Version 1.0: 24/06/09

General Certificate of Education

Chemistry 6421

CHM5 Thermodynamics and Further Inorganic Chemistry

Mark Scheme

2009 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.

Set and published by the Assessment and Qualifications Alliance.

The Assessment and Qualifications Alliance (AQA) is a company limited by guarantee registered in England and Wales (company number 3644723) and a registered charity (registered charity number 1073334).
Registered address: AQA, Devas Street, Manchester M15 6EX *Dr Michael Cresswell Director General*

Question	Part	Sub Part	Marking Guidance	Mark	Comments
1	(a)		Enthalpy <u>change</u> when <u>1 mol</u> of a substance/compound/ionic lattice/product; is formed from its elements; <u>All</u> substances in their standard states;	1 1 1	Allow heat change/heat energy change/heat absorbed Not energy change, not product<u>s</u> Or normal states under standard conditions If confused with ionisation energy or combustion or bond enthalpy etc CE=0 Ignore reference to standard conditions only
1	(b)		O^- repels electrons/both O^- and e^- are negative/idea of repulsion;	1	Allow (O^- ion) forced to accept an electron
1	(c)		Arrows on cycle and correct ΔH values/correct labels; $-\Delta H$ = +602 +150 +736 +1450 +248 +844 -142 ΔH*(lattice formation)* = -3888 (kJ mol^{-1});	1 1 1	Allow lattice enthalpy arrow going up Correct answer scores 3 +3888 scores 2 -2684 scores 1 Ignore incorrect or missing units
1	(d)		Ca^{2+} ions are smaller (than Ba^{2+} ions)/Ca^{2+} ions higher charge to size ratio/greater charge density; More attraction for O^{2-}/stronger attraction;	1 1	Must mention ions or M^{2+} Must imply between ions Mark independently CE if mention molecules

Question	Part	Sub Part	Marking Guidance	Mark	Comments
2	(a)	(i)	$BaO + H_2O \rightarrow Ba^{2+} + 2OH^-$;	1	Accept $Ba(OH)_2$
2	(a)	(ii)	Moles of BaO = 2.00/153.3 = 0.01305	1	Allow 0.013(0) – 0.0131
			$[Ba^{2+}] = 0.1305$ mol dm^{-3};	1	One mark for x 10 method mark
			$[OH^-] = 0.2609$ mol dm^{-3};	1	One mark for 2 x $[Ba^{2+}]$ method mark
			$[H^+] = K_w / [OH^-] = 3.83 \times 10^{-14}$	1	Method mark $K_w / [OH^-]$ or K_w / previous answer
			$pH = -\log_{10}[H^+] = 13.42$	1	Allow 13.40 to 13.43 5 for correct answer. Method mark for $-\log_{10}$ [answer 4] provided answer to 2dp 13.11 scores 4 (13.10 to 13.13) (omits factor 2) 12.41 scores 4 (12.40 to 12.43) (omits factor 10) 12.11 scores 3 (12.10 to 12.13) (omits x 2 and x 10)
2	(b)		$Mg(OH)_2$ (much) less soluble (than $Ba(OH)_2$)/$Ba(OH)_2$ more soluble (than $Mg(OH)_2$);	1	Allow $Mg(OH)_2$ sparingly soluble

Question	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)		$\Delta G = \Delta H - T\Delta S$	1	
3	(b)	(i)	Positive/+	1	
			More moles of gas products (2 mol gas gives 3 mol gas);	1	QWC Allow molecules instead of moles
			More disorder/increase in disorder/very disordered;	1	Mark independently even if + not given
3	(b)	(ii)	ΔH is negative and ΔS is positive/ $T\Delta S$ +ve/ $-T\Delta S$ -ve;	1	
			So ΔG will be negative (at all temperatures);	1	Mark independently and indep. of (b) (i)
3	(b)	(iii)	Too slow/activation energy too high/speeds up reaction;	1	higher yield is contradiction, scores 0
3	(c)	(i)	$\Delta H = \Sigma\Delta H(\text{formation products}) - \Sigma\Delta H(\text{formation reactants})$;	1	Allow correct cycle
			$= 4 \times -411 - (-720 + 4\times 3)$;	1	
			$= -936$ (kJ mol^{-1});	1	3 marks for correct value +936 scores 1 (-924 scores 1 – ie assumed ΔH_f(Na(l) = 0)
			$\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$;	1	
			$= 4 \times 72 + 30 - (329 + (4 \times 58)) = -243$ (J K^{-1} mol^{-1});	1	2 marks for correct value Penalise wrong units If answer - 0.243 must show units kJ K^{-1} mol^{-1}
3	(c)	(ii)	Limiting condition $\Delta G = 0$/ $0 = \Delta H - T\Delta S$/ $T = \Delta H/\Delta S$;	1	Using values given (allow use of these with own value for ΔH or ΔS)
			$= (-936 \times 1000)/-243$	1	$(-812 \times 1000)/-312$;
			= 3852 (K) – (allow range 3850 to 3852);	1	2603 (2600 to 2603) Allow consequential on answer to (c)(i) provided not –ve T. Penalise wrong units T = 3.85 scores M1 only

Question	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)		Gains electrons;	1	
4	(b)		Zero; By definition/by convention;	1 1	 Not reference electrode
4	(c)		Salt bridge transfers charge/ions/ to allow (electrical) connection between the two electrodes/ complete the circuit; Made from KCl etc; conducts electrons/ collects electrons/transfers electrons/gains electrons/loses electrons; Pt	1 1 1 1	Allow conduct electricity Not transfer electrons Any group 1 or ammonium chloride/nitrate/sulphate NOT 'salt' alone Must have idea of electron transfer Allow electron source/sink
4	(d)		(+)6/six/VI;	1	
4	(e)		$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $Zn \rightarrow Zn^{2+} + 2e^-$ $Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$	1 1 1	Allow spectator ions, $K_2Cr_2O_7$ etc Allow reverse equation Allow spectators
4	(f)		$Zn(s)\|Zn^{2+}(aq)\|\|Cr_2O_7^{2-}(aq),(H^+(aq)),Cr^{3+}(aq)(\|Pt)$	1	H^+, Pt, state symbols not essential Ignore water Ignore multiple ions Ignore SO_4^{2-} Allow I instead of , (comma) Allow extra | (phase boundary) at either end Allow X instead of Pt

Question	Part	Sub Part	Marking Guidance	Mark	Comments
General comments for Q5					Reagent must be a compound not an ion but mark on/mark on with wrong formula For no reaction do not allow nothing/no observation, do allow no change CE if no reagent given
5	(a)		*Reagent:* (dil) sulphuric acid/identified soluble sulphate; *Obs with $MgCl_2$:* no reaction/ no ppt; *Obs with $BaCl_2$:* white ppt;	1 1 1	*Reagent:* $NaOH/NH_3$ *Obs with $MgCl_2$:* white ppt *Obs with $BaCl_2$:* no reaction
5	(b)		*Reagent:* $NaHCO_3$ or allow Na_2CO_3 *Obs with CH_3COOH:* bubbles of gas; *Obs with CH_3COCH_3:* no reaction; *Equation*: $CH_3COOH + HCO_3^- \rightarrow CH_3COO^- + CO_2 + H_2O$ etc;	1 1 1 1	Allow correct acid/base indicator Correct acid indication No change $CH_3COOH \rightarrow CH_3COO^- + H^+$ *Allow Reagent:* Mg/Zn *Obs with CH_3COOH:* bubbles of gas *Obs with CH_3COCH_3:* no reaction *Equation*: $2CH_3COOH + Mg/Zn \rightarrow Mg^{2+}/Zn^{2+} + 2CH_3COO^- + H_2$ Allow (2,4)-dnph/Brady's reagent *Obs with CH_3COOH:* no change *Obs with CH_3COCH_3:* yellow/orange ppt *Equation*:$CH_3COCH_3 + (NO_2)_2C_6H_3NHNH_2 \rightarrow (NO_2)_2C_6H_3NHN=C(CH_3)_2 + H_2O$

5	(c)		*Reagent:* $AgNO_3$ *Obs with KF:* no change *Obs with KCl:* white ppt	1 1 1	Ignore NH_3 if $AgNO_3$ observation correct
5	(d)		*Reagent:* excess NaOH *Obs with $CrCl_3$:* green solution (or ppt dissolves) *Obs with $FeCl_2$:* green ppt	1 1 1	*Reagent:* NaOH *Obs with $CrCl_3$:* green ppt *Obs with $FeCl_2$:* green ppt goes brown on standing **OR** *Reagent:* NH_3 *Obs with $CrCl_3$:* green ppt *Obs with $FeCl_2$:* green ppt goes brown on standing **OR** *Reagent:* excess NH_3 (or conc) *Obs with $CrCl_3$:* purple solution *Obs with $FeCl_2$:* green ppt **OR** *Reagent:* Na_2CO_3 (or $NaHCO_3$) *Obs with $CrCl_3$:* green ppt gas evolved *Obs with $FeCl_2$:* green ppt or white ppt **OR** *Reagent:* H_2O_2/NaOH *Obs with $CrCl_3$:* yellow solution *Obs with $FeCl_2$:* brown ppt **OR** *Reagent:* Zn/HCl *Obs with $CrCl_3$:* blue solution *Obs with $FeCl_2$:* no change **Note** where two reagents necessary, only one must be fully specified e.g. Zn/H^+ scores the reagent mark

5	(e)		*Reagent:* excess NaOH *Obs with $AlCl_3$:* colourless solution with excess; *Obs with $MgCl_2$:* white ppt; *Equation*: $AlCl_3 + 6NaOH \rightarrow 3Na^+ + [Al(OH)_6]^{3-} + 3NaCl$ (or two equations)	1 1 1 1	'excess' can also be gained from M2 Or white ppt dissolves in excess Allow + $4NaOH \rightarrow Na^+ + [Al(OH)_4]^- + 3NaCl$ **OR** *Reagent:* $Na_2CO_3/NaHCO_3$ *Obs with $AlCl_3$:* bubbles (white ppt) *Obs with $MgCl_2$:* white ppt *Equation*: Any equation showing release of CO_2 **OR** *Reagent:* Acid base indicator *Obs with $AlCl_3$:* Correct acid indication *Obs with $MgCl_2$:* No change/neutral indication *Equation*: $[Al(H_20)_6]^{3+} \rightarrow [Al(H_20)_5(OH)]^{2+} + H^+$ **OR** *Reagent:* Mg/Zn *Obs with $AlCl_3$:* bubbles *Obs with $MgCl_2$:* no reaction *Equation*: $2[Al(H_20)_6]^{3+} + Mg/Zn \rightarrow 2[Al(H_20)_5(OH)]^{2+} + H_2 + Mg^{2+}/Zn^{2+}$

Question	Part	Sub Part	Marking Guidance	Mark	Comments
6	(a)		Power/ability of an element/atom to attract/pull/withdraw electrons/electron density; In a covalent bond/shared pair;	1 1	Not an electron Only allow if idea of attraction given in M1 If bond breaking or ionisation implied, CE=0
6	(b)		Na ion/Na^+ has low charge to size ratio/charge density/charge Aluminium ion/Al^{3+} has a high charge to size ratio/charge density/charge; Al^{3+} has higher charge density than Na^+ scores M1 and M2 Al^{3+} polarises Cl^- /chloride ion;	1 1 1	**Or** Big difference in electronegativity between Na and Cl; **Or** small difference in electronegativity between Al and Cl Electronegativity difference between Na and Cl > that between Al and Cl scores M1 and M2 Allow explanation or description of polarisation even if 'polarised' not stated
6	(c)	(i)	Ionic (lattice); Strong forces of attraction between ions;	1 1	 Or strong electrostatic attraction Mention of ions also scores first mark Any reference to molecules or atoms CE=0

6	(c)	(ii)	$SiCl_4$ molecular/molecules/simple covalent;	1	
			van der Waals'/vdW forces between molecules /VdW intermolecular forces/vdW IMF	1	Or London or temp dipole-dipole etc Mention of molecules here also scores M1
			PCl_5 ionic;	1	Lose this mark if confused with PCl_5 molecules
			PCl_4^+ PCl_6^-	1	Also scores M3
			Ionic forces stronger than van der Waals';	1	Allow van der Waals' forces weak, ionic bonds/forces strong
6	(d)		$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$	1	Allow without state symbols Allow $[Mg(H_2O)_6]^{2+}$ Ignore inclusion of aq in equation Equations must be balanced
			$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$	1	or + $4H_2O \rightarrow Si(OH)_4 + 4HCl$ HCl can be $H^+ + Cl^-$
			$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$	1	Or ionic Allow $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

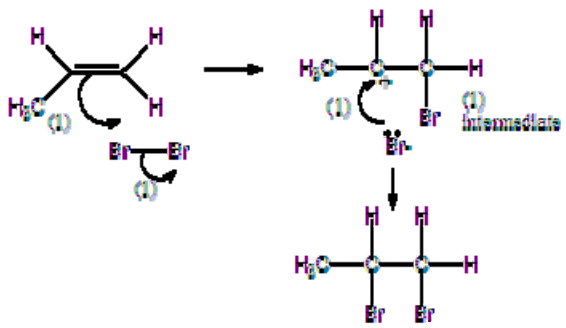
Question	Part	Sub Part	Marking Guidance	Mark	Comments
7	(a)		Electron pair donor/lone pair donor/Lewis base;	1	
			Number of electron pairs donated from ligands;	1	Allow number of co-ordinate bonds Not number of donor atoms Not number of ligands
7	(b)		**d** electrons can be excited/move to a higher energy level;	1	Allow there is an energy gap between d orbitals/can have d to d transitions
			By absorbing **visible** light/energy;	1	
			Remaining visible/coloured light reflected or transmitted;	1	**Or** in M2, if **some** visible light/energy is absorbed, this scores M2 and M3 If visible not mentioned in M3 but is mentioned in M2, can score this M3 mark

7	(c)	(i)	Add NH_3/ammonia; $[Co(NH_3)_6]^{2+}$ ions; Yellow/straw/pale brown;	1 1 1	Can be scored from an equation even if not balanced Colour must be correct for species given If no species do not allow colour mark **Or** Na_4EDTA/EDTA $[CoEDTA]^{2-}$ blue/purple (allow any colour not pink) **Or** $H_2NCH_2CH_2NH_2$ $[Co(H_2NCH_2CH_2NH_2)_3]^{2+}$ yellow (allow any colour not pink) **Or** $(COO)_2Na_2$ $[Co(C_2O_4)_3]^{4-}$ allow any colour not pink

7	(c)	(ii)	Add HCl/NaCl/KCl $[CoCl_4]^{2-}$ Blue (solution);	1 1 1	Not Cl^- but mark on, ignore concentration of solutions Not blue ppt

7	(c)	(iii)	Add NH_3 and H_2O_2/ O_2/air; $[Co(NH_3)_6]^{3+}$ ions; (Dark) brown (solution);	1 1 1 1	 Mark M1 and M2 independently

Question	Part	Sub Part	Marking Guidance	Mark	Comments
8	(a)		*Rate:* change of <u>concentration</u> with time; *Catalyst*: speeds up a reaction/alters rate; Without being chemically changed/used(up);	1 1	QWC Ignore reference to E_a and alternative route
8	(b)		(TM ions have) variable oxidation states; (Fe^{2+} ions) involved in alternative route/as intermediate $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ Activation energy lower; <u>Fe^{2+}</u> (involved in reaction but) regenerated	1 1 1 1 1 1	Mark first feature only in any list Allow any unambiguous explanation that Fe^{2+} is regenerated after involvement
8	(c)	(i)	Zeolite/alumino silicate/porous pot; $C_8H_{18} \rightarrow (CH_3)_3CCH_2CH_3$ (or C_6H_{14}) + C_2H_4	1 1	
8	(c)	(ii)	Pt; $CO + NO \rightarrow CO_2 + 1/2N_2$ (or $2NO \rightarrow O_2 + N_2$)	1 1	And/or Ir, Rh, Pd
8	(c)	(iii)	$AlCl_3/FeCl_3$ $C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$ (can use any acyl chloride) OR $C_6H_6 + RCOCl \rightarrow C_6H_5COR + HCl$	1 2	 Organic product (1), balanced equation (1) $C_6H_5CH_3CO$ could get equation mark but loses product mark

Question	Part	Sub Part	Marking Guidance	Mark	Comments
9	(a)			1 1 1 1	Curly arrow from C=C double bond to Br; Curly arrow from Br–Br bond to Br; Correct carbocation intermediate; Curly arrow from lone pair on $:Br^-$ to C^+ can score this mark (M4) if primary carbocation is shown; Ignore δ+ and δ-, penalise wrong + or – If HBr used instead of Br_2, max 2
9	(b)		$\cdot Br + CH_4 \rightarrow \cdot CH_3 + HBr$ $\cdot CH_3 + Br_2 \rightarrow CH_3Br + \cdot Br$	1 1	Allow free radical dot after $CH_3\cdot$
9	(c)	(i)	$K_c = [Br]^2/[Br_2]$;	1	
9	(c)	(ii)	Initial moles of Br_2 = 6.30/159.8 = 0.0394 Eqbm moles of $Br_2 = 0.8 \times 0.0394 = 0.0315$ Moles of Br = 0.01576 $[Br_2]$ = 0.0315/2 = 0.0158 mol dm^{-3} and [Br] = 0.01576/2 = 0.00788 $K_c = 0.00788^2/0.0158 = 3.93 \times 10^{-3}$ (mol dm^{-3})	1 1 1 1 1	Allow 0.039 to 0.040 (A1) Allow 0.031 to 0.032 (0.8 x A1) (A2) method mark Allow 0.15 to 0.16 (2 x (A1 – A2) or 0.4 x A1) method mark Method mark if both concentrations/2 (if not /2 CE – do not mark on) Allow 3.5 to 4.3×10^{-3} Allow consequential on incorrect [Br] and $[Br_2]$ only if M4 gained

9	(c)	(iii)	The value of K_c increases; The reaction is endothermic; The temperature increase is opposed by favouring the endothermic reaction;	1 1 1	CE if K_c does not increase Or the temperature increase is opposed by moving the equilibrium to lower the temperature/absorb heat/oppose the change