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ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6421

CHM5 Thermodynamics and Further Inorganic Chemistry

Mark Scheme

2006 examination - June series

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

CHM5

Section A

Question 1

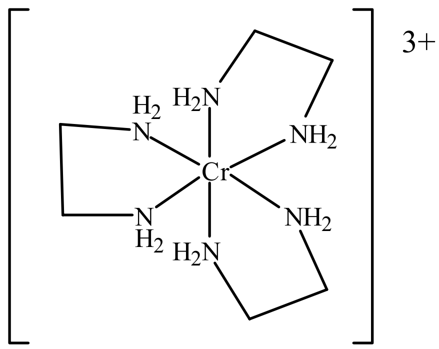
(a)	(i)	$Fe + 2HCl \rightarrow FeCl_2 + H_2$ (allow ionic formulae) or $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$	1
	(ii)	PV = nRT n = PV/RT (allow either formula but penalise contradiction)	1
		$n = \frac{110000 \times 102 \times 10^{-6}}{8.31 \times 298}$	1
		= 4.53×10^{-3} (mol) (answer must have at least 3 sig. figs. Ignore units)	1
	(iii)	Moles of iron = $4.5(3) \times 10^{-3}$ mol (allow conseq on (a)(ii)) (or = $4.2(5) \times 10^{-3}$ if candidate uses given moles of hydrogen)	1
		Mass of iron = $4.53 \times 10^{-3} \times 55.8 = 0.253$ g (mark is for method mass = moles × A_r) (Mass of iron can be 56)	1
	(iv)	$0.253 \times 100/0.263 = 96.1$ % (mark is for answer to 2 sig. figs.) (allow conseq on mass of iron. E.g. = 90% from $4.2(5) \times 10^{-3}$ moles of H_2 and Fe) (Do not allow answers greater than or equal to 100%)	1
(b)	(i)	$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (ignore state symbols)	1
		$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1
		$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$	1
	(ii)	Moles of dichromate = moles Fe^{2+}/6 (Allow conseq, mark is for method (a)(iii)/6) = $4.53 \times 10^{-3}/6 = 7.55 \times 10^{-4}$	1
		Volume of dichromate = moles/concentration (mark is for this method) (= $(7.55 \times 10^{-4} \times 1000)/0.0200$)	1
		V = 37.75 (cm^3) (allow 37.7 to 37.8, allow no units but penalise wrong units) (allow conseq on moles of dichromate) (if value of 3.63×10^{-3} used answer is 30.2 to 30.3, otherwise ans = moles Fe^{2+}/0.00012) (if mole ratio wrong and candidate does not divide by 6, max score is ONE for volume method)	1
	(iii)	($KMnO_4$) will also oxidise (or react with) Cl^- (or chloride or HCl)	1
		Total	***14***

Question 2

(a)		Particles are in maximum state of order (or perfect order or completely ordered or perfect crystal or minimum disorder or no disorder) (entropy is zero at 0 k by definition)	1
(b)		(Ice) melts (or freezes or changes from solid to liquid or from liquid to solid)	1
(c)		Increase in disorder (1)	1
		Bigger (at T_2)	1
		Second mark only given if first mark has been awarded	
(d)	(i)	Moles of water = 1.53/18 (= 0.085)	1
		Heat change per mole = 3.49/0.085 = 41.1 (kJ mol^{-1})	1
		(allow 41 to 41.1, two sig. figs.) (penalise –41 (negative value), also penalise wrong units but allow kJ only)	
	(ii)	$\Delta G = \Delta H - T\Delta S$	1
	(iii)	$\Delta H = T\Delta S$ or $\Delta S = \Delta H/T$	1
		(penalise if contradiction)	
		ΔS = 41.1/373 = 0.110 kJ K^{-1} (mol^{-1}) (or 110 (J K^{-1} (mol^{-1}))	1
		(allow 2 sig. figs.) (if use value given of 45, answer is 0.12 (or 120 to 121) (if ΔH is negative in (d) (i), allow negative answer) (if ΔH is negative in (d) (i), allow positive answer) (if ΔH is positive in (d) (i), penalise negative answer)	
		Correct units as above (mol^{-1} not essential)	1
		Total	***10***

Question 3

(a)		**A** $Cr(H_2O)_3(OH)_3$ (or $Co(OH)_3$	1
		B CO_2	1
		$2[Cr(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Cr(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$	1
		(or gives $2Cr(OH)_3 + 3CO_2 + 9H_2O$)	
(b)	(i)	NaOH	1
		(or KOH)	
	(ii)	+6	1
		(or 6 or +VI or VI)	
	(iii)	H_2O_2	1
		(orNa_2O_2 or BaO_2)	
		$[Cr(OH)_6]^{3-} + 2OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$	1
		(or $[Cr(OH)_6]^{3-} \rightarrow CrO_4^{2-} + 2H_2O + 2H^+ + 3e^-$)	
(c)	(i)		



		At least one $H_2NCH_2CH_2NH_2$ with correct structure and bonding to Cr via N	1
		6 co-ordination with 3 en drawn correctly	1
		Correct 3+ charge	1
		(Mark independently but must not have 6 monodentate ligands)	
	(ii)	Same (or similar) type of bonds broken and made	1
		Same number of bonds broken and made	1
		(or same co-ordination number)	
	(iii)	Entropy change (or ΔS) is positive	1
		(or increase in disorder)	
		Because there are more product particles than reactant particles	1
(d)		$[Cr(H_2O)_6]^{2+}$	1
		Reducing agent	1
		(mark independently)	
(e)	(i)	Ethanal (or CH_3CHO) (not CH_3COH)	1
	(ii)	Ethanoic acid (or correct formula)	1
		Total	***18***

Question 4

(a)	(i)	(K_p) = $(p_z)^2/(p_x)(p_y)^3$	1
		(penalise use of square brackets, allow ( ))	
	(ii)	**X** (22–6)/4 = 4 (MPa)	1
		(mark is for value 4 only, ignore units)	
		Y obtained by multiplying value for **X** by 3 (allow conseq on wrong value for **X**)	1
		Y 4.0 × 3 = 12 (MPa)	1
		(mark is for value 12 only)	
	(iii)	$K_p = 6.0^2/4.0\times12.0^3 = 5.21 \times 10^{-3}$	1
		(allow conseq on wrong values for **X** and **Y** e.g.$6^2/3\times9^3 = 0.165$)	
		(if K_p wrong in (a)(i) CE)	
		MPa^{-2}	1
		(allow any unit of P^{-2} provided ties to P used for K_p value)	
(b)		high pressure expensive (due to energy or plant costs)	1
		(Rate is) slow (at lower temperatures)	1
		Total	***8***

Question 5

(a)	(i)	Fe^{2+}	1
	(ii)	F_2O	1
	(iii)	Fe^{2+}	1
		Cl^-	1
		Use list principle if more than two answers	
(b)	(i)	e.m.f. = E(rhs) – E(lhs)	1
		= 1.52 – 0.77 = 0.75	1
		(0.75 scores first mark also)	
	(ii)	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	1
	(iii)	Decrease	1
		(Increase is CE, no further marks)	
		Equilibrium (or reaction) shifts to R (or L if refers to half equation in table)	1
		(or in favour of more Fe^{3+})	
		(or more Fe^{3+} formed)	
		(or more electrons formed)	
		Electrode potential (for Fe^{3+}/Fe^{2+}) less positive (or decreases)	1
		Total	***10***

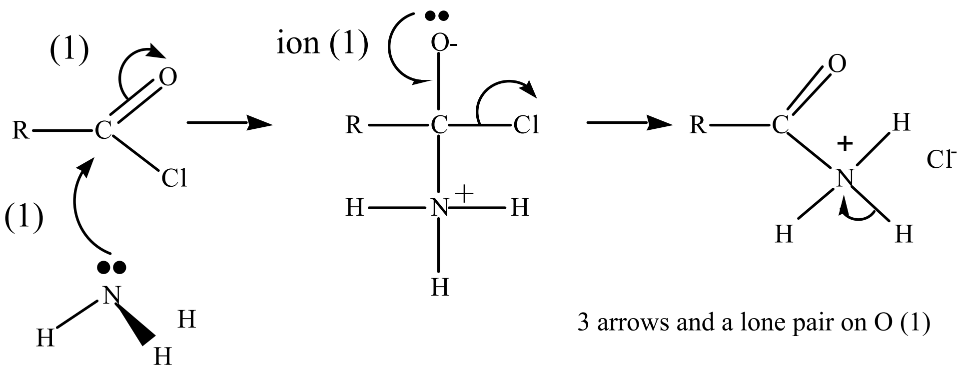
Section B

Question 6

(a) (i) $NH_3 + H_2O \rightarrow NH_4^- + OH^-$ 1
(allow NH_4OH as product)
Ammonia is a proton (or H^+) acceptor 1
Shape of the ammonium ion shown correctly as tetrahedral 1
(allow no charge or wrong charge)
(lose mark if wrong angle given)
(allow 'sticks')

(ii) $NH_3 + BF_3 \rightarrow H_3NBF_3$ 1
(allow NH_3BF_3 or BF_3NH_3)
(penalise Fl for F once only)
Ammonia is a lone pair donor 1
Shape of H_3NBF_3 shown as tetrahedral about N and B linked by N—B bond. 1

(b) 4



Correct name for product (e.g. ethanamide) 1

(c) Further substitution (or reaction) prevented (or 2° or 3° amine not formed) 1
Because ammonia is more likely to react with the haloalkane (rather than the amine product) 1
(or all the haloalkane is used up)
(or less amine is available)

(d) $2NH_3 + 2e^- \rightarrow 2NH_2^- + H_2$ 1
$2K + 2NH_3 \rightarrow 2K^+ \, 2NH_2^- + H_2$ 1
(or $\rightarrow 2KNH_2 + H_2$)

(e) Van der Waals' (or VdW) forces between methane molecules 1
(or VdW forces in methane)
Hydrogen bonding in <u>ammonia and water</u> 1
Hydrogen bonds are stronger than van der Waals' forces 1
(or VdW forces are the weakest)
Hydrogen bonds in water more extensive than ammonia because <u>O has two lone pairs</u> (N one) 1
(or Water forms more H bonds per molecule (than ammonia))
(or H bonds in water stronger because O more electronegative than N)
(or H bonds in water stronger because O—H bond more polar than N—H)
(Note that breaking covalent bond is CE but may not lose all 4 marks)

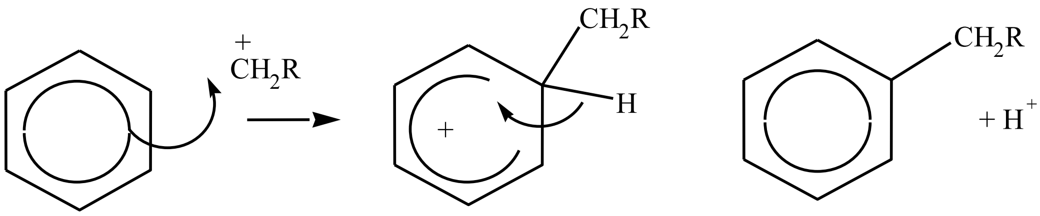
Total 19

Question 7

(a)	$MgCl_2$ is ionic	1
	$SiCl_4$ is molecular	1
	(or simple covalent)	
	Van der Waals' (or VdW) forces <u>between molecules</u>	1
	(or <u>intermolecular</u> VdW forces)	
	(QoL mark for forces between molecules clearly indicated)	
	Ionic forces (or bonds) stronger than VdW	1
	(must be a comparison to score the mark)	
	Therefore more energy required (to separate the particles in $MgCl_2$)	1
(b)	Charge on oxide <u>ion</u> bigger than on chlor<u>ide</u>	1
	(or oxide ion smaller than chloride)	
	(or charge density on oxide ion greater than chloride)	
	Therefore <u>electrostatic</u> attraction is stronger	1
	(QoL mark, can be given independent of first mark)	
(c)	MgO (is a white solid that) forms a suspension (or slightly soluble)	1
	$MgO + H_2O \rightarrow Mg(OH)_2$	1
	(or $\rightarrow Mg^{2+} + 2OH^{-}$)	
	pH is 8 to 10	1
	SO_2 dissolves	1
	(or forms (colourless) solution)	
	$SO_2 + H_2O \rightarrow H_2SO_3$	1
	(or $\rightarrow H^+ + HSO_3^-$)	
	(or $\rightarrow 2H^+ + SO_3^{2-}$)	
	pH is 1 to 4	1
	(mark both pH values independently of equations)	
(d)	$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$ species mark	1
	(or forms $Al(OH)_6^{3-}$ etc)	
	Balanced equation	1
	$Al(OH)_3 + 3H^+ + 3H_2O \rightarrow Al(H_2O)_6^{3+}$ species mark	1
	(or forms $[Al(H_2O)_5(OH)]^{2+}$, Al^{3+}, $AlCl_3$ (salt + water etc)	
	(Note must start equations with $Al(OH)_3$ or $Al(OH)_3(H_2O)_n$ where n = 1 to 3)	
	Balanced equation	1
	Total	***17***

Question 8

(a)	Reducing power increases	1
	SO_2	1
	S	1
	H_2S	1
	(Apply list principle to answers that give more than 3 reduction products)	
	$2I^- + SO_4^{2-} + 4H^+ \rightarrow I_2 + SO_2 + 2H_2O$ species correct	1
	(or $6I^- + SO_4^{2-} + 8H^+ \rightarrow 3I_2 + S + 4H_2O$)	
	(or $8I^- + SO_4^{2-} + 10H^+ \rightarrow 4I_2 + H_2S + 4H_2O$)	
	(Starting materials can be HI or NaI instead of I^- or H_2SO_4 instead of H^+)	
	Balanced equation (one only of the above)	1
(b)	$Cl_2 \rightarrow 2Cl^\bullet$	1
	$RCH_3 + Cl^\bullet \rightarrow RCH_2^\bullet + HCl$	1
	$RCH_2^\bullet + Cl_2 \rightarrow RCH_2Cl + Cl^\bullet$	1
	(Ignore termination steps and any arrows)	
(c)	Electrophilic substitution	1
	$RCH_2Cl + AlCl_3 \rightarrow RCH_2^+ + AlCl_4^-$	1
	(Ignore any arrows)	
		3



arrow (1) intermediate (1) and arrow (1)

(In intermediate, broken delocalised ring must cover at least 3 carbons and not extend beyond a line between carbons 2 and 6 on the benzene ring)

Total 14

Question 9

(a)	(Initially slow) because reaction is between two negative ions	1
	(or between two negative reactants or two negative species)	
	Which repel each other	1
	Then Mn^{2+} (or Mn^{3+}) (ions) are formed acting as an autocatalyst (QOL mark)	1
	(or answer such as Mn^{2+} ions formed in the reaction act as a catalyst)	
	$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 4CO_2$	1
	$MnO_4^- + 4Mn^{2+} + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$	1
	$C_2O_4^{2-} + 2Mn^{3+} \rightarrow 2Mn^{2+} + 2CO_2$	1
	(Note these equations may gain credit if they have spectator ions and/or be written as half equations)	
(b)	Active sites are where reactants are adsorbed onto a catalyst surface	1
	(or bind or react on a catalyst surface)	
	(do not allow absorbed)	
	(Number of active sites increases if) surface area is increased	1
	(or catalyst spread thinly)	
	(or on honeycomb)	
	(or powdered)	
	(or decreased particle size)	
	Active sites blocked by another species (or poison)	1
	(or species adsorbed more strongly)	
	(or species adsorbed irreversibly)	
	(or species not desorbed)	
	(Note, credit any answer that implies blocked but not just active site 'poisoned')	
	Sulphur (compounds) in Haber process	1
	(or lead in a catalytic converter)	
	(Note do not allow enzymes unless immobilised)	
	Total	***10***