



General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2007 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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Question 1

- (a) (i) 2 1
 (ii) 1 1
 (iii) 0 1
- (b) $k = \text{rate}/[\text{D}]^2[\text{E}]$ or $\frac{8.36 \times 10^{-4}}{(0.84)^2(1.16)}$ 1
 $= 1.0(2) \times 10^{-3}$ to 1.05×10^{-3} 1
 $\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$ 1
- Total 6 marks**

Question 2

- (a) mol $\text{Cl}_2 = 1.2(0)$ 1
 total mol = 3.8(0) no consequential marks on wrong mol Cl_2 in (a) unless obvious AE 1
- (b) mol fraction $\text{PCl}_5 = \frac{1.4}{3.8}$ (1) = 0.368 (or 0.37) allow $\frac{1.4}{\text{total mol}}$ from (a) 1
 mol fraction $\text{Cl}_2 = \frac{1.2}{3.8}$ (1) = 0.316 (or 0.32) allow $\frac{\text{mol Cl}_2}{\text{total mol}}$ from (a) 1
- (c) (i) (pp =) mol fraction \times total P or total P = $P_A + P_B + P_C \dots$ 1
 or $p_A = x_A \times P_T$
- (ii) pp $\text{PCl}_5 = 0.368 \times 125 = 46(.0)$ min 0.37 $\times 125 = 46.3$ max 1
 pp $\text{Cl}_2 = 0.316 \times 125 = 39.47$ 0.32 $\times 125 = 40(.0)$ 1
 Or conseq on (b)
- (d) $K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$ not numbers penalise [] but mark on allow extra () brackets needs all P 1
- (e) (i) no effect 1
 (ii) increase 1
- (f) $\frac{42.6^2}{36.9}$ If K_p wrong, allow units mark conseq within (f) 1
 49.2 (or $4.9.2 \times 10^4$ tied to Pa below) 1
 kPa 1

Total Mark 13

Question 3

- (a) (i) proton donor - alone 1
(ii) completely dissociated 1
- (b) (i) $7.05 \times 10^{-3} \times 10^3 / 50 = 0.14(1)$ 1
(ii) $-\log [H^+]$ or $\log 1/[H^+]$ 1
(iii) 0.85 or conseq on (b) penalise dp of final answer <2> once per paper 1
(iv) M1 pH = 1 $[H^+] = 0.1(0)$ (mol dm⁻³) if wrong, max 1 for M2 1
M2 $(7.05 \times 10^{-3})/0.10$ addition or subtraction loses M2 1
M3 vol = 7.05×10^{-2} dm³ or 70.5 cm³ Units tied (allow 71 but not 70) 1
- (c) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ not $\frac{[H^+]^2}{[HX]}$ but mark on 1
allow HA etc
- (ii) $K_a = \frac{[H^+]^2}{[HX]}$ If K_a expression wrong or missing: max 1 in 1
part (ii) for correct calculation
of pH from their $[H^+]$
- $[H^+] = \sqrt{(6.10 \times 10^{-5} \times 0.255)}$ or $\sqrt{(K_a \times [HX])}$
(= $\sqrt{1.55 \times 10^{-5}} = 3.94 \times 10^{-3}$) 1
- pH = 2.40 (if if write $\sqrt{\quad}$ but forget to take sq rt this 1
rounded to gives pH = 4.81 which can get 2 marks
 3.9×10^{-3} allow 2.41) max
- (d) (i) $[H^+] = 1.66 \times 10^{-4}$ 1
 $K_a = \frac{(1.66 \times 10^{-4})(2.98 \times 10^{-3})}{(6.85 \times 10^{-3})}$ if wrong method, no further
marks in d(i)
= 7.22×10^{-5}
pK_a = 4.14
- (ii) effect = none/ negligible/v small decrease/v small change; 1
not just pH goes down – must be v small decrease
- M1 Salt or Y⁻ reacts with extra H⁺ or
equm $HY \rightleftharpoons H^+ + Y^-$ shifts to LHS or
H⁺ is removed as eqm shifts to LHS
- M2 ∴ $[H^+]$ or **ratio** $[HY]/[Y^-]$ or **ratio** $[Y^-]/[HY]$ remains almost 1
constant only gained if M1 correct

Total 19 marks

Question 4

- (a)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{Si}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 allow $\text{Si}(\text{CH}_3)_4$ 1
- inert/non toxic/volatile or low bp Any
ignore cheap single intense peak/signal upfield of 2
others/(protons)very shielded
- (b) 2 1
- (c) (i) a = quartet or 4 allow explained alternative interpretation of splitting **by** 1
b = triplet or 3 rather than **of** these H
a causes triplet b causes triplet 1 1
- (ii) 3230 – 3550 (cm^{-1})
- (d) (i) butan(e)-1,4-diol or 1,4- butan(e)diol or 1,4-dihydroxybutane 1
- (ii) condensation or addition- elimination
- $$\text{---O---}(\text{CH}_2)_4\text{O---C(=O)---}(\text{CH}_2)_3\text{C(=O)---}$$
- must have both carbon chains and ester group to score at all
ester group (1)
 $(\text{CH}_2)_3$ (1) but -1 for each error 1
- (e) (i) 6(H) or 2 × CH_3 groups 1
- (ii) $(\text{R})\text{OCH}_3$ 1
- (iii) $\text{CH}_3\text{---CH}(\text{---})\text{O}$ penalise any extra H Not R attached to CH 1
- (iv)
$$\begin{array}{c} \text{H} \\ | \\ \text{H}_3\text{C}-\text{C}-\text{OCH}_3 \\ | \\ \text{OCH}_3 \end{array}$$
 1

Total 15 marks

Question 5(a) 2-aminopropanoic acid or 2-aminopropionic acid 1(b) (i)
$$\begin{array}{ccccccc} & & \text{CH}_3 & & \text{CH}_3 & & \\ & & | & & | & & \\ \text{H}_2\text{N} & - & \text{C} & - & \text{C} & - & \text{N} & - & \text{C} & - & \text{COOH} \\ & & | & & || & & | & & | & & \\ & & \text{H} & & \text{O} & & \text{H} & & \text{H} & & \end{array}$$
 Do NOT allow -CONH- or -COHN- 1

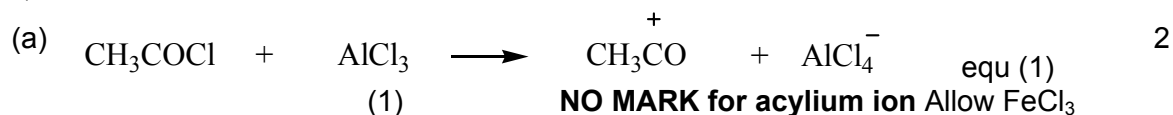
allow zwitterion

Not repeating unit(ii)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{N} - \text{C} - \text{COOCH}(\text{CH}_3)_2 \\ | \\ \text{H} \end{array}$$
 allow H_3N^+ or H_3N^+ 1not C₃H₇(iii)
$$\begin{array}{ccccccc} & & & & \text{CH}_3 & & \\ & & & & | & & \\ \text{H}_3\text{C} & - & \text{C} & - & \text{N} & - & \text{C} & - & \text{COOH} \\ & & || & & | & & | & & \\ & & \text{O} & & \text{H} & & \text{H} & & \end{array}$$
 allow -CONH- or -COHN- 1(nucleophilic) addition-elimination 1(c) (i) **X**
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ | \\ \text{H} \end{array}$$
 allow $^+\text{H}_3\text{N}-$ 1(ii) **Y**
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{N}^+ - \text{C} - \text{COO}^- \\ | \\ \text{H} \end{array}$$

if only mistake in **X**, is e.g. $^+\text{H}_2\text{N}-$ and this is repeated in **Y** but otherwise **Y** shows COO^- i.e. the candidate has realised the change from COOH to as pH rises, allow one for **Y** (ecf)

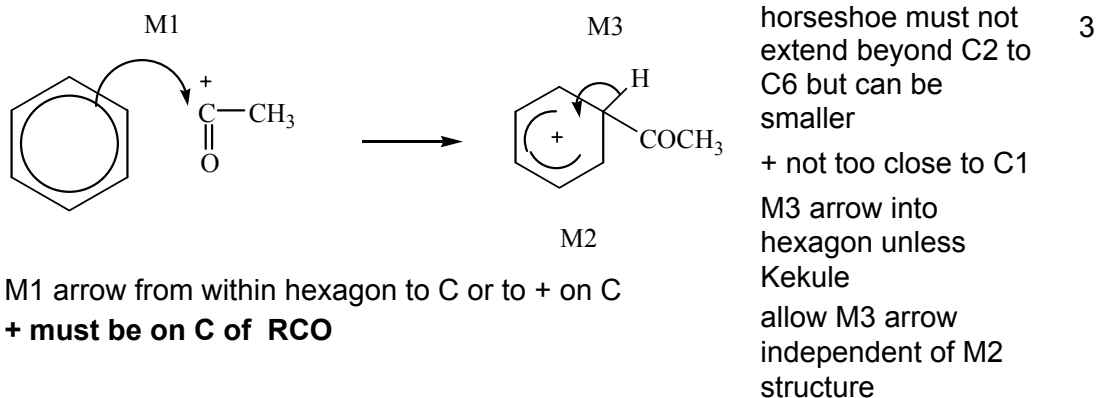
Total 7 marks

Question 6



position of + on electrophile can be on O or C or outside []

penalise wrong curly arrow in the equation or lone pair on AlCl_3 else ignore

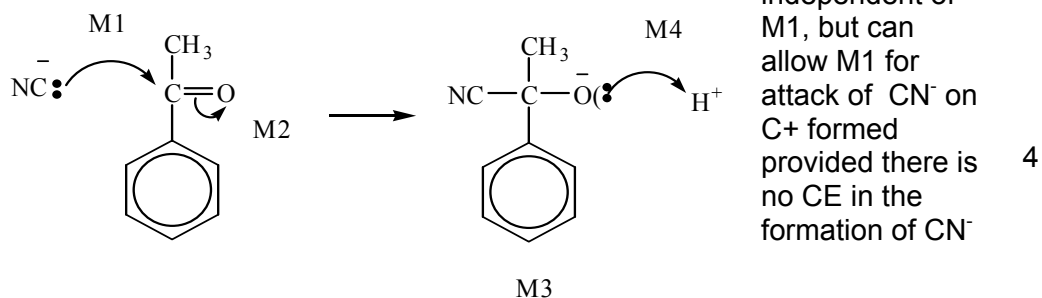


M1 arrow from within hexagon to C or to + on C
+ must be on C of RCO

electrophilic substitution **NOT F/C acylation**

1
Total 6

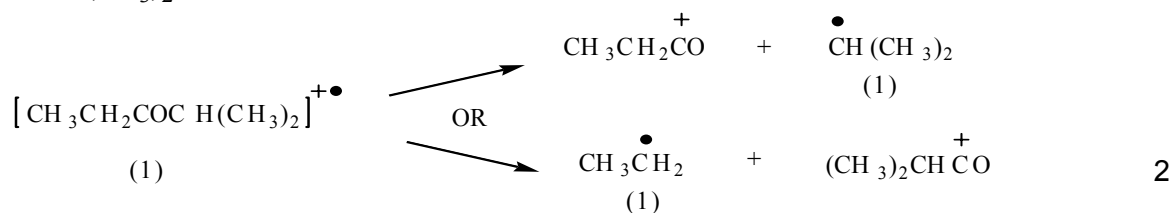
(b) (i) Nucleophilic addition



(ii) optically inactive or equal mixture of (both) enantiomers/optical isomers 1
 planar carbonyl group (stated or drawn) Not planar molecule 1
 attack from above or below or either side (stated or drawn) 1

Total 8

(c) 2-methylpentan-3-one no e inpentan-3-... 1
 $\overset{+}{\text{CH}_3\text{CH}_2\text{CO}}$ + can be on O or C or outside [] but not on alkyls 1
 $(\text{CH}_3)_2\overset{+}{\text{CHCO}}$ 1



allow $[\text{C}_6\text{H}_{12}\text{O}]^+$

Dot can be anywhere
 allow C_2H_5 or C_3H_7

+ on C or O or outside []

Total 5

Total 19 marks

Question 7

Incomplete reagent (e.g. carbonate) loses reagent mark, but mark on

If more than one test **including a different test on P and Q** ; give worst mark

if either reagent wrong - no marks at all

For “no reaction” allow “nothing”

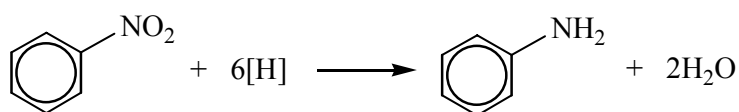
(a) (i)	reagent	Na ₂ CO ₃ / NaHCO ₃ named carbonate	UI litmus	PCl ₅ PCl ₃ SOCl ₂	Suitable metal	K ₂ Cr ₂ O ₇ / acidified or H ⁺	KMnO ₄ / acidified or H ⁺	1
	P	no reaction	No rxn	No rxn	No rxn	turns green	colourless or brown	1
	Q	effervescence or CO ₂ or dissolves	red	fumes	effervescence or H ₂ or dissolves	no rxn stays orange	no rxn stays purple	1

(ii)	reagent	H ₂ O	AgNO ₃	Na ₂ CO ₃ / NaHCO ₃ or named carbonate	Named alcohol	Named amine or ammonia	UI litmus	1
	R	(misty) fumes	(White) ppt or rapid_ppt	effervescence or CO ₂ or dissolves	Smell or fumes	fumes	red	1
	S	no rxn	no ppt or slow_ppt	no rxn	No rxn	No rxn	No rxn	1

No marks after wrong reagent in (ii) even if aq

6 marks

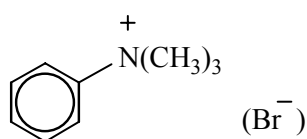
(b) (i)	Sn or Fe/HCl	conc or dil or neither	ignore extra NaOH	1
	Sn or Fe/H ₂ SO ₄	dil or neither	not HNO ₃	
	H ₂ /Ni	not NaBH ₄ LiAlH ₄ Na/C ₂ H ₅ OH		



C₆H₅ or 3H₂ organic species (1) balanced (1)

2

(ii)	nucleophilic substitution			1
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Be lenient on position of + 1

5 marks

Total 11