OCR
RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY **2816/01**

Unifying Concepts

Thursday 23 JUNE 2005 Afternoon 1 hour 15 minutes

Candidates answer on the question paper.
Additional materials:
Data Sheet for Chemistry
Scientific calculator

Candidate Name	Centre Number	Candidate Number

TIME 1 hour 15 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [ ] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE		
Qu	Max.	Mark
1	12	
2	18	
3	16	
4	14	
TOTAL	60	

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SP (SLM/KS) S76836/3

Answer **all** the questions.

1 This question looks at **two** different experiments that investigate rates of reaction.

(a) The decomposition of dinitrogen pentoxide, N_2O_5, at 45 °C was investigated. The reaction that takes place is shown below.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

In an experiment, N_2O_5 with a concentration of 0.60 mol dm^{-3} was decomposed at 45 °C.

At this temperature, the reaction has a constant half-life of 1200 s.

(i) How can you tell that this reaction is first order with respect to N_2O_5?

....

....[1]

(ii) Write down an expression for the rate equation of this decomposition.

....[1]

(iii) Complete the graph opposite to show how the [N_2O_5] changes over the first 3600 s of the reaction. [2]

(iv) The rate of this reaction can be determined from this graph.

Show on the graph how the rate can be measured after 1200 s. [1]

(v) The rate can also be calculated from the rate equation. The rate constant for this reaction is 6.2×10^{-4} s^{-1}.

Calculate the initial rate of this reaction. State the units.

rate = ... units.......................... [2]

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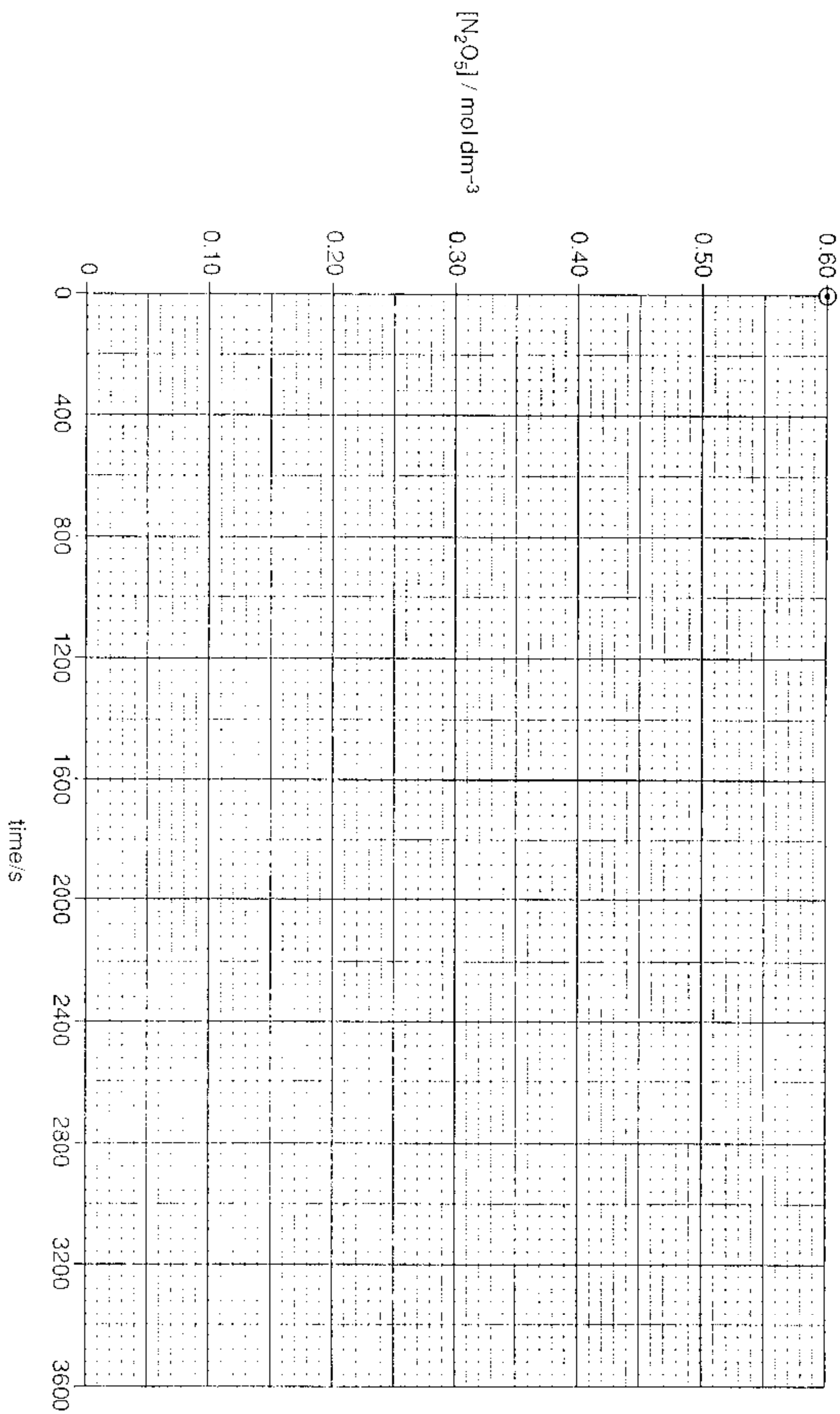

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(b) A student investigated the hydration of 2-methylpropene, $(CH_3)_2C{=}CH_2$, with dilute aqueous acid to form 2-methylpropan-2-ol, $(CH_3)_3COH$.

The following mechanism has been proposed for this hydration.

step 1 $(CH_3)_2C{=}CH_2 + H^+(aq) \longrightarrow (CH_3)_3C^+$ rate determining step

step 2 $(CH_3)_3C^+ + H_2O \longrightarrow (CH_3)_3COH + H^+(aq)$

(i) Step 1 is the rate-determining step for this hydration.

What is meant by the term *rate-determining step*?

....

....[1]

(ii) Write a balanced equation for the overall hydration reaction.

....[1]

(iii) Suggest the role of $H^+(aq)$ in this mechanism. Explain your reason.

....

....

....[2]

(iv) Use the mechanism above to suggest the rate equation for this hydration.

....[1]

[Total: 12]

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2 Methanol, $CH_3OH(g)$, is manufactured from carbon monoxide and hydrogen in an equilibrium reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91\,kJ\,mol^{-1}$$

(a) In this question, one mark is available for the quality of use and organisation of scientific terms.

Explain the advantages and disadvantages of running this reaction

- at a high pressure,
- at a high temperature.

....

....

....

....

....

....

....

....

....

....[5]

Quality of Written Communication [1]

(b) This equilibrium reaction is normally carried out at 10 MPa pressure and 550 K, and starting with a 1 : 2 CO : H_2 mixture. At equilibrium, only 10% of the CO has reacted.

(i) Deduce the equilibrium amounts, mole fractions and partial pressures of CO, H_2 and CH_3OH present at equilibrium. Write your answers in the table below.

Assume that you have started with a mixture of 1.0 mol CO and 2.0 mol H_2.

	CO	H_2	CH_3OH
initial amount /mol	1.0	2.0	0.0
equilibrium amount /mol	0.9		
mole fraction at equilibrium			
partial pressure at equilibrium /MPa			

[4]

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(ii) Write the expression for K_p for this equilibrium.

[2]

(iii) The CO : H_2 ratio in the starting mixture was changed from 1 : 2 to 1 : 3 and the mixture was allowed to reach equilibrium at the same temperature and pressure.

Explain, in terms of K_p, the effect of this change on the equilibrium yield of CH_3OH.

....

....

....

....

....[3]

(iv) In another experiment, the equilibrium partial pressures were:

CO, 3.70 MPa; H_2, 5.10 MPa; CH_3OH, 0.261 MPa.

Calculate the value of K_p for this equilibrium. Express your answer to an appropriate number of significant figures. State the units of K_p.

K_p = ... units............................[2]

(c) In the UK, the annual production of methanol is 500 000 tonnes. Methanol has many uses in fuels as a reliable and low pollution form of energy.

Suggest an equation for the combustion of methanol.

....[1]

[Total: 18]

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3 A student carried out an investigation with aqueous solutions of nitric acid, sodium hydroxide, ethanoic acid and water.

(a) Nitric acid, HNO_3, is a strong Brønsted-Lowry acid.

(i) Explain what is meant by a *strong acid* and a *Bronsted-Lowry acid.*

....

....

.... [2]

(ii) What is the conjugate base formed from HNO_3?

.... [1]

(b) The student diluted $0.015\,mol\,dm^{-3}$ nitric acid with an equal volume of water and measured the pH of the diluted acid at 25 °C.

(i) Calculate the pH of $0.015\,mol\,dm^{-3}$ nitric acid.

[2]

(ii) Calculate the pH of the diluted acid.

[1]

(c) The student measured the pH of a solution of sodium hydroxide as 13.54 at 25 °C.

$K_w = 1.0 \times 10^{-14}\ mol^2\,dm^{-6}$ at 25 °C.

(i) Write down an expression for the ionic product, K_w, for water.

.... [1]

(ii) Calculate the concentration, in $mol\,dm^{-3}$, of this solution of sodium hydroxide.

[2]

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(d) The student prepared two solutions.

- Solution **A** was made by mixing together 25 cm^3 0.010 mol dm^{-3} aqueous sodium hydroxide with 50 cm^3 0.010 mol dm^{-3} ethanoic acid, CH_3COOH. Solution **A** is a buffer solution.
- Solution **B** was made by mixing together 25 cm^3 0.020 mol dm^{-3} aqueous sodium hydroxide with 50 cm^3 0.010 mol dm^{-3} ethanoic acid, CH_3COOH. Solution **B** is **not** a buffer solution.

(i) What is meant by a *buffer solution*?

....

....[1]

(ii) Explain why Solution **A** is a buffer solution whereas Solution **B** is **not**.

....

....

....

....

....

....

....[4]

(e) The student measured the pH of water as 7.0 at 25 °C. The student then warmed the water to 40 °C and measured the pH as 6.7.

What do these results tell you about the tendency of water to ionise as it gets warmer? Explain your reasoning in terms of equilibrium.

....

....

....

....[2]

[Total: 16]

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4 *In your answers to the questions that follow, show all of your working.*

At room temperature and pressure, r.t.p., 1 mol of gas molecules has a volume of 24 dm^3.

Whilst digging his garden, a chemistry student found what appeared to be a piece of bronze, possibly from the Bronze Age. The student knew that bronze was an alloy of copper with other metals including tin. He carried out three experiments on samples of the bronze.

(a) **Experiment 1**

He dissolved a small piece of the bronze, weighing 0.28 g, in concentrated (16 mol dm^{-3}) nitric acid, HNO_3. 5 cm^3 of a blue solution **C** containing Cu^{2+} ions was formed together with a brown gas with the molecular formula NO_2.

Equation **4.1** represents the equation for the reaction between copper and concentrated nitric acid.

$$Cu + 4H^+ + 2NO_3^- \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O \qquad \text{equation } \mathbf{4.1}$$

The student analysed the blue colour from the Cu^{2+} ions in solution **C** using a colorimeter. He found out that the concentration of Cu^{2+} ions in solution **C** was 0.68 mol dm^{-3}.

The student concentrated the solution and obtained some blue crystals of a compound **A** with a percentage composition by mass of Cu, 26.29%; N, 11.60%; O, 59.63%; H, 2.48%. This composition included 3 waters of crystallisation.

- Calculate the percentage of copper in the bronze relic. [3]
- Calculate the empirical formula of **A**. [2]
- How would the formula of **A** normally be shown on a bottle of the chemical? [2]

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(b) Experiment 2

The student dissolved another small piece of the bronze relic in dilute (8 mol dm^{-3}) nitric acid. A blue solution containing Cu^{2+} ions was again formed but this time a colourless gas was produced with the molecular formula NO.

Equation **4.2** represents the **unbalanced** equation for this second reaction.

$$Cu + H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + H_2O \qquad \text{equation } \mathbf{4.2}$$

- By considering oxidation numbers, balance equation **4.2**. [3]

(c) Experiment 3

The student heated a third small piece of the bronze relic with concentrated sulphuric acid. The copper in the bronze relic reacted to produce a blue solution and 90 cm^3 of a gas **B**, measured at r.t.p.. The mass of the gas **B** collected was 0.24 g.

- Suggest a possible identity of gas **B**.
- Suggest a likely balanced equation for this reaction. [4]

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[Total: 14]

END OF QUESTION PAPER

Abbreviations, annotations and conventions used in the Mark Scheme	/	= alternative and acceptable answers for the same marking point
	;	= separates marking points
	NOT	= answers which are not worthy of credit
	( )	= words which are not essential to gain credit
	___	= (underlining) key words which **must** be used to gain credit
	ecf	= error carried forward
	AW	= alternative wording
	ora	= or reverse argument

Question			Expected Answers	Marks
1	(a)	(i)	constant half-life ✓	[1]
		(ii)	rate = k $[N_2O_5]$ ✓ Common error will be to use '2' from equation.	[1]
		(iii)	curve downwards getting less steep ✓ curve goes through 1200,0.30; 2400,0.15; 3600,0.075 ✓	[2]
		(iv)	tangent shown on graph at t = 1200 s ✓	[1]
		(v)	3.7(2) x 10^{4} ✓ mol dm^{-3} s^{-1} ✓ ecf possible from (ii) using $[N_2O_5]^x$ (2nd order answer: 2.2(3) x 10^{4})	[2]
	(b)	(i)	slow step ✓	[1]
		(ii)	$(CH_3)_2C{=}CH_2$ + H_2O ⟶ $(CH_3)_3COH$ ✓	[1]
		(iii)	H^+ is a catalyst ✓ H^+ used in first step **and** formed in second step/ regenerated/ not used up ✓	[2]
		(iv)	rate = k $[(CH_3)_2C{=}CH_2]$ $[H^+]$ ✓ common error will be use of H_2O instead of H^+	[1]
				Total: 12

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Abbreviations, annotations and conventions used in the Mark Scheme		
	/ = alternative and acceptable answers for the same marking point ; = separates marking points NOT = answers which are not worthy of credit ( ) = words which are not essential to gain credit ___ = (underlining) key words which **must** be used to gain credit ecf = error carried forward AW = alternative wording ora = or reverse argument	

Question	Expected Answers	Marks
2 (a)	**High Pressure** Equilibrium ⟶ right as fewer moles on right hand side and the shift reduces number of molecules/compensates for increasing pressure ✓ Rate increases/ more collisions ✓	[2]
	High temperature Equilibrium ⟶ left as equilibrium goes to the left to compensate for increased temperature/absorbs the energy/in endothermic direction (ora) ✓ Rate increases/ more successful collisions ✓	[2]
	Other effect High pressures expensive/ high temperatures expensive /high pressures cause safety problems ✓	[1]
QoWC:	One correct statement followed by correct explanation ✓	[1]
(b) (i)	CO H_2 CH_3OH 1.0 2.0 0.0 0.9 1.8 ✓ 0.1 ✓ 0.9/2.8 or 0.321 or 0.32/0.3 1.8/2.8 or 0.643 or 0.64/0.6 0.1/2.8 or 0.036 or 0.04 ✓ 3.21 (MPa) 6.43 (MPa) 0.36 (MPa) ✓ In 3rd and 4th rows, ecf from previous row	[4]
(ii)	$K_p = \frac{p(CH_3OH)}{p(CO) \times p(H_2)^2}$ ✓✓ 1 mark for K_c / use of any [ ] /inverted/power missing.	[2]
(iii)	K_p stays the same ✓ Equilibrium position moves to the right/yield increases ✓ in response to increase in reactants ✓	[3]
(iv)	$K_p = \frac{0.261}{3.70 \times 5.10^2} = 2.71 \times 10^{-3}$ ✓ MPa^{-2} ✓ calc value 2.7120546×10^{-3}; answer and/or units ecf from (ii)	[2]
(c)	$CH_3OH + 1.5O_2 \longrightarrow CO_2 + 2H_2O$ ✓	[1]
		Total: 18

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Question	**Expected Answers**	**Marks**
3 (a) (i)	completely dissociates/ionised ✓ proton donor ✓	[2]
(ii)	NO_3 ✓	[1]
(b) (i)	pH = $-\log[H^+]$ / $-\log(0.015)$ ✓ = 1.82 / 1.8 ✓ (Not 2)	[2]
(ii)	$[H^+]$ = 0.0075 mol dm^{-3} pH = $-\log(0.0075)$ = 2.12 / 2.1 ✓	[1]
(c) (i)	$K_w = [H^+(aq)]\,[OH^-(aq)]$ ✓ *state symbols not needed*	[1]
(ii)	$[H^+(aq)] = 10^{-pH} = 10^{-13.54}$ = 2.88/2.9 × 10^{-14} mol dm^{-3} ✓ [NaOH] / $[OH^-(aq)] = \frac{K_w}{[H^+(aq)]} = \frac{1.0 \times 10^{-14}}{2.88 \times 10^{-14}}$ = 0.347 / 0.35 mol dm^{-3} ✓	[2]
(d) (i)	a solution that minimises/resists/opposes pH changes ✓	[1]
(ii)	The buffer must contain both CH_3COOH and CH_3COONa / CH_3COO^- /weak acid and conjugate base ✓ Solution **A** is a mixture of CH_3COOH and CH_3COONa / / has an excess of acid /is acidic ✓ Solution **B**, contains only CH_3COONa/ only CH_3COO^- /only the salt/ is neutral ✓ $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$ / acid/alkali has been neutralised/ $CH_3COOH(aq)$ and NaOH react together ✓	[4]
(e)	$[H^+]$ increases ✓ H_2O ionises more / for $H_2O \rightleftharpoons H^+ + OH^-$, equilibrium moves to the right ✓ exo/endo is 'noise'	[2]
		Total: 15

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Question	**Expected Answers**	**Marks**
4 (a)	moles of Cu = 0.68 x 5/1000 = 0.0034 ✓ mass of Cu = 0.0034 x 63.5 = 0.216 g ✓ % Cu = 0.216/0.28 = 77% ✓	[3]
	ratios: Cu = 26.29/63.5 = 0.41 OR 1 N= 11.6/14 = 0.83 OR 2 O = 59.63/16 = 3.73 OR 9 H= 2.48/1 = 2.48 OR 6 ✓ empirical formula = $CuN_2O_9H_6$ ✓	[2]
	Formula with $3H_2O$ shown separately scores 1: i.e. $CuN_2O_6.3H_2O$ ✓ Correct formula shown with $(NO_3)_2$ scores 2nd mark: $Cu(NO_3)_2.3H_2O$ ✓ (Correct answer automatically scores both marks)	[2]
(b)	$Cu \longrightarrow Cu^{2+}$: Cu from 0 to +2 ✓ $NO_3^- \longrightarrow NO$: N from +5 to +2 ✓ $3Cu + 8H^+ + 2NO_3^- \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$ ✓ 'simple balance' as the only creditworthy response scores 1 mark: i.e. $Cu + 4H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + 2H_2O$	[3]
(c)	moles of A = 90/24000 = 3.75×10^{-3} ✓ M_r of A = 0.24/ 3.75×10^{-3} = 64 ✓ Gas is SO_2 ✓ $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ / $Cu + 4H^+ + SO_4^{2-} \longrightarrow Cu^{2+} + SO_2 + 2H_2O$ / $Cu + 3H^+ + HSO_4^- \longrightarrow Cu^{2+} + SO_2 + 2H_2O$ ✓	[4]
		Total: 14

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