UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

0651889794

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2011**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **all** questions.

You may lose marks if you do not show your working or if you do not use 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	
7	
8	
Total	

This document consists of **17** printed pages and **3** blank pages.

DC (NF/SW) 50350

UNIVERSITY *of* CAMBRIDGE
International Examinations

[Turn over

Section A

For Examiner's Use

Answer **all** questions in the spaces provided.

1 **(a)** The halogens chlorine and bromine react readily with hydrogen.

$$X_2(g) + H_2(g) \longrightarrow 2HX(g) \qquad [X = Cl \text{ or } Br]$$

(i) Describe how you could carry out this reaction using chlorine.

....

(ii) Describe **two** observations you would make if this reaction was carried out with bromine.

....

....

(iii) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^\ominus$ for this reaction when

X = C*l*,

$\Delta H^\ominus$ = ... $kJ\,mol^{-1}$

X = Br.

$\Delta H^\ominus$ = ... $kJ\,mol^{-1}$

(iv) What is the major reason for the difference in these two $\Delta H^\ominus$ values?

....

[8]

For Examiner's Use

(b) Some halogens also react readily with methane.

$$CH_4(g) + X_2(g) \rightarrow CH_3X(g) + HX(g)$$

(i) What conditions are needed to carry out this reaction when X is bromine, Br?

....

(ii) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^{\ominus}$ of this reaction for the situation where X is iodine, I.

$\Delta H^{\ominus}$ = ... $kJ\,mol^{-1}$

(iii) Hence suggest why it is not possible to make iodomethane, CH_3I, by this reaction.

....

[4]

(c) Halogenoalkanes can undergo *homolytic fission* in the upper atmosphere.

(i) Explain the term *homolytic fission*.

....

....

(ii) Suggest the most likely organic radical that would be formed by the homolytic fission of bromochloromethane, CH_2BrCl. Explain your answer.

....

....

....

[3]

(d) The reaction between propane and chlorine produces a mixture of many compounds, four of which are structural isomers with the molecular formula $C_3H_6Cl_2$.
Draw the structural or skeletal formulae of these isomers, and indicate any chiral atoms with an asterisk (*).

[3]

[Total: 18]

2 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.

For Examiner's Use

$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\text{methanol}}{2CH_3OH} \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{acetal } \mathbf{A}}{CH_3CH(OCH_3)_2} + H_2O$$

(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	$[CH_3CHO]$ / $mol\,dm^{-3}$	$[CH_3OH]$ / $mol\,dm^{-3}$	$[H^+]$ / $mol\,dm^{-3}$	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

(i) Use the data in the table to determine the order with respect to each reactant.

order with respect to $[CH_3CHO]$ ....

order with respect to $[CH_3OH]$ ....

order with respect to $[H^+]$ ....

(ii) Use your results from part **(i)** to write the rate equation for the reaction.

....

(iii) State the units of the rate constant in the rate equation ....

(iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 $mol\,dm^{-3}$.

relative rate = ...

[6]

For Examiner's Use

(b) The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	[acetal **A**] / mol dm^{-3}	$[H_2O]$ / mol dm^{-3}
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20–***x***)			***x***	
at equilibrium				0.025	

(i) Complete the second row of the table in terms of ***x***, the concentration of acetal **A** at equilibrium. You may wish to consult the chemical equation opposite.

(ii) Using the [acetal **A**] as given, 0.025 mol dm^{-3}, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.

(iii) Write the expression for the equilibrium constant for this reaction, K_c, stating its units.

K_c = ... units = ...

(iv) Use your values in the third row of the table to calculate the value of K_c.

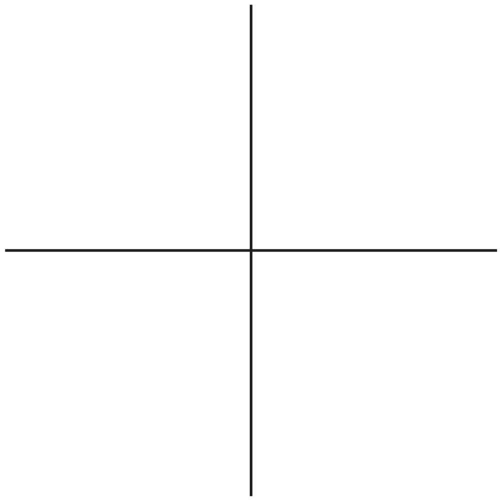
K_c = ...

[9]

[Total: 15]

For Examiner's Use

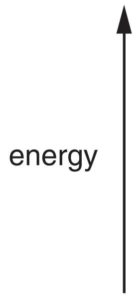
3 **(a)** On the following diagram draw a clear **labelled** sketch to describe the shape and symmetry of a typical d-orbital.



[2]

(b) Although the five d-orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups.

(i) Draw an orbital energy diagram to show this, indicating the number of orbitals in each group.



(ii) Use your diagram as an aid in explaining the following.

- Transition element complexes are often coloured.

....

....

....

....

- The colour of a complex of a given transition element often changes when the ligands around it are changed.

....

....

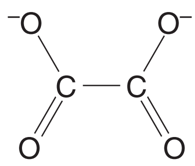
....

[7]

For Examiner's Use

(c) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$.

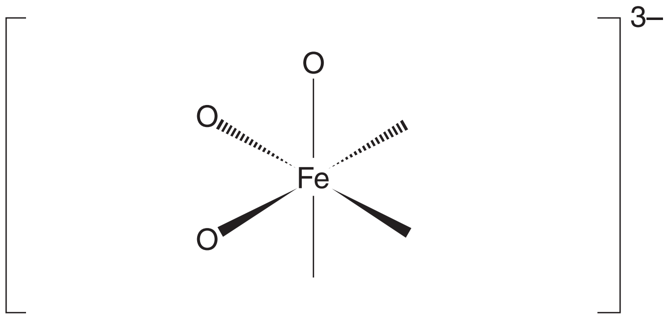
The structure of the ethanedioate ion is as follows.



(i) Calculate the oxidation number of carbon in this ion. ....

(ii) Calculate the oxidation number of iron in $[Fe(C_2O_4)_3]^{3-}$. ....

(iii) The iron atom in the $[Fe(C_2O_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Complete the following **displayed** formula of this ion.



(iv) In sunlight the complex decomposes into potassium ethanedioate, iron(II) ethanedioate and carbon dioxide.

Use oxidation numbers to help you balance the following equation for this decomposition.

$K_3Fe(C_2O_4)_3 \rightarrow$ ....$K_2C_2O_4$ + ...FeC_2O_4 + ...CO_2

[5]

[Total: 14]

For Examiner's Use

4 (a) (i) Write the equation for a reaction in which ethylamine, $C_2H_5NH_2$, acts as a Brønsted-Lowry base.

....

(ii) Ammonia, ethylamine and phenylamine, $C_6H_5NH_2$, are three nitrogen-containing bases.

Place these three compounds in order of basicity, with the most basic first.

most basic		least basic

(iii) Explain why you have placed the three compounds in this order.

....

....

....

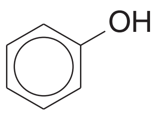
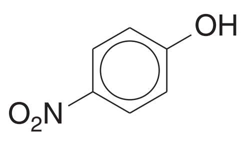
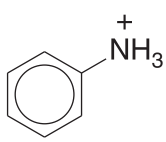
....

[4]

(b) (i) Write an equation for a reaction in which phenol, C_6H_5OH, acts as a Brønsted-Lowry acid.

....

The pK_a values for phenol, 4-nitrophenol and the phenylammonium ion are given in the table.

compound	pK_a
	10.0
	7.2
	4.6

(ii) Suggest an explanation for the difference in the pK_a values of phenol and nitrophenol.

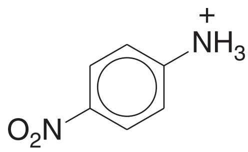
....

....

....

....

(iii) Using the information in the table opposite, predict which of the following pK_a values is the most likely for the 4-nitrophenylammonium ion.



Place a tick (✓) in the box beside the value you have chosen.

pK_a	
1.0	
4.5	
7.0	
10.0	

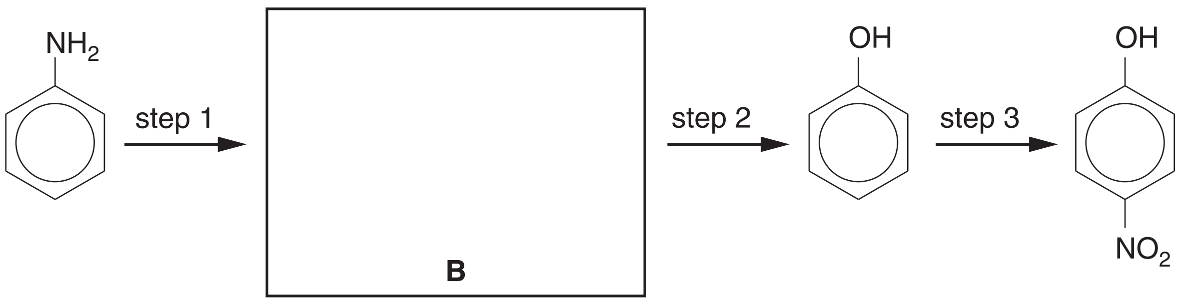
(iv) Explain your answer to part **(iii)**.

....

....

....
[5]

(c) Phenylamine can be converted to 4-nitrophenol by the following steps.



(i) Suggest the identity of intermediate **B** by drawing its structure in the box above.

(ii) Suggest reagents and conditions for the three steps in the above scheme.

	reagent(s)	conditions
step 1		
step 2		
step 3		

[5]

[Total: 14]

For Examiner's Use

5 Compound **C** has the molecular formula $C_7H_{14}O$. Treating **C** with hot concentrated acidified $KMnO_4$(aq) produces two compounds, **D**, C_4H_8O, and **E**, $C_3H_4O_3$. The results of four tests carried out on these three compounds are shown in the following table.

test reagent	result of test with		
	compound **C**	compound **D**	compound **E**
Br_2(aq)	decolourises	no reaction	no reaction
Na(s)	fizzes	no reaction	fizzes
I_2(aq) + OH^-(aq)	no reaction	yellow precipitate	yellow precipitate
2,4-dinitrophenylhydrazine	no reaction	orange precipitate	orange precipitate

(a) State the functional groups which the above four reagents test for.

(i) Br_2(aq)

....

(ii) Na(s)

....

(iii) I_2(aq) + OH^-(aq)

....

(iv) 2,4-dinitrophenylhydrazine

....

[4]

(b) Based upon the results of the above tests, suggest structures for compounds **D** and **E**.

D, C_4H_8O **E**, $C_3H_4O_3$

[2]

(c) Compound **C** exists as two stereoisomers.

For Examiner's Use

Draw the structural formula of **each** of the two isomers, and state the type of stereoisomerism involved.

type of stereoisomerism ....
[3]

[Total: 9]

Section B

Answer **all** questions in the spaces provided.

For Examiner's Use

6 Proteins exist in an enormous variety of sizes and structures in living organisms. They have a wide range of functions which are dependent upon their structures. The structure and properties of an individual protein are a result of the primary structure – the sequence of amino acids that form the protein.

(a) Proteins are described as condensation polymers.

(i) Write a balanced equation for the condensation reaction between two glycine molecules, $H_2NCH_2CO_2H$.

(ii) Draw the skeletal formula for the organic product.

[2]

(b) X-ray analysis has shown that in many proteins there are regions with a regular arrangement within the polypeptide chain. This is called the secondary structure and exists in two main forms.

(i) State the two forms of secondary structure found in proteins.

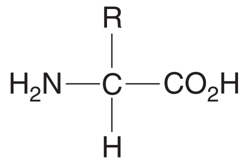
....

....

(ii) Draw a diagram to illustrate **one** form of secondary structure.

[4]

(c) There are around 20 different common amino acids found in humans most of which have the same general structure.



The nature of the group R affects which bonds are formed as the secondary structure of the protein is further folded to give the tertiary structure.

Complete the table indicating the type of **tertiary** bonding that each pair of the amino acid residues is likely to produce.

residue 1	residue 2	type of tertiary bonding
$–HNCH(CH_2CH_2CH_2CH_2NH_2)CO–$	$–HNCH(CH_2CH_2CO_2H)CO–$	
$–HNCH(CH_3)CO–$	$–HNCH(CH_3)CO–$	
$–HNCH(CH_2SH)CO–$	$–HNCH(CH_2SH)CO–$	
$–HNCH(CH_2OH)CO–$	$–HNCH(CH_2CO_2H)CO–$	

[4]

[Total: 10]

For Examiner's Use

For Examiner's Use

7 One of the key areas of investigation in understanding the structures of polypeptides and proteins is the sequence of amino acids that make up the polypeptide chains.

(a) One of the methods used to determine the amino acids present in a polypeptide chain is electrophoresis.

Sketch and label the apparatus used to carry out electrophoresis.

[4]

(b) In electrophoresis, different amino acids move in different directions and at different speeds.

(i) What factors determine the *direction of travel* of an amino acid?

....

....

....

(ii) What factors determine the *speed of movement* of an amino acid?

....

....

[3]

(c) Another important technique used to examine the structure of proteins is X-ray crystallography. In this technique the position of individual atoms can be determined, and the distances between them measured.

For Examiner's Use

(i) Hydrogen atoms never produce images using X-ray crystallography. Explain why this is the case.

....

....

(ii) Suggest and explain which one of the atoms in a molecule of cysteine, $H_2NCH(CH_2SH)CO_2H$, would show up most clearly using X-ray crystallography.

....

....
[3]

[Total: 10]

For Examiner's Use

8 In today's world we make use of a wide range of different polymers. These polymers are often substitutes for traditional materials, but may have more useful properties.

(a) Complete the table identifying one traditional material that has been replaced by each polymer.

traditional material	modern polymer and its use
	PVC in packaging
	Terylene in fabrics
	polycarbonate bottle

[2]

(b) Throwing away articles made from polymers after use is a major environmental concern for **two** main reasons. Identify **each** of these reasons and suggest a strategy that has been adopted to try to overcome each of these.

reasons : ....

....

....

strategy 1 : ....

....

strategy 2 : ....

....

[3]

(c) One suggestion for the disposal of polymers is to use them as a fuel to provide energy for small-scale power stations or district heating schemes.
Identify one polymer which would be **unsuitable** for this use, explaining the reason behind this.

For Examiner's Use

polymer ....

reason ....

....

.... [2]

(d) Polymers can be either thermoplastic or thermosetting.

Name a thermoplastic polymer. ....

State which type of polymerisation produces thermoplastic polymers, explaining your answer in terms of the structure of the polymer.

....

....

....

.... [3]

[Total: 10]

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