AQA

ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark scheme January 2003

GCE

Chemistry

Unit CHM5

LI
MA
BL

SECTION A

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

1 (a) At high temperatures, aluminium chloride exists in the vapour phase as the molecule $AlCl_3$. On cooling, two molecules of $AlCl_3$ combine by co-ordinate bonding to form molecules of Al_2Cl_6.

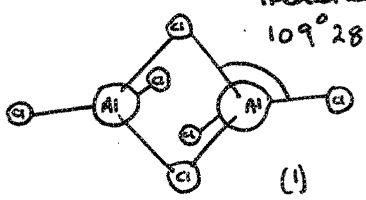
(i) State the shape of the $AlCl_3$ molecule and give the bond angle.

Linked to a correct shape

Shape .... Trigonal planar .... (1)

Bond angle .... 120° .... (1)

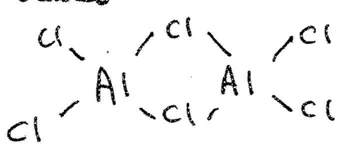
(ii) Sketch the structure of Al_2Cl_6 and mark on your sketch the value of **one** of the bond angles.



(1)

Predicted 109°28' (Allow 104 – 109.5) (1)
or correct values

Allow



(iii) Explain how two $AlCl_3$ molecules are able to bond together.

Lone electron pair on chlorine .... (1)

Electron deficient Al (accepts lone pair) .... (1)

(6 marks)

(b) (i) Describe what is observed when anhydrous $AlCl_3$ is added to an excess of water. Identify the major aluminium-containing species formed and predict the pH of the final solution.

Mark Separately

Observation .... Dissolves / exothermic reaction .... (1)

Major aluminium-containing species .... $[Al(H_2O)_6]^{3+}$ .... (1)

pH of final solution .... 2/3/4 .... (1)

(ii) Describe what you would observe when aqueous sodium carbonate is added to aqueous aluminium chloride. Write an equation for the reaction.

Mark Separately

Observations .... Gas evolved .... (1)

.... White precipitate formed .... (1)

Equation $2[Al(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Al(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$

Species (1) Balanced (1)

(7 marks)

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2 (a) Write equations for the reactions which occur when the following compounds are added separately to water. In each case, predict the approximate pH of the solution formed when one mole of each compound is added to 1 dm^3 of water.

Sodium oxide

Equation $Na_2O + H_2O \rightarrow 2NaOH$ (1)

pH of solution formed 14 (1)

Sulphur dioxide

Equation $SO_2 + H_2O \rightarrow H_2SO_3$ (1)

pH of solution formed 1 – 3 (1)

(4 marks)

(b) When silicon dioxide and carbon are heated in a stream of chlorine gas, silicon tetrachloride and carbon monoxide are formed.

(i) Write an equation for this reaction.

$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$ (1)

or $SiO_2 + C + 2Cl_2 \longrightarrow SiCl_4 + CO_2$

(ii) State what is observed when silicon tetrachloride is added to water. Write an equation for the reaction which occurs.

Observations (Gelatinous) {Solid / Gel} precipitate formed (1)

Exothermic reaction or gas evolved (1)

Equation $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ (1)

or $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$

(iii) Explain, in terms of their structure and bonding, why silicon tetrachloride has a lower melting point than phosphorus pentachloride.

$SiCl_4$ (is molecular), weak vdw forces between molecules (1); PCl_5 is ionic (1); ion – ion attraction stronger than vdw forces (1)

(7 marks)

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3 Use the data in the table below to answer the questions which follow.

Substance	$Fe_2O_3(s)$	Fe(s)	C(s)	CO(g)	$CO_2(g)$
$\Delta H_f^\ominus$/kJ mol^{-1}	–824.2	0	0	–110.5	–393.5
$S^\ominus$/J K^{-1}mol^{-1}	87.4	27.3	5.7	197.6	213.6

(a) The following equation shows one of the reactions which can occur in the extraction of iron.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

(i) Calculate the standard enthalpy change and the standard entropy change for this reaction.

Standard enthalpy change $\Delta H_R = \sum \Delta H_f$ products $- \sum \Delta H_f$ reactants

or a cycle (1)

$\Delta H_R = ([2\times0] + [3\times-393.5]) - (-824.2 + [3\times-110.5])$ (1)

$= -24.8$ (kJ mol^{-1}) (1)

Allow +24.8 max one

Standard entropy change $\Delta S = \sum S$ products $- \sum S$ reactants (1)

$\Delta S = ([2\times27.3] + [3\times213.6]) - (87.4 + [3\times197.6])$ (1)

$= (54.6 + 640.8) - (87.4 + 592.8)$

$= 15.2$ (J K^{-1} mol^{-1}) (1)

Allow –15.2 max one

(ii) Explain why this reaction is feasible at all temperatures.

$\Delta G = \Delta H - T\Delta S$

or ΔS positive or correct calc (1)

ΔH is negative and $-T\Delta S$ is negative (1)

Hence ΔG is always negative (1)

or feasible when $\Delta G \leq 0$

(9 marks)

(b) The reaction shown by the following equation can also occur in the extraction of iron.

$$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g) \quad \Delta H^\ominus = +492.7 \text{ kJ mol}^{-1}$$

The standard entropy change, $\Delta S^\ominus$, for this reaction is $+542.6 \text{ J K}^{-1} \text{ mol}^{-1}$

Use this information to calculate the temperature at which this reaction becomes feasible.

$\Delta G = 0 = \Delta H - T\Delta S$ Hence $\Delta H = T\Delta S$ (1)

Penalise missing 1000 by one mark

$T = \Delta H / \Delta S = 492.7 \times 1000 / 542.6$ (1)

$= 908$ K (1)

(3 marks)

(c) Calculate the temperature at which the standard free-energy change, $\Delta G^\ominus$, has the same value for the reactions in parts (a) and (b).

$\Delta G(b) = \Delta G(a)$

Penalise missing 1000 by one mark

$(492.7 \times 10^3 - T \times 542.6) = (-24.8 \times 10^3 - T \times 15.2)$ (1)

$517.5 \times 10^3 = 527.4\ T$ (1)

$T = 981.2$ K Allow 980 – 982 (1)

(3 marks)

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TURN OVER FOR THE NEXT QUESTION

4 Use the standard electrode potential data in the table below to answer the questions which follow.

	$E^\ominus/V$
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.70
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17

(a) Name the standard reference electrode against which all other electrode potentials are measured.

(Standard) hydrogen (electrode) (1)

(1 mark)

(b) When the standard electrode potential for $Fe^{3+}(aq)/Fe^{2+}(aq)$ is measured, a platinum electrode is required.

(i) What is the function of the platinum electrode?

To allow transfer of electrons / provide a reaction surface (1)

(ii) What are the standard conditions which apply to $Fe^{3+}(aq)/Fe^{2+}(aq)$ when measuring this potential?

298 K (1)

Both $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ have a concentration QoL

of 1 mol dm^{-3} (1) OR $[H^+]$ = 1 mol dm^{-3}

NOT zero current

or 100 kPa

(3 marks)

(c) The cell represented below was set up under standard conditions.

$$Pt|H_2SO_3(aq), SO_4^{2-}(aq)||MnO_4^-(aq), Mn^{2+}(aq)|Pt$$

Calculate the e.m.f. of this cell and write an equation for the spontaneous cell reaction.

Cell e.m.f. +1.34 V (1)

Equation $2MnO_4^- + 5H_2SO_3 \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O + 4H^+$

Correct species/order (1)

Balanced and cancelled (1)

Allow one for $2MnO_4^- + 5H_2SO_3 \rightarrow 2Mn^{2+} + 5SO_4^{2-}$ *(3 marks)*

(d) (i) Which one of the species given in the table is the strongest oxidising agent?

$Ce^{4+}(aq)$ (1)

(ii) Which of the species in the table could convert $Fe^{2+}(aq)$ into $Fe^{3+}(aq)$ but could not convert $Mn^{2+}(aq)$ into $MnO_4^-(aq)$?

$VO_2^+(aq)$ (1) ; Cl_2 (1)

Penalise additional answers to zero *(3 marks)*

(e) Use data from the table of standard electrode potentials to deduce the cell which would have a standard e.m.f. of 0.93 V. Represent this cell using the convention shown in part (c).

$Pt|Fe^{2+}(aq), Fe^{3+}(aq)||Ce^{4+}(aq), Ce^{3+}(aq)|Pt$

(2 marks)

Correct species (1)
Correct order (1)
(Deduct one mark for each error)

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TURN OVER FOR THE NEXT QUESTION

5 (a) Give **one** example of a bidentate ligand.

$C_2O_4^{2-}$ or $H_2NCH_2CH_2NH_2$ (1)

(1 mark)

(b) Give **one** example of a linear complex ion formed by a transition metal.

$[AgCl_2]^-$ or $[Ag(CN)_2]^-$ or $[Ag(NH_3)_2]^+$ (1)

(1 mark)

(c) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs with a change in **both** the co-ordination number and the overall charge of the complex ion.

eg $[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$

(2 marks)

Correct complex species (1) Balanced (1) Only allow if species correct

(d) Write an equation for a substitution reaction in which the complete replacement of ligands in a complex ion occurs without a change in either the co-ordination number or the overall charge of the complex ion.

eg $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$

(2 marks)

Correct complex species (1) Balanced (1) Only allow if species correct

(e) When a solution containing $[Co(H_2O)_6]^{2+}$ ions is treated with a solution containing $EDTA^{4-}$ ions, a more stable complex is formed. Write an equation for this reaction and explain why the complex is more stable.

Equation $[Co(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Co(EDTA)]^{2-} + 6H_2O$ (1)

Explanation More molecules on right hand side (1)

Entropy increases (1)

(3 marks)

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Section B Question 6 Answers

(a) $Cu \rightarrow Cu^{2+} + 2e^-$ (1)

$NO_3^- + 2H^+ + e^- \rightarrow H_2O + NO_2$ (1)

$Cu + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + 2H_2O + 2NO_2$ (1) **3**

or $Cu + 2HNO_3 + 2H^+ \rightarrow Cu^{2+} + 2H_2O + 2NO_2$

(b) Moles Cu = 1.25/63.5 = 0.0197 to 0.020 (1)

Moles NO = 2/3 × 0.0197 = 0.0131 (1)

PV = nRT (1)

V = nRT/P = 0.0131 × 8.31 × 330 / 98000 (1)

(Allow "n" consequentially to moles NO but not to moles Cu)

= 3.67×10^{-4} (1)

units m^3 (1) **6**

or equivalent

(c) Yellow-green copper species $[CuCl_4]^{2-}$ (1)

Equation; $Cu + [CuCl_4]^{2-} + 4Cl^- \rightarrow 2[CuCl_4]^{3-}$ Species (1)

Balance (1)

Copper acts as a reducing agent (1)

Not coloured as d sub-shell full (1)

Copper in CuCl is in oxidation state +1 or

No absorption of light as electron transitions not possible (1)

6

Section B Question 7 Answers

(a) reactants brought together/ increased concentration on surface or increased collision frequency (1)

reactants must be correctly orientated (1)

reaction on the surface (1)

products desorbed (1)

example of a catalysed reaction (not a named process) (1)

a suitable catalyst for this reaction (1)

(Penalise incorrect second reactions and catalysts))

If adsorption too weak reactants not brought together (1)

e.g. silver (1)

If adsorption too strong products not desorbed (1)

e.g. tungsten (1) Max 8

(b) Equations

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ (1)

$Zn + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+}$ (1)

Method

Titrate measured volume solution against $K_2Cr_2O_7$ (1)

Reduce same volume solution with zinc (1)

Filter off excess zinc (1)

Titrate for total Fe^{n+} using $K_2Cr_2O_7$ (1)

Percentage $Fe^{3+} = 100 \times$(titre 2 - titre1)/ titre 2 or equivalent (1) 7

Section B Question 8 Answers.

(a) Identity of **X**; 2-methylpropene (1)

Absorption at 1650 cm^{-1} indicates an alkene present (1)
[OR a chemical answer e.g. $Br_2(aq)$ brown to colourless]

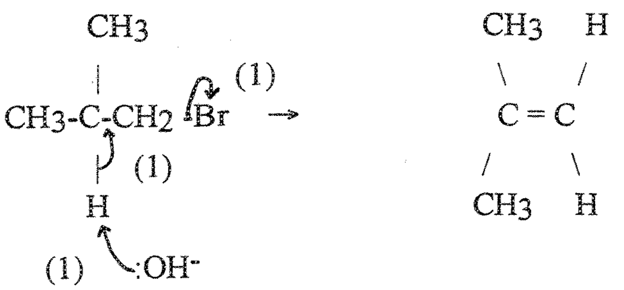
2

(b) Reagents

Step 1 KOH (Allow NaOH) (1) Alcoholic (1) Warm (1)
(Only allow solvent and warm if reagent correct)

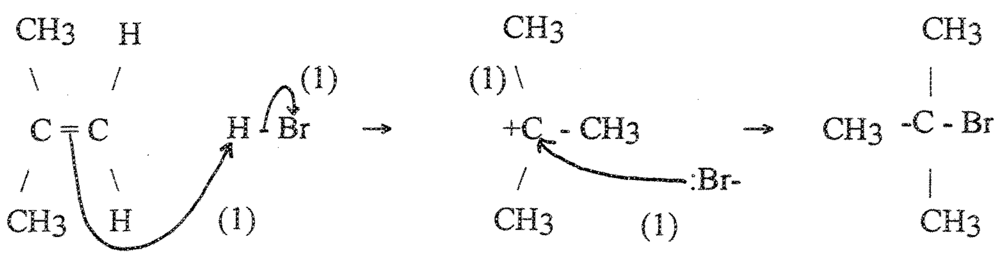
Step 2 HBr (1)

Mechanism A → **X**



or a carbocation mechanism

Mechanism **X** → B



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(c) A gives three peaks (1)
B gives one peak (1)
Allow one for
"A has more peaks than B" when no number of peaks given

2

Section B Question 9 Answers

(a)	$HCl + NH_3 \rightarrow NH_4Cl$	(1)	
	Ammonia reacts as a base or nucleophile	(1)	
	$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$	(1)	
	Ammonia acts as a ligand	(1)	
	$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$	(2)	
	(Allow one mark if second product is HCl)		
	Ammonia behaves as a nucleophile	(1)	
			7
(b)	Pentane is non-polar	(1)	
	van der Waals forces between molecules	(1)	
	Butanone has a polar C=O bond	(1)	
	Dipole-dipole attraction between molecules	(1)	
	Propanoic acid has very polar O-H groups	(1)	
	Hydrogen bonding between molecules	(1)	
	vdw < dipole - dipole attraction < hydrogen bonding	(1)	
	Link to energy needed to separate molecules	(1)	
	(Last mark only allowed when clearly stated and all three interactions are correct)		**8**