



General Certificate of Education

Chemistry 6421

**CHM4 Further Physical and Organic
Chemistry**

Mark Scheme

2009 examination - January 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.

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Marking Guidance			
Question	Part	Sub Part	Marking Guidance
1	(a)	(i)	$-\log[\text{H}^+]$; 1
			Allow $\log 1/[\text{H}^+]$ or full definition in words. Penalise ()
1	(a)	(ii)	0.82; 1
			Penalise pH to <2dp> once in the paper
1	(b)	(i)	$\text{mol KOH} = \frac{60}{1000} \times 0.0850 = 5.1 \times 10^{-3}$; 1
			Mark for answer
1	(b)	(ii)	$\text{mol HCl} = \frac{30}{1000} \times 0.150 = 4.5 \times 10^{-3}$; 1
			Mark for answer

1	(b)	(iii)	<p>M1 XS mol KOH = 6.0×10^{-4} if XS acid can only score b(i), b(ii) and M2 (vol);</p> <p>M2 total volume = 90 cm^3;</p> <p>M3 $[\text{OH}^-] = 6.0 \times 10^{-4} \times \frac{1000}{90}$ (= 6.67×10^{-3} or 6.7×10^{-3});</p> <p>M4 $[\text{H}^+] = \frac{10^{-14}}{6.67 \times 10^{-3}}$ (or 1.50×10^{-12} or 1.49×10^{-12});</p> <p>OR pOH = 2.18; OR pOH = 2.17;</p>	1	<p>Conseq on their b(i) – b(ii)</p> <p>If vol missed or wrong (apart from obvious AE), lose M2 and next mark gained, e.g. if vol = 60 cm^3 lose M2 and M3 (0.010) but can gain M4 for pOH = 2.00 and M5 for pH = 12.00 if no vol: M4 gained for $[\text{H}^+] = 1.67 \times 10^{-11}$ or pOH = 3.22 M5 for pH = 10.78 AE (-1) if 1000 missed (pH = 8.82). AE (-1) if 1000/90 upside down, (pH = 9.73) If wrong method (e.g. addition of moles) only score max 2 for M1 and M2 Must involve substitution of numbers not just rearrangement of K_w If no use of K_w or pOH – no further marks (ie pH = 2.18 gets M1, M2, M3 only)</p>
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			M5 pH = 11. <u>82</u> ; OR 11. <u>83</u> ;	1	Penalise pH to <2dp> once in the paper.
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Question	Part	Sub Part	Marking Guidance	Mark	Comments
2	(a)	(i)	$K_a = \frac{[H^+][X^-]}{[HX]}$ <p>allow even if followed by $\frac{[H^+]^2}{[HX]}$;</p> <p>Allow HX for HA</p>	1	<p>But not $\frac{[H^+]^2}{[HX]}$ alone, although this can score for part (ii) if not gained there.</p> <p>Penalise () rather than [] once in the question.</p> <p>If Ka expression wrong: score max 1 for correct $[H^+]$</p>
		(ii)	$[H^+] = 3.3(1) \times 10^{-4};$ $K_a = \frac{[H^+]^2}{[HX]} \text{ or } \frac{[3.31 \times 10^{-4}]^2}{[0.15]}$	1 1	<p>Ignore units.</p> <p>If $[H^+]$ is wrong (apart from obvious AE) or missing and the final answer is wrong, they can gain the second mark for either $[H^+]^2/[HA]$ or using their numbers, but not the third mark i.e. they can get 1 out of three for section a(ii).</p> <p>Ignore units.</p> <p>Use of 3.3×10^{-4} gives 7.26×10^{-7}</p>
2	(a)		$= 7.3(1) \times 10^{-7} \text{ or } 7.3(0) \times 10^{-7};$	1	

2	(b)	<p>M1 Either $[Y^-] = 0.06 \text{ mol dm}^{-3}$ (from 2×0.03);</p> <p>OR</p> <p>Moles HY = 0.125 (from $500 \times 10^{-3} \times 0.250$);</p> <p>M2 $[H^+] = \frac{K_a \times [HY]}{[Y^-]}$ or $\frac{(2.65 \times 10^{-4})(0.25)}{0.06}$;</p> <p>OR</p> <p>$\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$ or $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$;</p> <p>M3 = $1.1(0) \times 10^{-3}$;</p> <p>OR</p> <p>$\text{p}K_a = 3.58$;</p> <p>M4 2.96;</p>	1	<p>If factor of two not used (or used wrongly except AE) then lose M1 and the next mark gained (i.e. max 2): This gives M3 = 2.21 $\times 10^{-3}$; M4 = 2.66 If wrong method (e.g. addition or subtraction of moles or use of square root) score M1 only Penalise () rather than [] once in the question. If $[HY]/[Y^-]$ upside down in H^+ expression, lose M2 and M3, can score M4 for $\text{pH} = 4.20$</p>
			1	<p>Penalise pH to <2dp> once in the paper.</p>

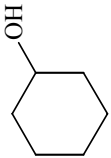
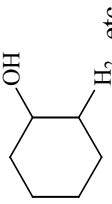
Question	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)	(i)	M1 mol CO = 0.36 - 0.12 = 0.24;	1	Mark for answer if wrong, CE so lose M1 and next mark gained. Mark for answer if multiplying 0.12 by 2 is missed, CE so lose M2 and next mark gained in part (a)(i.e. max 2 for part(a))
			M2 mol H ₂ = 0.64 - 2(0.12) = 0.40;	1	
3	(a)	(ii)	M3 Total no moles = 0.76;	1	If both M1+ M2 lost for CE no marks in (a) (ii) (if mol H ₂ = 0.52, total no moles = 0.24 + 0.52 + 0.12 = 0.88) If Σ of their mol is wrong, no marks in (a)(ii) unless clear AE If multiplying 2(0.12) is missed: max 2 for 0.24 = 0.27(3) 0.88
			M4 Mole fraction = $\frac{0.24}{0.76} = 0.316$ or 0.32 or $\frac{6}{19}$;	1	
3	(b)	(i)	(pp =) mol fraction \times total P;	1	
			OR Allow symbols;		
3	(b)	(ii)	84.6 - 86;	1	Conseq on (a)(ii) 0.27(3) gives 72.36 - 73.2 ignore units
3	(c)	(i)	125 (kPa);		

3	(c)	(ii)	$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2};$	1	If K_p wrong, allow units mark only consequ to their K_p Penalise [] but mark on;
3	(c)	(iii)	$\frac{125}{75 \times 300^2};$	1	Answer = their (c)(i) × (1.48 × 10 ⁻⁷) Conseq on their K_p allow mol ⁻² dm ⁶ if K given with []
			1.85 × 10 ⁻⁵ or 1.9 × 10 ⁻⁵ kPa ⁻² or 1.85 × 10 ⁻¹¹ if in Pa; or Pa ⁻² (tied to answer above)	1	
3	(d)	(i)	Increased;	1	
			No effect;	1	
3	(d)	(ii)	Decreased;	1	
			Decreased;	1	

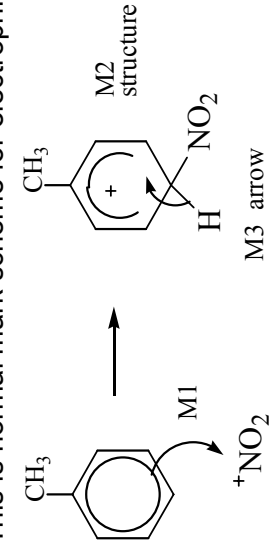
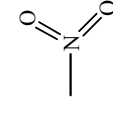
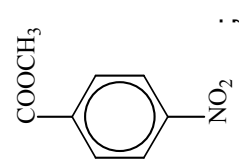
Question	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)		<u>3-bromo-3-methylpentane</u> ;	1	Ignore commas or hyphens or spaces, but otherwise must be correct, including order of bromo before methyl. QOL
4	(b)	(i)	KOH or NaOH;	1	If reagent wrong or missing, no mark for conditions. Any mention of conc sulphuric loses both reagent and condition marks. Not ethanoic.
			(Hot) alcoholic or (hot) ethanolic;	1	
			Elimination (mark independently)	1	Allow <i>basic elimination</i> but penalise other qualifications
4	(b)	(ii)	$ \begin{array}{c} \text{CH}_2 \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3\text{CH}_2 \quad \text{CH}_2\text{CH}_3 \end{array} $	1	Allow C ₂ H ₅ .
4	(c)	(i)	cis-trans or geometric(al) or E-Z;	1	Not cis alone but could score in c(ii).
4	(c)	(ii)	Restricted or no <u>rotation about C=C / double bond</u> ;	1	
			(Two) <u>different</u> groups on <u>each</u> end (not side) or wtte;	1	Not just different groups attached to C=C

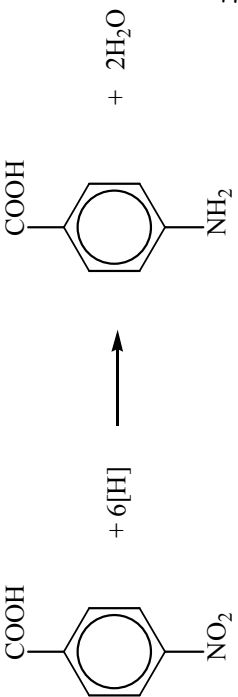
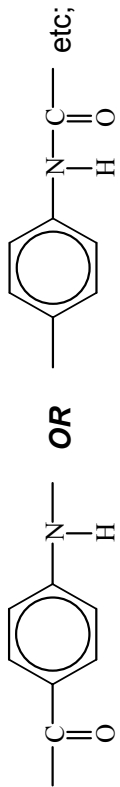
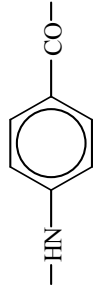
4	(d)	(i)	(two) isotopes of <u>Br</u> (with or without <u>correct numbers</u>); OR ^{79}Br ^{81}Br ; OR <u>Br</u> has two mass numbers; (Approx) equal abundance;	Mention of isomers gets zero for part (d)(i). If mentioned, mass numbers must be correct.	
					1
					1
4	(d)	(ii)	$\text{CH}_3\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}_2\text{CH}_3$; +	Allow C_2H_5 + on central C or outside brackets NOT radical cation (but mark on) if not tertiary or missing no further mark. NOT just Br is good leaving group.	
			Tertiary or 3° or III° carbocation stated or described or most stable cation or discussion of ease of formation e.g. C–Br bond weak or easily breaks'		1

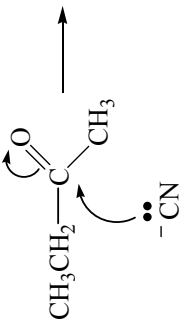
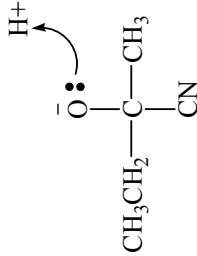
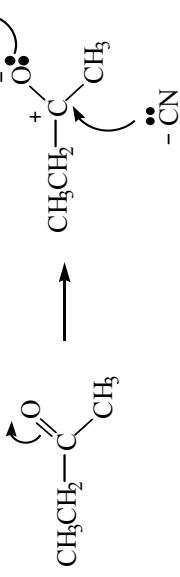
Question	Part	Sub Part	Marking Guidance	Mark	Comments
5	(a)	(i)	O-H alcohols ;	1	Not O-H alone and not O-H acids
		(ii)	C-H;	1	
5	(a)	(ii)	(Unreacted) alcohol or C or any alcohol or water or moisture;	1	
5	(b)	(i)	<u>Three</u> CH ₃ groups;	1	Allow C(CH ₃) ₃
5	(b)	(ii)	CH next to CH ₃	1	i.e. Structure fragment with or without R or OH mention of ROCH ₃ or OH linked to δ loses mark.
			OR CH ₃ CH OR (splitting) linked to adjacent/coupling;		
5	(b)	(iii)	$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array} ;$	2	Apply list principle if more than one answer given here and below penalise bond drawn as -HO one mark (once per paper)
		(i)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{OH} \end{array} \quad \text{or} \quad \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CH}-\text{C}-\text{CH}_3 \\ \\ \text{OH} \end{array} ;$	1	Allow C ₂ H ₅ but NOT C ₃ H ₇ .

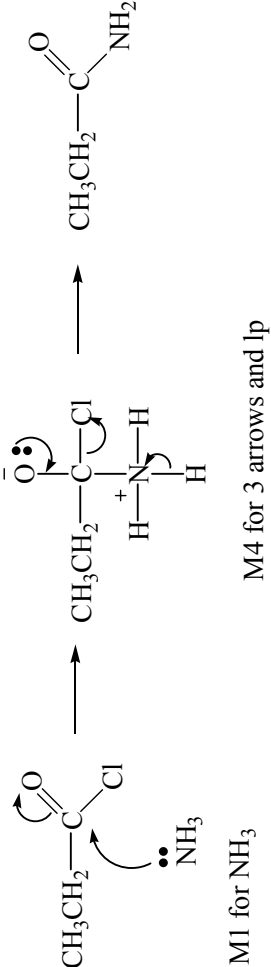
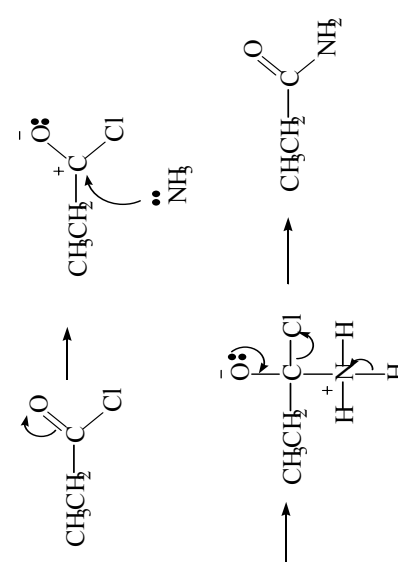
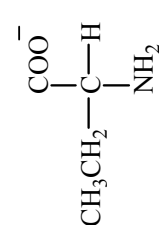
5	(c)	(ii)	<p>Erratum sheet gives 6 peaks</p> $ \begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_2\text{CH}_3 \\ \quad \\ \text{H} \quad \text{OH} \end{array} $ <p>OR</p> $ \begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_2\text{OH} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} $ <p>OR</p> $ \begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \\ \\ \text{H} \end{array} ; $	1	<p>Only if it appears that the erratum was not issued, i.e. qu is for 4 peaks, allow the original C (although it is not an isomer of C)</p> $ \begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array} $
5	(d)			1	<p>Allow methylcyclopentanols and other alkyl cyclic alcohols. Penalise</p>

Question	Part	Sub Part	Marking Guidance	Mark	Comments	
6	(a)	(i)	$\frac{9.45 \times 10^{-4}}{(0.76)(1.22)^2}$;	1	Mark is for insertion of numbers. If upside down, score only units mark consequential on their expression for k	
			8.35 × 10 ⁻⁴ to 8.4 × 10 ⁻⁴ ; mol ⁻² dm ⁶ s ⁻¹ ;			1
						1
6	(a)	(ii)	4.7 × 10 ⁻⁴ to 4.8 × 10 ⁻⁴ ;	1	Ignore units. Conseq on their k multiplied by [(0.76 × 2) × (½ × 1.22) ²] i.e. k × 0.5656	
6	(b)	(i)	2;	1		
6	(b)	(ii)	0;	1		

Question	Part	Sub Part	Marking Guidance	Mark	Comments
7	(a)		<p>Base or proton acceptor;</p> <p><u>Electrophilic substitution</u>;</p> <p>This is normal mark scheme for electrophilic substitution;</p> 	1 1 3	<p>M1 arrow from within hexagon to N or to + on N.</p> <p>Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1</p> <p>M3 arrow into hexagon unless Kekule</p> <p>allow M3 arrow independent of M2 structure.</p> <p>Ignore NO₂ attempted structures e.g</p> 
7	(b)		<p>Oxidation or redox;</p> 	1 1	<p>Not reduction.</p> <p>Allow – CO₂CH₃.</p>

7	(c)	Sn OR Fe/HCl (conc or dil or neither) allow dil H ₂ SO ₄ OR Ni/H ₂ ;	<p style="text-align: center;">  </p>	1 1	<p>Not NaBH₄ Not LiAlH₄ Not Na/C₂H₅OH Not conc H₂SO₄ nor any HNO₃</p> <p>Allow 3H₂ Allow O₂NC₆H₄COOH</p>
7	(d)	Condensation; Peptide/amide;	<p style="text-align: center;">  </p>	1 1	<p>Allow addition-elimination. Must have trailing bonds ignore <i>n</i> NOT double unit allow</p> <p style="text-align: center;">  </p>

Question	Part	Sub Part	Marking Guidance	Mark	Comments
8	(a)		<p>M3 for both arrows and lp </p> <p>M4 for lp and arrow and H⁺ </p> <p>M1 for CN⁻ M2 for butanone</p> <p>M1 for nucleophile cyanide, allow minus sign on N or C but penalise missing - (lp on C is part of M3)</p> <p>M2 for butanone</p> <p>M3 for both arrows and lp (which must be on C) ignore missing - (this is penalised in M1)</p> <p>M4 for lp and arrow and H⁺</p> <p><u>2-hydroxy-2-methylbutanenitrile</u> allow 2-hydroxy-2-methylbutanenitrile QOL;</p>	4	<p>If final product wrong, no penalty for error in structure, but no mark for name of wrong product.</p> <p>If C=O shown breaking first (as below), can gain M1 and M2 for reagents, not M3, but can gain M4.</p>  <p>If mistake in given intermediate ion, lose M4</p> <p>Allow commas or missing hyphens but otherwise must be as here. Ignore -1- before nitrile but penalise other numbers here</p>

8	(b)	<p>M2 propanoyl chloride</p>  <p>M1 for NH₃</p> <p>M3 for 2 arrows and lp</p> <p>M4 for 3 arrows and lp</p> <p>M1 for nucleophile NH₃, penalise minus sign on NH₃ (lp on N is part of M3)</p> <p>M2 for propanoyl chloride</p> <p>M3 for 2 arrows and lp (which must be on N)</p> <p>M4 for 3 arrows and lp (can be in two stages) allow NH₃ to remove H⁺ but not Cl⁻ (if Cl⁻ removes H⁺ then lose M4) (Nucleophilic) addition-elimination;</p> <p>Propanamide;</p>	4	<p>if C=O shown breaking first (as below) can gain M1 and M2 for reagents, not M3, but can gain M4</p>  <p>If mistake in given intermediate ion, lose M4</p> <p>If final product wrong, no penalty for error in structure, but no mark for name of wrong product.</p> <p>Not acylation alone, but do not penalise acylation given together with addition-elimination.</p> <p>Ignore -1- before amide but penalise other numbers here.</p>
8	(c)	<p>Zwitterion;</p>  <p>(with or without Na⁺);</p>	1	<p>Allow COONa or CO₂Na but not COO⁻Na.</p>

8	(d)	<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> <p style="margin-top: 10px;">(1)</p> </div> <div style="margin: 0 20px;">→</div> <div style="text-align: center;"> <p style="margin-top: 10px;">(1)</p> </div> <div style="margin-left: 20px;">+ CH₃COOH</div> </div> <p style="text-align: right; margin-right: 20px;">(1) ... >>></p> <p>CH₃COCl is</p> <ul style="list-style-type: none"> • corrosive or toxic or dangerous. • reactive or vulnerable to hydrolysis or difficult to store. • produces HCl or poisonous/toxic/harmful gases/fumes. • reaction too vigorous or gets too hot. • more expensive. 	3	<p>Allow CH₃COOCOCH₃ for anhydride.</p> <p>Allow CO₂H for acid group.</p> <p>If extra products e.g. water, lose CH₃COOH mark.</p> <p>Or converse for anhydride.</p> <p>Any two from the 5 answer lines shown (i.e. corrosive and toxic scores only 1).</p> <p>But apply list principle if more than 2 answers given (but ignore rate) .</p>
		2		