RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY

2815/01

Trends and Patterns

Tuesday **24 JUNE 2003** Morning 1 hour

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

Candidate Name	Centre Number	Candidate Number

TIME 1 hour

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	18	
2	15	
3	12	
TOTAL	45	

This question paper consists of 10 printed pages and 2 blank pages.

[Turn over

For Examiner's Use

Answer **all** the questions.

1 Calcium carbonate thermally decomposes into calcium oxide and carbon dioxide as shown in the equation.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

(a) Show that the thermal decomposition of calcium carbonate is **not** a redox reaction. Use oxidation states in your answer.

....

....

.... [2]

(b) Magnesium carbonate also thermally decomposes. Describe and explain the difference in the ease of thermal decomposition between magnesium carbonate and calcium carbonate. Use ideas about charge density and polarisation in your answer.

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....

....

.... [3]

(c) Calculate the enthalpy change of reaction, ΔH_r, for the thermal decomposition of calcium carbonate using the enthalpy changes of formation given in the table.

compound	enthalpy change of formation, ΔH_f / kJ mol^{-1}
$CaCO_3(s)$	–1207
$CaO(s)$	–635
$CO_2(g)$	–393

answer .... kJ mol^{-1} [2]

[Turn over

For Examiner's Use

(d) The lattice enthalpy of magnesium oxide is –3916 kJ mol^{-1}.

Explain, with the aid of a suitable equation, what is meant by the statement the 'lattice enthalpy of magnesium oxide is –3916 kJ mol^{-1}'.

....

....

....

.... [3]

(e) The table below shows the enthalpy changes needed to calculate the lattice enthalpy of magnesium oxide.

process	equation	enthalpy change / kJ mol^{-1}
first ionisation energy of magnesium	$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$	+735
second ionisation energy of magnesium	$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$	+1445
first electron affinity of oxygen	$O(g) + e^{-} \rightarrow O^{-}(g)$	–141
second electron affinity of oxygen	$O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$	+878
enthalpy change of formation for magnesium oxide	$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$	–602
enthalpy change of atomisation for magnesium	$Mg(s) \rightarrow Mg(g)$	+150
....	$\frac{1}{2}O_2(g) \rightarrow O(g)$	+247

(i) Complete the table by writing in the missing process. [1]

(ii) Explain why the second ionisation energy of magnesium is **more endothermic** than the first ionisation energy.

....

....

....[2]

(iii) Draw a labelled Born-Haber cycle using the information in the table. Show, by calculation, that the lattice enthalpy of magnesium oxide is –3916 kJ mol^{-1}.

[4]

~~**(f)** State **one** use for magnesium oxide that relies on its high lattice enthalpy.~~

.... [1]

[Total: 18]

For Examiner's Use

2 Aqueous copper(II) sulphate reacts with an excess of aqueous ammonia to give a dark blue solution. The solution contains the octahedral complex ion, $[Cu(NH_3)_x(H_2O)_y]^{2+}$.

The formula of this complex ion can be determined using colorimetry.

- A student makes up six different mixtures of 1.00 mol dm^{-3} aqueous ammonia and 0.500 mol dm^{-3} aqueous copper(II) sulphate and water.
- She filters the mixtures to remove any precipitate that forms.
- The filtrate is a dark blue solution that contains the complex ion, $[Cu(NH_3)_x(H_2O)_y]^{2+}$.
- The student places the blue solution into a colorimeter and measures the absorbance of the solution.

The table below shows the relative absorbance of each mixture.

mixture	one	two	three	four	five	six
volume of 0.500 mol dm^{-3} $CuSO_4(aq)$ / cm^3	5.00	5.00	5.00	5.00	5.00	5.00
volume of 1.00 mol dm^{-3} $NH_3(aq)$ / cm^3	3.00	6.00	9.00	11.00	15.00	18.00
volume of $H_2O(l)$ / cm^3	17.00	14.00	11.00	9.00	5.00	2.00
relative absorbance	0.29	0.57	0.86	0.95	0.94	0.95

(a) Copper is a transition element. One typical property of a transition element is that it forms coloured complex ions.

State **two** other typical properties of a transition element.

1. ....

2. .... [2]

(b) The precipitate formed when the student makes some of the mixtures is copper(II) hydroxide.

(i) Write an ionic equation to show the formation of copper(II) hydroxide from its ions.

.... [1]

(ii) If this precipitate is **not** removed, an inaccurate absorbance reading is obtained. Suggest why.

....

.... [1]

For Examiner's Use

(e) In the octahedral complex, $[Cu(NH_3)_x(H_2O)_y]^{2+}$, ammonia is a ligand.

(i) Explain why ammonia can behave as a ligand.

....

.... [1]

(ii) The bond angle around the nitrogen atom in an ammonia molecule is 107° but it is 109.5° in the octahedral complex. Explain why the bond angles differ.

....

....

....

....

.... [2]

(f) Aqueous copper(II) ions react with concentrated hydrochloric acid to give a yellow solution of $[CuCl_4]^{2-}(aq)$. This reaction is an example of ligand substitution.

(i) Write an equation to show the formation of $[CuCl_4]^{2-}(aq)$.

[1]

(ii) Draw the shape of the $[CuCl_4]^{2-}$ ion.

[1]

[Total: 15]

For Examiner's Use

Answer **all** the questions.

1 Copper is an element that has many uses, both as a metal and in its compounds.

(a) By reference to a suitably labelled diagram, describe how you would measure the standard electrode potential of the Cu^{2+}/Cu electrode.

....

....

....

....

....[6]

(b) Complete the electronic structures of

a Cu atom $1s^2 2s^2 2p^6$ ....

a Cu^+ ion $1s^2 2s^2 2p^6$ ....

a Cu^{2+} ion $1s^2 2s^2 2p^6$ .... [3]

(b) The compound 1,2-diaminoethane, $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$, is a bidentate ligand.

(i) Explain the meaning of the term *ligand*.

....

....[2]

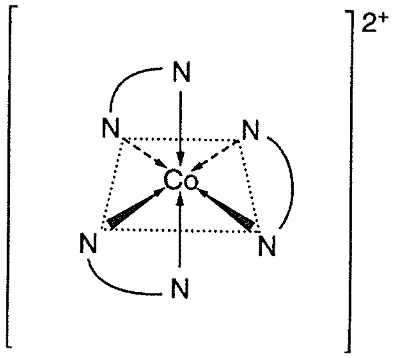
(ii) Suggest the meaning of the term *bidentate*.

....

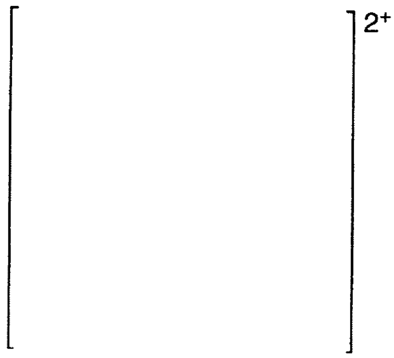
....[1]

(c) Cobalt(II) ions form a complex with the ligand 1,2-diaminoethane. The structure of an isomer of this complex is shown below (**structure A**).

is used to represent 1,2-diaminoethane.



structure A



structure B

(i) In the space above (labelled **structure B**), draw the structure of another isomer of this complex. [1]

(ii) Name this type of isomerism. Explain why the complex shows this type of isomerism.

....

....

....[2]

[Total: 11]

For Examiner's Use

3 Some standard electrode (redox) potentials involving copper and its ions are given in the table below.

electrode reaction	$E^{\ominus}$/V
$Cu^{+} + e^{-} \rightleftharpoons Cu$	+ 0.52
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+ 0.34
$Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$	+ 0.15

(a) Use these data to explain why the reaction below is likely to occur.

$$2Cu^{+} \rightarrow Cu^{2+} + Cu$$

....

....

....

....[1]

(b) This type of reaction can be called *disproportionation*. Explain the meaning of this term.

....

....

....[2]

(c) Some copper(I) compounds are stable. Suggest a condition under which copper(I) compounds are stable.

....

....

....[1]

For Examiner's Use

(d) When aqueous potassium iodide is added to aqueous copper(II) sulphate, a white solid and a yellow/brown solution are formed.

(i) Complete and balance the following equation for the reaction between copper(II) ions and iodide ions.

$Cu^{2+}(aq)$ + $I^{-}(aq)$ → [2]

(ii) Including starting materials, use your answer to **(i)** to explain the observations above.

....

....

....

....[3]

(e) Apart from its use to make pigments, give one use of copper. State the property which makes it suitable for this use.

use ....

property .... [1]

[Total: 10]

For Examiner's Use

4 Compounds of chromium and manganese exist in a wide variety of oxidation states and these compounds can be used in redox reactions.

(a) Under certain conditions dichromate(VI) ions, $Cr_2O_7^{2-}$, can oxidise manganese(II) ions, Mn^{2+}.

In this reaction, dichromate(VI) ions are reduced to chromium(III) ions according to the equation below.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$$

In an experiment, it was found that 20.0 cm^3 of 0.100 mol dm^{-3} potassium dichromate(VI) were needed to oxidise 30.0 cm^3 of 0.200 mol dm^{-3} manganese(II) sulphate.

(i) Calculate the amount of $Cr_2O_7^{2-}$ used in the reaction.

.... mol [1]

(ii) Calculate the amount of Mn^{2+} used in the reaction.

.... mol [1]

(iii) Deduce the number of moles of Mn^{2+} that are oxidised by one mole of $Cr_2O_7^{2-}$.

[1]

(iv) Deduce the oxidation state of manganese, after the manganese(II) sulphate has been oxidised. Show your reasoning.

[2]

(b) A student added aqueous sodium hydroxide to aqueous potassium dichromate(VI) and noticed that the colour changed from orange to yellow. He thought that this was due to a change in the oxidation state of the chromium.
Comment on the validity of this conclusion.

....

....

....

....

....[4]

[Total: 9]

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]

(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]

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

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]

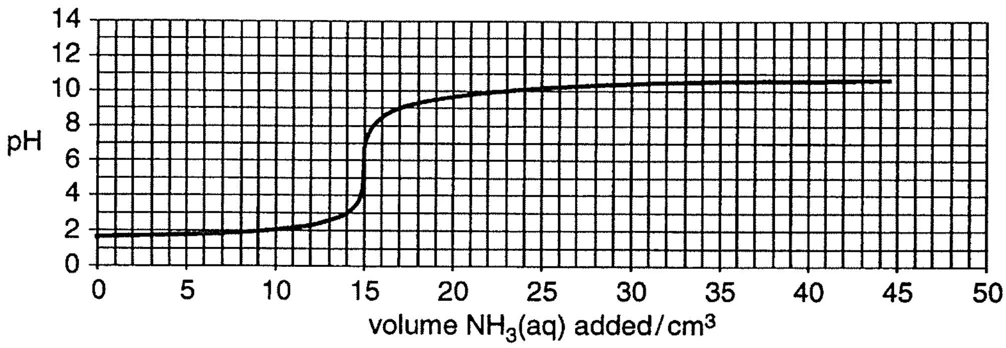
(iii) Calculate the pH of 0.0200 $mol\,dm^{-3}$ $HCl(aq)$.

[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]

[Turn over

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 × 10^{-4} mol dm^{-3}).

[3]

[Total: 10]