



General Certificate of Education

Chemistry 5421

**CHM4 Further Physical and Inorganic
Chemistry**

Mark Scheme

June examination - 2009 series

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SECTION A

Q	Part	Sub Part	Marking Guidance	Mark	Comments
1	(a)	(i)	Expt 2 $\underline{1.8} \times 10^{-3}$ or $\frac{6.75}{k}$	1	If k used for the calculation: if rounded to 3.8×10^3 allow answer 1.78×10^3
			Expt 3 $\underline{8.1} \times 10^{-5}$ or $k \times (2.16 \times 10^{-8})$	1	If k used for the calculation: if rounded to 3.8×10^3 allow answer 8.2×10^{-5} and if calc rounded to $(3.8 \times 10^3) (2.2 \times 10^{-8}) = 8.4 \times 10^{-5}$
			Expt 4 $\underline{6.7} \times 10^{-4}$ or $\sqrt{(1.67 \times 10^{-3} / k)}$	1	If k used for the calculation: if rounded to 3.8×10^3 allow answer 6.6×10^{-4}
			Allow 0.7×10^{-3} or 7×10^{-4}		
1	(a)	(ii)	$k = \frac{\text{rate}}{[P][Q]^2} = \frac{1.8 \times 10^{-5}}{(1.2 \times 10^{-3})(2.0 \times 10^{-3})^2}$	1	Mark is for insertion of numbers If upside down, score only units mark consequential on their expression for k
			3750 or 3.75×10^3 or 3.8×10^3	1	If k is wrong, check whether apparently wrong answers in part(i) are correct conseq to wrong k .
			$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$	1	Any order
1	(b)		Horizontal straight line	1	Be generous, they need not use a ruler.

Q	Part	Sub Part	Marking Guidance	Mark	Comments
2	(a)		<p>The Statement : mol fraction = $\frac{\text{mol NO}_2}{\text{total moles}}$</p> <p>mol N₂O₄ = 1.20 - ½(0.36) = 1.0(2)</p> <p>total moles = 1.0(2) + 0.36 = 1.36 or 1.38 or 1.4</p> <p>mol fraction of NO₂ = $\frac{0.36}{1.38} = 0.26$ allow $\frac{6}{23}$</p> <p>allow (0.36/1.36) = 0.264 to (0.36/1.4) = 0.257</p>	M1 M2 M3	<p>either in this form or using their numbers, gets max 1 if answer to par (a) is wrong because of wrong no of moles (CE) of either NO₂ or N₂O₄ or total</p> <p>If AE earlier, this mark is for (previous answer + 0.36)</p> <p>If AE earlier, this mark is for $\frac{0.36}{\text{previous answer}}$</p>
2	(b)	(i)	pp = mol fract × Total Pressure	1	Or allow symbols
2	(b)	(ii)	<p>ppNO₂ = 0.28 × 180 = 50(.4)</p> <p>ppN₂O₄ = 180 – 50.4 = 129.6 or 130</p>	1 1	<p>Mark for answer</p> <p>Mark for answer = (180 – previous answer)</p>
2	(c)	(i)	$K_p = \frac{(p\text{NO}_2)^2}{p\text{N}_2\text{O}_4}$	1	if K _p wrong, allow units mark only conseq to their K _p penalise [] but mark on;
2	(c)	(ii)	<p>$\frac{49.6^2}{132.0}$</p> <p>18.6 or 19</p> <p>kPa</p>	1 1 1	conseq on their K _p allow mol dm ⁻³ if K given with []

Penalise pH to <2dp> once in the paper

Q	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)	(i)	$\text{pH} = -\log[\text{H}^+]$	1	Penalise () once in question
3	(a)	(ii)	$\text{mol HCl} = (5.0 \times 10^{-3}) \times 0.135 = 6.75 \times 10^{-4}$ (or 6.8×10^{-4}) $\text{pH} = 3.17$	1 1	Mark is for answer – if wrong, no further mark in part (a)(ii) Lose this mark if moles divided by 0.995
3	(b)	(i)	$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CHClCOO}^-]}{[\text{CH}_3\text{CHClCOOH}]}$ allow molecular formulae or minor slip in formulae	M1	Penalise () once in question Penalise $[\text{H}^+]^2/[\text{CH}_3\text{CHClCOOH}]$ but this can score M2 Not allow $[\text{H}^+][\text{A}^-]/[\text{HA}]$
3	(b)	(ii)	$\frac{[\text{H}^+]^2}{[\text{CH}_3\text{CHClCOOH}]}$ $[\text{H}^+] = \sqrt{(1.48 \times 10^{-3} \times 0.350)} = 2.28 \times 10^{-2}$ $\text{pH} = 1.64$ (can give three ticks here for (b)(ii))	M2 M3 M4	Allow $[\text{H}^+]^2/[\text{HA}]$ or minor slip in formula Mark for 2.28×10^{-2} (allow 2.3×10^{-2} - this still gives 1.64) use of quadratic gives 1.66 3.29 gets 2 marks if $\sqrt{\quad}$ visible in calculation, but square root not taken (AE), else gets 1
3	(c)		Decrease but mark on if incorrect increase T increases dissociation /favours forward reaction / moves to right / favours endothermic reaction \therefore increases $[\text{H}^+]$ or more H^+	1 1 1	

3	(d)	Optical (plane) <u>polarised light</u> or <u>polarimeter</u> (light) <u>rotated in opposite</u> (or <u>wtte</u>) directions QOL	1	If wrong type, no further marks but mark on from just <i>stereoisomerism</i>
			1	
			1	
3	(e)	$[H^+] = 10^{-4.69} = 2.0(4) \times 10^{-5}$ or $pK_a = 4.69 - \log \left(\frac{0.10}{0.15} \right)$ $K_a = \frac{(2.04 \times 10^{-5})(0.10)}{(0.15)}$ or $pK_a = 4.86$ or 4.87 $= 1.36 \times 10^{-5}$ (allow 1.3×10^{-5} to 1.4×10^{-5})	M1	If $[H^+]$ wrong, due to CE, allow numbers in expression for one mark out of three for M2
			M2	If 0.10/0.15 upside down or if moles added to or subtracted from salt or acid, can only score M1
			M3	ignore units

Q	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)	(i)	proton acceptor	1	
4	(a)	(ii)	butylamine alkyl group is electron releasing/ increases e density on N/has (+) inductive effect lone pair more available	1 1 1	Or formula - if wrong, no further marks in (a)(ii)
4	(b)		$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{N}^+ \\ \\ \text{CH}_3 \end{array}$	1	Allow C ₂ H ₅
4	(c)	(i)	$\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3 \text{ (Br}^-)$	1	Mark part (ii) independent of part (i)
4	(c)	(ii)	quaternary ammonium (salt) or tetraalkylammonium (salt) (QOL) (cationic) surfactant/ fabric softener/water repellents / fungicides / emulsifiers/ paper softeners/antistatic agents/corrosion inhibitors/ disinfectants/antistatic agents (e.g. in shampoo)/hair conditioners /spermicidal jellies/detergents	1 1	Or quaternary alkylammonium (salt)
4	(d)	(i)	<u>N</u> -methylethanamide	1	Allow <u>N</u> -methylacetamide

4	(d)	(ii)	<p>(Nucleophilic) addition-elimination</p> <p>M1 M3 for structure M4 for 3 arrows and lone pair</p>	1 4	<p>Penalise electrophilic</p> <p>M2 not allowed independent of M1, but allow M1 for correct attack on C+ +C=O loses M2</p> <p>only allow M4 after correct or very close M3 lose M4 for Cl⁻ removing H⁺ in mechanism, but ignore HCl as a product</p>
4	(e)	(i)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COO}^- \\ \\ \text{H} \end{array}$	1	
4	(e)	(ii)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ \\ \text{H} \end{array}$	1	allow -CO ₂ H don't penalise position of + on NH ₃
4	(e)	(iii)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{N} - \text{C} - \text{COOCH}_3 \\ \\ \text{H} \end{array}$ <p>or H_3N^+</p>	1	Allow -CO ₂ CH ₃

Q	Part	Sub Part	Marking Guidance	Mark	Comments
5	(a)	(i)	<p>HCl or HBr ignore g aq conc etc</p> <p>AlCl₃ or AlBr₃ FeCl₃ FeBr₃ ignore g aq conc etc</p> <p>CH₂CH₂ + HCl → CH₃CH₂ + AlCl₃</p>	1 1 1	The two substances can be in either order Ignore position of + or – on ions Allow C ₂ H ₄
5	(a)	(ii)	<p><u>electrophilic substitution</u></p> <p>CH₂CH₃⁺ M3 arrow</p> <p>Allow Kekule structures</p> <p>Be lenient on position of + in electrophile unless definitely on CH₃</p>	1 3	Not Friedel Crafts M1 arrow from within hexagon to C of CH ₂ or to + on C of CH ₂ horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H in M3
5	(b)		<p>chloroethane usually made from ethene or more difficult to make</p> <p>ethene is a (by)product of cracking</p>	1	Not just cheaper - indication of cost must be qualified Not just ethene is more readily available
5	(c)		<p>Addition or radical or step (QOL)</p>	1 1	Ignore <i>n</i> or brackets, but must have trailing bonds Not additional

6	(e)		c doublet or duplet d doublet or duplet	1 1		2
6	(f)		$\text{CH}_3\text{CH}_2\text{O}^+ \text{ or } \text{C}_4\text{H}_5\text{O}_2^+$ $\left[\text{H}_3\text{CH}_2\text{C}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3 \right]^+ \cdot \rightarrow \text{CH}_3\text{CH}_2^+ + \cdot$ $\text{OCOCOOCH}_2\text{CH}_3$ <p>(1) for Molecular ion (1) for RHS of equation</p> <p>Allow + on CH₃CH₂ or dot on radical anywhere allow (COO)₂C₂H₅ etc</p>	1 2	+ on O or outside brackets Allow molecular formulae $[\text{C}_6\text{H}_{10}\text{O}_4]^+ \cdot \rightarrow \text{C}_2\text{H}_5^+ + [\text{C}_4\text{H}_5\text{O}_4] \cdot$	3

Q	Part	Sub Part	Marking Guidance	Mark	Comments
7			X propene or $\text{CH}_3\text{CH}=\text{CH}_2$ contradiction loses the mark	1	Ignore C_3H_6
			Y propan-1-ol or 1- propanol or $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ contradiction loses the mark	1	Not propan-2-ol nor $\text{C}_3\text{H}_7\text{OH}$ Ignore propanol if correct structure also give If reagent wrong or missing, no mark for conditions, but allow conditions following minor slip in formula Ignore temperature throughout
			Reaction 1 KOH or NaOH	1	Any mention of conc sulphuric loses both reagent and condition marks Incomplete reagent e.g. OH^- penalise once but can score conditions marks in both Reaction 1 and 3
			(Hot) alcoholic or ethanolic	1	Not ethanoic
			Reaction 2 HBr or $\text{KBr}/\text{H}_2\text{SO}_4$ (with or without conc or dil)	1	Not KBr alone ignore extra (conc) H_2SO_4
			Reaction 3 KOH or NaOH	1	Any mention of conc sulphuric loses both reagent and condition marks
			(Warm) aqueous	1	
Reaction 4 $\text{K}_2\text{Cr}_2\text{O}_7/\text{acidified}$ or H^+ or $\text{KMnO}_4/\text{acidified}$ or H^+ reflux	1 1	Not Fehlings/Tollens penalise incomplete reagent again			

Q	Part	Sub Part	Marking Guidance	Mark	Comments		
8	(a)		$\text{mol HCl} = \frac{20.8}{10^3} \times 0.150 = 3.12 \times 10^{-3}$ $[\text{CO}_3^{2-}] = (3.12 \times 10^{-3}) \times 10^3/25$ $= 0.125 \text{ (mol dm}^{-3}\text{) or 0.13}$	allow 3.1×10^{-3} 0.124 or 0.12	M1 M2 M3	Mark for answer Treat $\frac{25}{10^3} \times 0.150$ as AE and allow conseq M2 and M3 Mark for previous answer $\times 1000/25$	3
8	(b)		2nd volume/amount HCl is used to react with (original HCO_3^-) + (HCO_3^- formed in Reaction 1) $\text{vol HCl for original } \text{HCO}_3^- = 33.25 - 20.80 = 12.45 \text{ cm}^3$ $\text{mol HCl} = (12.45 \times 10^{-3}) \times 0.150$ $= 1.87 \times 10^{-3}$ $= \text{mol } \text{HCO}_3^- \text{ in } 25 \text{ cm}^3$ $[\text{HCO}_3^-] = (1.87 \times 10^{-3}) \times 1000/25 = 0.0748 \text{ or } 0.075$	M4 M5 M6 M7	If no subtraction, allow max 1 for mol HCl or H^+ added in second step or second mol HCl added $= \frac{33.25}{10^3} \times 0.150$ $= 4.99 \times 10^{-3}$ or $5(.0) \times 10^{-3}$ or Mol HCl used with $\text{HCO}_3^- = 4.99 \times 10^{-3} - 3.12 \times 10^{-3} = 1.87 \times 10^{-3}$	4	