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ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6421

CHM5 Thermodynamics and Further Inorganic Chemistry

Mark Scheme

2008 examination - June series

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CHM5

SECTION A

Question 1

(a) Proton (or H^+) acceptor (1)

(b) Electron (or lone) pair donor (1)

(c) Electron (or lone) pair donor (1)

(Ignore answers that talk about attraction to +ve centre)

(allow Lewis base)

(d) $NH_3 + H^+ \rightarrow NH_4^+$ (1)

(or $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$)

(allow Cl^- as a spectator)

(e) $4NH_3 + [Cu(H_2O)_6]^{2+} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

Correct copper species (both) (1)

(allow no square brackets or other shapes of brackets)

balanced equation (1)

(only with correct species)

colour of reagent: Blue (1)

Colour of product: (Dark) blue (1)

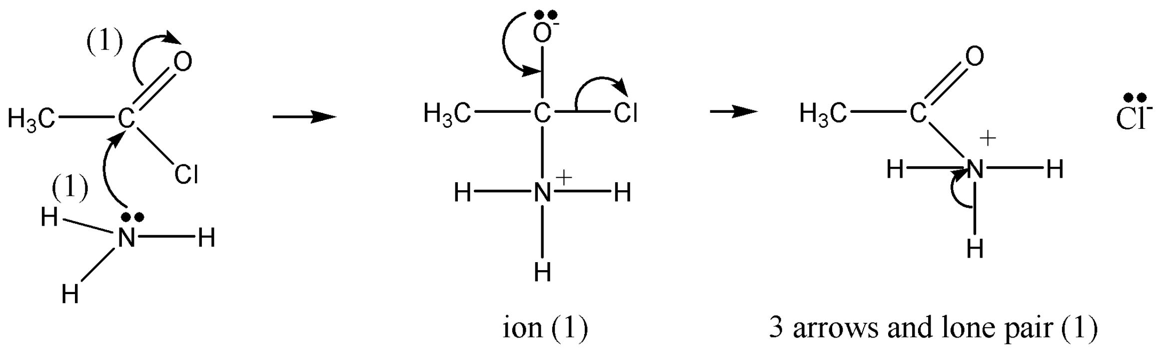
(note NOT purple, NOT blue ppt)

(Note mark colours independently correct)

(f) $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$ (1)

(allow $CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$)

(nucleophilic) addition-elimination (1)



(final Cl^- not essential)

(ignore final proton donation to base even if arrow etc wrong)

arrow from lone pair on ammonia to C (1)

arrow from C=O to O (1)

intermediate with + and – charges (1)

3 arrows and lone pair on O (1)

Total 14 marks

Question 2

(a)	$\Delta G = \Delta H - T\Delta S$	(1)
(b)	(Boiling is a) spontaneous (or feasible) (change)	(1)
	(or (water and water vapour are at) equilibrium)	
(c)	When $\Delta G = 0$ $\Delta S = \Delta H/T$	(1)
	$= 23.4 \times 1000/240$	
	$=97.5$ (J K^{-1} mol^{-1})	(1)
	(units not essential but 97.5 with wrong units scores 1/2)	
	(note 0.0975 (kJ K^{-1} mol^{-1}) scores 1/2)	
	(allow 2 marks for correct answer)	
	(allow range 97 to 98)	
	(note, if –ve answer, can score first mark only)	
(d)	H bonding in both	(1)
	Stronger in HF	(1)
	(or more energy needed to overcome forces)	
	Because H—F is more polar than H—N	(1)
	(or electronegativity of F > N)	
	(or F is more electronegative or F is the most electronegative)	
	Note	
	(if breaking covalent bonds or ionic bonds C.E. = 0/3)	
	(allow 1/3 (second mark) for intermolecular forces in HF stronger without specifying nature of force or when comparing H bonding in HF with dipole-dipole or VdW in NH_3)	

Total 7 marks

Question 3

(a) $1/2N_2 + 3/2H_2 \rightarrow NH_3$ (1)

(must be this equation not a multiple)

(ignore state symbols)

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

(must have Σ (or equivalent) and no Δ on RHS)

$= 193 – (192/2 + 3/2 \times 131)$ (1)

(this also scores first mark)

$= -99.5$ ($J\ K^{-1}\ mol^{-1}$) (1)

(units not essential but penalise wrong units one mark)

(allow 3 for correct answer)

(allow range -99 to -100)

(if equation doubled allow 2/3 for –198 to -200)

(allow 1/3 for +99.5)

(can only score 1/3 (first mark) if answer is –130 and equation stated correctly)

(c) (i) $\Delta G = \Delta H - T\Delta S$

$= -46.2 - (700 \times -99.5)/1000$ (1)

(or $= -46.2 - (700 \times x)/1000$ if using given value or value from (b))

$= +\ 23.45$ kJ mol^{-1} (1)

(allow range 23 to 24)

(units must be given, penalise wrong units)

Allow 2 for consequential marking from answer to (b) e.g.

(if answer to (b) is +99.5 allow -115 to -116)

(if answer to (b) is –199 allow 46 to 47 or 93 to 94)

(if answer to (b) is –130 allow 44 to 45)

(if used given answer of –125 allow 41 to 42)

(ii) Decreases (or becomes more negative) (1)

(d) To speed up reaction (1)

(or fast reaction)

(or give more molecules $E > E_a$)

Total 8 marks

Question 4

(a)	(i)	W Pt (or in words)	(1)
		X KCl, NH_4Cl etc (allow any simple soluble salt and ignore water, paper, agar etc)	(1)
		Y Mg	(1)
		Z $MgCl_2$	(1)
		(aq not essential)	
		(allow any identified soluble Mg salt)	
	(ii)	$Pt|H_2(g)|H^+(aq)||Mg^{2+}(aq)|Mg$	
		(allow $Mg|Mg^{2+}(aq)||H^+(aq)|H_2|Pt$)	(1)
		Species	
		(ignore state symbols)	
		(allow any coefficients)	
		Correct order	(1)
		(order is consequential on correct species)	
		(can score this mark (not first mark) if phase boundary solidus omitted)	
		(If Pt omitted max 1)	
(b)	(i)	0.84 (V)	(1)
	(ii)	(+)3	(1)
		(or III)	
		(or Mn^{3+} or Mn(III))	
	(iii)	$2MnO_2 + 2H_2O + Zn \rightarrow 2MnO(OH) + 2OH^- + Zn^{2+}$	(1)
		(allow multiples)	
		(allow $Zn(OH)_2$)	
		(arrow can be equilibrium arrow)	
	(iv)	*Oxidising agent* MnO_2	(1)
		(allow in words manganese oxide)	
		Reducing agent Zn	(1)

	(v)	Zn (or MnO_2) used up	(1)
		(or concentration of products increases)	
		(or electrode(s) worn away)	
		(allow polarisation or explanation in terms of ion migration)	
		(note if equation reversed allow conseq i.e. Zn^{2+} or MnO(OH) used up)	
(c)	(i)	$4H^+ + SO_4^{2-} + 2e^- \rightarrow SO_2 + 2H_2O$	(1)
		(or $2H^+ + H_2SO_4$ etc)	
		$2Br^- \rightarrow Br_2 + 2e^-$	(1)
		$4H^+ + SO_4^{2-} + 2Br^- \rightarrow SO_2 + 2H_2O + Br_2$	(1)
		(or $2H_2SO_4 + 2KBr \rightarrow K_2SO_4 + SO_2 + 2H_2O + Br_2$)	
		(allow production of SO_3^{2-} for last mark but not for half equation i.e. 1/2)	
	(ii)	H_2SO_4 cannot oxidise Cl^-	(1)
		(or Cl^- ions (or KCl) cannot reduce H_2SO_4)	
		(or Cl_2 strong(er) oxidising agent (than H_2SO_4))	
		(or Cl^- weak reducing agent)	
		(allow any correct E^0 argument)	
		$H_2SO_4 + KCl \rightarrow KHSO_4 + HCl$	(1)
		(or $H_2SO_4 + 2KCl \rightarrow K_2SO_4 + 2HCl$)	
		(or $H^+ + Cl^- \rightarrow HCl$ or any correct equation to give HCl)	

Total 17 marks

Question 5

(a)		Curve Y starts at origin and is steeper than curve A	(1)
		Finishes at the same level as curve A	(1)
(b)		Curve X starts at the origin and is below curve B	(1)
		Approaches the same level as curve B	(1)
(c)		Order is 1 (or first order)	(1)
		(Note C.E. if order not equal to 1)	
		When concentration (of iodine) is <u>doubled</u> gradient (or rate) doubles	(1)
		(or when concentration (of iodine) is <u>halved</u> gradient (or rate) halves	
(d)	(i)	$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$	(1)
		$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ (either order)	(1)
		(allow correct equations that are not ionic)	
	(ii)	Alternative route	(1)
		Not used up (or is regenerated) (or not chemically changed) (or not in overall equation)	(1)
		Speeds up reaction (or changes rate)	
		Lowers activation energy	
		(any two of these four)	

(e)	(i)	Different phase (or state) from reactants	(1)
		(or implied eg silver is a solid, reactants are gases	
	(ii)	Reactants <u>ad</u>sorb weakly (or poorly) (onto surface of silver) QWC mark	(1)
	(iii)	Reaction may be too fast	(1)
		(note candidates must give the idea of reaction rate)	
		Explosion	(1)
		(or uncontrolled)	
		(note do not accept further oxidation arguments)	

Total 14 marks

SECTION B

Question 6

(a) (i) Note incorrect reagent (e.g. $BaCO_3$) CE = 0 but if Ba^{2+} or Ba^+ implied, lose reagent mark and mark on

If two reagents given (one for each member of pair), mark first and ignore second

Reagent	$BaCl_2/H^+$ or $Ba(NO_3)_2$	$Ba(OH)_2$	Ba	(1)
Obs with $CuSO_4$	(White) ppt	White and blue ppts	White and blue ppts	(1)
Obs with $Cu(NO_3)_2$	No change or green or yellow solution	Blue ppt	Blue ppt	(1)

$CuSO_4(aq) + BaCl_2 \rightarrow BaSO_4(s) + CuCl_2(aq)$ (1)

(or $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$)

(ignore state symbols)

(If use Ba, also need an equation to show production of $Ba(OH)_2$ or Ba^{2+})

(ii) If reagent incompletely given (e.g. OH^-), lose reagent mark and mark on

Reagent	NaOH	xs NaOH	NH_3	xs NH_3 (or conc)	Na_2CO_3 (or $NaHCO_3$)	(1)
Obs with $CrCl_3$	Green ppt	Green solution	Green ppt	Purple solution	Green ppt gas evolved	(1)
Obs with $FeCl_2$	Green ppt goes brown on standing	Green ppt	Green ppt goes brown on standing	Green ppt	Green ppt or white ppt	(1)

Note other answers possible e.g. Zn/HCl (1) blue solution (1) no reaction (1)

Equations for reactions with $CrCl_3$ (Note square brackets for complexes & ss optional) (1)

NaOH $Cr(H_2O)_6^{3+} + 3OH^- \rightarrow Cr(H_2O)_3(OH)_3 + 3H_2O$

(or $CrCl_3 + 3OH^- \rightarrow Cr(OH)_3 + 3Cl^-$) etc

xs NaOH $[Cr(H_2O)_6]^{3+} + 6OH^- \rightarrow [Cr(OH)_6]^{3-} + 6H_2O$

(or $CrCl_3 + 6NaOH \rightarrow Cr(OH)_6^{3-} + 6Na^+ + 3Cl^-$)

(allow formation of $[Cr(H_2O)_2(OH)_4]^-$ & $[Cr(H_2O)(OH)_5]^{2-}$,

NH_3	As NaOH but can have + $NH_3 \rightarrow NH_4^+$ instead of + $OH^- \rightarrow H_2O$	
xs NH_3	$[Cr(H_2O)_6]^{3+} + 6NH_3 \rightarrow [Cr(NH_3)_6]^{3+} + 6H_2O$	
Na_2CO_3	$2[Cr(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2Cr(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$	
$NaHCO_3$	$[Cr(H_2O)_6]^{3+} + 3HCO_3^{2-} \rightarrow Cr(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$	
Equations for reactions with $FeCl_2$		(1)
NaOH	$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(H_2O)_4(OH)_2 + 2H_2O)$	
(& xs)	(or $FeCl_2 + 2NaOH \rightarrow Fe(OH)_2 + 2NaCl$)	
NH_3 & xs	As NaOH but can have + $NH_3 \rightarrow NH_4^+$ instead of + $OH^- \rightarrow H_2O$	
Na_2CO_3	$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$	
	(or $FeCl_2 + Na_2CO_3 \rightarrow FeCO_3 + 2NaCl$)	
$NaHCO_3$	As NaOH or Na_2CO_3	

(b) (i) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 10CO_2 + 8H_2O + 2Mn^{2+}$ (1)

(ii) Moles $C_2O_4^{2-}$ = vol in $dm^3 \times$ conc = $17.6/1000 \times 0.1 = 0.00176$ (this answer only) (1)

Moles MnO_4^- = 2/5 × moles $C_2O_4^{2-}$ (this mark is for 2/5) (1)

= 2/5 × 0.00176 = 0.000704 (or 7.04×10^{-4}) (1)

(This answer only which also scores the previous 2 marks)

(iii) Mass of 1 mol of unknown = 0.1/0.000704 = 142 (1)

(or if M_r assumed, mass of 1.0 g (or 0.1 g for 25 cm^3) can be calculated from no. of moles × M_r

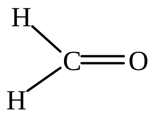
(must show working using answer from (b) (ii) to score this mark)

Unknown corresponds to $NaMnO_4$ (1)

(this mark only given if previous mark for working also given)

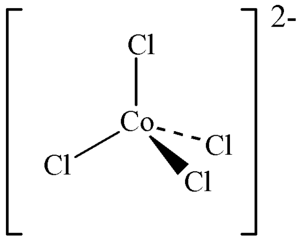
Total 15 marks

Question 7

(a) (i)  (1)

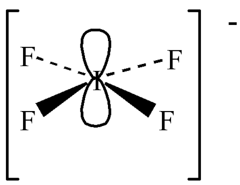
(must show single and double bonds)

Trigonal planar (allow triangular planar) (1)

(ii)  (1)

(Charge optional (and in other shapes in (iii) and (iv))

tetrahedral (1)

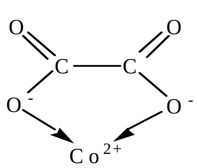
(iii)  (1)

Note lone pairs not necessary

Square planar (allow octahedral if lone pairs shown) (1)

(iv) $[NC—Ag—CN]^-$ (allow CN or NC linkage) (1)

linear (1)

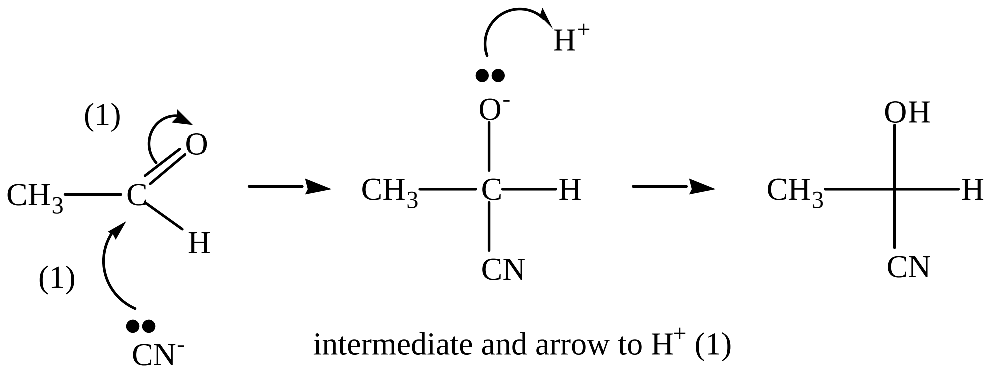
(b)  (2)

structure of ligand (1) bonds to Co (1) (allow with or without charges)

(note if more than one ligand shown, all must be correct)

(Second mark only given if first mark gained)

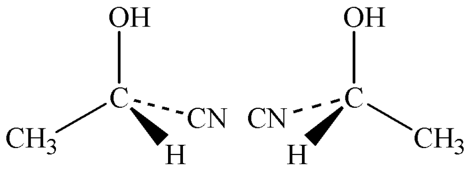
(c) (3)



intermediate and arrow to H^+ (1)

(Equal chance of) attack on each side of carbon (or molecule or double bond) (1)

(allow from above and below the plane)

 (1)

Note, do not allow structures with bond angle of 90^0

Allow CN or NC linkages as above

Total 15 marks

Question 8

(a) $H^{\ominus}_{sol} = H_{lattice} + \sum H^{\ominus}_{hyd}$ so $H_{lattice} = H^{\ominus}_{sol} - \sum H^{\ominus}_{hyd}$ (or cycle) (1)

For NaCl = +3.9 +406 +364 = (+) 774 (kJ mol^{-1}) (1)

(allow 773.5 to 774)

For $MgCl_2$ = -155 + 1920 +728 = (+) 2493 (kJ mol^{-1}) (1)

If either of last two answers is correct first mark is also scored

(if both answers numerically correct but negative signs allow 1/3)

(b) Attraction (or force or bonding) between <u>ions</u> weaker (<u>ions</u> for QWC) (1)

(or <u>ionic</u> bonding weaker)

Charge on $Na^{(+)}$ or less than that on $Mg^{(2+)}$ (1)

(Do not allow polarisation argument)

(c) Al($^{3+}$ ions) have higher charge/size ratio than $Mg^{(2+)}$ (allow just charge) (1)

(If answer refers to m/z C.E. = 0)

Attract water molecules more strongly (1)

(d) $K_a = [H^+][A^-]/[HA]$ (1)

(allow incorrect or omitted use of [] for concentration of Al ions)

(Where A^- is $[Al(H_2O)_5(OH)]^{2+}$ and HA is $[Al(H_2O)_6]^{3+}$)

$K_a = [H^+]^2/[HA]$ when $[H^+]=[A^-]$ therefore $[H^+] = \sqrt{K_a[HA]}$ (1)

(this mark also scores the first mark)

$[H^+] = \sqrt{1.26 \times 10^{-5} \times 2.0} = 5.02 \times 10^{-3}$ (mol dm^{-3}) (1)

pH = 2.30 (1)

(pH must be quoted to 2 d.p.) (QWC mark)

(Note pH = 2.30 scores 4)

(Note pH mark can be given consequentially on a wrong value for $[H^+]$

(e) $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$ (1)

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

(Note other equations possible)

pH = -1 to 1 (1)

Total 13 marks

Question 9

(a) Heat required = mass $\times$ sp ht capacity $\times$ rise in temp = $1000 \times 4.18 \times 80 = 334400$ J (1)

(allow 334000 to 335000 J or 334 to 335 kJ)

Number of moles of methanol required to provide this = $334400/(715 \times 1000)$ (1)

(method mark for heat/(enthalpy of combustion) but both values must be in the same units)

= 0.4677 mol (1)

(allow 0.46 to 0.47)

But efficiency is only 0.5 therefore moles required = $0.4677 \times 2 = 0.9354$ (1)

(note 0.935 scores 4)

(note this mark of 1 is for the factor of 2 and can be scored anywhere in the answer even if the rest of the calculation is wrong)

Mass = moles $\times$ M_r = $0.935 \times 32 = 29.9$ g (1)

(allow 29 to 30.1 g allow answers to 2 sig figs)

(note correct answer scores 5)

(note answer of 14.5 to 15.1 scores 4/5)

(b) $K_c = [CH_3OH]/[H_2]^2[CO]$ (1)

Moles at equilibrium of H_2 = 0.4 (1)

CO = 0.2 (1)

Concentration = moles/vol = moles/1.5 (1)

(can score this from next mark also)

$K_c = (0.8/1.5) /(0.4/1.5)^2 \times (0.2/1.5)$ (1)

56.25 (1)

(allow 55.5 to 56.5)

(note correct answer scores 6)

(note an answer of 25 (not divided by vol to get concentration) scores 3/6)

$mol^{-2}dm^6$ (1)

(note mark units independently)

(Note if moles of H_2 wrong and moles CO wrong, max mark is 3 for

K_c expression, moles/ vol expression for concentration and units)

(c) **Methyl ethanoate**: 2 peaks (1)

Each is a singlet (1)

Ethyl methanoate: 3 peaks (1)

Singlet, triplet, quartet all three scores 2 marks, (or two out of three 1 mark) (1)

(Note must give number of peaks to score next mark(s)) (QWC)

(But if number of peaks can be unambiguously implied from splitting answer can score 1/2 for number of peaks (2 peaks then 3 peaks))

Total 17 marks