ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2007 examination - June 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.

Set and published by the Assessment and Qualifications Alliance.

The Assessment and Qualifications Alliance (AQA) is a company limited by guarantee registered in England and Wales (company number 3644723) and a registered charity (registered charity number 1073334).
Registered address: AQA, Devas Street, Manchester M15 6EX *Dr Michael Cresswell Director General*

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)

$= \frac{90.8^2}{10.6^2 \text{ x } 1.42}$ one mark for insertion of correct numbers into acorrect expression *These can be in either order* (1)

= 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) T_2 (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 = mole fraction × total pressure (1)

(iii) mark consequentially on (i) OR one mark for correct rearrangement of expression to give P = …. (1)

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

must specify substances

$P = \frac{0.75^2}{0.17^2 \text{ x } 0.08 \text{ x } 1.42}$ 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)

(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)) 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)
$[H^+]$	$= \sqrt{(1.35 \times 10^{-5} \times 0.55)} = 2.72 \times 10^{-3}$	5.13 (if miss square root) 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)

$[H^+] = \frac{Ka \times [CH_3CH_2COOH]}{[CH_3CH_2COO^-]}$ *

or $= \frac{(1.35 \times 10^{-5})(1.42 \times 10^{-2}/V)}{(2.3 \times 10^{-3}/V)}$ $\qquad \frac{(1.4 \times 10^{-5})(1.4 \times 10^{-2}/V)}{(2.3 \times 10^{-3}/V)}$ (1)

$= 8.33 \times 10^{-5}$ $\qquad = 8.5 \times 10^{-5}$ (1)

pH = 4.08 $\qquad$ pH = 4.07

Total 9

* expression may be pH = pKa + log[salt/acid] or pKa – log[acid/salt]

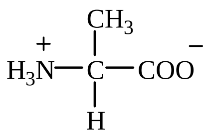
† if addition, 3.96-3.97 gets two in part (iv)

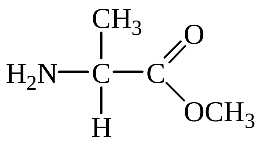
Question 4

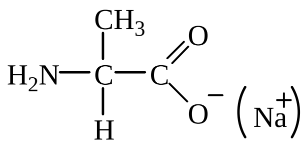
(a)	(i)	k =	$\dfrac{0.65}{(0.15)(0.24)^2}$	if *k* upside down, max 1 for consequential units	(1)
		=	75.23 to 74.7	mol^{2}dm^{-6}s$^{(+}$	(1)
			mol^{-2}dm^{6}s^{-1}		(1)
	(ii)	0.081 (min sig. figs required) (ignore wrong units) may be consequential on their *k* i.e. (1.08×10^{-3}) × their *k*			(1)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

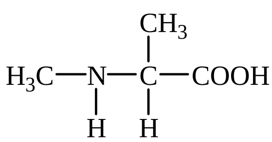
Total 6

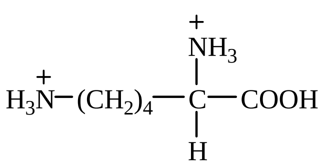
Question 5

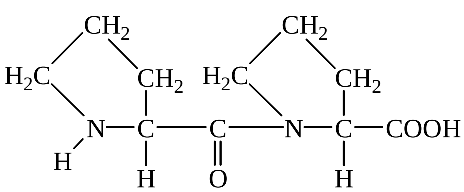
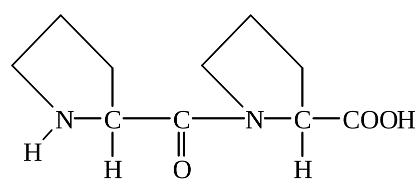
(a) (i)  (1)

(ii)  (1)

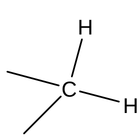
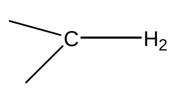
 Not allow covalent O-Na (1)

 (1)

(b)  (1)

(c)   (1)

allow –CON and zwitterions and dipeptide – cyclic(-H_2O) **Total 6**

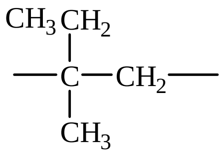
allow  but not 

Question 6

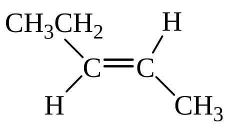
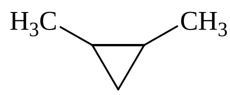
(a) (i) 2-methylbutan-1-ol (numbers essential) (1)

(ii) optical (1)

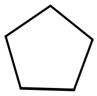
(b) (i) elimination — not nucleophilic nor any other qualification (1)
not just dehydration

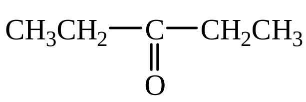
(ii)  penalise $–CH_3CH_2$ each time (1)

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

(iii)  or  (1)

allow $C_2H_5CH=CHCH_3$

(iv)  (1)

(c) (i)  (1)

allow $C_2H_5COC_2H_5$

(ii) reflux (**QOL**) (1)

(d) **I** M (1)
II J (1)
III K (1)
IV L (1)

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

(ii) M1 compare with spectrum of known compound / database (1)
M1 must be gained to score M2

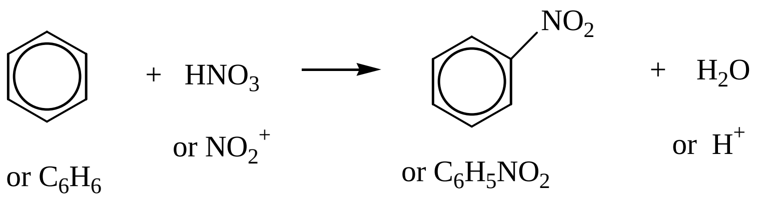
M2 exact match or fingerprint unique (1)

Total 16

Question 7

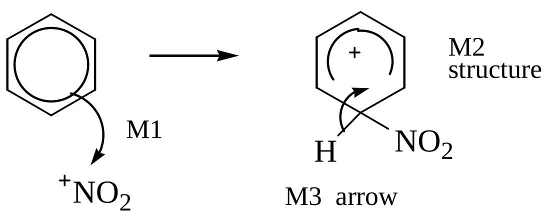
(a) conc HNO_3 — if both conc missing can score one for both acids (1)
conc H_2SO_4 — if omitted can score one for reagents in the equation (1)
ignore temp/reflux etc

$HNO_3 + 2\,H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (or in two equations) (1)
or $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + H_2O + HSO_4^-$
or $HNO_3 + H^+ \rightarrow NO_2^+ + H_2O$



(1)

electrophilic substitution (1)



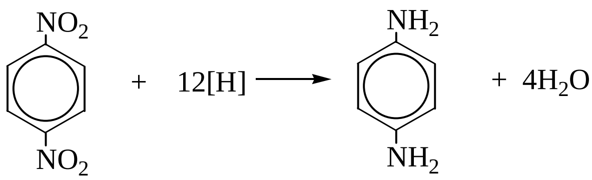
M1 arrow from within hexagon to N or to + on N
don't penalise position of + on N of $^+NO_2$
horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1
M3 arrow into hexagon unless Kekule (3)

(b) 1,4-dinitrobenzene (1)

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

Sn or Fe/H_2SO_4 (dil or neither) — **not** HNO_3 at all

or H_2/Ni — **not** $NaBH_4$/ $LiAlH_4$ or Na/C_2H_5OH

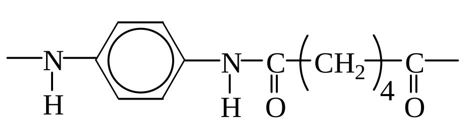


allow $C_6H_4(NO_2)_2$ and $C_6H_4(NH_2)_2$ (1)

allow $6H_2$

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)



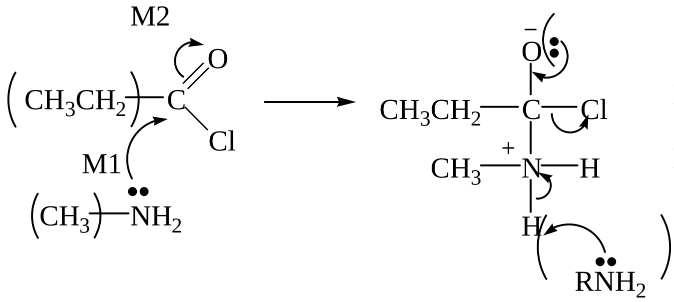
not C_4H_8
ignore [ ] or n
but must have trailing bonds (2)

allow -NHCO- (2)

Total 16

Question 8

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

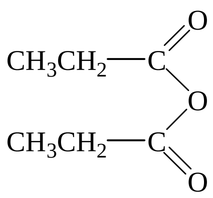


M3 for structure

M4 for 3 arrows and lone pair (4)

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

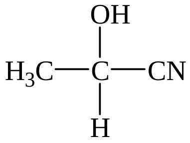
(ii)



allow C_2H_5 so minimum is $(C_2H_5CO)_2O$ (1)

(iii) $CH_3CH_2CONHCH_3^{+\cdot} \rightarrow CH_3CH_2CO^+ + CH_3NH^\cdot$ (3)
* or $C_4H_9NO^{+\cdot}$
(1) (1) (1)
be lenient on position of + and dot

(b) Reaction 1 Nucleophilic addition (1)



(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 $CH_3CONHCH_3^{+\cdot} \rightarrow CH_3CON^+ + HCH_3$ or CH_4