General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2006 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.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates’ reactions to a particular paper. Assumptions about future mark schemes on the basis of one year’s document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.
CHM4

SECTION A

Question 1

(a) 
\[\exp 2 \quad 4.0 \times 10^{-3}\]  
\[\exp 3 \quad 0.45 \times 10^{-5}\]  
\[\exp 4 \quad 9.0 \times 10^{-3}\]  

(b) 
\[\frac{1.8 \times 10^{-5}}{(3.0 \times 10^{-3})^2(1.0 \times 10^{-3})}\]  
\[2000\]  
\[\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}\]  

Total 6

Question 2

(a) 
(i) \[[H^+]][OH^-]\]  
- \log [H^+]  

(ii) \[[H^+] = [OH^-]\]  

(iii) \[(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}\]  

(iv) \[[H^+] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}} (= 4.02 \times 10^{-11})\]  
\[\text{pH} = 10.40\]  

(b) 
(i) \[\text{Ka} = \frac{[H^+][\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]\]  
\[= \frac{[H^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]\]  

\[[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125} (= 1.30 \times 10^{-3})\]  
\[\text{pH} = 2.89\]
(c)  
(i) \[(50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}\]  
(ii) \[(6.25 \times 10^{-3}) - (1.0 \times 10^{-3}) = 5.25 \times 10^{-3}\]  
(iii) mol salt formed = 1.0 \times 10^{-3}  
\[
\text{[H}^+\] = Ka \times \frac{[\text{CH}_3\text{CH}_2\text{COOH}]}{[\text{CH}_3\text{CH}_2\text{COO}^-]} 
\[
= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V} 
(= 7.088 \times 10^{-5}) 
\]
\[\text{pH} = 4.15\]  

Total 16

Question 3

(a)  
(i) C + 3D \rightleftharpoons 2A + B  
(ii) mol dm\(^3\)  
(iii) (forward reaction is) exothermic or more products formed  

(b)  
(i) for N\(_2\)O\(_4\) Mr = 92.0  
\[
\text{Mol} = \frac{36.8}{92.0} = 0.400 
\]
(ii) mol N\(_2\)O\(_4\) reacted = 0.400 - 0.180 = 0.220  
mol NO\(_2\) formed = 0.440  
(iii) \[Kc = \frac{(\text{NO}_2)^2}{(\text{N}_2\text{O}_4)}\]  
\[
= \frac{(0.44/16)^2}{(0.18/16)} 
= 0.067\]  
(iv) move to NO\(_2\)/ to right/ forwards  
none  

Total 12
Question 4

(a) nucleophilic addition

(b) (i) 2-hydroxybutanenitrile

(ii) (allow 1 for amide even if not C₄H₇NO, i.e. RCONH₂)
     (if not amide, allow one for any isomer of C₄H₇NO which shows geometric isomerism)

(c) (i) CH₃CH₂—C—OH

     COOCH₃

(ii) CH₃CH₂—C—COOH

(iii) CH₃CH=CHCOOH

Total 11
**Question 5**

(a) dimethylamine 1

(b) nucleophilic substitution 1

(c) quaternary ammonium salt 1

\[(\text{cationic}) \text{ surfactant / bactericide / detergent / fabric softener or conditioner/ hair conditioner} \] 1

(d) 1

\[
\begin{array}{c}
\text{CH}_3\text{COO}^- \quad \text{CH}_2\text{NH}_3^+ \\
\text{(allow CH}_3\text{COOH or CH}_3\text{COO}^- \text{NH}_4^+) \\
\end{array}
\]

Total 10

**Question 6**

(a) polyamide or nylon (2,4) 1

\[(\text{allow nylon without numbers but if numbers are present they must be correct})\]

condensation 1

(b) 1

(c) ionic bonding in aminoethanoic acid 1

\[(\text{can only score if includes that aminoethanoic is ionic})\]

stronger attractions than Hydrogen bonding in hydroxyethanoic 1

\[(\text{e.g. stronger Hydrogen bonding in aminoethanoic acid scores } 0)\]

\[(\text{mention of electrostatic forces between molecules scores } 0)\]

Total 5
SECTION B

Question 7

(a) ethyl benzene

chloroethane or bromoethane (or ethene and hydrogen chloride/bromide)

aluminium chloride/bromide or iron(III) chloride /bromide or iron + chorine/bromine

\[ \text{CH}_3\text{CH}_2\text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CH}_2^+ + \text{AlCl}_4^- \]

electrophilic substitution

(b) 

\[ \text{CH}_3\text{CH}_2\text{COCl} / \text{propanoyl chloride or (CH}_3\text{CH}_2\text{CO})_2\text{O / propanoic anhydride} \]

NaBH\(_4\) or LiAlH\(_4\) or H\(_2\)/Ni (not Sn/Fe with HCl)

Total 11

Question 8

(a) (i) 3 peaks or shown in a list

\[ m/z = 126, 128 \text{ and } 130 \ (56 + 70/72/74) \ (all \ 3 \ scores \ 2) \]
\[ \text{(if 56 wrong allow } x + 70/72/74 \text{) for } 1 \ (x \ cannot \ be \ zero) \]
\[ \text{(any two scores } 1) \]

(ii)

\[ [\text{C}_4\text{H}_8\text{Cl}_2]^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}^+ + \cdot \text{CH}_2\text{Cl} \]

(1) (1) (1)

allow wrong structure for structure dot can be anywhere
(b) (i) optical
   equal mixture of enantiomers
   (optically) inactive or effects cancel
   plane polarised light use stereospecific reagent (QoL)
   rotated in opposite/different directions (QoL)
   reacts with one isomer only

(ii) carbocation
   planar - (must refer to carbocation or intermediate)
   attack from either side equally likely – (must refer to carbocation /intermediate)

7 max

(c) (i) 2 peaks (if 4 peaks allow splitting only)
   ratio 6:2 or 3:1
   doublet (6 or 3)
   quartet (2 or 1)

(ii) S

\[
\begin{align*}
H_3C & \xrightarrow{Cl} \xrightarrow{C} \xrightarrow{CH_2CH_3} \\
& \xrightarrow{Cl}
\end{align*}
\]

1

T

\[
\begin{align*}
H_3C & \xrightarrow{CH_3} \xrightarrow{C} \xrightarrow{CH_2Cl} \\
& \xrightarrow{Cl}
\end{align*}
\]

1

Total 19