

General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2007 examination - June series

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CHM 4

Question 1

(a) (i)
$$kPa^{-1}$$
 not $1/kPa$ (1)

(ii)
$$pO_2 = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 K_p}$$
 one mark for correct rearrangement of expression to give $pO_2 =$ (1)

$$= \frac{90.8^2}{10.6^2 \times 1.42}$$
 one mark for insertion of correct numbers into acorrect expression

These can be in either order

$$= 51.7 \text{ (allow } 51.6 - 51.9)$$
 (1)

(ii)
$$pp = mole fraction \times total pressure$$
 (1)

(iii) mark consequentially on (i) OR one mark for (1) correct rearrangement of expression to give
$$P = \dots$$

$$K_p = \frac{(\text{mol fn SO}_3)^2 \times P^2}{[(\text{mol fn SO}_2)^2 \times P^2][(\text{mol fn O}_2) \times P]}$$

must specify substances

one mark for insertion of correct numbers into a correct expression
$$These steps can be in either order$$
 (1)

$$= 171 (kPa)$$
 (1)

Total 14
Question 2

(a) (i)
$$pH = -log[H^+]$$
 must be [] allow $log \frac{1}{[H^+]}$ (1)

(b) (i)
$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
 ignore spectator ions (1) $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ OR $\rightarrow H_2CO_3$ (1)

(iii)
$$\frac{40}{10^3} \times 0.150 = 6.0 \times 10^{-3}$$
 (1)

(iv) mol HCl =
$$12.0 \times 10^{-3}$$
 (consequential on (iii)) must score this to gain 2nd mark) (1)

conc =
$$\frac{12.0 \times 10^{-3}}{50.0 \times 10^{-3}}$$
 = 0.24 mol dm⁻³ (1)

Total 9

Question 3 penalise pH with decimal places ≠ 2 once per paper

(a)
$$K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]}$$
 (1)
$$[H^+] = \sqrt{(1.35 \times 10^{-5} \times 0.55)} = 2.72 \times 10^{-3}$$
 gets 2 (1)

$$[H^{+}] = \sqrt{(1.35 \times 10^{-5} \times 0.55)} = 2.72 \times 10^{-3}$$
 gets 2 (1)

$$pH = 2.56 \text{ or } 2.57$$
 (1)

(b) (i)
$$30.0 \times 10^{-3} \times 0.55 = 1.65 \times 10^{-2}$$
 or 0.017 (at least 2sig figs) (1)

(ii)
$$10.0 \times 10^{-3} \times 0.23 = 2.30 \times 10^{-3} \text{ or } 0.0023 \text{ (at least 2 sig figs)}$$
 (1)

(iii)
$$(1.65 \times 10^{-2}) - (2.30 \times 10^{-3}) = 1.42 \times 10^{-2}$$
 i.e. (i) – (ii) above (1)

if addition not subtraction, also penalise first mark gained in (iv)†

if any mention of [H⁺]²/[HA] max 1 for moles of salt (iv)

mol CH₃CH₂COONa =
$$2.30 \times 10^{-3}$$
 (may be scored in the expression) (1)

$$[H^{+}] = \frac{\text{Ka x } [\text{CH}_{3}\text{CH}_{2}\text{COOH}]}{[\text{CH}_{3}\text{CH}_{2}\text{COO}^{-}]} *$$
or
$$= \frac{(1.35 \times 10^{-5}) (1.42 \times 10^{-2}/\text{V})}{(2.3 \times 10^{-3}/\text{V})} \frac{(1.4 \times 10^{-5}) (1.4 \times 10^{-2}/\text{V})}{(2.3 \times 10^{-3}/\text{V})}$$
(1)

$$= 8.33 \times 10^{-5}$$
 $= 8.5 \times 10^{-5}$ (1)
pH = 4.08 pH = 4.07

- expression may be pH = pKa + log[salt/acid] or pKa log[acid/salt]
- † if addition, 3.96-3.97 gets two in part (iv)

(a) (i)
$$k = \frac{0.65}{(0.15)(0.24)^2}$$
 if k upside down, (1)
$$\max 1 \text{ for consequential units}$$
$$= 75.23 \text{ to } 74.7$$

$$\min^{-2} \text{dm}^{-6} \text{s}^{-1}$$
 (1)

- (ii) 0.081 (min sig. figs required) (ignore wrong units) may be consequential on their k i.e. $(1.08 \times 10^{-3}) \times \text{their } k$
- (b) (i) 2 (1) (1)

(a) (i)
$$CH_3 - H_3N - C - COO$$

(ii)
$$\begin{array}{c} CH_3 \\ H_2N - C - C \\ H \end{array}$$
 OCH₃

(b)
$$+ NH_3$$
 $+ CH_2)_4 - C - COOH$ $+ COOH$ $+ COOH$ $+ COOH$

allow –CON and zwitterions and dipeptide – cyclic(-H₂O) Total 6

allow but not
$$C \longrightarrow H_2$$

- (a) (i) 2-methylbutan-1-ol (numbers essential) (1)
 - (ii) optical (1)
- (b) (i) elimination not nucleophilic nor any other qualification (1) not just dehydration

(ii)
$$CH_3CH_2$$
 penalise $-CH_3CH_2$ each time
$$-C - CH_2 - CH_3 - CH_$$

addition or radical (QOL) i.e. not additional

(iii)
$$CH_3CH_2$$
 H or CH_3 CH_3 allow $C_2H_5CH=CHCH_3$ (1)

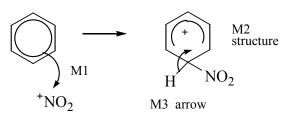
(c) (i)
$$CH_3CH_2$$
— C — CH_2CH_3 (1) CH_3CH_5 allow $C_2H_5COC_2H_5$

(e) (i)
$$400 - 1500 \text{ cm}^{-1}$$
 allow range from [0-600] to [1200 - 1500] (1)

(a) $conc\ HNO_3$ if both conc missing can score one for both acids (1) $conc\ H_2SO_4$ if omitted can score one for reagents in the equation ignore temp/reflux etc

 $HNO_3 + 2 H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (or in two equations) or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$ or $HNO_3 + H^+ \rightarrow NO_2^+ + H_2O$

electrophilic substitution (1)



M1 arrow from within hexagon to N or to + on N don't penalise position of + on N of +NO₂ (3) horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule

(b) 1,4-dinitrobenzene (1)

Sn or Fe/HCl (conc or dil or neither) ignore extra NaOH (1)

Sn or Fe/H₂SO₄ (dil or neither) **not** HNO₃ at all or H₂/Ni **not** NaBH₄/ LiAlH₄ or Na/C₂H₅OH

lone pair or electron pair on N in Y
delocalised into ring (QOL)
less available for protonation than lp in Z

(1)
(1)

$$\begin{array}{c}
M2 \\
CH_3CH_2 \\
\hline
C1 \\
CH_3 \\
\hline
CH_3 \\
CH_3 \\
\hline
CH_3 \\
CH_3 \\
\hline
CH_3 \\
CH_3 \\
\hline
CH_3 \\
C$$

must show a bond to -NH₂ to gain M1 penalise :Cl⁻ attacking H in M4

(ii) allow
$$C_2H_5$$
 so minimum is
$$(C_2H_5CO)_2O$$

$$CH_3CH_2 - C$$

$$CH_3CH_2 - C$$

$$(1)$$

(iii)
$$CH_3CH_2CONHCH_3^{+} \rightarrow CH_3CH_2CO^{+} + CH_3NH^{-}$$

* or $C_4H_9NO^{+}$
(1) (1) (1)
be lenient on position of + and dot

(b) Reaction 1 Nucleophilic addition (1)

$$\begin{array}{c}
OH \\
H_3C \longrightarrow C \longrightarrow CN \\
\downarrow \\
H
\end{array}$$
(1)

Reaction 2
$$H_2/Ni$$
 Na/ethanol or LiAlH₄ (1) hydrogenation or reduction reduction (1)

Total 14

* if you suspect erratum sheet was not circulated, CH_3CON^+ is 57 allow $CH_3CONHCH_3^{+} \rightarrow CH_3CON^+ + HCH_3$ or CH_4