GCE 2004
June Series

ASSESSMENT and QUALIFICATIONS ALLIANCE

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× electron affinity of chlorine 1

(v) Lattice formation enthalpy of $MgCl_2$ 1

(b) Equation $2MgCl(s) \rightarrow MgCl_2(s) + Mg(s)$ 1
State symbols not required but penalise if incorrect

Calculation ΔH reaction $= \Sigma \Delta H_f$ products $- \Sigma \Delta H_f$ reactants 1
$= -653 - (2 \times -133)$ 1
$= -427$ (kJmol^{-1}) 1

Allow +427 to score (1) mark
Other answers; award (1) for a correct ΔH reaction expression

(c) ΔH soln $MgCl_2 = -\Delta H$ Lat.form. $+ \Delta H$ hyd.$Mg^{2+} + 2\Delta H$ hyd.Cl^- 1

or cycle
$= 2502 - 1920 - (2 \times 364)$ 1
$= -146$ (kJmol^{-1}) 1
Allow + 146 to score (1) mark
Other answers; award (1) for a correct ΔH soln $MgCl_2$ expression/cycle

Total 12

Question 2

Each section to be marked independently

(a)	(i)	Ionic		1
	(ii)	Sodium/Na		1
	(iii)	$Na_2O + H_2O \rightarrow 2NaOH$ *Ignore state symbols*		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. $CaO + SiO_2 \rightarrow CaSiO_3$	Base Balanced	1 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) MnO_4^- / Mn^{2+} has a more positive $E^{\ominus}$ value than Cl_2 / Cl^- or data used 1

and will oxidise Cl^- or change Cl^- to Cl_2 1
Allow converse answers

(ii) NO_3^- / HNO_2 has a more positive $E^{\ominus}$ value then Fe^{3+} / Fe^{2+} or data used 1

and will oxidise Fe^{2+} or change Fe^{2+} to Fe^{3+} 1

(e) (i) 0.5 1

(ii) $2Mn^{2+} + 8H_2O + 5S_2O_8^{2-} \rightarrow 10SO_4^{2-} + 2MnO_4^- + 16H^+$

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
or ion in which co-ordination number exceeds oxidation state 1

(iii) The number of co-ordinate bonds formed to a central metal ion
or number of electron pairs donated or donor atoms 1

(b) *Allow the reverse of each substitution*

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

Complex ions 1

Balanced 1

Allow partial substitution

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

Complex ions 1

Balanced 1

or H_2O or NH_3 or $C_2O_4^{2-}$ by Cl^-

e.g. (iii) $[Co(H_2O)_6]^{2+} + 3C_2O_4^{2-} \rightarrow [Co(C_2O_4)_3]^{4-} + 6H_2O$

Complex ions 1

Balanced 1

Allow all substitution except
(i) NH_3 by H_2O
(ii) more than 2Cl^- substituted for NH_3 or H_2O

e.g. (iv) $[Co(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Co(EDTA)]^{2-} + 6H_2O$

Complex ions 1

Balanced 1

or H_2O *or* NH_3 *by* $C_2O_4^{2-}$ *and* NH_3 *or* Cl^- *by* $EDTA^{4-}$

(c) (i) $[Fe(H_2O)_6]^{2+}$ 1

(ii) $Fe(OH)_2$ or $Fe(OH)_2(H_2O)x$ where $x = 0$ to 4 1

(iii) Fe^{2+} is oxidised to Fe^{3+} or $Fe(OH)_3$ 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) $2CO + 2NO \rightarrow 2CO_2 + N_2$ 1
or $4CO + 2NO_2 \rightarrow 4CO_2 + N_2$
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

$[Fe(H_2O)_6]^{3+}$ is a Bronsted-Lowry acid 1

Donated protons 1
NB mark separately

(b) (i) $K_a = [\{ Fe(H_2O)_5(OH)\}^{2+}][H^+]/ [\{Fe(H_2O)_6\}^{3+}]$ *NB* [ ] *essential* 1

$pH = -\log[H^+]$ *or* $[H^+] = 3.02 \times 10^{-2}$ 1

Hence $[H^+] = [\{ Fe(H_2O)_5(OH)\}^{2+}]$ 1

$K_a = [H^+]^2 / [\{Fe(H_2O)\}^{3+}]$ $(= 3.02 \times 10^{-2})^2 / 0.15)$ 1

$K_a = 6.08 \times 10^{-3}$ *(Allow 6.0 to 6.1 × 10^{-3})* 1

$pK_a = 2.22$ (3 significant figures needed but ignore units) 1
NB allow value of pK_a consequentially to value of K_a
allow pK_a = - $\log K_a$ (1) if stated but no value of pK_a calculated

(ii) *Mark consequentially to the value of K_a obtained in (b)(i)*
New $[\{Fe(H_2O)\}^{3+}] = 0.250/4$ $(= 0.0625)$ 1
$K_a = 6.08 \times 10^{-3} = [H^+]^2 / 0.0625$
$[H^+] = \sqrt{(6.08 \times 10^{-3} \times 0.0625)}$ $(= \sqrt{3.80 \times 10^{-4}})$ 1
$pH = -\log 0.01949 = 1.71$ 1

NB *(i) Using the given value of $K_a = 4.50 \times 10^{-3}$ and 0.0625*
$[H^+] = 0.0168$ and pH = 1.78 (Scores the full 3 marks)

(ii) Penalise two marks if $[\{Fe(H_2O)\}^{3+}] = 0.250/n$ where $n \neq 4$
Allow $[H^+] = \sqrt{(6.08 \times 10^{-3} \times 0.250/n)}$ (1)

(iii) Using $K_a = 4.50 \times 10^{-3}$ and 0.0833
pH = 1.71 ***BEWARE*** *of this answer it scores only 1 mark*

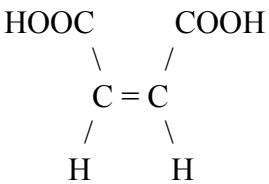
(c) Fe^{2+} ion has a smaller charge to size ratio or charge density 1
Less polarising than Fe^{3+} / less weakening effect on O - H bonds or
Hydrolysis equilibrium displace more to the left 1

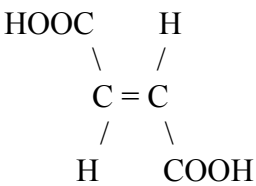
Total 15

SECTION B

Question 7

(a) 1





1

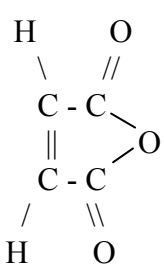
NB *The bonds shown in the structure must be to correct*

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

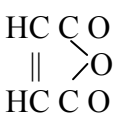
No rotation about C=C axis 1

Structure

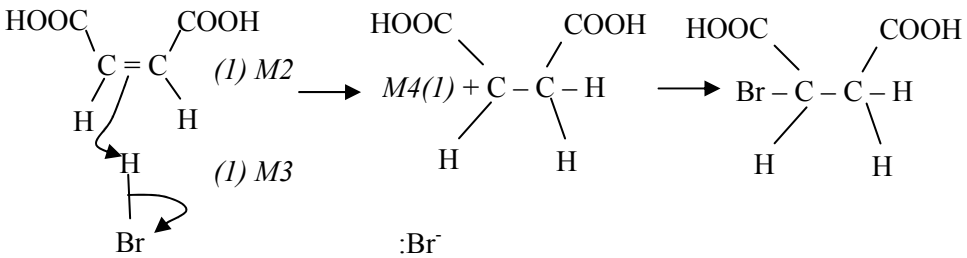


1

Allow



(b) Br_2 / HBr / H_2SO_4 / H^+ / Br^+ / NO_2^+ *(Mark M1)*



4

NB If electrophile H^+ / Br^+ / 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. $2NaOH + HO_2CCHCHCO_2H \rightarrow NaO_2CCHCHCO_2Na + 2H_2O$

Both H replaced	1
Balanced for atoms and charges	1

NB Allow ionic equations and $2NaOH + C_4H_4O_4 \rightarrow C_4H_2O_4Na_2 + 2H_2O$
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* $K_p = ({}_pY)^3 . ({}_pZ)^2 / ({}_pW)^2 . ({}_pX)$ *NB [ ] wrong* 1
M2 temperature 1
M3 increase 1
M4 particles have more energy or greater velocity/speed 1
M5 more collisions with E > Ea or 1
more successful collisions
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 CH_3COCl expensive

NB *Allow converse answers*
Do not allow reactions with other reagents e.g. water or ease of separation

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

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

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

Allow – 84 to score (1) mark

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

$= -21.6 - 298 \times 84/1000$ 1
$= -46.6$ kJ mol^{-1} or $-46\,600$ J mol^{-1} 1
Allow (2) for – 46.6 without units
(Mark ΔG consequentially to incorrect ΔS)
(e.g. $\Delta S = -84$ gives $\Delta G = +3.4$ kJ mol^{-1})

Total 15

Question 9

(a) $Mg + 2HCl \rightarrow MgCl_2 + H_2$ 1

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$ 1

Allow ionic equations

(b) Hydrogen collection

Using a gas syringe or measuring cylinder/ graduated vessel over water 1

Allow if shown in a diagram

Measurements (i) P 1

(ii) T 1

(iii) V 1

Use ideal gas equation to calculate mol hydrogen or mass/*M*r 1

Mol H_2 = mol Mg (Mark consequentially to equation) 1

(c) $MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$ Species 1

Balanced 1

Allow an ionic equation

$Mg(OH)_2 \rightarrow MgO + H_2O$ 1

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

EITHER

Mol MgO obtained stage 2 = mass MgO/*M*rMgO 1

= 6.41/ 40.(3) = 0.159 *Allow 0.16* 1
Allow method mark if formula of magnesium oxide or M_r incorrect.

Moles of Mg = moles of H_2 hence

Mol original MgO = mol MgO from stage 2 - mol H_2 1
= 0.159 - 0.0528 = 0.106 *Allow 0.11* 1

Mark consequentially to moles of magnesium oxide determined above

OR

Mass MgO formed from Mg = 0.0528× M_r MgO {or 40.(3)} (1)

= 2.13 g *Allow 2.1* (1)
Allow method mark if formula of magnesium oxide or Mr incorrect.

Mass original MgO = total mass MgO - mass formed from Mg (1)
= 6.41 – 2.13 = 4.28 g *Allow 4.3* (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