



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) $p_{O_2} = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 K_p}$ one mark for correct rearrangement of expression to give $p_{O_2} = \dots$ (1) $= \frac{90.8^2}{10.6^2 \times 1.42}$ one mark for insertion of correct numbers into a correct expression (1)
These can be in either order $= 51.7$ (allow 51.6 – 51.9) (1)(b) (i) increase (1)
equilibrium moves to fewer gas moles or fewer moles on RHS (1)

(ii) none (1)

(iii) T₂ (1)
equilibrium moves in endothermic direction or to LHS (1)
or forward reaction is exothermic...

(c) (i) 0.08 (NOT 0.085) (1)

(ii) $pp = \text{mole fraction} \times \text{total pressure}$ (1)(iii) mark consequentially on (i) (1)
OR one mark for correct rearrangement of expression to give $P = \dots$ (1)

$$K_p = \frac{(\text{mol fn } SO_3)^2 \times P^2}{[(\text{mol fn } SO_2)^2 \times P^2][(\text{mol fn } O_2) \times P]}$$

must specify substances

 $P = \frac{0.75^2}{0.17^2 \times 0.08 \times 1.42}$ one mark for insertion of correct numbers into a correct expression (1)
These steps can be in either order $= 171$ (kPa) (1)**Total 14****Question 2**(a) (i) $pH = -\log[H^+]$ must be [] allow $\log \frac{1}{[H^+]}$ (1)

(ii) 0.437 or 0.44 (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)

- (ii) metacresol purple (1)
bromophenol blue (1)
- (iii) $\frac{40}{10^3} \times 0.150 = 6.0 \times 10^{-3}$ (1)
- (iv) mol HCl = 12.0×10^{-3} (consequential on (iii)) (1)
must score this to gain 2nd mark)
- conc = $\frac{12.0 \times 10^{-3}}{50.0 \times 10^{-3}} = 0.24 \text{ mol dm}^{-3}$ (1)

Total 9**Question 3** penalise pH with decimal places $\neq 2$ once per paper

- (a) $K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]}$ (1)
5.13 (if miss square root)
[H⁺] = $\sqrt{(1.35 \times 10^{-5} \times 0.55)} = 2.72 \times 10^{-3}$ gets 2 (1)
- pH = 2.56 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) $10.0 \times 10^{-3} \times 0.23 = 2.30 \times 10^{-3}$ or 0.0023 (at least 2sig 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)†

- (iv) if any mention of $[H^+]^2/[HA]$ max 1 for moles of salt
- mol $CH_3CH_2COONa = 2.30 \times 10^{-3}$ (may be scored in the expression) (1)
- $[H^+] = \frac{K_a \times [CH_3CH_2COOH]}{[CH_3CH_2COO^-]}$ *
- or $= \frac{(1.35 \times 10^{-5})(1.42 \times 10^{-2}/V)}{(2.3 \times 10^{-3}/V)}$ $\frac{(1.4 \times 10^{-5})(1.4 \times 10^{-2}/V)}{(2.3 \times 10^{-3}/V)}$ (1)
- $= 8.33 \times 10^{-5}$ $= 8.5 \times 10^{-5}$ (1)
- pH = 4.08 pH = 4.07

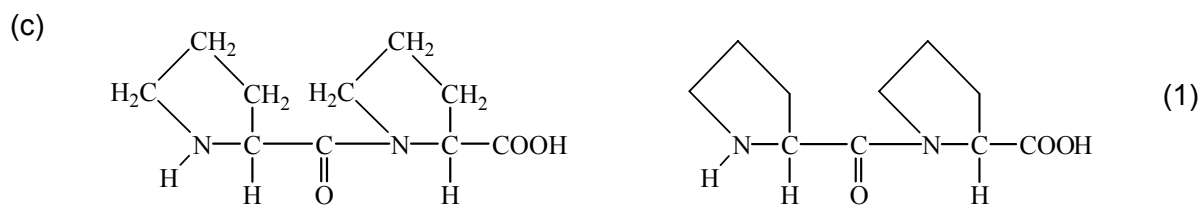
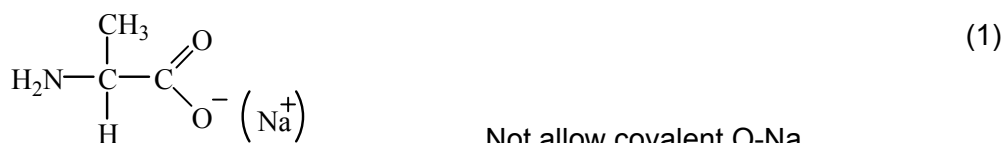
Total 9* expression may be $pH = pK_a + \log[\text{salt/acid}]$ or $pK_a - \log[\text{acid/salt}]$

† if addition, 3.96-3.97 gets two in part (iv)

Question 4

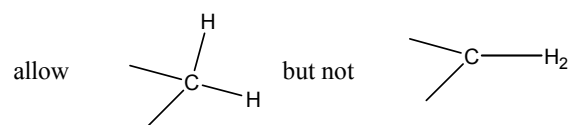
- (a) (i) $k = \frac{0.65}{(0.15)(0.24)^2}$ if k upside down, (1)
max 1 for consequential units
 $= \frac{75.23 \text{ to } 74.7}{\text{mol}^{-2}\text{dm}^6\text{s}^{-1}}$ $\text{mol}^2\text{dm}^{-6}\text{s}^{(+)}$ (1)
(1)
- (ii) 0.081 (min sig. figs required) (ignore wrong units) (1)
may be consequential on their k i.e. $(1.08 \times 10^{-3}) \times$ their k
- (b) (i) 2 (1)
(ii) 0 (1)

Total 6

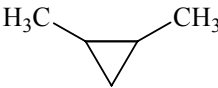

Question 5

allow -CON and zwitterions and dipeptide – cyclic($\text{-H}_2\text{O}$)

Total 6



Question 6

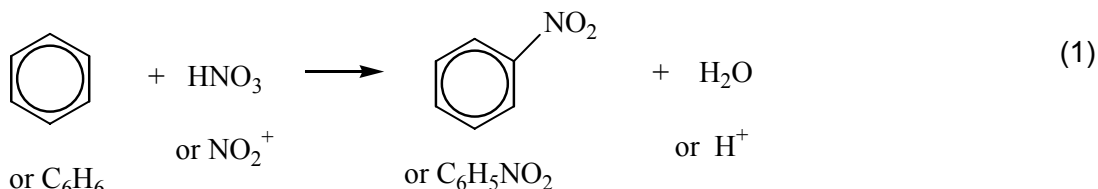
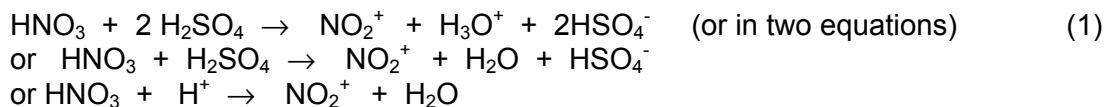
- (a) (i) 2-methylbutan-1-ol (numbers essential) (1)
- (ii) optical (1)
- (b) (i) elimination not nucleophilic nor any other qualification
not just dehydration (1)
- (ii)
$$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ | \\ \text{---C---CH}_2\text{---} \\ | \\ \text{CH}_3 \end{array}$$
 penalise $-\text{CH}_3\text{CH}_2$ each time (1)
- addition or radical (**QOL**)
i.e. not additional
- (iii)
$$\begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array}$$
 or  (1)
- allow $\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_3$
- (iv)  (1)
- (c) (i)
$$\text{CH}_3\text{CH}_2\text{---C---CH}_2\text{CH}_3$$

$$\quad \quad \quad \parallel$$
$$\quad \quad \quad \text{O}$$
 allow $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ (1)
- (ii) reflux (**QOL**) (1)
- (d) **I** M (1)
II J (1)
III K (1)
IV L (1)
- (e) (i) $400 - 1500 \text{ cm}^{-1}$ allow range from [0-600] to [1200 - 1500] (1)
- (ii) M1 compare with spectrum of known compound / database
M1 must be gained to score M2 (1)
- M2 exact match or fingerprint unique (1)

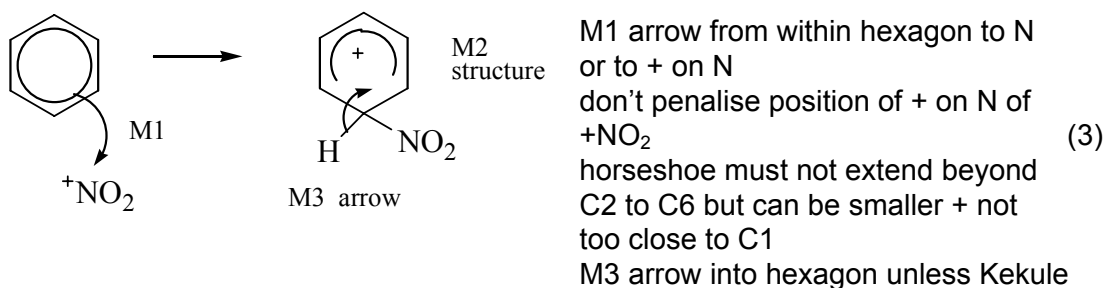
Total 16

Question 7

- (a) conc HNO₃ if both conc missing can score one for both acids (1)
 conc H₂SO₄ if omitted can score one for reagents in the equation (1)
 ignore temp/reflux etc



electrophilic substitution (1)

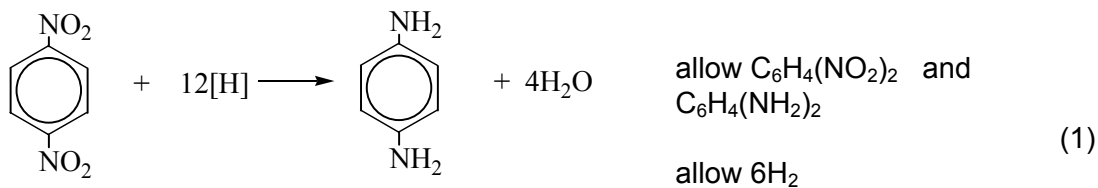


- (b) 1,4-dinitrobenzene (1)

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 (1)

delocalised into ring (QOL) (1)

less available for protonation than lp in Z (1)

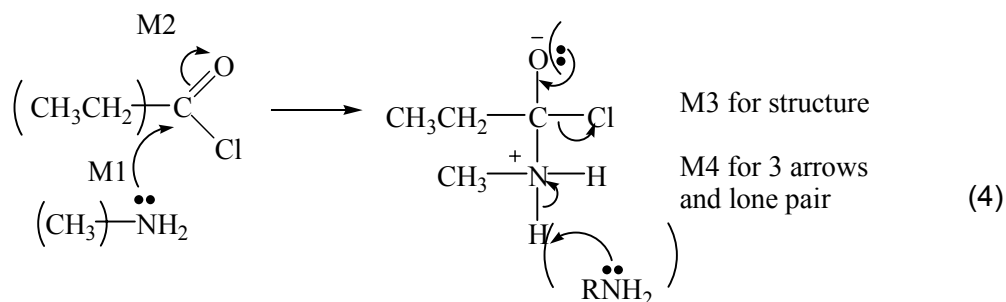
- (c)  not C₄H₈ ignore [] or n but must have trailing bonds (2)

allow -NHCO- (2)

Total 16

Question 8

- (a) (i) N-methylpropanamide (1)
nucleophilic addition-elimination (1)



must show a bond to -NH_2 to gain M1
penalise :Cl^- attacking H in M4

- (ii) $\text{CH}_3\text{CH}_2\text{-C}(=\text{O})\text{-O-C}(=\text{O})\text{-CH}_2\text{CH}_3$ allow C_2H_5 so minimum is $(\text{C}_2\text{H}_5\text{CO})_2\text{O}$ (1)

- (iii) $\text{CH}_3\text{CH}_2\text{CONHCH}_3^+ \rightarrow \text{CH}_3\text{CH}_2\text{CO}^+ + \text{CH}_3\text{NH}^+$ (3)
* or $\text{C}_4\text{H}_9\text{NO}^+$
(1) (1) (1)
be lenient on position of + and dot

- (b) Reaction 1 Nucleophilic addition (1)



- Reaction 2 H_2/Ni Na/ethanol or LiAlH_4 (1)
hydrogenation or reduction reduction (1)

Total 14

- * if you suspect erratum sheet was not circulated, CH_3CON^+ is 57
allow $\text{CH}_3\text{CONHCH}_3^+ \rightarrow \text{CH}_3\text{CON}^+ + \text{HCH}_3$ or CH_4