OCR
RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS
Advanced GCE

CHEMISTRY **2816/01**

Unifying Concepts in Chemistry

Wednesday **18 JUNE 2003** 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	**14**	
2	**14**	
3	**13**	
4	**10**	
5	**9**	
TOTAL	**60**	

This question paper consists of 11 printed pages and 1 blank page.

For Examiner's Use

Answer **all** the questions.

1 Bromine can be formed by the oxidation of bromide ions. This question compares the rates of two reactions that produce bromine.

(a) Bromine is formed by the oxidation of bromide ions with acidified bromate(V) ions.

$$5Br^-(aq) + 6H^+(aq) + BrO_3^-(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

This reaction was carried out several times using different concentrations of the three reactants. The initial rate of each experimental run was calculated and the results are shown below. In each case, initial concentrations are shown.

experiment	$[Br^-(aq)]$ /mol dm^{-3}	$[H^+(aq)]$ /mol dm^{-3}	$[BrO_3^-(aq)]$ /mol dm^{-3}	initial rate /10^{-3} mol dm^{-3} s^{-1}
1	0.10	0.10	0.10	1.2
2	0.10	0.10	0.20	2.4
3	0.30	0.10	0.10	3.6
4	0.10	0.20	0.20	9.6

(i) For each reactant, deduce the order of reaction. Show your reasoning.

$Br^-(aq)$ ....

....

....

$H^+(aq)$ ....

....

....

$BrO_3^-(aq)$ ....

....

....[6]

(ii) Deduce the rate equation.

....[1]

For Examiner's Use

(iii) Calculate the rate constant, *k*, for this reaction. State the units for *k*.

rate constant, *k* .... units ....[3]

(b) Bromine can **also** be formed by the oxidation of hydrogen bromide with oxygen.

The following mechanism has been suggested for this multi-step reaction.

step 1	$HBr + O_2 \longrightarrow HBrO_2$
step 2	$HBrO_2 + HBr \longrightarrow 2HBrO$
step 3	$HBrO + HBr \longrightarrow Br_2 + H_2O$
step 4	$HBrO + HBr \longrightarrow Br_2 + H_2O$ (a repeat of step 3)

(i) Explain the term *rate-determining step*.

....

....[1]

(ii) The rate equation for this reaction is: rate = $k[HBr][O_2]$.

Explain which of the four steps above is the **rate-determining step** for this reaction.

....

....

....[2]

(iii) Determine the **overall** equation for this reaction.

....[1]

[Total: 14]

[Turn over

For Examiner's Use

2 Phosgene, $COCl_2$, is a highly toxic gas, used in making organic chemicals, dyestuffs and resins. Phosgene can be manufactured by the reaction of carbon monoxide and chlorine in the presence of a catalyst.

An equilibrium system exists between carbon monoxide, chlorine and phosgene.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H = -108\,\text{kJ mol}^{-1}$$

(a) Explain how changes in temperature and pressure could be used to increase the equilibrium yield of $COCl_2$.

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....[4]

(b) The equilibrium partial pressures in this system are shown below.

compound	CO	Cl_2	$COCl_2$
partial pressure / Pa	2.5×10^{-6}	2.5×10^{-6}	4.13×10^{-5}

(i) What is meant by the term *partial pressure*?

....

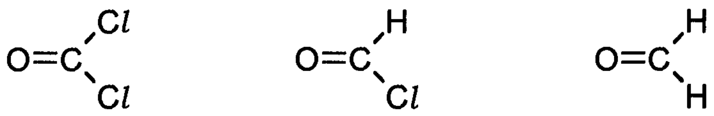
....[1]

(ii) Write the expression for K_p in this equilibrium system and calculate the numerical value of K_p.

[3]

For Examiner's Use

(c) Phosgene is a polar molecule. The diagram below shows a molecule of phosgene and two related molecules, **A** and **B**.



phosgene **A** **B**

(i) Add the partial charges (δ+ and δ–) to the diagrams of the three molecules above. [2]

(ii) Molecule **A** is the most polar of the three molecules.

Suggest why this is so.

....

....

....[2]

(iii) Compound **A** reacts with water as follows.

Phosgene also reacts with water.

Suggest an equation for this reaction.

[2]

[Total: 14]

[Turn over

3 Hydrogen chloride is used in the manufacture of many chemical compounds, including those used in metallurgy and food processing.

(a) There are two main industrial methods for preparing hydrogen chloride:

- by direct combination of chlorine and hydrogen gases,
- as a by-product of the chlorination of many organic hydrocarbons.

Write equations to show the formation of HCl from

(i) chlorine and hydrogen

....[1]

(ii) chlorine and hexane, C_6H_{14}.

....[1]

(b) Hydrochloric acid is usually sold as a solution prepared by dissolving hydrogen chloride gas in water.

A science technician bought 15.0 dm^3 of 8.00 $mol\,dm^{-3}$ hydrochloric acid which had been made by dissolving hydrogen chloride gas in water.

1 mol of gas molecules occupies 24.0 dm^3 at room temperature and pressure, r.t.p.

(i) Calculate the volume of hydrogen chloride gas at r.t.p. that dissolved to produce this hydrochloric acid.

[2]

(ii) Outline, with quantities, how the technician could make up 1.00 dm^3 of 0.0200 $mol\,dm^{-3}$ hydrochloric acid from the 8.00 $mol\,dm^{-3}$ stock solution of hydrochloric acid.

[2]

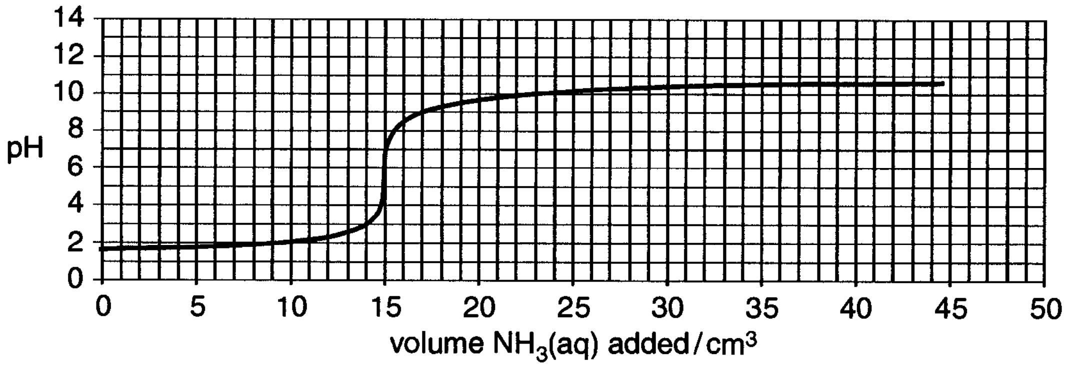
(iii) Calculate the pH of 0.0200 $mol\,dm^{-3}$ $HCl(aq)$.

[2]

(c) Hydrochloric acid can be neutralised with aqueous ammonia to form ammonium chloride.

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

The technician titrated the 0.0200 mol dm^{-3} hydrochloric acid prepared in **(b)(ii)** with aqueous ammonia.
A 20.0 cm^3 sample of the 0.0200 mol dm^{-3} HCl(aq) was placed in a conical flask and the NH_3(aq) was added from a burette until the pH no longer changed.
The pH curve for this titration is shown below.



(i) How can you tell from this pH curve that aqueous ammonia is a weak base?

....

....[1]

(ii) Use the information above to calculate the concentration, in mol dm^{-3}, of the aqueous ammonia.

[2]

(iii) The pH ranges in which the pH changes for three indicators are shown below.

indicator	pH range
alizarin yellow	10.1–12.0
methyl yellow	2.9–4.0
chlorophenol red	4.8–6.4

Explain which of the three indicators is most suitable for this titration.

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....[2]

[Total: 13]

For Examiner's Use

4 Buffer solutions have many uses in medicine and in cosmetics and toiletries. Buffer solutions can be prepared by mixing aqueous solutions of methanoic acid, HCOOH, and sodium methanoate, HCOONa.

(a) In this part, one mark is available for the quality of written communication.

Describe what a buffer solution is and how a buffer solution works.

Use the HCOOH/HCOONa buffer solution in your answer.

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....[6]

Quality of Written Communication [1]

(b) Calculate the pH of a buffer solution containing equal volumes of 2.5 mol dm^{-3} HCOONa and 1.0 mol dm^{-3} HCOOH ($K_a = 1.6 \times 10^{-4}$ mol dm^{-3}).

[3]

[Total: 10]

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TURN OVER FOR QUESTION 5

[Turn over

For Examiner's Use

5 Read the section below and use your knowledge and understanding of chemistry to answer the questions that follow.

Compound **X** is a dicarboxylic acid, M_r = 90, present in many foods such as cocoa, green vegetables and rhubarb. Compound **X** may be harmful to humans because it reacts with calcium ions in the bloodstream to form solid particles. These are then deposited in the kidneys as 'kidney stones'.

Analysis of a kidney stone showed that it was made up almost entirely of a single compound **Y** with the percentage composition by mass: Ca, 31.3%; C, 18.7%; O, 50.0%.

Some people develop kidney stones more readily than others. Compound **X** is very soluble in water and people susceptible to kidney stones are advised to drink large quantities of water to flush this compound from their bodies.

- Calculate the empirical formula of compound **Y**, the main compound in kidney stones. [2]
- A kidney stone with a mass of 2.0 g was removed from a patient. Calculate the number of calcium ions that have been removed from the bloodstream to form this kidney stone. $L = 6.02 \times 10^{23}\ mol^{-1}$ [3]
- Deduce the molecular formula of compound **X** and suggest its structural formula. [2]
- Explain why compound **X** is very soluble in water. [2]

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2816/01 Unifying Concepts

June 2003

Mark Scheme

The following annotations may be used when marking:

X	=	incorrect response (errors may also be underlined)
^	=	omission mark
bod	=	benefit of the doubt (where professional judgement has been used)
ecf	=	error carried forward (in consequential marking)
con	=	contradiction (in cases where candidates contradict themselves in the same response)
sf	=	error in the number of significant figures

Abbreviations, annotations and conventions used in the Mark Scheme:

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

1. **(a)** **(i)** $Br^-(aq)$ 1st order ✓

$[Br^-(aq)]$ triples rate triples ✓

[2]

$H^+(aq)$ 2nd order ✓

$[H^+(aq)]$ doubles rate quadruples ✓

[2]

$BrO_3^-(aq)$ 1st order ✓

$[BrO_3^-(aq)]$ doubles rate doubles ✓

[2]

(ii) rate = $k[Br^-(aq)]\,[H^+(aq)]^2\,[BrO_3^-(aq)]$ ✓ (state symbols **not** needed)

[1]

(iii)

$$k = \frac{\text{rate}}{[Br^-(aq)]\,[H^+(aq)]^2\,[BrO_3^-(aq)]} = \frac{1.2 \times 10^{-3}}{0.1 \times 0.1^2 \times 0.1} ✓ =$$

rate constant, k:= 12 ✓ units: $dm^9\ mol^{-3}\ s^{-1}$ ✓

(0.0833 would score 1 mark)

[3]

(b) **(i)** slowest step✓

[1]

(ii) rate equation shows reaction is 1st order wrt HBr and 1st order wrt O_2 ✓

which corresponds to molecules in step 1 ✓

[2]

(iii) $4HBr + O_2 \longrightarrow 2Br_2 + 2H_2O$ ✓

[1]

[Total: 14]

2. **(a)** decrease temperature ✓ exothermic direction ✓

increase pressure ✓ favours side with fewer molecules✓

[4]

(b) **(i)** The contribution of a gas to the pressure in a gas mixture /

mole fraction x total pressure ✓

[1]

(ii)

$$K_p = \frac{p\,COCl_2(g)}{p\,CO(g) \times p\,Cl_2(g)}$$ ✓✓

If any [ ] then only ✓ for K_p expression

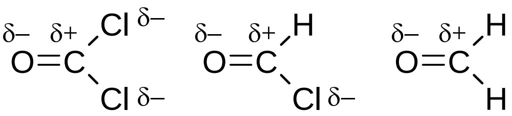
If upside down with **no** concentration terms [ ], ✓ only

$$K_p = \frac{4.13 \times 10^{-5}}{2.5 \times 10^{-6} \times 2.5 \times 10^{-6}} = 6.6 \times 10^{6}$$ ✓ Pa^{-1}

If expression is upside down, then answer consequentially is 1.51×10^{-7}.

[3]

(c) **(i)**



A **B**

C=O dipole ✓; δ– on chlorines ✓

C=O dipole shown correctly on one structure without any contradiction scores 1 mark

[2]

(ii) **A** has 2 δ- / **A** has 2 electronegative atoms / **A** has more electronegative elements than **B** ✓

$COCl_2$ is symmetrical / **A** is **not** symmetrical ✓

dipoles cancel in $COCl_2$ ✓

3 marking points gives [2] max

(iii) $COCl_2 + 2H_2O \longrightarrow H_2CO_3 + 2HCl$ ✓✓

OR

$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$ ✓✓

OR

$COCl_2 + H_2O \longrightarrow O{=}COHCl + HCl$ ✓

[2]

[Total: 14]

3. **(a)** **(i)** $H_2 + Cl_2 \longrightarrow 2HCl$ ✓

[1]

(ii) $C_6H_{14} + Cl_2 \longrightarrow C_6H_{13}Cl + HCl$ ✓

[1]

(b) **(i)** moles HCl = 8 x 15 = 120 mol ✓

volume HCl(g) = 120 x 24 = 2880 (dm^3) ✓

[2]

(ii) solution must be diluted by 8.00/0.0200 = 400 times ✓

To 2.50 cm^3 of 8.00 mol dm^{-3} HCl✓ add sufficient water to make 1 dm^3 of solution.

[2]

(iii) pH= $-\log[H^+]$ ✓ = 1.70 ✓

[2]

(c) **(i)** Final pH is approx 11 / equivalence point <7 ✓

[1]

(ii) volume of NH_3(aq) that reacts is 15 cm^3 ✓

amount of HCl used = 0.0200 x 20.00/1000 = 4×10^{-4}
concentration of NH_3(aq) = 4×10^{-4} x 1000/15 = 0.0267 mol dm^{-3} ✓

[2]

(iii) chlorophenol red ✓

pH range coincides with pH change **during sharp rise** OR pH 4-7 /

coincides with equivalence point ✓

[2]

[Total: 13]

4. (a) A solution that minimises changes in pH (after addition of acid/alkali) ✓

equilibrium: HCOOH $\rightleftharpoons$ $HCOO^-$ + H^+

/ HCOOH and $HCOO^-$ / weak acid and its conjugate base ✓

HCOOH reacts with added alkali / HCOOH + $OH^- \longrightarrow H_2O + COO^-$/

added alkali reacts with H^+ / $H^+ + OH^- \longrightarrow H_2O$✓

$\longrightarrow$ $HCOO^-$ / Equilibrium moves to right (to counteract change) ✓

$HCOO^-$ reacts with added acid or H^+ ✓

$\longrightarrow$ HCOOH / Equilibrium moves to left (to counteract change) ✓

[6]

qwc: communicates in terms of relevant equilibrium ✓ [1]

(b) For a buffer, $K_a = [H^+] \times [HCOO^-]/[HCOOH]$ ✓

$[H^+] = K_a \times [HCOOH]/[HCOO^-] = 1.6 \times 10^{-4} \times 1/2.5 = 6.4 \times 10^{-5}$ mol dm^{-3}✓

$pH = -\log[H^+] = -\log(6.4 \times 10^{-5}) = 4.19$ / 4.2 ✓

OR

$pH = pK_a - \log [HCOOH]/[HCOO^-]$ ✓

$pK_a = 3.8$ ✓

pH = 3.8 + 0.4 = 4.2 ✓

NOTES

3.19 worth ✓✓ (incorrect power of 10)

3.4 worth ✓✓ (use of $[HCOOH]/[HCOO^-]$)

[3]

[Total: 10]

5.

	Ca	:	C	:	O
	Ca	:	C	:	O
=	31.3/40.1	:	18.7/12	:	50.0/16 ✓
=	0.78	:	1.56	:	3.125
=	1	:	2	:	4

Empirical formula of **Y** = CaC_2O_4 ✓

[2]

mass of Ca in kidney stone = 2 x 31.3/100 = 0.626 g ✓
moles of Ca in kidney stone = 0.626/40.1 = 0.0156 mol ✓
number of Ca^{2+} ions removed = $6.02 \times 10^{23} \times 0.0156 = 9.39 \times 10^{21}$ ions ✓

0.0156 mol Ca is 2 marks (molar mass 128.1 g mol^{-1})

OR

moles of Ca = 2/128.1 ✓ = 0.0156 mol ✓

number of Ca^{2+} ions removed = $6.02 \times 10^{23} \times 0.0156 = 9.39 \times 10^{21}$ ions ✓

*For consequential marking of last point, must be evidence of **moles** x L*

[3]

Molecular formula of **X** = $H_2C_2O_4$ ✓
Structural formula = $(COOH)_2$ ✓

[2]

Oxalic acid forms hydrogen bonds with water ✓
2 x O–H in structure / 2 x COOH groups / no hydrocarbon chain / diagram showing at least 2 H bonds with water per oxalic acid molecule ✓

[2]
[Total: 9]