General Certificate of Education

Chemistry (6421)

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2008 examination - January series
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Question 1

(a)  
(i)  \( K_w = [H^+][OH^-] \) if wrong only score in (ii) and (iii) except if \([H_2O] = 1 \) * 1

(ii) 2.34 \times 10^{-7}  
penalise 2.3 \times 10^{-7} i.e. 2 sfs once in the question 1

(iii) 2.34 \times 10^{-7}  
conseq = (ii) 1

(iv) 5.48 to 5.50 \times 10^{-14}  
conseq = (ii) \times (iii) 1

*if \([H_2O] = 1 \) can score for correct answer here

(b)  
\[ [H^+] = \frac{10^{-14}}{0.136} \] (1)  = 7.35 \times 10^{-14}  
OR  pOH = 0.87 1

pH = 13.13 1

Total 6

Question 2

(a)  
M1  \( K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]} \) if wrong, score max 1 for M3 from their \([H^+] \) 1

penalise round brackets once in the qu

M2  \([H^+] = \sqrt{(1.35 \times 10^{-5} \times 0.169)} \) (1)  = 1.51 \times 10^{-3} 1

If \(\sqrt{\text{visible}} \) can score 2 for 5.64

M3  pH = 2.82  
allow 1 for correct pH from their \([H^+] \) 1

(b)  
(i)  CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O  
penalise 1

OR  CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H_2O  
covalent Na

(ii)  mol propanoic acid = 0.250 \text{ } - \text{ } 0.015 = 0.235  
penalise rounding to 1

mol propanoate ions = 0.190 + 0.015 = 0.205  
2sfs once 1

(iii)  
M1  \([H^+] = \frac{K_a \times [CH_3CH_2COOH]}{[CH_3CH_2COO^-]} \) correct rearrangement, 1

as here or with their numbers even if x

allow \(\frac{K_a \times [HA]}{[A^-]} \) 1

M2  = \frac{(1.35 \times 10^{-5}) (0.235)}{0.205}  
insertion of correct numbers 1

(= 1.548 \times 10^{-5})

M3  4.81  
allow 1 for correct pH from their \([H^+] \) 1

Total 9
Question 3

(a) \[ K_c = \frac{[H_2]^3[C_2H_2]}{[CH_4]^2} \]

if round brackets, penalise here but mark on
if \( K_c \) wrong can score only M1 and conseq units

(b) M1 dividing by volume
if moles used instead of conc can score only M3* (+ units M4);
can score this in M2

\[ M2 \quad K_c = \frac{0.28}{0.25} \times \frac{0.12}{0.25} \times \frac{0.44}{0.25} \]

\[ (= \frac{(1.12)^3(0.48)}{(1.76)^2}) \]

M3 = 0.218 or 0.22
* 1.36 \times 10^{-2} if vol not used
allow 0.217 – 0.22

M4 mol² dm⁻⁶

(c) to right or to product(s) or forwards
Increase

(d) to left or to reagent or backwards
no effect

(e) total no moles = 0.84
if CE, no second mark

\[ \frac{0.12}{0.84} = 0.14(3) \]

allow \( \frac{1}{7} \)

(f) \[ 0.143 \times 2.78 \times 10^4 = 3.97 \times 10^3 \] (allow 3.89– 4.00 \times 10^3 & 2 sfs i.e. 3.9 – 4.0)
conseq on (e):
penalise wrong units

(g) mol \( H_2 \) = 2.1
mark independently

mol \( C_2H_2 \) = 0.7

Total 14
**Question 4**

(a) (i) A

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \equiv \text{C} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

must show C=C

1

(ii) C

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

or (CH\(_3\))\(_3\)CCHO NOT (CH\(_3\))\(_3\)CCOH

1

D

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

allow C\(_2\)H\(_5\) and C\(_2\)H\(_5\)COC\(_2\)H\(_5\)

1

(iii) E

CH\(_3\)CH\(_2\)COOH or C\(_2\)H\(_5\)CO\(_2\)H

1

F

HCOOCH\(_2\)CH\(_3\) or HCO\(_2\)CH\(_2\)CH\(_3\)

1

(iv) G

CH\(_3\)CH=CHCH\(_2\)CH\(_2\)CH\(_3\) CH\(_3\)CH=CHCH(CH\(_3\))_2

1

CH\(_3\)CH=CHC\(_3\)H \quad CH\(_3\)CH\(_2\)CH=CHCH\(_2\)CH\(_3\)

1

CH\(_3\)

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

must show C=C in alkenes

1

H

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

allow C\(_2\)H\(_3\) or CHCH\(_2\)

1

(v) I

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

or (CH\(_3\))\(_2\)C(OH)C\(_2\)H\(_5\)

1

J

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \equiv \text{C} \\
\text{OH} & \quad \text{CH}_3
\end{align*}
\]

or (CH\(_3\))\(_3\)CCH\(_2\)OH

1
(b)  
(i)  5  
(ii) a singlet QWC  
       b triplet QWC  

Total 13

Question 5

(a)  
(i)  

(ii) H₂N-CH₂CH₂-COOH not H₂N-C₂H₄-COOH  
(iii) ethan(e)-1,2-diamine allow ethylene diamine or 1,2-diaminoethane but penalise wrong numbers  
       butan(e)(-1,4)-dioic acid NOT dibutanoic acid  

(b)  
(i) addition not additional  
(ii) 3-methylpent-2-ene  

(c)  
(i) HOCH₂CH₂OH  
       HOOCCH₂CH₂COOH or ClOOCCH₂CH₂COCl  
(ii) HOCH₂CH₂COO⁻ allow -COONa but not covalently bonded Na  

(d)  
(i) van der Waals allow vdW or London forces or dispersion forces  
(ii) dipole- dipole QWC Not temporary dipole- induced dipole  

Total 11

Question 6  
all answers to 3 sfs penalise fewer once

(a)  
(i) Expt 2 2.68 ×10⁻⁴  
       Expt 3 10.7(2) ×10⁻⁴  
       Expt 4 2.08 ×10⁻³  

(ii)  

k = \frac{\text{rate}}{[X]^2} or \frac{2.68 \times 10^{-4}}{(1.20 \times 10^{-3})^2}  

= 186  

mol⁻¹ dm³ s⁻¹ allow mol⁻¹ dm³ for misprint  

1
(b) increases (exponentially) allow straight line but not  

Total 7

Question 7

(a) \[ \text{AlCl}_3 \text{ or AlBr}_3 \text{ FeCl}_3 \text{ FeBr}_3 \]

\[ \text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CH}_2^+ + \text{AlCl}_4^- \]
ignore arrows unless wrong e.g. from lp on Al

\[ \text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl} \]
allow words if all reagents and products described correctly

electrophilic substitution

\[ \text{ethylbenzene} \text{ ignore numbers allow phenylethane} \]

phenylethene or poly(phenylethene) or styrene or poly(styrene)
or formula or repeating unit

9 marks

(b) nucleophilic substitution

\[ \text{N-ethylphenylamine or N-phenylethylamine} \]

6 marks

Total 15
Question 8

(a) (nucleophilic) addition-elimination  

\[
\begin{align*}
\text{M1:} & \quad \text{Cl}^- \quad \text{OH}^- \\
\text{M2:} & \quad \text{C}_6\text{H}_5 \quad \text{C} \quad \text{Cl}^- \\
\end{align*}
\]

M3 for structure  
M4 for 3 arrows and lone pair

NB Different from Qu 7b → do not penalise M4 if Cl\(^-\) removes H\(^+\)  

5 marks

NB There are four fragment ions in parts (b) and (c).  
If these are written with a negative charge or with a radical dot they are all wrong, but if they are written with no charge at all, penalise the first two without + then allow the rest.

(b)  
m/z 105 \( \text{C}_6\text{H}_5\text{CO}^+ \) or \( \text{C}_6\text{H}_5\text{CO}^+ \)  

1 mark  
m/z 77 \( \text{C}_6\text{H}_5^+ \) or \( \text{C}_6\text{H}_5^+ \) but not Wheland horseshoe intermediate  

1 mark  
\( \text{C}_6\text{H}_5\text{COOCCH}_3^- \) → \( \text{C}_6\text{H}_5\text{CO}^+ \) + \( \cdot\text{OCH}_3 \) allow dot anywhere  

2 marks  
(1) (1) (for balanced equation)

4 marks

(c)  
m/z 43 \( \text{CH}_3\text{CO}^+ \)  
V is \( \text{CH}_3\text{COOC}_6\text{H}_5 \)  

1 mark  
m/z 91 \( \text{C}_6\text{H}_5\text{CH}_2^+ \) or \( +\text{C}_6\text{H}_5\text{CH}_3 \)  

1 mark  
W is \( \text{HCOOCH}_2\text{C}_6\text{H}_5 \) \( \text{HCOOC}_6\text{H}_4\text{CH}_3 \)  

4 marks
(d) (i) OH or acid or (absorption at) 2500-3000 cm\(^{-1}\)  
(present in acid not in ester)  
1 mark

(ii) use of fingerprint region or (exact match with) known spectrum  
1 mark

2 marks

Total 15