

# Mark Scheme (Final) January 2009

GCE

GCE Chemistry (6246/02)

## General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

### Using the mark scheme

- 1 / means that the responses are alternatives and either answer should receive full credit.
- 2 ( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
- 3 [ ] words inside square brackets are instructions or guidance for examiners.
- 4 Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
- 5 ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

### Quality of Written Communication

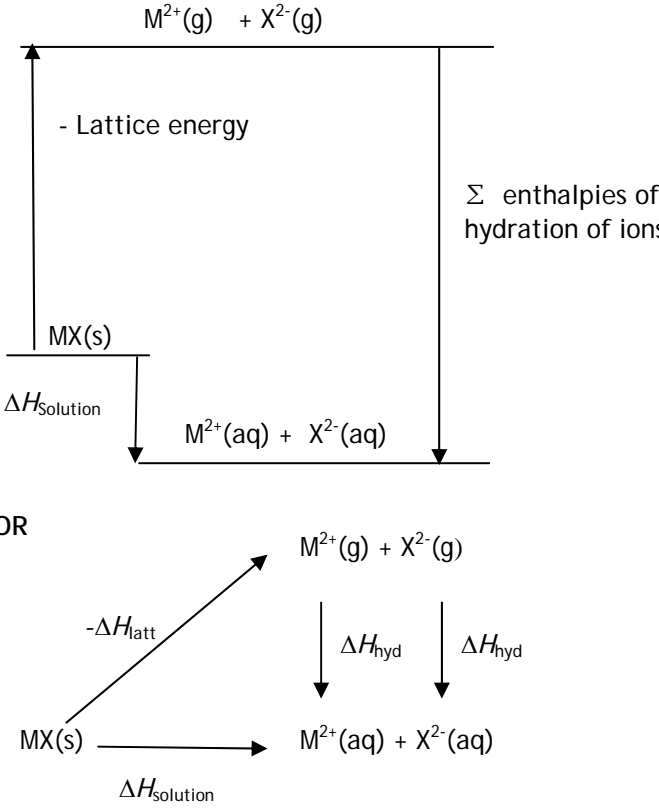
Questions which involve the writing of continuous prose will expect candidates to:

- show clarity of expression
- construct and present coherent arguments
- demonstrate an effective use of grammar, punctuation and spelling.

Full marks will be awarded if the candidate has demonstrated the above abilities.

Questions where QWC is likely to be particularly important are indicated "QWC" in the mark scheme BUT this does not preclude others.



Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)(i)	 <p>Species with state symbols charge must be +2/-2 (1) <math>\Delta H_{\text{solution}}</math> labelled on arrow showing solid to aqueous ions (1) LE and enthalpies of hydration of ions labelled (1)</p>	<p>Allow lattice energy with arrow the other way and positive sign.</p> <p>I think we allow it as the question is not direction specific</p>	$\Delta H_{\text{solubility}}$	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)(ii)	<p><b>1<sup>st</sup> mark</b> EITHER Solubility is balance between lattice energy and hydration energy OR heat released on hydration must compensate for heat needed to break up lattice OR <math>\Delta H_{\text{Solution}} = -\text{lattice energy} + \sum \text{hydration energies}</math> (1) This equation scores the mark and could be in quoted as part of the energy cycle</p> <p><b>2<sup>nd</sup> mark</b> Both lattice energy and hydration energy decrease as cations get larger/ ionic radius increases (1)</p> <p><b>3<sup>rd</sup> mark</b> But hydration energy decreases more /lattice energy decreases less / both decrease but <math>\Delta H_{\text{LE}}</math> is less significant( because of large anion size) (1)</p> <p><b>4<sup>th</sup> mark</b> So enthalpy of solution becomes more endothermic down the group / less exothermic (hence less soluble)(1) <b>Stand alone</b></p>	<p>Ions (place of cations) Become less exothermic</p> <p>Reference to atoms not ions penalise once</p> <p>If no change in LE in second mark carry forward this error to third mark? This does not apply to hydration energy</p>		4

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(i)	<p>van der Waals / London / dispersion / induced dipole/instantaneous dipole - instantaneous dipole (1) Hydrogen bond(1)</p> <p>Ignore Dipole-dipole interactions but if give THREE answers one of which is wrong max 1</p>			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(ii)	The acid /COOH group (1) Can form hydrogen bonds with the water(1)			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(iii)	Energy released on formation of intermolecular forces (between aspirin and water) is less than the energy required to overcome the existing intermolecular forces OWTTE Or Large hydrophobic benzene ring /non-polar ring/non-polar group leads to low solubility Or Hydrogen bonds formed fail to overcome the hydrophobic effect of the benzene ring (1)	"strength of forces" instead of "energy"	Any reference to breaking of molecule or bonds with molecules score zero	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(iv)	It is ionic and the ions can be hydrated providing enough energy to cause it to dissolve or Strong interaction between water and ions (1)			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(i)	Methanol / CH <sub>3</sub> OH (1)			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(ii)	Ethanoyl chloride / CH <sub>3</sub> COCl(1)	(CH <sub>3</sub> CO) <sub>2</sub> O or name	CH <sub>3</sub> COCl solution	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(iii)	Sodium hydroxide / NaOH OR sodium carbonate / Na <sub>2</sub> CO <sub>3</sub> OR sodium hydrogen carbonate/NaHCO <sub>3</sub> (1)			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (d)	$\text{CH}_3\text{COOC}_6\text{H}_4\text{CO}_2\text{Na} + \text{HCl} \longrightarrow \text{CH}_3\text{COOC}_6\text{H}_4\text{CO}_2\text{H} + \text{NaCl}(1)$ <p>Salicylic acid is a weaker acid / HCl is a stronger acid / Salicylate ions are a base(1)</p>		If draw benzene ring it must be correct	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (e)	$\begin{array}{c} \text{O} \\    \\ \text{CH}_2 - \text{O} - \text{C} - \text{R}_1 \\   \\ \text{CH} - \text{O} - \text{C} - \text{R}_2 \\   \\ \text{CH}_2 - \text{O} - \text{C} - \text{R}_3 \\    \\ \text{O} \end{array} + 3\text{CH}_3\text{OH} \longrightarrow \text{R}_1\text{CO}_2\text{CH}_3 + \text{R}_2\text{CO}_2\text{CH}_3 + \text{R}_3\text{CO}_2\text{CH}_3 + \begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \end{array}$ <p>1 mark for three esters + 1 mark for glycerol (stand alone)</p>			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (a)	$\begin{array}{c} \text{H}^{\times} \text{O}^{\circ} \text{C}^{\times} \text{O}^{\times} \text{O}^{\times} \text{N}^{\circ} \\ \text{H}^{\times} \text{O}^{\circ} \text{C}^{\times} \text{O}^{\times} \text{O}^{\times} \text{N}^{\circ} \\ \text{H}^{\times} \text{O}^{\circ} \text{C}^{\times} \text{O}^{\times} \text{O}^{\times} \text{N}^{\circ} \end{array}$	Dots or crosses		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (b)(i)	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$ $K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{[\text{H}^+]^2}{[\text{HCN}]}$ $\frac{[\text{H}^+]^2}{0.220} = 4.90 \times 10^{-10} \text{ (1)}$ $[\text{H}^+] = \sqrt{4.90 \times 10^{-10} \times 0.220} = 1.038 \times 10^{-5} \text{ (1)}$ $\text{pH} = -\log_{10} 1.038 \times 10^{-5} = 4.98(4) \text{ (1) Allow 5.00}$ <p>Correct answer with no working (3)</p>			3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (b)(ii)	100 % dissociation would give $0.220 \text{ mol dm}^{-3}$ Actual figure $1.038 \times 10^{-5} \text{ mol dm}^{-3}$ % dissociation = $\frac{1.038 \times 10^{-5}}{0.220} \times 100(1)$ $= 4.72 \times 10^{-3} \%$ <b>Answer must be the 3 sig. figs</b> Cq on $[\text{H}^+]$ (i)	If use $1.04 \times 10^{-5}$ then get $4.73 \times 10^{-3} \%$		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c)(i)	<p>First two arrows (1)            Intermediate (1) including charge            Arrow to H of HCN/<math>\text{H}^+</math> (1)            Arrow can come from negative sign            Arrow must go from bond to C of HCN not N            Ignore <math>\delta+</math> and <math>\delta-</math> unless wrong way round</p>	$\text{H}^+$ in place of HCN		3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c)(ii)	(A nucleophile is a) species that can donate a (lone) pair of electrons to form a covalent bond (1).		Just "species which attacks a positive / $\delta^+$ site" A negative ion	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c)(iii)	cyanide ion / $\text{CN}^-$ (1)  HCN is a weak acid so $\text{CN}^-$ removed $\text{CN}^-$ reacts with $\text{H}^+$ $\text{CN}^-$ is a base so reacts with $\text{H}^+$ (1)	Equation and statement that equilibrium moves to LHS		2



Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)	$\text{CH}_3\text{Cl} + \text{KCN} \longrightarrow \text{CH}_3\text{CN} + \text{KCl}$ OR $\text{CH}_3\text{Cl} + \text{CN}^- \longrightarrow \text{CH}_3\text{CN} + \text{Cl}^-$ (1) Ignore state symbols Nucleophilic substitution(1)			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (e)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H} - \text{C} = \text{C} - \text{H} \end{array} \xrightarrow{\text{Br}_2} \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{Br} - \text{C} - \text{C} - \text{Br} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad (1) \quad \text{Allow Cl}_2$ $\downarrow \text{KCN} + \text{HCN} \text{ ignore solvent}$ $\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{NC} - \text{C} - \text{C} - \text{CN} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad (1)$ <p>(Dilute) acid or alkali</p> $\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{HCO}_2\text{C} - \text{C} - \text{CO}_2\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad (1)$ <p>PCl<sub>5</sub> or PCl<sub>3</sub> or SOCl<sub>2</sub></p> $\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{ClCO}_2\text{C} - \text{C} - \text{CO}_2\text{Cl} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ <p>LiAlH<sub>4</sub></p> $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ <p><b>Marking</b>  1 mark for each of the three intermediate compounds</p> <p>5 reagents = (3)  3 reagents = (2)  2 reagents = (1)</p> <p>The reagent marks can only be awarded for parts of correct sequences</p>	<p>Other routes can score but they must go via a cyanide (in question)</p> <p>Correct route via a Grignard reagent to the acid chloride scores Max 5 (it does not answer the question actually asked)</p> <p>Allow Na /ethanol  Or  Hydrogen/  Ni  In place of  LiAlH<sub>4</sub></p>		6

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(i)	Value of $K$ will decrease (1) <i>This mark is stand alone</i>  $\therefore [\text{SO}_3]$ must decrease so that the fraction equals the new /lower $K$ (1) <b>Not stand alone</b>			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(ii) QWC	No change in value of $K$ (1) <i>This mark is stand alone</i>  the fraction gets smaller /decreases (because there are more molecules on the left) (1)  Equilibrium moves to the right (so that the fraction equals the value of $K$ ) so concentration of $\text{SO}_3$ increases (1)			3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(iii)	No change in value of $K$ (or in the value of the fraction) No change in equilibrium yield of $\text{SO}_3$ (1)	No change because catalysts only alter rate not yield OWTTE		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (b)	Average KE of molecules increases/molecules move faster/molecules have more energy / (1)  a greater fraction of collisions will have energy greater than activation energy(1)  Greater <b>proportion</b> of collisions are successful (1)			3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(i)	Temperature must be high enough to give a reasonable rate(1) Too high and yield would drop dramatically(1) e.g. High temp gives a low yield but low temp will slow the rate and so a compromise is chosen" (2)			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(ii)	Higher pressure not necessary as conversion 425°C and 2 atm is very high / ~98% (1) Ignore costs			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(iii)	Since reaction is exothermic the temperature will rise (1) Which would decrease the yield unless cooled (1)	Allow reference to equilibrium moving for second mark?		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(i)	$2\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^+ + 2\text{HSO}_4^-$ OR $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_2^+ + \text{HSO}_4^-$ (1)  OR both of: $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ then $\text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$  OR $\text{H}_2\text{NO}_3^+ + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^+ + \text{HSO}_4^-$			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(ii)	The sulphuric acid is a stronger acid and so protonates the nitric acid OR Nitric acid is a weaker acid and so is protonated (1)			1

Question	Correct Answer	Acceptable	Reject	Mark
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Number	Mechanism	Answers		
4 (d)(iii)	<p>1 mark for arrow from ring on to N of the <math>\text{NO}_2^+</math>  1 mark for intermediate with positive charge shown and delocalisation not extending over carbon attached to <math>\text{NO}_2</math> but covering the other carbons  1 mark for arrow from C - H bond into ring</p>			3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(iv)	<p>OR drawn structure of any dinitromethyl benzene  OR  Any valid name for a dinitroderivative</p>			1