General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2007 examination – January series
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**Question 1**

(a)  
(i) 2  
(ii) 1  
(iii) 0  

(b) \( k = \frac{\text{rate}/[D]^2[E]}{(0.84)^2(1.16)} \)  
\( = 1.0(2) \times 10^{-3} \) to \( 1.05 \times 10^{-3} \)  
\( \text{mol}^{-2}\text{dm}^6\text{s}^{-1} \)  

Total 6 marks

**Question 2**

(a) \( \text{mol Cl}_2 = 1.2(0) \)  
\( \text{total mol} = 3.8(0) \)  
no consequential marks on wrong mol Cl\(_2\) in (a) unless obvious AE  

(b) mol fraction PCl\(_5\)  
\( = \frac{1.4}{3.8} \)  
(1) = 0.368 (or 0.37)  
allow \( \frac{1.4}{\text{total mol}} \) from (a)  

mol fraction Cl\(_2\)  
\( = \frac{1.2}{3.8} \)  
(1) = 0.316 (or 0.32)  
allow \( \frac{\text{mol Cl}_2}{\text{total mol}} \) from (a)  

(c) (i) (pp =) mol fraction \( \times \) total P  
or \( p_A = x_A \times P_T \)  

(ii) pp PCl\(_5\)  
\( = 0.368 \times 125 = 46(0) \)  
\( 0.37 \times 125 = 46.3 \)  

pp Cl\(_2\)  
\( = 0.316 \times 125 = 39.47 \)  
\( 0.32 \times 125 = 40(0) \)  

Or conseq on (b)  

(d) \( K_p = \frac{p_{PCl_5} \times p_{Cl_2}}{p_{PCl_5}} \)  
not numbers  
penalise [ ] but mark on allow extra  
mark on all P ( ) brackets needs  

(e) (i) no effect  
(ii) increase  

(f) \( \frac{42.6^2}{36.9} = 49.2 \)  
(4.92 \times 10^4 tied to Pa below)  

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) \[\log [H^+] \text{ or } \log 1/[H^+]\] 1
(iii) 0.85 or conseq on (b) penalise dp of final answer <2> once per paper 1
(iv) M1 pH = 1 \[ [H^+] = 0.1(0) \text{ (mol dm}^{-3}\text{) } \text{ if wrong, max 1 for M2 } 1\]
M2 \[(7.05 \times 10^{-3})/0.10\] addition or subtraction loses M2 1
M3 vol = \[7.05 \times 10^{-2}\text{ _dm}^3\text{ or 70.5_cm}^3\] Units tied (allow 71 but not 70) 1

(c) (i) \[K_a = \frac{[H^+][X^-]}{[HX]} \text{ not } \frac{[H^+]^2}{[HX]} \text{ but mark on } 1\]
allow HA etc

(ii) \[K_a = \frac{[H^+]^2}{[HX]} \text{ If } K_a \text{ expression wrong or missing: max 1 in part (ii) for correct calculation of pH from their } [H^+] \] 1

\[
[H^+] = \sqrt{6.10 \times 10^{-5} \times 0.255} \text{ or } \sqrt{(Ka \times [HX])}
\]
\[= \sqrt{1.55 \times 10^{-5}} = 3.94 \times 10^{-3}\] 1
pH = 2.40 (if write \[\sqrt{\text{but forget to take sq rt this gives pH = 4.81 which can get 2 marks}}\] 1
rounded to \[3.9 \times 10^{-3} \text{ allow 2.41} \text{ max} \]

(d) (i) \[[H^+] = 1.66 \times 10^{-4}\] 1
\[K_a = \frac{(1.66\times10^{-4})(2.98\times10^{-3})}{(6.85\times10^{-3})} \text{ if wrong method, no further marks in d(i)}\]
\[= 7.22 \times 10^{-5}\]
pK_a = 4.14 1

(ii) effect = none/ negligible/v small decrease/v small change; not just pH goes down -- must be v small decrease
M1 Salt or Y^- reacts with extra H^+ or
equm HY \Longrightarrow H^+ + Y^- shifts to LHS or
H^+ is removed as eqm shifts to LHS
M2 \[\therefore[H^+] \text{ or ratio } [HY]/[Y^-] \text{ or ratio } [Y^-]/[HY] \text{ remains almost constant only gained if M1 correct} \] 1

Total 19 marks
Question 4

(a) \[
\begin{align*}
\text{CH}_3 & \quad \text{Si} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{Si} & \quad \text{CH}_3 \\
\text{CH}_3 & & \\
\end{align*}
\]
allow \( \text{Si(CH}_3)_4 \)\n
inert/non toxic/volatile or low bp \( \text{Any} \)
ignore cheap single intense peak/signal upfield of others/(protons)very shielded \( \text{2} \)

(b) \( \text{2} \) \( \text{1} \)

(c) (i) \( a = \text{quartet or 4} \) allow explained alternative interpretation of splitting \( \text{by} \) \( \text{1} \)
\( b = \text{triplet or 3} \) rather than \( \text{of these H} \)
\( a \text{ causes triplet} \) \( b \text{ causes triplet} 1 \)

(ii) \( 3230 – 3550 \text{ (cm}^{-1} \text{)} \) \( \text{1} \)

(d) (i) butan(e)-1,4-diol or 1,4- butan(e)diol or 1,4-dihydroxybutane \( \text{1} \)
(ii) condensation or addition- elimination
\[
\begin{align*}
\text{O} & \quad \text{CH}_2 \quad \text{O} & \quad \text{CH}_2 \quad \text{O} \quad \text{C} \\
\text{(CH}_2)_3 & & & & \text{3} & & \text{O} \\
\end{align*}
\]
must have both carbon chains and ester group to score at all ester group \( (1) \)
\( (\text{CH}_2)_3 \text{ (1)} \) but \( -1 \text{ for each error} \) \( \text{1} \)

(e) (i) \( 6(\text{H}) \) or \( 2 \times \text{CH}_3 \text{ groups} \) \( \text{1} \)
(ii) \( \text{(R)OCH}_3 \) \( \text{1} \)
(iii) \( \text{CH}_3(\text{–} \text{CH}(-\text{O}) \) penalise any extra \( \text{H} \) Not \( \text{R} \) attached to \( \text{CH} \) \( \text{1} \)
(iv) \[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{OCH}_3 \\
\text{H}_3\text{C} & & \text{OCH}_3 \\
\end{align*}
\]

Total \( 15 \text{ marks} \)
Question 5

(a) 2-aminopropanoic acid or 2-aminopropionic acid 1

(b) (i) \[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{C} \\
\text{H} \quad \text{O} \quad \text{H} \quad \text{H}
\end{array}
\]

Do NOT allow -CONH- or -COHN-

allow zwitterion

Not repeating unit

(ii) \[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{C} \quad \text{COOCH(CH}_3\text{)}_2 \\
\text{H}
\end{array}
\]

allow \( + \text{H}_3\text{N} \) or \( + \text{H}_3\text{N} \)

not \( \text{C}_3\text{H}_7 \)

(iii) \[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{COOH} \\
\text{O} \quad \text{H} \quad \text{H}
\end{array}
\]

(nucleophilic) addition-elimination 1

(c) (i) \[
\begin{array}{c}
\text{X} \quad \text{C} \quad \text{COOH} \\
\text{H}_3\text{N} \quad \text{H}
\end{array}
\]

allow \( ^+\text{H}_3\text{N} \) 1

(ii) \[
\begin{array}{c}
\text{Y} \quad \text{C} \quad \text{COO}^- \\
\text{H}_3\text{N} \quad \text{H}
\end{array}
\]

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

Total 7 marks
Question 6

(a) \[ \text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^- \] (1)

**NO MARK for acylium ion**

Allow FeCl₃

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

penalise wrong curly arrow in the equation or lone pair on AlCl₃ else ignore

electrophilic substitution **NOT F/C acylation**

(b) (i) Nucleophilic addition

(ii) optically inactive or equal mixture of (both) enantiomers/optical isomers

planar carbonyl group (stated or drawn) Not planar molecule

attack from above or below or either side (stated or drawn)

(c) 2-methylpentan-3-one no e in …..pentan-3-…

\[ \text{CH}_3\text{CH}_2\text{CO} + \] can be on O or C or outside [ ] but not on alkyls

[CH₃CH₂COC H(CH₃)₂]⁺ OR

allow [C₆H₁₂O]⁺. Dot can be anywhere allow C₂H₅ or C₃H₇

Total 6

Total 8

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 \( \text{Na}_2\text{CO}_3/ \text{NaHCO}_3 \) named carbonate

<table>
<thead>
<tr>
<th>P</th>
<th>No reaction</th>
<th>No rxn</th>
<th>No rxn</th>
<th>turns green</th>
<th>colourless or brown</th>
</tr>
</thead>
</table>

| Q | effervescence or CO\(_2\) or dissolves | fumes effervescence or H\(_2\) or dissolves | no rxn | stays orange | stays purple |

(ii) reagent \( \text{H}_2\text{O} \) \( \text{AgNO}_3 \) \( \text{Na}_2\text{CO}_3/ \text{NaHCO}_3 \) named carbonate

<table>
<thead>
<tr>
<th>R</th>
<th>(misty) fumes (White) ppt or rapid_ppt</th>
<th>effervescence or CO(_2) or dissolves</th>
<th>Smell fumes</th>
<th>red</th>
</tr>
</thead>
</table>

| S | no rxn | no ppt or slow_ppt | no rxn | No rxn | No rxn | No rxn |

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 \( \text{NaOH} \) 1
Sn or Fe/H\(_2\)SO\(_4\) dil or neither not \( \text{HNO}_3 \) 1
H\(_2\)/Ni not \( \text{NaBH}_4 \) \( \text{LiAlH}_4 \) \( \text{Na/C}_2\text{H}_5\text{OH} \) 1

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NO}_2 + 6[\text{H}] & \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O} \\
\text{C}_6\text{H}_5 & \text{or } 3\text{H}_2 \quad \text{organic species (1) balanced (1)}
\end{align*}
\]

(ii) nucleophilic substitution 1

Be lenient on position of + 1

5 marks

Total 11