



ASSESSMENT and
QUALIFICATIONS
ALLIANCE

Mark scheme January 2004

GCE

Chemistry

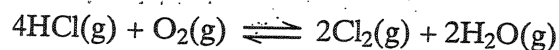
Unit CHM5

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SECTION A

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

- 1 Chlorine is formed in a reversible reaction as shown by the equation



- (a) Use the data below to calculate the standard enthalpy change, ΔH^\ominus , and the standard entropy change, ΔS^\ominus , for this reaction.

Substance	HCl(g)	O ₂ (g)	Cl ₂ (g)	H ₂ O(g)
$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	-92	0	0	-242
$S^\ominus/\text{J K}^{-1}\text{mol}^{-1}$	187	205	223	189

Standard enthalpy change, ΔH^\ominus $\Delta H_R = \sum \Delta H_f^\ominus \text{products} - \sum \Delta H_f^\ominus \text{reactants}$

$$\begin{aligned} \Delta H_R &= (0 + [2 \times -242]) - (4 \times -92) && \text{or cycle} && (1) \\ &= -484 + 368 && && (1) \\ &= -116 \text{ (kJ mol}^{-1}\text{)} && \text{Allow max one for } +116 && (1) \end{aligned}$$

Standard entropy change, ΔS^\ominus $\Delta S = \sum S^\ominus \text{products} - \sum S^\ominus \text{reactants}$ (1)

$$\begin{aligned} \Delta S &= ([2 \times 223] + [2 \times 189]) - (205 + [4 \times 187]) && (1) \\ &= 824 - 953 \\ &= -129 \text{ (J K}^{-1}\text{ mol}^{-1}\text{)} && \text{Allow max one for } +129 && (1) \end{aligned}$$

(6 marks)

- (b) The data below apply to a different gas phase reversible reaction.

Standard enthalpy change, $\Delta H^\ominus = +208 \text{ kJ mol}^{-1}$

Standard entropy change, $\Delta S^\ominus = +253 \text{ J K}^{-1} \text{ mol}^{-1}$

- (i) Deduce the effect of an increase in temperature on the position of the equilibrium in this reaction. Use Le Chatelier's principle to explain your answer.

Mark
Separately

Effect Equilibrium displaced to right / to products (1)

Explanation Reaction is endothermic (1)

Constraint reduced (1)

- (ii) Calculate the minimum temperature at which this reaction is feasible.

Feasible when $\Delta G \leq 0$ (1)

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

$T = \Delta H / \Delta S = 208 \times 1000 / 253$ (1)

$= 822 \text{ K}$ (1)

(7 marks)

TURN OVER FOR THE NEXT QUESTION

Turn over 

- 2 (a) Silicon dioxide is a solid with a high melting point. When a mixture of silicon dioxide and carbon is heated in a stream of chlorine, silicon tetrachloride and carbon monoxide are formed. At room temperature, silicon tetrachloride is a colourless liquid.

- (i) State the type of bonding and structure present in solid silicon dioxide and explain why it has a high melting point.

Type of bonding Covalent (1)

Type of structure Macromolecular (1)

Reason for high melting point Many strong (covalent) bonds
must be broken (1)

- (ii) Write an equation for the reaction described above in which silicon tetrachloride is formed.



- (iii) State the type of bonding present in silicon tetrachloride molecules. Explain why silicon tetrachloride has a low melting point.

Type of bonding Covalent (1)

Q of L

Reason for low melting point Intermolecular
v d w forces between
molecules (1)

(6 marks)

- (b) Describe what you would observe and write an equation for the reaction occurring when silicon tetrachloride is added to an excess of water.

Observations (white / colourless) precipitate or gel (1)

..... Vigorous / exothermic reaction or gas evolved (max 2) (1)

Equation $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4 + 4\text{HCl}$ (1)

or $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$ (3 marks)

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- 3 The Group II element **A** burns when heated in chlorine forming the solid chloride **B** which has a high melting point.

When aqueous sodium hydroxide is added to an aqueous solution of **B** a white precipitate **C** is formed.

Precipitate **C** does not dissolve when an excess of aqueous sodium hydroxide is added but does dissolve when aqueous sulphuric acid is added.

- (a) State the type of bonding present in **B**.

Ionic (1)
(1 mark)

- (b) Identify **B**.

MgCl₂ (Allow other Group II chlorides except BeCl₂) (1)
(1 mark)

- (c) Write an equation for the formation of chloride **B** from element **A**.

Mg + Cl₂ → MgCl₂ (Conseq to (b)) (1)
(1 mark)

- (d) Identify the precipitate **C**.

Mg(OH)₂ (Only allow this answer) (1)
(1 mark)

- (e) Write an equation for the reaction in which **C** is formed.

MgCl₂ + 2NaOH → Mg(OH)₂ + 2NaCl (1)
[Allow conseq to a hydroxide in (d)] (1 mark)

- (f) Write an equation for the reaction of **C** with aqueous sulphuric acid.

Mg(OH)₂ + H₂SO₄ → MgSO₄ + 2H₂O (1)
Only Allow for MgO or Mg(OH)₂ (1 mark)

TURN OVER FOR THE NEXT QUESTION

Turn over 

4 Use the data below, where appropriate, to answer the questions which follow.

Standard electrode potentials	E^\ominus/V
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.09
$2\text{BrO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 10\text{e}^- \rightarrow \text{Br}_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$	+1.52

Each of the above can be reversed under suitable conditions.

- (a) State the hydrogen ion concentration and the hydrogen gas pressure when, at 298 K, the potential of the hydrogen electrode is 0.00 V.

Hydrogen ion concentration 1.00 mol dm⁻³ (1)

Hydrogen gas pressure 100 kPa (1)

(2 marks)

- (b) The electrode potential of a hydrogen electrode changes when the hydrogen ion concentration is reduced. Explain, using Le Chatelier's principle, why this change occurs and state how the electrode potential of the hydrogen electrode changes.

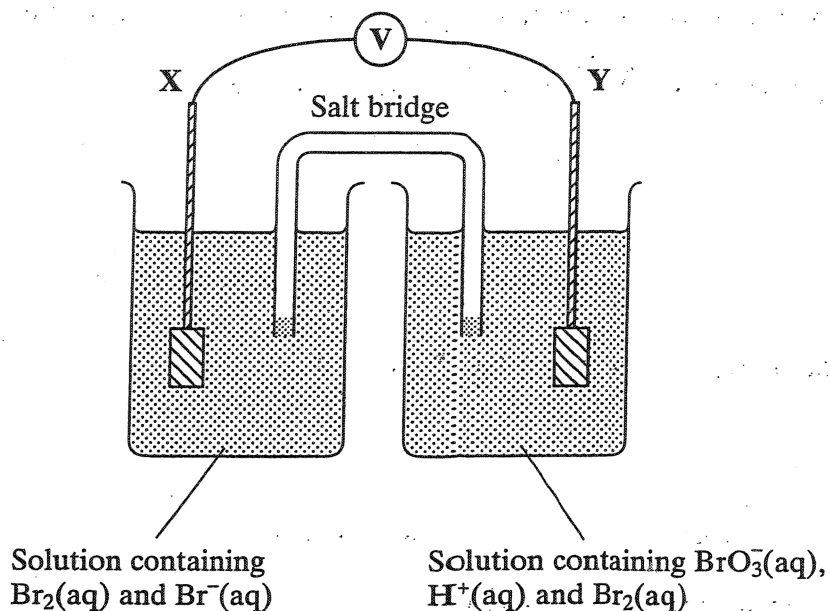
Explanation of change Equilibrium displaced to left (1)

..... to reduce constraint (1)

Change in electrode potential Becomes negative or decreases (1)

(Allow more negative) (3 marks)

- (c) A diagram of a cell using platinum electrodes X and Y is shown below.



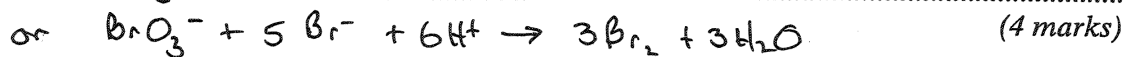
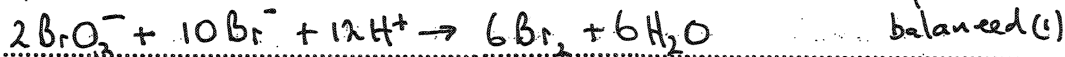
- (i) Use the data above to calculate the e.m.f. of the above cell under standard conditions.

..... 0.43 V (1)

- (ii) Write a half-equation for the reaction occurring at electrode X and an overall equation for the cell reaction which occurs when electrodes X and Y are connected.



Overall equation species (1)



TURN OVER FOR THE NEXT QUESTION

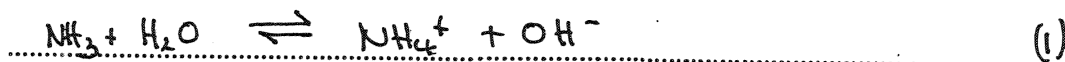
Turn over

- 5 (a) By reference to the forces between molecules, explain why ammonia is very soluble in water.

Hydrogen bonding (1)
 between H_2O and NH_3 (1)
 (2 marks)

- (b) Aqueous solutions of ammonia have a pH greater than 7.

- (i) Write an equation for the reaction of ammonia with water.



- (ii) Explain why the pH of a solution containing 1.0 mol dm^{-3} of ammonia is less than 14 at 298 K.

Ammonia is a weak base [Not partially ionised] (1)
 Equilibrium to left or incomplete reaction (1)
 (3 marks)

- (c) An ammonium ion in aqueous solution can behave as a Brønsted-Lowry acid. State what is meant by the term *Brønsted-Lowry acid*.

A proton donor (1)
 (1 mark)

- (d) State what is meant by the term *buffer solution*. Identify a reagent which could be added to a solution of ammonia in order to form a buffer solution.

Buffer solution A solution which resists change in pH (1)

when small amounts of acid or base added or on dilution (1)

Reagent NH_4Cl (Allow a correct strong acid) (1)

(3 marks)

(e) An acidic buffer solution is obtained when sodium ethanoate is dissolved in aqueous ethanoic acid.

- (i) Calculate the pH of the buffer solution formed at 298 K when 0.125 mol of sodium ethanoate is dissolved in 250 cm³ of a 1.00 mol dm⁻³ solution of ethanoic acid. The acid dissociation constant, K_a , for ethanoic acid is 1.70×10^{-5} mol dm⁻³ at 298 K.

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (1)$$

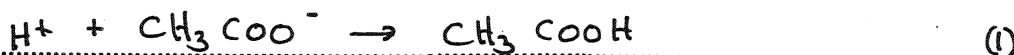
$$= \frac{[H^+][0.125 \times 4]}{1.00}$$

$$[H^+] = \frac{1.70 \times 10^{-5}}{0.125 \times 4} = 3.40 \times 10^{-5} \quad (1)$$

$$pH = -\log_{10} [H^+] = 4.47 \quad (1)$$

(Allow pH consequ. to $[H^+]$ if 2 place decimals given)

- (ii) Write an ionic equation for the reaction which occurs when a small volume of dilute hydrochloric acid is added to this buffer solution.



(5 marks)

TURN OVER FOR THE NEXT QUESTION

Turn over 

- 6 (a) Explain why complex ions with partially filled d sub-levels are usually coloured.

Electrons (excited) transitions from ground to excited state (1)

Energy absorbed from (light) visible (spectrum) (1)

(2 marks)

- (b) (i) When aqueous ammonia was added to an aqueous solution of cobalt(II) sulphate, a blue precipitate **M** was formed. Identify the cobalt-containing species present in aqueous cobalt(II) sulphate and the precipitate **M**.

Cobalt-containing species $[Co(H_2O)_6]^{2+}$ (1)

Precipitate **M** $Co(H_2O)_4(OH)_2$ or $Co(OH)_2$ (1)

- (ii) Precipitate **M** dissolved when an excess of concentrated aqueous ammonia was added. The solution formed was pale brown due to the presence of the cobalt-containing species **P**. Identify **P**.

$[Co(NH_3)_6]^{2+}$ (1)

- (iii) On standing in air, the colour of the solution containing **P** slowly darkened as the cobalt-containing species **Q** was formed. State the type of reaction occurring when **P** changes into **Q** and identify the reactant responsible for this change.

Type of reaction Co^{2+} oxidised to Co^{3+} (1)

Reactant responsible Oxygen (1)

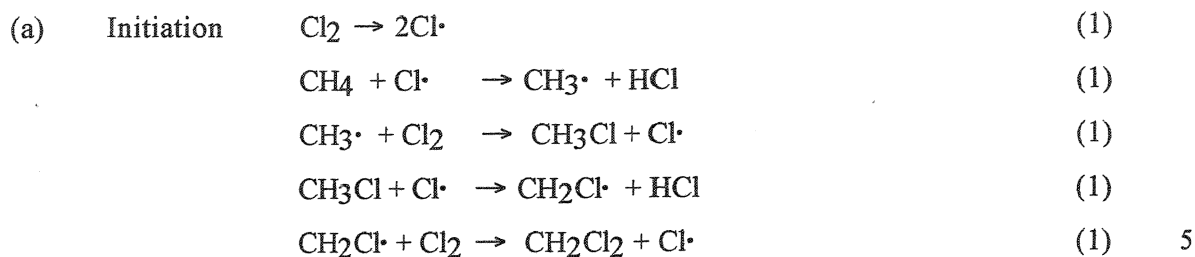
- (iv) When potassium iodide was added to the solution containing **Q** and the mixture was acidified, a dark red-brown colour due to the presence of **R** was produced. On addition of starch solution the mixture turned blue-black. Identify **R** and explain its formation.

Identity of **R** Iodine (1)

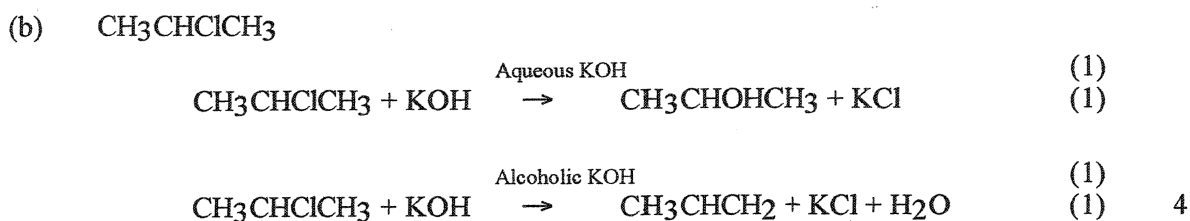
Explanation I^- oxidised (by Co^{3+} which is reduced to Co^{2+}) (1)

(7 marks)

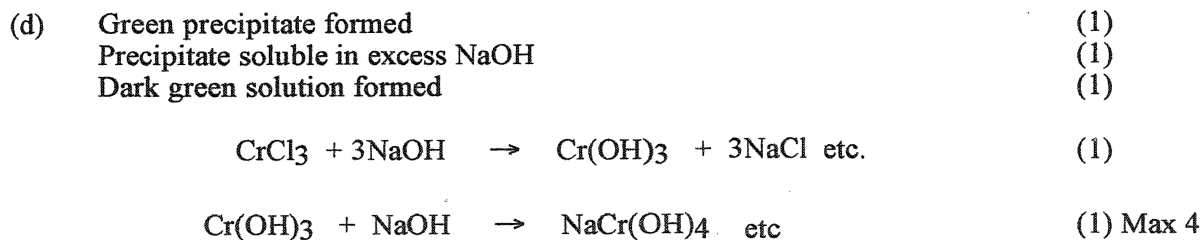
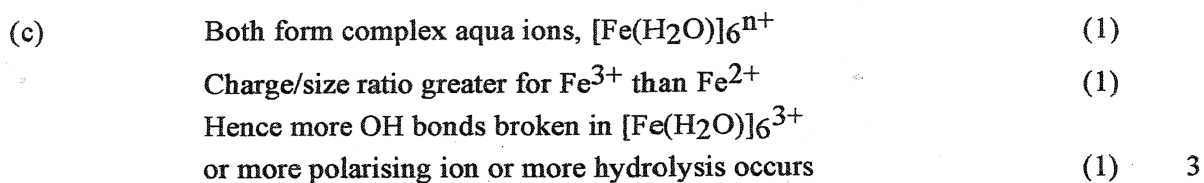
Q7 Answers



Note Additional answers ignored even if incorrect but contradictions penalised.



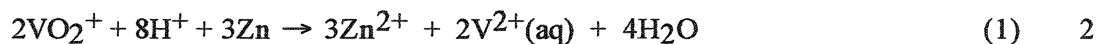
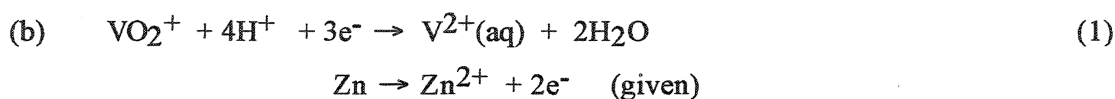
Note Solvent mark only allowed if a correct product given



Q 8 Answers.

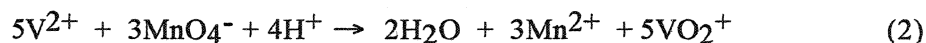
- (a)(i) Heterogeneous:- In a different phase to reactants (1)
 Catalyst:- Increases reaction rate (1)
 Alternative route or route described (1)
 Lower E_a (1)
 Unchanged at end of reaction (1) Max 4
- (ii) Feature:- **Q of L** Variable oxidation states shown by vanadium (1)
 Equations $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ (1)
 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$ (1) 3

7



$Mol\ KMnO_4 = mv/1000 = 0.0200 \times 38.5/1000 = 7.70 \times 10^{-4}$ (1)

Mole ratio MnO_4^- to $V(II)$ = 3: 5 deduced
 or equation



$Mol\ V(II) = 7.70 \times 10^{-4} \times 5/3$ (1) $= 1.283 \times 10^{-3}$

$Mass\ V = 1.283 \times 10^{-3} \times 50.9$ (1) $= 0.0653\ g$

$\% V\ in\ sample = 0.06532 \times 100/0.160 = 40.8$ (1) 6

8

Q 9 Answers 'Stick structures' penalised once only in this question.

(a) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ reduced by
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (1)

oxidised to $\text{CH}_3(\text{CH}_2)_2\text{CHO}$ (1)

and $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ (1)

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (1)

oxidised to $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ (1)

Equation $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ (1) 6

Note Deduct one if all three compounds given as reducing agents.

(b) Tollens' reduced by
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (1)

oxidised to $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ (1)

Equation $[\text{Ag}(\text{NH}_3)_2]^+ + \text{e}^- \rightarrow \text{Ag} + 2\text{NH}_3$ (1) 3

(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (1)

Product $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OOCCH}_3$ (1)

$(\text{CH}_3)_3\text{COH}$ (1)

Product $(\text{CH}_3)_3\text{COOCCH}_3$ (1) 4

(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ has five peaks (1)

$(\text{CH}_3)_3\text{COH}$ has two peaks (1) 2

Q10 Answers

- (a)(i) Extraction by C reduction of oxide
 Iron (1)

$$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$$
 (1)
- Extraction by electrolysis
 Aluminium (1)

$$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$$
 (1)
- Extraction by metal displacement
 Titanium (1)

$$\text{TiCl}_4 + 4\text{Na} \rightarrow \text{Ti} + 4\text{NaCl}$$

 or
$$\text{TiCl}_4 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgCl}_2$$
 (1) 6
- (ii) The reactive metal must first be extracted (1)
 This extraction will required a great deal of energy or electrolysis (1) 2
- (iii)
$$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \rightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$$
 Species (1)
 Balanced (1) 2 10
- (b) Linear complex e.g. $[\text{Ag}(\text{NH}_3)_2]^+$ (1)
 Tetrahedral complex e.g. $[\text{CoCl}_4]^{2-}$ (1)
 Octahedral complex e.g. $[\text{Fe}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$
 Species (1)
 Charge (1) 4 4