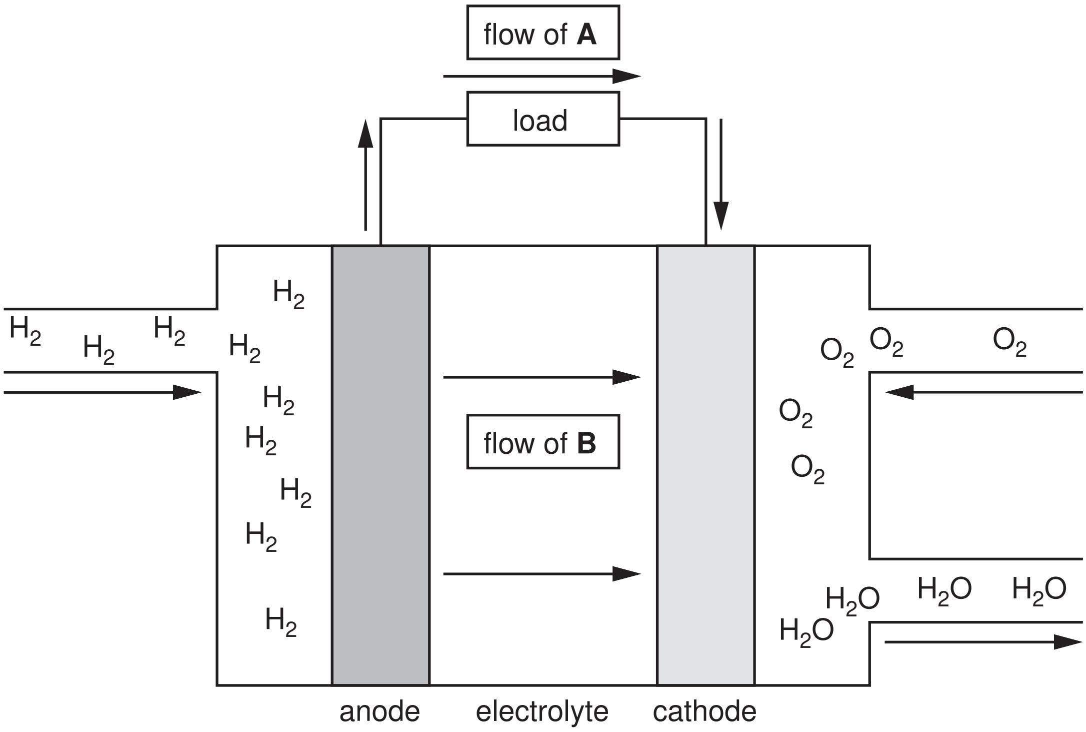


Fig. 3.1

(a) Identify the particles represented by:

A .... **B** .... [2]

(b) The cathode in this fuel cell is coated with a catalyst. Suggest a suitable material for this catalyst.

.... [1]

(c) Write the equation for the reaction occurring at each electrode.

cathode reaction ....

anode reaction .... [2]

(d) **(i)** One of the advantages of fuel cells over the use of fossil fuels is that the only by-product is water.
Suggest two **other** advantages of fuel cells over the use of fossil fuels in motor vehicles.

....

....

....

.... [2]

(ii) Apart from cost, suggest two disadvantages of using fuel cells rather than fossil fuels in motor vehicles.

....

....

....

.... [2]

For Examiner's Use

(e) The zinc/silver oxide cell is used for button cells in watch batteries and is based on the following half-cells:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\qquad E^\ominus = -0.76\,V$

$Ag_2O(s) + H_2O(l) + 2e^- \rightleftharpoons 2Ag(s) + 2OH^-(aq)$ $\qquad E^\ominus = +0.34\,V$

(i) Complete the left-hand side of the notation that describes this cell diagram. [1]

.... $||[Ag_2O(s) + H_2O(l)],[2Ag(s) + 2OH^-(aq)]|Ag(s)$

(ii) State which species is oxidised and which is reduced in this cell during use.

species being oxidised ....

species being reduced .... [2]

(iii) Write an overall equation for the reaction taking place in the cell during use.

.... [1]

(iv) Calculate the standard cell potential for the zinc/silver oxide cell.

$E^\ominus_{cell}$ = ... [1]

(v) Use your answer to part **(iv)** to calculate the standard Gibbs energy change ($\Delta_r G^\ominus$) for the reaction in this cell.

.... $kJ\,mol^{-1}$ [1]

(vi) Use your answer to part **(v)** to calculate the equilibrium constant (K_c) for the reaction in part **(iii)**.

K_c = ... [2]

[Total: 17]

[Turn over

4 In most metals the atoms pack in one of three possible ways. One of these is called *body-centred cubic (bcc)*, in which there is 32% empty space between the atoms. In the other two common metal structures there is only 26% empty space, so these structures are described as *close-packed*.

(a) Give the coordination number of a metal atom in a *close-packed* metal structure.

.... [1]

(b) Complete the table to give the names and layer structures of the two close-packed metal structures.

name	layer structure

[4]

(c) Explain the differences between the lattice structures of sodium chloride, $NaCl$, and calcium fluoride, CaF_2, by completing the following sentences.

(i) $NaCl$ can be considered to consist of a close-packed structure of sodium ions with chloride ions occupying the .... holes. [1]

(ii) CaF_2 can be considered to consist of a close-packed lattice of .... ions with .... ions occupying the .... holes. [2]

(d) Table 4.1 gives the electronegativities of sodium, silver and the halogens.

Table 4.1

element	sodium	silver	fluorine	chlorine	bromine	iodine
electronegativity	0.87	1.87	4.19	2.87	2.69	2.36

Table 4.2 gives the theoretical (from the Born-Landé equation) and experimental (from a Born-Haber cycle) lattice energies for the sodium and silver halides.

Table 4.2

compound	experimental lattice energy / $kJ\,mol^{-1}$	theoretical lattice energy / $kJ\,mol^{-1}$
NaF	918	912
NaC*l*	780	770
NaBr	742	735
NaI	705	687
AgF	958	920
AgC*l*	905	833
AgBr	891	816
AgI	889	778

(i) Use the data in Table 4.1 to explain why there is generally good agreement between the experimental and theoretical values of the lattice energies for the sodium halides.

....

....

....

.... [2]

(ii) Identify and explain the trend that is evident in the magnitudes of the differences between the experimental and theoretical values of the lattice energies for the silver halides.

....

....

....

.... [3]

For Examiner's Use

(e) Restless Legs Syndrome (RLS), also known as Wittmaack-Ekbom's syndrome, is a condition characterised by an uncontrollable urge to move one's legs to alleviate odd or uncomfortable sensations. The condition is not well understood but one possible cause is thought to be low iron levels in the body. Conversely, if iron levels are too high then this can also cause problems as free iron readily produces insoluble compounds and either iron(II) or iron(III) can catalyse the Fenton reaction, which leads to cell damage and eventually cell death.

(i) What is the name of the iron-containing protein found in red-blood cells?

.... [1]

(ii) What role does ferritin play in preventing the problems associated with high or low levels of iron?

....

....

....

.... [2]

(f) With reference to the data in equations 4.1 and 4.2 explain why solutions of iron(II) compounds in the laboratory are normally made up and stored in the presence of acid.

equation 4.1 $Fe(OH)_3 (s) + e^- \longrightarrow Fe(OH)_2 (s) + OH^-(aq)$ $E^\ominus = -0.56\,V$

equation 4.2 $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ $E^\ominus = +0.77\,V$

....

....

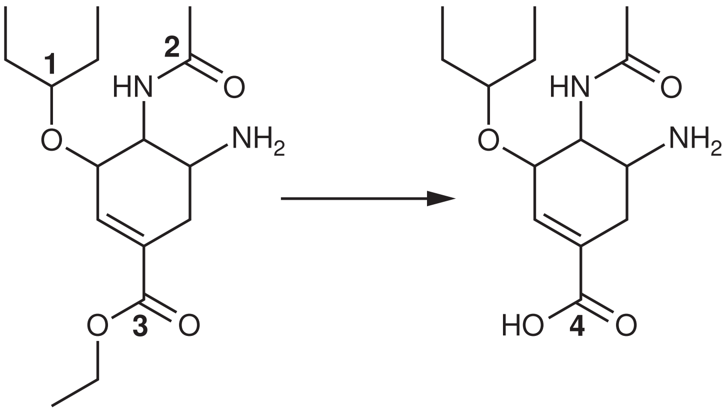
....

....

.... [3]

[Total: 19]

5 Oseltamivir is an anti-viral drug that is converted to its active form, GS 4071, in the body after being administered.



oseltamivir GS 4071

(a) State the names of the functional group levels of the carbon atoms numbered **1** and **2** in the structure of oseltamivir.

carbon **1** ....

carbon **2** .... [2]

(b) With reference to the functional group levels of the carbon atoms numbered **3** and **4**, what type of reaction is involved in the conversion of oseltamivir into GS 4071? Explain your answer.

....

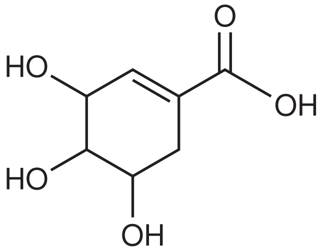
....

.... [2]

(c) Use skeletal formulae to give the structures of all three products formed from the hydrolysis of the ester and amide links in oseltamivir by hot aqueous hydrochloric acid.

[4]

Oseltamivir can be produced from shikimic acid, which occurs naturally in star anise.



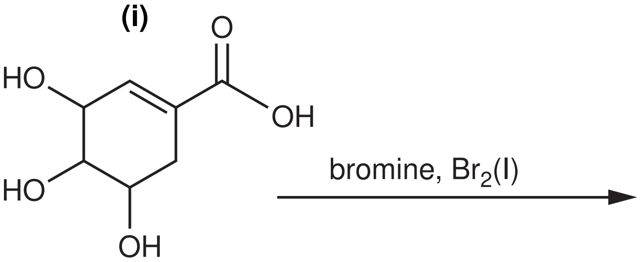
shikimic acid

(d) Give the molecular formula of shikimic acid.

.... [1]

(e) Give the structure of the organic product when shikimic acid reacts with each of the following reagents.

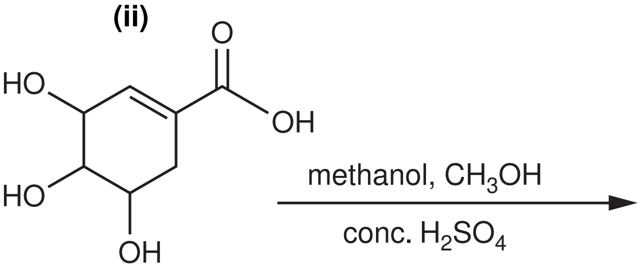
(i)



shikimic acid

[1]

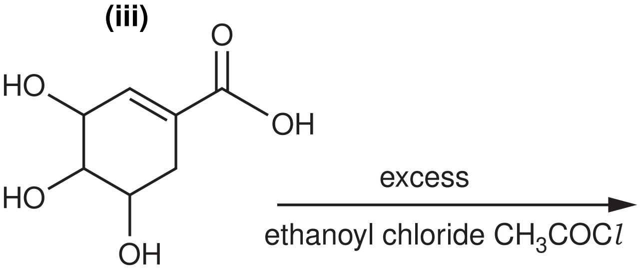
(ii)



shikimic acid

[1]

(iii)



shikimic acid

[2]

For Examiner's Use

(f) Using the numbers on the diagram of shikimic acid's structure in Fig. 5.1 indicate (by putting numbers in the boxes) which carbon atoms in the molecule are responsible for each signal in its ^{13}C NMR spectrum in Fig. 5.2. The precise order of carbons within the group of two and the group of three are not required.

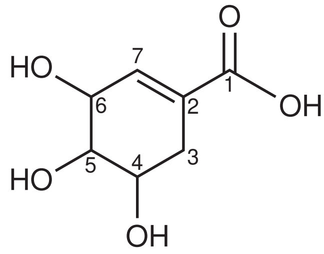
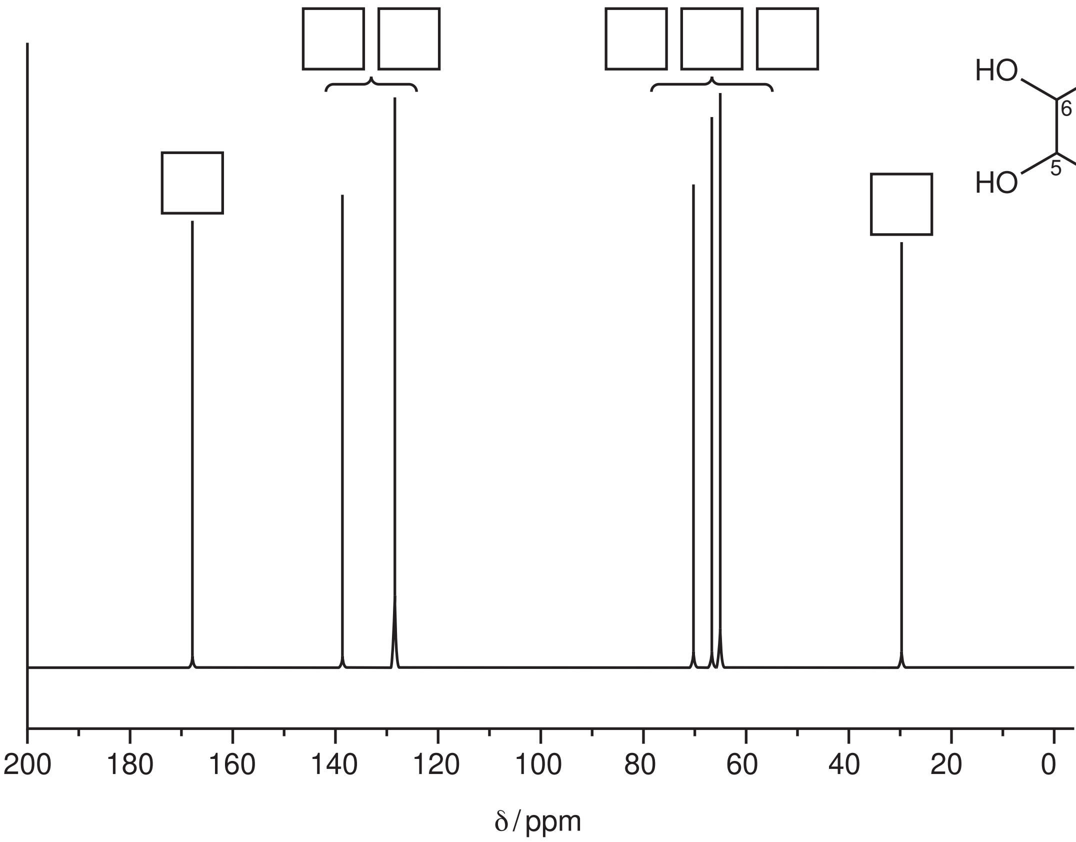


Fig. 5.1



[3]

Fig. 5.2

(g) Under suitable conditions shikimic acid reacts with HBr in a 1:1 ratio to produce a mixture of two products each with the molecular formula $C_7H_{11}BrO_5$.

(i) Give the full name of the mechanism of this reaction.

.... [1]

(ii) Draw the structures of the two possible products.

[2]

(iii) Suggest why one of the two products will be present in greater quantities.

....

....

.... [2]

[Total: 21]

For Examiner's Use

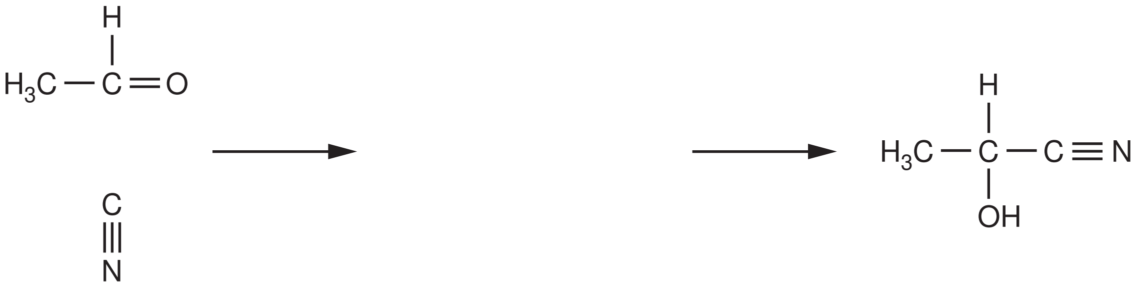
6 When a carbonyl compound reacts with an acidified solution of potassium cyanide an hydroxynitrile is produced. An example of such a reaction is shown in equation 6.1. This type of reaction is useful because it provides a means of adding another carbon atom to the carbon chain.

equation 6.1 $CH_3CHO + KCN + H_2SO_4 \rightarrow CH_3CH(OH)CN + KHSO_4$

(a) Give the full name of the mechanism of this reaction.

.... [1]

(b) **(i)** Complete the mechanism shown in Fig. 6.1 by adding all necessary curly arrows, lone pairs and full or partial charges and by showing the intermediate stage.



[4]

Fig. 6.1

(ii) Explain why the product of this reaction is not optically active.

.... [1]

(c) The pK_a values for ethanoic acid and some substituted acids are given in Table 6.1.

Table 6.1

acid	pK_a
ethanoic	4.8
chloroethanoic	2.9
dichloroethanoic	1.3
trichloroethanoic	0.7

(i) Give the expression for K_a for ethanoic acid.

[1]

(ii) Define pK_a.

.... [1]

For Examiner's Use

(iii) Use the data in Table 6.1 to identify and explain the pattern in the strengths of the acids.

....

....

....

....

....

....

....

.... [4]

(d) 2-chloropropanoic acid, $CH_3CHClCOOH$, is a chiral molecule and exists as a pair of *enantiomers*.

(i) Define the term *enantiomers*.

....

.... [1]

(ii) The structure shown in Fig. 6.2 is the R-enantiomer of 2-chloropropanoic acid.

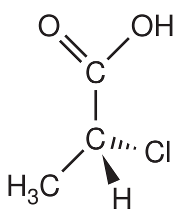


Fig. 6.2

Use the Cahn-Ingold-Prelog priority rules to explain why this is identified as the R-enantiomer.

....

....

....

....

....

.... [3]

For Examiner's Use

(iii) What is the physical property that can be used to distinguish between the enantiomers?

....

....

.... [1]

(iv) Explain the notation used to distinguish between the enantiomers in terms of this property.

....

....

.... [2]

[Total: 19]