



General Certificate of Education

Chemistry 6421

**CHM4 Further Physical and Organic
Chemistry**

Mark Scheme

2008 examination - June series

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CHM4**SECTION A****Question 1**

(a) 1.42 pH to < or > 2dp penalised once per paper (1)

(b) $[H^+] = 0.038/2$ or 0.019 (1)

pH = 1.72 (1)

(c) (i) (only) partly or slightly dissociated/ionised NOT “not completely ionised” (1)

proton donor (1)

(ii) $K_a = \frac{[H^+][X^-]}{[HX]}$ Ignore use of HA etc (1)

(iii) $[H^+] = 10^{-3.48} = 3.3(1) \times 10^{-4}$ (1)

$K_a = \frac{[H^+]^2}{[HX]}$ here or in part(ii) or $\frac{(3.31 \times 10^{-4})^2}{0.063}$ (1)

= $1.7(4) \times 10^{-6}$ (ignore units even if wrong) (1)

(d) (i) 4.20 allow 4.19 – 4.21 (1)

(ii) mol NaOH = $10.0 \times 10^{-3} \times 0.130 = 1.30 \times 10^{-3}$ or 0.0013 (M1)

mol HA left = $0.055 - 0.0013 = 0.0537$ (M2)

mol A⁻ present = $0.025 + 0.0013 = 0.0263$ (M3)

$[H^+] = \frac{K_a \times [HA]}{[A^-]}$ or $\frac{(2.87 \times 10^{-5})(0.0537/V)}{(0.0263/V)} (= 5.86 \times 10^{-5})$ (M4)

If [HA] and [A] wrong way round - no further marks

pH = 4.23 (M5)

The essential part of this calculation is the subtraction/addition of 1.30×10^{-3} moles

- If no subtraction/addition at all - max 1 for M1
- If one subtraction/addition missing or chemically wrong – lose M2 or M3 and next mark gained = max 3 (see * below)

If subtraction/addition reversed - max 2 for M1 and M5 ($[H^+] = 6.82 \times 10^{-5}$) pH = 4.17

$0.0537/0.110 = 0.488$ $0.0263/0.110 = 0.239$

* $\frac{(2.87 \times 10^{-5})(0.0550/V)}{(0.0263/V)} = 6.00 \times 10^{-5}$ pH = 4.22

* $\frac{(2.87 \times 10^{-5})(0.0537/V)}{(0.0250/V)} = 6.16 \times 10^{-5}$ pH = 4.21

Total 15 marks

Question 2

(a) order wrt **A** = 2 (1)

order wrt **B** = 1 (1)

(b) (i) (rate =) $k [\text{C}][\text{D}]^2$ (1)

(ii) $k = \frac{1.45 \times 10^{-4}}{(2.50 \times 10^{-2})(6.65 \times 10^{-2})^2}$ NOT $\frac{\text{rate}}{[\text{C}][\text{D}]^2}$ (1)

= 1.3(1) (1)

$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$ allow units conseq to wrong rate equation in (b)(i)

Total 6 marks

Question 3

(a) (i) $pp = \text{mole fraction} \times \text{total pressure}$ (1)

or $pp \text{ hydrazine} = 0.22 \times 150$

$= 33 \text{ (kPa)}$ ignore units even if wrong (NB 2 marks for 33) (1)

(ii) $pp \text{ N}_2 + pp \text{ H}_2 = 150 - 33 = 117$ Or $\text{mol fn N}_2 + \text{mol fn H}_2 = 0.78$ (1)

$pp \text{ N}_2 = \frac{1}{3} \times 117 = 39$ $pp \text{ N}_2 = 0.26 \times 150 = 39$ (1)

$pp \text{ H}_2 = \frac{2}{3} \times 117 = 78$ $pp \text{ H}_2 = 0.52 \times 150 = 78$ (1)

conseq on (i) but must show working

Allow one for $pp \text{ H}_2 = 2 \times pp \text{ N}_2$

also allow one for $pp \text{ H}_2$ if you can see that their answer has been achieved by subtracting (their $pp \text{ N}_2\text{H}_4$ + their $pp \text{ N}_2$) from 150

(b) (i) $K_p = \frac{P_{\text{N}_2} \times P_{\text{H}_2}^2}{P_{\text{N}_2\text{H}_4}}$ Penalise [] but mark on
if K_p wrong, no marks for calc (1)

(ii) $K_p = \frac{27 \times 48^2}{75}$ If numbers reversed, score units mark only (1)

$= 829 \text{ or } 830$ (or $829 \text{ or } 830 \times 10^6$ tied to Pa below) (1)

kPa^2 or conseq on their wrong K_p in (b)(i) (1)

(c) equm moves to fewer (gas) moles (not just to LHS) (1)

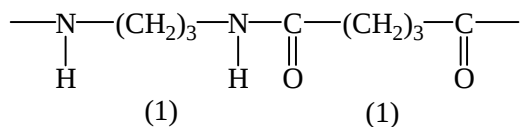
to counter increase P or to reduce P (1)

Total 11 marks

Question 4

(a) Condensation or addition-elimination

(1)



Penalise missing ties in polymers
once per question

(2)

Allow CONH and COHN

Must have both C chains and an attempt at a peptide link to score at all, then -1 per error

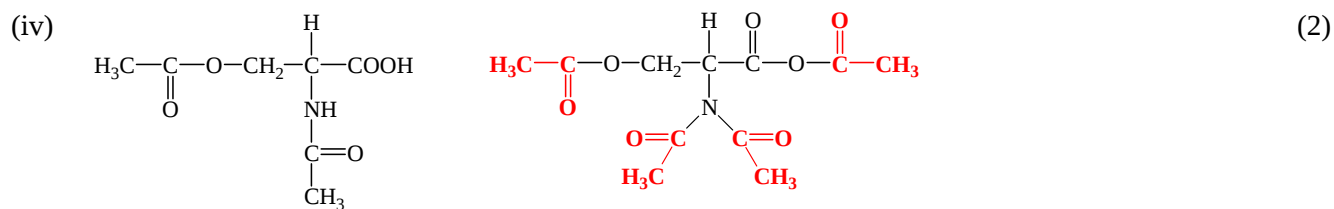
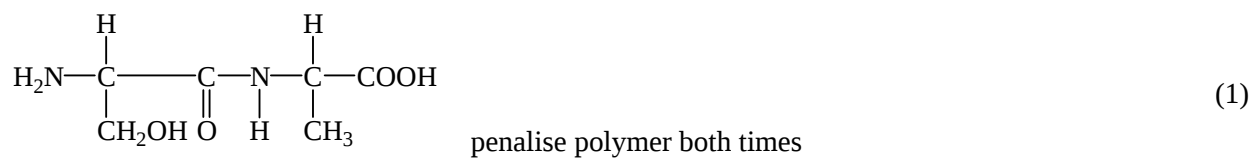
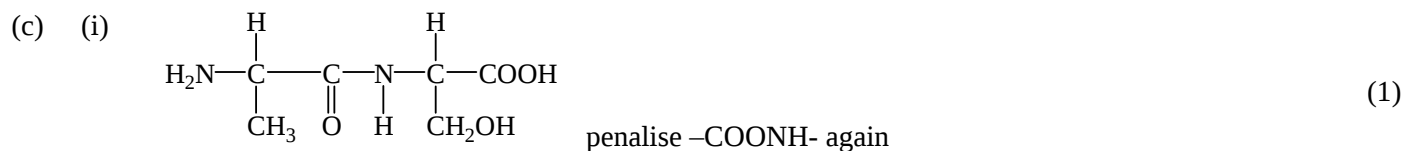
OOC-(CH₂)₃-COO counts as 1 mistake

(b) (i) H₂C=CHallow -OCOCH₃ and -O₂CCH₃

(1)

(ii) ---CH₂---CH---

(1)



CH₃CO can in theory be attached in 4 places as shown in above (RHS)

max 2 marks for any two attachments

If three attachments +2-1 = 1 mark; if four attachments +2-2 = 0 marks

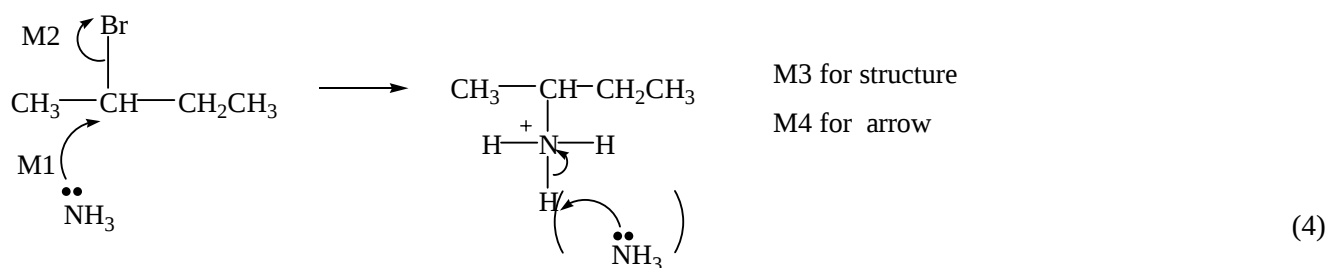
Total 11 marks

Question 5

(a) (i) electrophilic addition (1)

(ii) $\text{CH}_3\text{-CH=CH-CH}_3$ must show C=C (1)

(b) nucleophilic substitution (1)



Allow SN1

lose M4 if :Br^- used to remove H^+

(c) (i) $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_{11}\text{N}$ (1)

$M_r = 137$ $M_r = 73$ (both M_r values) or $10/137$ ($= 0.0730$)

0.0730×73 ($= 5.33$) (1)

$53.4\% = 0.534 \times 5.33 = 2.85 \text{ g}$ (allow rounding) (1)

(ii) further substitution or **G** reacts with F or further reaction or II/III
etc amines formed NOT just “other products formed” (1)

(d) 4 (1)

a doublet or 2 (1)

b triplet or 3 (1)

- (e) (i)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{NH}_2 \\ | \\ \text{CH}_3 \end{array}$$
 (1)
- (ii)
$$\begin{array}{c} \text{CH}_3 - \text{N} - \text{CH}(\text{CH}_3)_2 \\ | \\ \text{H} \end{array}$$
 (1)
- (iii)
$$\begin{array}{c} \text{CH}_3 - \text{N} - \text{CH}_2\text{CH}_3 \text{ or } \text{C}_2\text{H}_5 \\ | \\ \text{CH}_3 \end{array}$$
 (1)

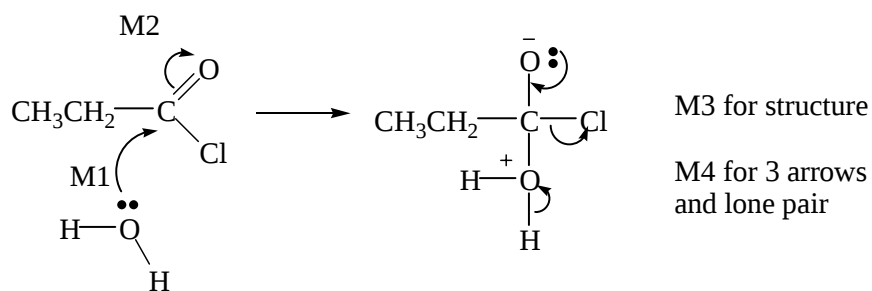
Total 17 marks

Question 6

allow molecular formulae $\text{C}_3\text{H}_5\text{OCl} + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_6\text{O}_2 + \text{HCl}$

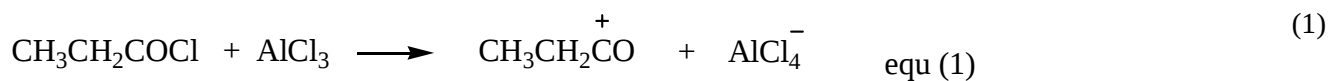
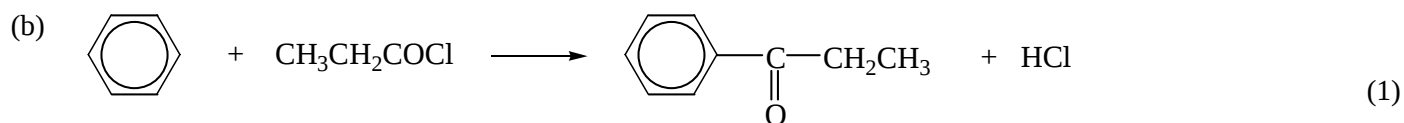
Penalise CH_3COCl once in the question

(nucleophilic) addition-elimination (1)



Allow M1 only for attack of water on acylium ion but not M2 separately (4)

Total 6 marks

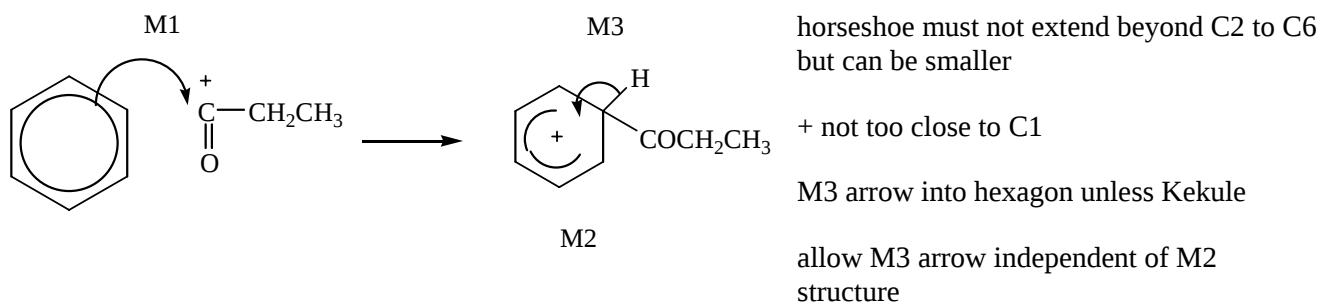


Ignore arrows except if from Al

Be lenient on position of + in equation



electrophilic substitution (1)



M1 arrow from within hexagon to C or to + on C

+ must be on C of RCO in mechanism (3)

(8 marks)

Total 14 marks

Question 7

- (a) 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 for one test; if either reagent wrong - no marks at all

For “no reaction” allow “nothing”

Wrong reagent is CE = zero

(i)	reagent	Br ₂ not Br₂/uv	KMnO ₄ / acidified or H ⁺	(1)
	P	no reaction	no reaction or stays purple	(1)
	Q	bromine decolourised	colourless or brown	(1)

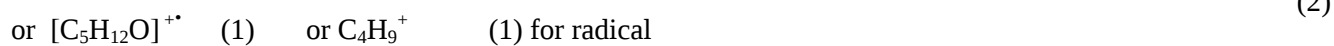
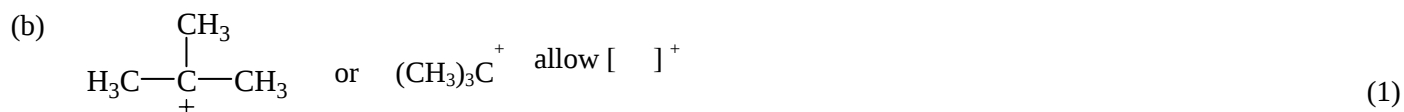
(ii)	reagent	Na ₂ CO ₃ / NaHCO ₃	UI	PCl ₅ PCl ₃	Suitable	(1)
		named carbonate	litmus	SOCl ₂	metal	
	R	no reaction	No reaction	No reaction	No reaction	(1)
	S	effervescence or CO ₂ or dissolves	red	fumes	effervescence or H ₂ or dissolves	(1)

Alternate:

(ii)	reagent	Bradys or 2,4,dnph	I ₂ /NaOH or NaOCl/KI	named alcohol /acid (catalyst)	(1)
	R	Orange/yellow ppt	Yellow ppt	No reaction	(1)
	S	No reaction	No reaction	Smell	(1)

(iii)	reagent	K ₂ Cr ₂ O ₇ /	KMnO ₄ /	(1)
		acidified or H ⁺	acidified or H ⁺	
	T	turns green	colourless or brown	(1)
	U	no reaction	no reaction	(1)
		stays orange	stays purple	

(9 marks)



(3 marks)



V ethanoic anhydride (1)

W dimethylethan(e)dioate (ignore numbers) (1)

V has peak at $\delta = 2.1-2.6$ (and **W** doesn't) **or**

W has peak at $\delta = 3.7-4.1$ (and **V** doesn't) (1)

Allow δ for **W** is higher than δ for **V** or peak for **W** is further to left etc

but if use numbers both must be correct.

(4 marks)

Total 16 marks