

GCE 2004

June Series



Mark Scheme

Chemistry

(Subject Code CHM5)

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CHM5 Thermodynamics and Further Inorganic Chemistry**SECTION A****Question 1**

- (a) (i) ΔH atomisation/sublimation of magnesium 1
- (ii) Bond/dissociation enthalpy of Cl-Cl
OR $2 \times H$ atomisation of chlorine 1
- (iii) Second ionisation enthalpy of magnesium 1
- (iv) $2 \times$ electron affinity of chlorine 1
- (v) Lattice formation enthalpy of MgCl_2 1
- (b) Equation $2\text{MgCl(s)} \rightarrow \text{MgCl}_2\text{(s)} + \text{Mg(s)}$ 1
State symbols not required but penalise if incorrect
- Calculation $\Delta H_{\text{reaction}} = \Sigma \Delta H_{\text{f products}} - \Sigma \Delta H_{\text{f reactants}}$ 1
 $= -653 - (2 \times -133)$ 1
 $= -427 \text{ (kJmol}^{-1}\text{)}$ 1
- Allow +427 to score (1) mark*
Other answers; award (1) for a correct ΔH reaction expression
- (c) $\Delta H_{\text{soln MgCl}_2} = -\Delta H_{\text{Lat.form.}} + \Delta H_{\text{hyd.Mg}^{2+}} + 2\Delta H_{\text{hyd.Cl}^-}$ 1
- or cycle
 $= 2502 - 1920 - (2 \times 364)$ 1
 $= -146 \text{ (kJmol}^{-1}\text{)}$ 1
- Allow +146 to score (1) mark*
Other answers; award (1) for a correct $\Delta H_{\text{soln MgCl}_2}$ expression/cycle

Total 12

Question 2

Each section to be marked independently

(a)	(i)	Ionic	1
	(ii)	Sodium/Na	1
	(iii)	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$ <i>Ignore state symbols</i>	1
(b)	(i)	Covalent	1
	(ii)	Phosphorus/P	1
	(iii)	H_3PO_4 or other acid with P in oxidation state (V) or (III)	1
(c)	(i)	Macromolecular/giant covalent/giant molecular	1
	(ii)	Silicon/Si	1
	(iii)	e.g. $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$	
		Base	1
		Balanced	1

Total 10

Question 3

- (a) (i) Orange 1
- (ii) Red-violet/ruby/violet/ green 1
- (iii) Purple 1
- (b) Fe^{2+} or Fe(II) 1
- (c) (i) 6 or (VI) 1
- (ii) 3 or (III) 1
- (d) (i) $\text{MnO}_4^- / \text{Mn}^{2+}$ has a more positive E^\ominus value than $\text{Cl}_2 / \text{Cl}^-$ 1
or data used
- and will oxidise Cl^- or change Cl^- to Cl_2 1
Allow converse answers
- (ii) $\text{NO}_3^- / \text{HNO}_2$ has a more positive E^\ominus value than $\text{Fe}^{3+} / \text{Fe}^{2+}$ 1
or data used
- and will oxidise Fe^{2+} or change Fe^{2+} to Fe^{3+} 1
- (e) (i) 0.5 1
- (ii) $2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}_2\text{O}_8^{2-} \rightarrow 10\text{SO}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+$
Both SO_4^{2-} and MnO_4^- on right 1
Balanced 1

Total 13

Question 4

- (a) (i) An atom, ion or molecule which can donate a lone electron pair 1
- (ii) A central metal ion/species surrounded by co-ordinately bonded ligands 1
or ion in which co-ordination number exceeds oxidation state
- (iii) The number of co-ordinate bonds formed to a central metal ion 1
or number of electron pairs donated or donor atoms
- (b) *Allow the reverse of each substitution*
- (i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$ 1
Complex ions
Balanced 1
Allow partial substitution
- (ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow \text{CoCl}_4^{2-} + 6\text{H}_2\text{O}$ 1
Complex ions
Balanced 1
or H₂O or NH₃ or C₂O₄²⁻ by Cl
- e.g. (iii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow [\text{Co}(\text{C}_2\text{O}_4)_3]^{4-} + 6\text{H}_2\text{O}$ 1
Complex ions
Balanced 1
Allow all substitution except
(i) NH₃ by H₂O
(ii) more than 2Cl⁻ substituted for NH₃ or H₂O
- e.g. (iv) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + \text{EDTA}^{4-} \rightarrow [\text{Co}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$ 1
Complex ions
Balanced 1
or H₂O or NH₃ by C₂O₄²⁻ and NH₃ or Cl⁻ by EDTA⁴⁻
- (c) (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ 1
(ii) $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_x$ where $x = 0$ to 4 1
(iii) Fe^{2+} is oxidised to Fe^{3+} or $\text{Fe}(\text{OH})_3$ 1
By oxygen in the air 1

Total 15

Question 5

- (a) A catalyst in the same phase/phase as the reactants 1
- (b) (i) A reaction in which a product acts as a catalyst 1
- (ii) Mn^{2+} or Mn^{3+} 1
“Self-catalysing” not allowed
- (c) (i) $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$ 1
or $4\text{CO} + 2\text{NO}_2 \rightarrow 4\text{CO}_2 + \text{N}_2$
C not allowed as a product
Reducing agent CO 1
- (ii) Pt, Pd or Rh 1
Deposited on a ceramic honeycomb or matrix or mesh or sponge 1
To increase surface area of catalyst 1
- (d) (i) Reactants cannot move on surface or products not desorbed or 1
Active sites blocked
- (ii) Reactants not brought together or 1
No increase in reactant concentration on catalyst surface or
Reactants not held long enough for a reaction to occur or
Reactant bonds not weakened

Total 10

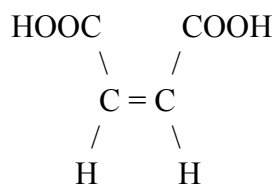
Question 6

- (a) FeCl_3 is a Lewis acid 1
- Accepts electron pairs (from water) 1
- $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is a Bronsted-Lowry acid 1
- Donated protons 1
- NB mark separately*
- (b) (i) $K_a = \frac{[\{\text{Fe}(\text{H}_2\text{O})_5(\text{OH})\}^{2+}][\text{H}^+]}{[\{\text{Fe}(\text{H}_2\text{O})_6\}^{3+}]}$ *NB []* 1
- essential*
- $\text{pH} = -\log[\text{H}^+] \text{ or } [\text{H}^+] = 3.02 \times 10^{-2}$ 1
- Hence $[\text{H}^+] = [\{\text{Fe}(\text{H}_2\text{O})_5(\text{OH})\}^{2+}]$ 1
- $K_a = \frac{[\text{H}^+]^2}{[\{\text{Fe}(\text{H}_2\text{O})\}^{3+}]}$ (= $3.02 \times 10^{-2} / 0.15$) 1
- $K_a = 6.08 \times 10^{-3}$ (*Allow 6.0 to 6.1×10^{-3}*) 1
- $\text{p}K_a = 2.22$ (3 significant figures needed but ignore units) 1
- NB allow value of $\text{p}K_a$ sequentially to value of K_a*
- allow $\text{p}K_a = -\log K_a$ (1) if stated but no value of $\text{p}K_a$ calculated*
- (ii) *Mark sequentially to the value of K_a obtained in (b)(i)*
- New $[\{\text{Fe}(\text{H}_2\text{O})\}^{3+}] = 0.250/4$ (= 0.0625) 1
- $K_a = 6.08 \times 10^{-3} = [\text{H}^+]^2 / 0.0625$
- $[\text{H}^+] = \sqrt{(6.08 \times 10^{-3} \times 0.0625)}$ (= $\sqrt{3.80 \times 10^{-4}}$) 1
- $\text{pH} = -\log 0.01949 = 1.71$ 1
- NB** (i) *Using the given value of $K_a = 4.50 \times 10^{-3}$ and 0.0625*
- $[\text{H}^+] = 0.0168$ and $\text{pH} = 1.78$ (Scores the full 3 marks)*
- (ii) *Penalise two marks if $[\{\text{Fe}(\text{H}_2\text{O})\}^{3+}] = 0.250/n$ where $n \neq 4$*
- Allow $[\text{H}^+] = \sqrt{(6.08 \times 10^{-3} \times 0.250/n)}$ (1)*
- (iii) *Using $K_a = 4.50 \times 10^{-3}$ and 0.0833*
- $\text{pH} = 1.71$ **BEWARE** of this answer it scores only 1 mark*
- (c) Fe^{2+} ion has a smaller charge to size ratio or charge density 1
- Less polarising than Fe^{3+} / less weakening effect on O - H bonds or 1
- Hydrolysis equilibrium displace more to the left

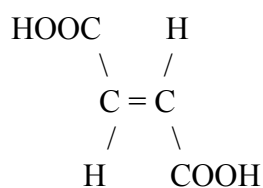
Total 15

SECTION B**Question 7**

(a)



1



1

NB The bonds shown in the structure must be to correct

Isomerism: Geometric or cis-trans

1

If written answer is correct, ignore incorrect labelling of structures.

If no written answer, allow correctly labelled structures.

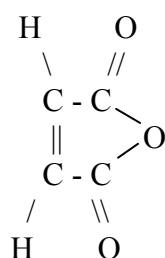
Both COOH groups must be on the same side/ close together/ cis .

1

No rotation about C=C axis

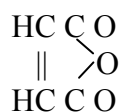
1

Structure

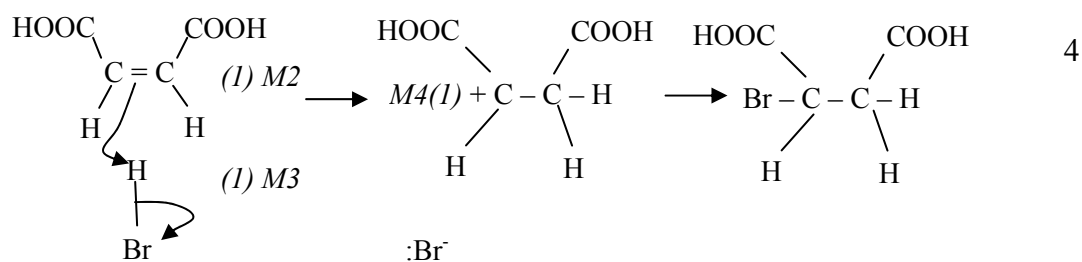


1

Allow



(b) $\text{Br}_2 / \text{HBr} / \text{H}_2\text{SO}_4 / \text{H}^+ / \text{Br}^+ / \text{NO}_2^+$ (Mark M1)



*NB If electrophile $\text{H}^+ / \text{Br}^+ / \text{NO}_2^+$ allow M1, M2 and M4
If the acid is incorrect, M2 and M3 can still be scored
Allow M4 consequentially if a repeat error from part (a)*

(c) e.g. $2\text{NaOH} + \text{HO}_2\text{CCHCHCO}_2\text{H} \rightarrow \text{NaO}_2\text{CCHCHCO}_2\text{Na} + 2\text{H}_2\text{O}$

Both H replaced 1
Balanced for atoms and charges 1

*NB Allow ionic equations and $2\text{NaOH} + \text{C}_4\text{H}_4\text{O}_4 \rightarrow \text{C}_4\text{H}_2\text{O}_4\text{Na}_2 + 2\text{H}_2\text{O}$
Allow one if structure incorrect but molecular formula correct
Allow one for a correct equation showing one H replaced*

(d) M1 Two peaks 1
M2 No splitting or singlets 1
M3 (Two) non-equivalent protons or two proton environments 1
M4 No adjacent protons 1
M5 Same area under the two peaks or same relative intensity 1
Max 3

NB Doublet could score M1 and M3 or M5 (Max 2)

More than two peaks CE = 0

Apply the “list principle” to incorrect answers if more than 3 given

Total 15

Question 8

- (a) *M1* $K_p = \frac{(p_Y)^3 \cdot (p_Z)^2}{(p_W)^2 \cdot (p_X)}$ NB [] wrong 1
M2 temperature 1
M3 increase 1
M4 particles have more energy or greater velocity/speed 1
M5 more collisions with $E > E_a$ or
more successful collisions 1
M6 reaction exothermic or converse 1
M7 equilibrium moves in the left 1

Marks for other answers

Increase in pressure or concentration allow *M1, M5, M6* Max 3

Addition of a catalyst; allow *M1, M5, M6* Max 3

Decrease in temperature; allow *M1, M2, M6* Max 3

Two or more changes made; allow *M1, M6* Max 2

- (b) (i) Advantage; reaction goes to completion, not reversible or faster 1

Disadvantage; reaction vigorous/dangerous (*exothermic must be qualified*) 1

or HCl(g) evolved/toxic
or CH₃COCl expensive

NB Allow converse answers

Do not allow reactions with other reagents e.g. water or ease of separation

- (ii) $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$ 1

$$\Delta S = (259 + 187) - (201 + 161) \quad 1$$

$$\Delta S = 84 \text{ (JK}^{-1} \text{ mol}^{-1}) \text{ (Ignore units)} \quad 1$$

Allow -84 to score (1) mark

$$\Delta G = \Delta H - T\Delta S \quad 1$$

$$= -21.6 - 298 \times 84/1000 \quad 1$$

$$= -46.6 \text{ kJ mol}^{-1} \text{ or } -46\,600 \text{ J mol}^{-1} \quad 1$$

Allow (2) for -46.6 without units

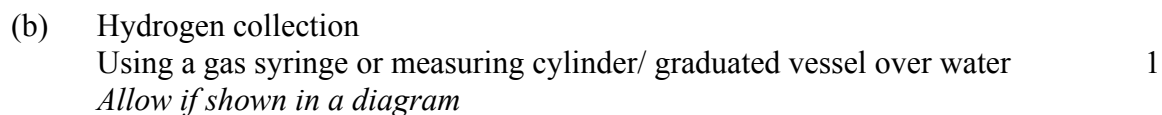
(Mark ΔG consequentially to incorrect ΔS)

(e.g. $\Delta S = -84$ gives $\Delta G = +3.4 \text{ kJ mol}^{-1}$)

Total 15

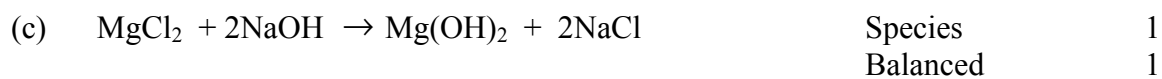
Question 9

Allow ionic equations



Measurements (i) P 1
(ii) T 1
(iii) V 1

Use ideal gas equation to calculate mol hydrogen or mass/Mr 1
Mol H_2 = mol Mg (Mark consequentially to equation) 1



Allow an ionic equation



- (d) **Allow 2 significant figures in these calculations and ignore additional figures.**

EITHER

$$\text{Mol MgO obtained stage 2} = \text{mass MgO} / M_r \text{MgO} \quad 1$$

$$= 6.41 / 40.(3) = 0.159 \quad \text{Allow } 0.16 \quad 1$$

Allow method mark if formula of magnesium oxide or M_r incorrect.

Moles of Mg = moles of H_2 hence

$$\text{Mol original MgO} = \text{mol MgO from stage 2} - \text{mol H}_2 \quad 1$$

$$= 0.159 - 0.0528 = 0.106 \quad \text{Allow } 0.11 \quad 1$$

Mark consequentially to moles of magnesium oxide determined above

OR

$$\text{Mass MgO formed from Mg} = 0.0528 \times M_r \text{MgO} \{ \text{or } 40.(3) \} \quad (1)$$

$$= 2.13 \text{ g} \quad \text{Allow } 2.1 \quad (1)$$

Allow method mark if formula of magnesium oxide or M_r incorrect.

$$\text{Mass original MgO} = \text{total mass MgO} - \text{mass formed from Mg} \quad (1)$$

$$= 6.41 - 2.13 = 4.28 \text{ g} \quad \text{Allow } 4.3 \quad (1)$$

Mark consequentially mass of magnesium oxide determined above

NB

As there is an error in part (d), the mass of sample should have been 6.25 NOT 2.65, award full marks to any candidate who has crossed out their correct first answer.

Total 15