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**  

(b) \([H^+] = 0.038/2\) or \(0.019\)  
\[\text{pH} = 1.72\]  

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

proton donor  

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

(iii) \([H^+] = 10^{-3.48} = 3.3(1) \times 10^{-4}\)  
\[K_a = \frac{[H^+]^2}{[HX]}\] here or in part(ii) or \(\frac{(3.31 \times 10^{-4})^2}{0.063}\)  
\[= 1.7(4) \times 10^{-6}\] (ignore units even if wrong)
(d) (i) \[ 4.20 \text{ allow 4.19 – 4.21} \] (1)

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

\[
\text{mol HA left} = 0.055 - 0.0013 = 0.0537 \quad (\text{M2})
\]

\[
\text{mol A}^- \text{ present} = 0.025 + 0.0013 = 0.0263 \quad (\text{M3})
\]

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

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

\[\text{pH} = 4.23 \quad (\text{M5})\]

The essential part of this calculation is the subtraction/addition of \(1.30 \times 10^{-3}\) 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

\[
0.0537/0.110 = 0.488 \quad 0.0263/0.110 = 0.239
\]

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

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

Total 15 marks
Question 2

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

order wrt B = 1 ........................................ (1)

(b) (i) (rate =) \( k [C][D]^2 \) ........................................ (1)

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

= 1.3(1) ........................................ (1)

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

Total 6 marks
**Question 3**

(a) (i) \[ pp = \text{mole fraction} \times \text{total pressure} \]  
\[ \text{or } pp \text{ hydrazine} = 0.22 \times 150 \]  
\[ = 33 \text{ (kPa)} \]  
Ignore units even if wrong \( \text{(NB 2 marks for 33)} \) \( \text{(1)} \)

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

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

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

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) \[ K_p = \frac{P_{N_2} \times P_{H_2}^2}{P_{N_2\text{H}_4}} \]  
Penalise \[ \] but mark on

\[ \text{if } K_p \text{ wrong, no marks for calc} \]  
\( \text{(1)} \)

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

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

\[ \text{kPa}^2 \]  
Or conseq on their wrong \( K_p \) in (b)(i) \( \text{(1)} \)

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

To counter increase P or to reduce P \( \text{(1)} \)

**Total 11 marks**
Question 4

(a) Condensation or addition-elimination

\[
\begin{align*}
\text{N–}(\text{CH}_2)_3\text{N–}(\text{CH}_2)_3\text{C} & \quad \text{Penalise missing ties in polymers} \\
\text{H} & \quad \text{once per question} \\
\text{H} & \quad \text{Allow CONH and COHN} \\
\text{O} & \quad \text{(1)} \\
\text{O} & \quad \text{(1)}
\end{align*}
\]

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

OOC-(CH$_2$)$_3$-COO counts as 1 mistake

(b) (i) \[
\begin{align*}
\text{H}_2\text{C} & \quad \text{allow –OCOCH}_3 \quad \text{and } -\text{O}_2\text{CCH}_3 \\
\text{O} & \quad \text{(1)} \\
\text{C} & \quad \text{(1)} \\
\text{O} & \quad \text{(1)} \\
\text{CH}_3 & \quad \text{(1)}
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_2 & \\
\text{CH} & \\
\text{OH} & \quad \text{(1)}
\end{align*}
\]
(c) (i) 

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{C} & \quad \text{N} & \quad \text{C} & \quad \text{COOH} \\
\text{CH}_3 & \quad \text{O} & \quad \text{H} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

penalise –COONH- again

(1)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{C} & \quad \text{N} & \quad \text{C} & \quad \text{COOH} \\
\text{CH}_2\text{OH} & \quad \text{O} & \quad \text{H} & \quad \text{CH}_3 \\
\end{align*}
\]

penalise polymer both times

(1)

(ii) 

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{C} & \quad \text{COO}^- \\
\text{O} & \quad \text{H} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

(1)

(iii) 

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{C} & \quad \text{COOCH}_3 \\
\text{CH}_3 & \quad \text{OR} & \quad \text{-NH}_3^+ \\
\end{align*}
\]

(1)

(iv) 

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} & \quad \text{CH}_2 & \quad \text{C} & \quad \text{COOH} \\
\text{NH} & \quad \text{O} & \quad \text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} & \quad \text{CH}_2 & \quad \text{C} & \quad \text{O} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{C} & \quad \text{O} & \quad \text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}
\]

CH$_3$CO 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

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

(b) nucleophilic substitution

\[
\text{CH}_3\text{-CH-CH}_2\text{CH}_3 \xrightarrow{\text{M1}} \text{CH}_3\text{-CH-CH}_2\text{CH}_3 + \text{NH}_3
\]

- Allow SN1
- lose M4 if :Br used to remove H⁺

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

\[
M_r = 137 \quad M_r = 73 \quad \text{(both Mr values)} \quad \text{or} \quad 10/137 \quad (= 0.0730)
\]

\[
0.0730 \times 73 \quad (= 5.33)
\]

\[
53.4\% \quad = \quad 0.534 \times 5.33 \quad = \quad 2.85 \text{ g (allow rounding)}
\]

(ii) further substitution or \( \text{G} \) reacts with F or further reaction or II/III etc amines formed NOT just “other products formed”

(d) 4

- \( a \) doublet or 2

- \( b \) triplet or 3
(e) (i) \[\text{CH}_3\text{C} - \text{NH}_2\text{C} - \text{CH}_3\] (1)

(ii) \[\text{CH}_3\text{N} - \text{CH(CH}_3\text{)}_2\text{H}\] (1)

(iii) \[\text{CH}_3\text{N} - \text{CH}_2\text{CH}_3\text{ or C}_2\text{H}_5\] (1)

Total 17 marks
**Question 6**

(a) \[ \text{CH}_3\text{CH}_2\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HCl} \] 

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 \( \text{CH}_3\text{COCl} \) once in the question

(nucleophilic) addition-elimination

\[ \text{CH}_3\text{CH}_2\overset{\text{Cl}}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad \overset{\text{H}}{\text{O}} \quad \overset{\text{H}}{\text{H}} \quad \overset{\text{Cl}}{\text{C}} \rightarrow \text{CH}_3\text{CH}_2\overset{\text{O}}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad \overset{\text{H}}{\text{O}} \quad \overset{\text{H}}{\text{H}} \]

M2

M3 for structure

M4 for 3 arrows and lone pair

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

Total 6 marks
(b) 

+ \[
\begin{align*}
\text{C}_6\text{H}_6 & + \text{C}_3\text{H}_5\text{OCl} & \rightarrow & \text{C}_9\text{H}_{10}\text{O} + \text{HCl} \\
\text{CH}_3\text{CH}_2\text{COCl} & + \text{AlCl}_3 & \rightarrow & \text{CH}_3\text{CH}_2\text{CO} + \text{AlCl}_4^- \\
\text{AlCl}_3 & + \text{H}^+ & \rightarrow & \text{AlCl}_3 + \text{HCl}
\end{align*}
\]

(1)

Ignore arrows except if from Al

Be lenient on position of + in equation

\[
\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}
\]

(1)

electrophilic substitution

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

+ must be on C of RCO in mechanism

(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  Br₂  not Br₂/uv  KMnO₄/ acidified or H⁺

P  no reaction  no reaction or stays purple
Q  bromine decolourised  colourless or brown

(ii) reagent  Na₂CO₃/ NaHCO₃  UI  PCl₅  PCl₃  Suitable

named carbonate  litmus  SOCl₂  metal
R  no reaction  No reaction  No reaction  No reaction
S  effervescence or CO₂  red  fumes  effervescence or H₂ or dissolves

Alternate:

(ii) reagent  Bradys or 2,4,dnph  I₂/NaOH or NaOCl/KI

R  Orange/yellow ppt  Yellow ppt  No reaction
S  No reaction  No reaction  Smell

(iii) reagent  K₂Cr₂O₇/  KMnO₄/

acidified or H⁺  acidified or H⁺
T  turns green  colourless or brown
U  no reaction  no reaction
stays orange  stays purple

(9 marks)
(b) \[
\begin{align*}
\text{H}_3\text{C} & \text{C} \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \\
\text{+} & \text{+}
\end{align*}
\]
\text{or } (\text{CH}_3)_3\text{C}^+ \text{ allow } [ \quad ]^+ 
\quad (1)

\left[(\text{CH}_3)_3\text{CCH}_2\text{OH}\right]^- \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{CH}_3\text{OH} \text{ or } \text{CH}_3\text{O} \text{ (allow dot anywhere)}
\quad (2)

\text{or } [\text{C}_5\text{H}_12\text{O}]^- \quad (1) \text{ or } \text{C}_4\text{H}_9^+ \quad (1) \text{ for radical}

(3 marks)

(c) \text{CDCl}_3 \text{ or } \text{CCl}_4 \text{ or } \text{D}_2\text{O} \text{ or } \text{C}_6\text{D}_6
\quad (1)

\text{V} \text{ ethanoic anhydride}
\quad (1)

\text{W} \text{ dimethylethan(e)dioate (ignore numbers)}
\quad (1)

\text{V} \text{ has peak at } \delta = 2.1 - 2.6 \text{ (and } \text{W} \text{ doesn’t) or}

\text{W} \text{ has peak at } \delta = 3.7 - 4.1 \text{ (and } \text{V} \text{ doesn’t)}
\quad (1)

Allow \delta \text{ for } \text{W} \text{ is higher than } \delta \text{ for } \text{V} \text{ or peak for } \text{W} \text{ is further to left etc}

but if use numbers both must be correct.

(4 marks)

\textbf{Total 16 marks}