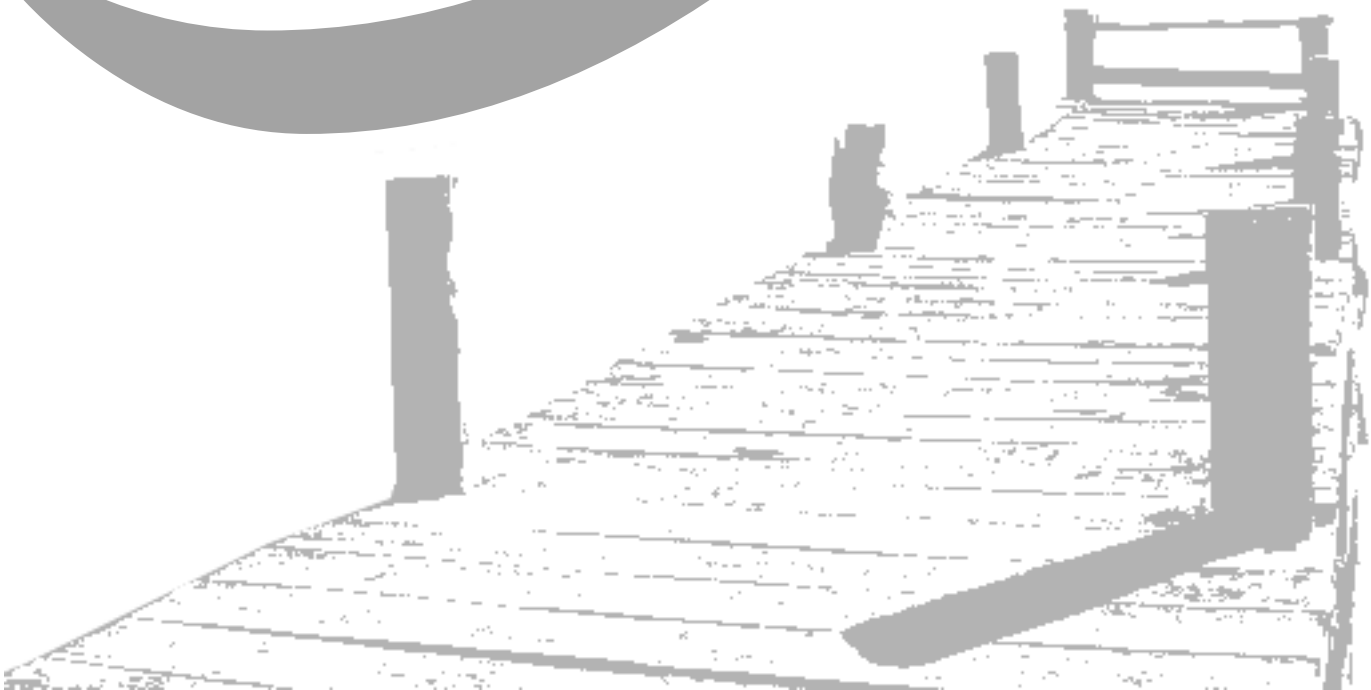
GCE
AS and A Level

Chemistry

AS exams 2009 onwards
A2 exams 2010 onwards

Unit 4:
Specimen question paper

Version 1.1



Surname		Other Names	
Centre Number						Candidate Number				
Candidate Signature										

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General Certificate of Education
2009
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY CHEM4
Unit 4 Kinetics, Equilibria and Organic Chemistry

SPECIMEN PAPER

For this paper you must have
- A calculator
- Data Sheet / Periodic Table

Time allowed: 1¾ hours

Instructions
- Use blue or black ink or ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.

Information
- The maximum mark for this paper is 100.
- The marks for the questions are shown in brackets.
- You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use			
Number	Mark	Number	Mark
1		6	
2		7	
3		8	
4		9	
5		10	
Total (Column 1)			
Total (Column 2)			
TOTAL			
Examiner's Initials			

SECTION A

Answer **all** questions in the spaces provided

1 Kinetic studies enable chemists to suggest mechanisms for reactions.

(a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/ mol $dm^{-3}s^{-1}$
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

(i) Deduce the order of reaction with respect to **A**.

.....

.....

(ii) Deduce the order of reaction with respect to **B**.

.....

.....

(2 marks)

(b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O_2 at a constant temperature.

Experiment	Initial concentration of NO/mol dm^{-3}	Initial concentration of O_2/mol dm^{-3}	Initial rate/ mol $dm^{-3}s^{-1}$
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[NO]^2[O_2]$$

(i) Use the data from Experiment **4** to calculate a value for the rate constant, *k*, at this temperature, and state its units.

Value of k .....

.....

Units of k .....

.....

(ii) Calculate a value for the initial rate in Experiment **5**.

.....

.....

(iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.

Step 1 $NO + NO \rightarrow N_2O_2$

Step 2 $N_2O_2 + O_2 \rightarrow 2NO_2$

Which did the scientist suggest was the rate–determining step?

.....

(5 marks)

7

2 The study of equilibrium constants enables chemists to calculate the composition of equilibrium mixtures.

(a) The expression for an equilibrium constant, K_c, for a homogeneous equilibrium is given below.

$$K_c = \frac{[C]^2[D]}{[E][F]^3}$$

(i) Write an equation for the forward reaction.

.....

(ii) Deduce the units of K_c

.....

.....

(iii) State what can be deduced from the fact that the value of K_c is larger when the equilibrium is established at a lower temperature.

.....

(3 marks)

(b) When a 0.218 mol sample of hydrogen iodide was heated in a flask of volume V dm^3, the following equilibrium was established at 700 K.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The equilibrium mixture was found to contain 0.023 mol of hydrogen.

(i) Calculate the number of moles of iodine and the number of moles of hydrogen iodide in the equilibrium mixture.

Number of moles of iodine .....

Number of moles of hydrogen iodide .....

.....

(ii) Write an expression for K_c for the equilibrium.

.....

.....

(iii) State why the volume of the flask need not be known when calculating a value for K_c.

.....

.....

(iv) Calculate the value of K_c at 700 K.

.....

.....

.....

.....

(v) Calculate the value of K_c at 700 K for the equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

.....

.....

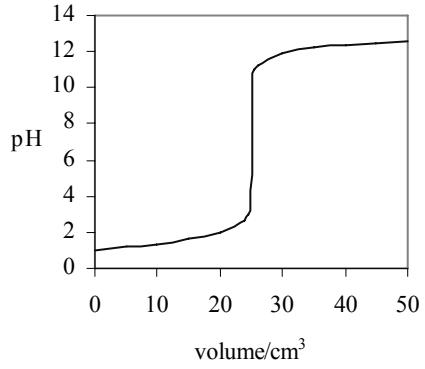
(7 marks)

10

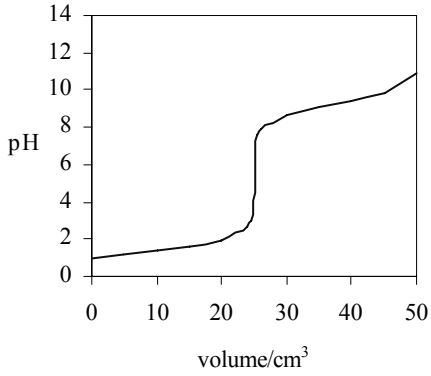
Turn over for the next question

3 Indicators and pH curves can be used to determine the end point in a titration.

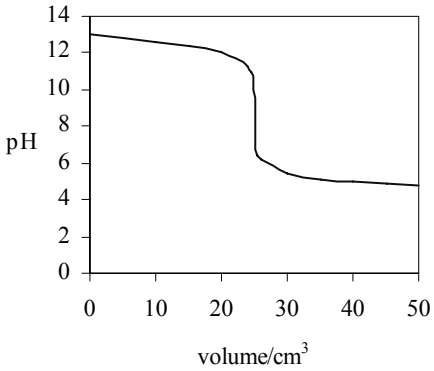
(a) The pH curves labelled **J, K, L** and **M** for combinations of different acids and bases are shown below. All solutions have a concentration of 0.1 mol dm^{-3}.



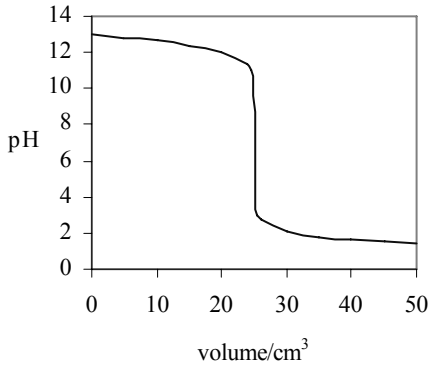
J



K



L



M

(i) Select from **J**, **K**, **L** and **M** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid.....

ethanoic acid to 25 cm^3 of sodium hydroxide .....

sodium hydroxide to 25 cm^3 of hydrochloric acid .....

(ii) A table of acid–base indicators and the pH ranges over which they change colour is shown below.

Indicator	pH range
Thymol blue	1.2 – 2.8
Bromophenol blue	3.0 – 4.6
Methyl red	4.2 – 6.3
Cresolphthalein	8.2 – 9.8
Thymolphthalein	9.3 – 10.5

Select from the list above an indicator which could be used in the titration which produces curve **J** but not in the titration which produces curve **K**.

.....

(4 marks)

(b) The acid dissociation constant, K_a, for the weak acid, ethanoic acid, has a value of 1.74×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

(i) Write an expression for the term pH.

.....

(ii) Calculate the pH of a 0.15 mol dm^{-3} solution of ethanoic acid. Give your answer to 2 decimal places.

.....

.....

.....

.....

(4 marks)

8

4 Buffer solutions are important in biological systems and in industry to maintain almost constant pH values.

(a) In the human body, one important buffer system in blood involves the hydrogencarbonate ion, HCO_3^-, and carbonic acid, H_2CO_3, which is formed when carbon dioxide dissolves in water.

(i) Use the following equation to explain how this buffer maintains a constant pH of 7.41 even if a small amount of acid enters the bloodstream.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

.....

.....

.....

(ii) In a sample of blood with a pH of 7.41, the concentration of $HCO_3^-(aq)$ ions is 2.50×10^{-2} mol dm^{-3} and the concentration of $H_2CO_3(aq)$ is 1.25×10^{-3} mol dm^{-3}. Calculate a value for the acid dissociation constant, K_a, for carbonic acid at this temperature.

.....

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.....

(5 marks)

(b) In industry, the pH of a solution used to dye cloth must be controlled or else the colour varies.

A solution of dye in a beaker is buffered by the presence of ethanoic acid and sodium ethanoate. In the solution, the concentration of ethanoic acid is 0.15 mol dm^{-3} and the concentration of sodium ethanoate is 0.10 mol dm^{-3}. The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(i) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffered solution.

Calculate the number of moles of hydrochloric acid added.

.....

(ii) Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid.

Mol of ethanoic acid after addition .....

.....

Mol of sodium ethanoate after addition .....

.....

(iii) Hence calculate the pH of this new solution. Give your answer to 2 decimal places.

.....

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.....

.....

(6 marks)

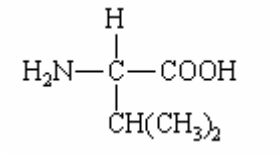
11

Turn over for the next question

5 Fibres are made from natural and from synthetic polymers. Both types of polymer have advantages and disadvantages.

(a) Amino acids are the building blocks of naturally-occurring polymers called proteins.

Consider the following amino acid.



(i) Draw the structure of the amino acid species present in a solution at pH 12.

(ii) Use your understanding of amino acid chemistry to deduce the structure of the dipeptide formed from two molecules of this amino acid and illustrate your answer with a sketch showing the structure of the dipeptide.

(iii) Protein chains are often arranged in the shape of a helix. Name the type of interaction that is responsible for holding the protein chain in this shape.

.....

(3 marks)

(b) Alkenes are the building blocks of synthetic addition polymers.

Consider the hydrocarbon **G**, $(CH_3)_2C{=}CHCH_3$, which can be polymerised.

(i) Draw the repeating unit of the polymer.

(ii) Draw the structure of an isomer of **G** which shows *E-Z* isomerism.

(iii) Draw the structure of an isomer of **G** which does not react with bromine water.

(3 marks)

(c) Draw the repeating unit of the polymer formed by the reaction between butanedioic acid and hexane-1,6-diamine.

(2 marks)

(d) Two plastic objects were manufactured, one from the polyalkene represented by the repeating unit in part (b)(i) and the other from the polyamide represented by the repeating unit in part (c).

After use it was suggested that both objects be disposed of as landfill.

(i) Describe an experiment in which you could compare the biodegradability of these two objects.

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(3 marks)

(ii) Describe an advantage or a disadvantage of a different method of disposal of such objects compared with landfill.

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(3 marks)

14

Turn over for the next question

6 It is necessary to use several analytical techniques to determine the structure of an unknown compound.

An analytical chemist was asked to determine the structure of compound **Q** which was found in a waste tank in a mixture of volatile liquids.

Compound **Q** has the molecular formula C_4H_7ClO. It is a volatile liquid which does not produce misty fumes when added to water.

(a) Suggest how the chemist could obtain a sample of **Q** for analysis from the mixture of volatile liquids.

.....

(1 mark)

(b) The infra-red spectrum of Q contains a major absorption at 1724 cm^{-1}. Identify the bond which causes this absorption.

.....

(1 mark)

(c) The mass spectrum of Q contains two molecular ion peaks at *m/z* = 106 and *m/z* = 108. It also has a major peak at *m/z* = 43.

(i) Suggest why there are two molecular ion peaks.

.....

(ii) A fragment ion produced from **Q** has *m/*z = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

Fragment ion .....

Equation.....

(3 marks)

(d) The proton n.m.r. spectrum of **Q** was recorded.

(i) Suggest a suitable solvent for use in recording this spectrum of **Q**.

.....

(ii) Give the formula of the standard reference compound used in recording proton n.m.r. spectra.

.....

(2 marks)

(e) The proton n.m.r. spectrum of Q shows 3 peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting patterns.

	Peak 1	Peak 2	Peak 3
Integration value	3	3	1
Splitting pattern	doublet	singlet	quartet
Number of adjacent, non-equivalent protons	1		

(1 mark)

(f) Using the information in parts (a), (b) and (d) deduce the structure of compound **Q.**

(1 mark)

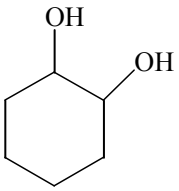
(g) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1 mark)

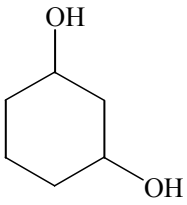
10

Turn over for the next question

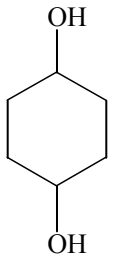
7 Three cyclic alcohols, cyclohexan–1,2-diol, cyclohexan–1,3-diol and cyclohexan–1,4-diol were compared using ^{13}C n.m.r. spectroscopy.



cyclohexan-1,2-diol

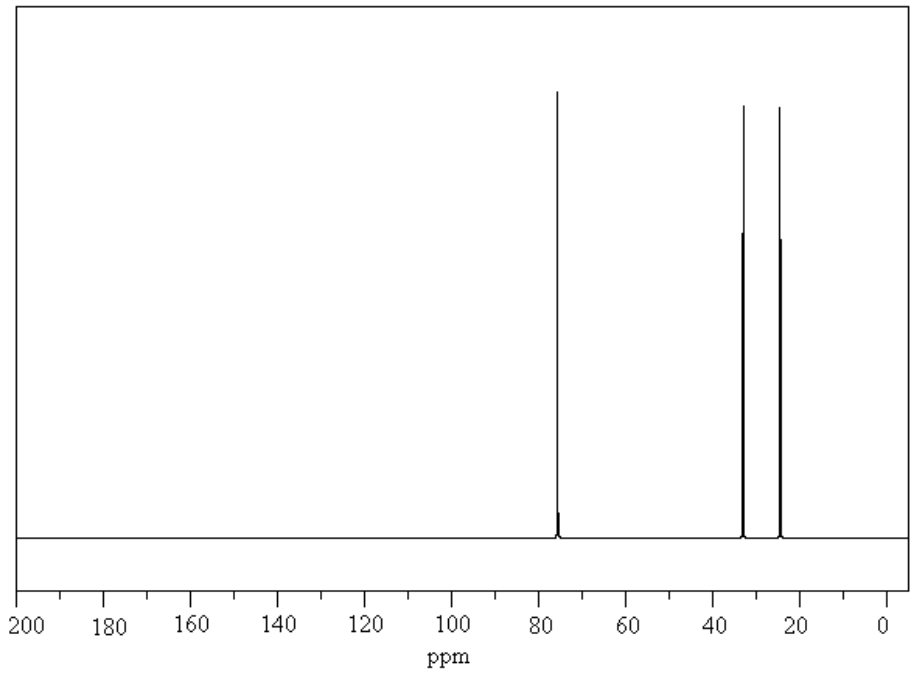


cyclohexan-1,3-diol



cyclohexan-1,4-diol

The ^{13}C n.m.r. spectrum of cyclohexan–1,2-diol is shown below.



(a) Explain why there are three peaks.

.....

.....

.....

(ii) Proton n.m.r. chemical shift data is shown in Table 1 on the reverse of the Periodic Table. Chemical shift values for ^{13}C vary similarly with chemical environment.

Suggest the δ value of the peak in the spectrum above which corresponds to the absorption for carbon atom 1 in cyclohexan–1,2-diol.

.....

(b) (i) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan–1,3-diol.

.....

(ii) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan–1,4-diol.

.....

(c) Suggest why the structures drawn above represents several stereoisomers.

.....

(5 marks)

5

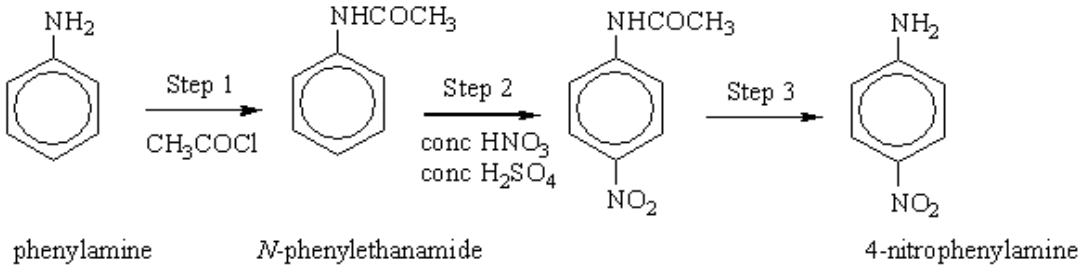
Turn over for the next question

SECTION B

Answer questions 8, 9 and 10 in the space provided on pages 20 to 24 of this booklet.

8 Synthetic dyes can be manufactured starting from compounds such as 4-nitrophenylamine.

A synthesis of 4-nitrophenylamine starting from phenylamine is shown below.



(a) An equation for formation of *N*-phenylethanamide in Step 1 of the synthesis is shown below.

$$2C_6H_5NH_2 + CH_3COCl \rightarrow \underset{\textit{N}\text{-phenylethanamide}}{C_6H_5NHCOCH_3} + C_6H_5NH_3Cl$$

(i) Calculate the % atom economy for the production of *N*-phenylethanamide (*M*r = 135.0).

(ii) In a process where 10.0 kg of phenylamine are used, the yield of *N*-phenylethanamide obtained is 5.38 kg.

Calculate the percentage yield of *N*-phenylethanamide.

(iii) Comment on your answers to parts (i) and (ii) with reference to the commercial viability of the process.

(7 marks)

(b) Name and outline a mechanism for the reaction in Step 1.

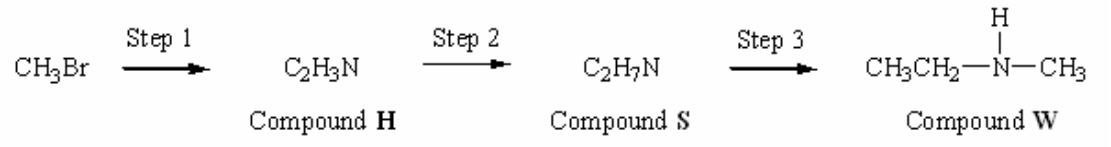
(5 marks)

(c) The mechanism of Step 2 involves attack by an electrophile. Write an equation showing the formation of the electrophile. Outline a mechanism for the reaction of this electrophile with benzene.

(4 marks)

16

9 Compound **W** can be formed via compounds **H** and **S** in the three-step synthesis shown below.



Identify compounds **H** and **S** and give reagents and conditions for Steps 1 and 2.

State the **type** of compound of which **W** is an example.

W reacts with a large excess of bromomethane to form a solid product. Draw the structure of this product and name the type of mechanism for this reaction.

(9 marks)

10 A chemist has discovered that the labels have fallen off four bottles each of which contains a different organic liquid. These liquids are known to be propan-2-ol, propanal, hexene and 1-bromopropane.

Suggest a series of test-tube reactions which a chemist could use to confirm the identities of the four compounds. State the reagents used and the observations expected.

(10 marks)

END OF QUESTIONS

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