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ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2007 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.

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Dr Michael Cresswell Director General

Question 1

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

(b) k = rate/$[D]^2[E]$ or $\frac{8 \cdot 36 \times 10^{-4}}{(0.84)^2(1.16)}$ 1

= 1.0(2) × 10^{-3} to 1.05 × 10^{-3} 1

$mol^{-2}dm^6s^{-1}$ 1

Total 6 marks

Question 2

(a) mol Cl_2 = 1.2(0) 1

total mol = 3.8(0) no consequential marks on wrong mol Cl_2 in (a) unless obvious AE 1

(b) mol fraction PCl_5 = $\frac{1.4}{3.8}$ (1) = 0.368 (or 0.37) allow $\frac{1.4}{\textit{total mol}}$ from (a) 1

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) 1

(c) (i) (pp =) mol fraction × total P **or** total P = P_A + P_B + P_C ….
or p_A = x_A × P_T 1

	min	max	
(ii)	pp PCl_5 = 0.368 × 125 = 46(.0)	0.37 × 125 = 46.3	1
	pp Cl_2 = 0.316 × 125 = 39.47	0.32 × 125 = 40(.0)	1

Or conseq on (b)

(d) K_p = $\frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$ **not numbers** penalise [ ] but mark on allow extra ( ) brackets needs all P 1

(e) (i) no effect 1
(ii) increase 1

(f) $\frac{42.6^2}{36.9}$ If Kp wrong, allow units mark conseq within (f) 1

49.2 (or 4.9.2 ×10^4 tied to Pa below) 1

kPa 1

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) $-\log [H^+]$ 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 $[H^+] = 0.1(0)$ (mol dm^{-3}) if wrong, max 1 for M2 1
M2 $(7.05 \times 10^{-3})/0.10$ addition or subtraction loses M2 1
M3 vol = 7.05×10^{-2} dm^3 or 70.5 cm^3 Units tied (allow 71 but not 70) 1

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

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

$[H^+] = \sqrt{(6.10 \times 10^{-5} \times 0.255)}$ or $\sqrt{(Ka \times [HX])}$

$(= \sqrt{1.55 \times 10^{-5}} = 3.94 \times 10^{-3})$ 1

pH = 2.40 (if rounded to 3.9×10^{-3} allow 2.41) if write √ but forget to take sq rt this gives pH = 4.81 which can get 2 marks max 1

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

(ii) effect = none/ negligible/v small decrease/v small change; 1
not just pH goes down – must be v small decrease

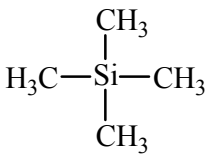
M1 Salt or Y^- reacts with extra H^+ **or**
equm $HY \rightleftharpoons H^+ + Y^-$ shifts to LHS **or**

H^+ is removed as eqm shifts to LHS

M2 $\therefore [H^+]$ or **ratio** $[HY]/[Y^-]$ or **ratio** $[Y^-]/[HY]$ remains almost constant only gained if M1 correct 1

Total 19 marks

Question 4

(a)  allow $Si(CH_3)_4$ 1

inert/non toxic/volatile or low bp
ignore cheap single intense peak/signal upfield of others/(protons)very shielded
Any 2

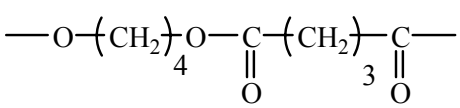
(b) 2 1

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

(ii) 3230 – 3550 (cm^{-1})

(d) (i) butan(e)-1,4-diol or 1,4- butan(e)diol or 1,4-dihydroxybutane 1

(ii) condensation or addition- elimination

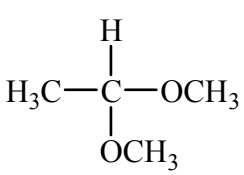


must have both carbon chains and ester group to score at all
ester group (1)
$(CH_2)_3$ (1) but -1 for each error 1

(e) (i) 6(H) or 2 × CH_3 groups 1

(ii) $(R)OCH_3$ 1

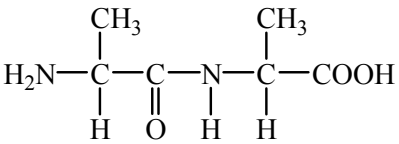
(iii) $CH_3(—)CH(-O)$ penalise any extra H Not R attached to CH 1

(iv)  1

Total 15 marks

Question 5

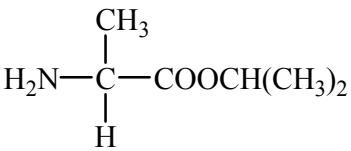
(a) 2-aminopropanoic acid or 2-aminopropionic acid 1

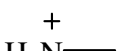
(b) (i)  1

Do NOT allow -CONH- or -COHN-

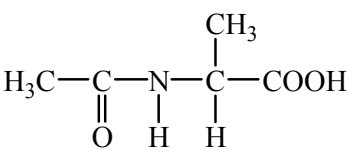
allow zwitterion

Not repeating unit

(ii)  1

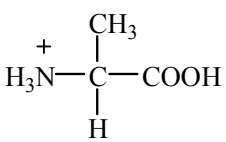
allow  or 

not C_3H_7

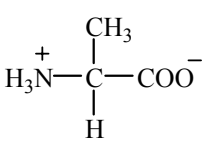
(iii)  1

allow –CONH- or -COHN-

(nucleophilic) addition-elimination 1

(c) (i) **X**  1

allow $^{+}H_3N$-

(ii) **Y** 

if only mistake in **X**, is e.g. $^{+}H_2N$- and this is repeated in **Y** but otherwise **Y** shows COO^{-} i.e. the candidate has realised the change from COOH to as pH rises, allow one for **Y** (ecf)

Total 7 marks

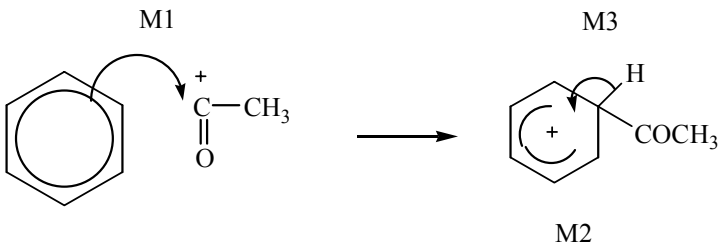
Question 6

(a) $CH_3COCl + AlCl_3 \longrightarrow CH_3\overset{+}{C}O + AlCl_4^-$ equ (1) 2

(1) **NO MARK for acylium ion** Allow $FeCl_3$

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

penalise wrong curly arrow in the equation or lone pair on $AlCl_3$ else ignore



horseshoe must not extend beyond C2 to C6 but can be smaller

+ not too close to C1

M3 arrow into hexagon unless Kekule

allow M3 arrow independent of M2 structure

3

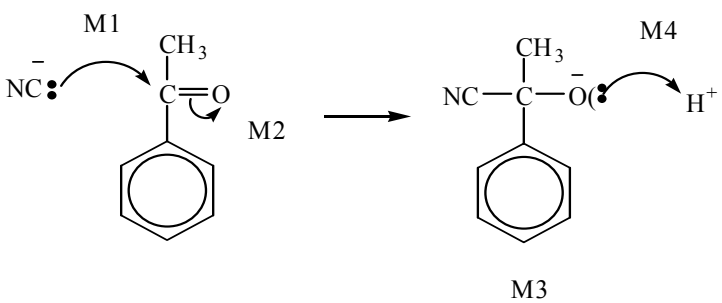
M1 arrow from within hexagon to C or to + on C

+ must be on C of RCO

electrophilic substitution **NOT F/C acylation** 1

Total 6

(b) (i) Nucleophilic addition 1



M2 not allowed independent of M1, but can allow M1 for attack of CN^- on C+ formed provided there is no CE in the formation of CN^- 4

(ii) optically inactive or <u>equal</u> mixture of (both) enantiomers/optical isomers 1

planar carbonyl group (stated or drawn) Not planar molecule 1

attack from above or below or either side (stated or drawn) 1

Total 8

(c) <u>2-methylpentan-3-one</u> no e in …..pentan-3-… 1

$CH_3CH_2\overset{+}{C}O$ + can be on O or C or outside [ ] but not on alkyls 1

$(CH_3)_2\overset{+}{C}HCO$ 1

$[CH_3CH_2COCH(CH_3)_2]^{+\bullet}$ (1)

OR

$CH_3\overset{+}{C}H_2CO$ + $\overset{\bullet}{C}H(CH_3)_2$ (1)

$CH_3\overset{\bullet}{C}H_2$ (1) + $(CH_3)_2CH\overset{+}{C}O$ 2

allow $[C_6H_{12}O]^{+\cdot}$ Dot can be anywhere + on C or O or outside [ ]

allow C_2H_5 or C_3H_7

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"

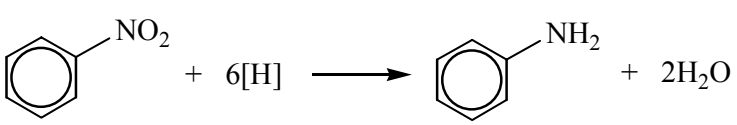
(a)	(i)	reagent	Na_2CO_3/ $NaHCO_3$ named carbonate	UI litmus	PCl_5 PCl_3 $SOCl_2$	Suitable metal	$K_2Cr_2O_7$/ acidified or H^+	$KMnO_4$/ acidified or H^+	1
		P	no reaction	No rxn	No rxn	No rxn	turns green	colourless or brown	1
		Q	effervescence or CO_2 or dissolves	red	fumes	effervescence or H_2 or dissolves	no rxn stays orange	no rxn stays purple	1
	(ii)	reagent	H_2O	$AgNO_3$	Na_2CO_3/ $NaHCO_3$ or named carbonate	Named alcohol	Named amine or ammonia	UI litmus	1
		R	(misty) fumes	(White) ppt or rapid_ppt	effervescence or CO_2 or dissolves	Smell or fumes	fumes	red	1
		S	no rxn	no ppt or slow_ppt	no rxn	No rxn	No rxn	No rxn	1

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 NaOH 1

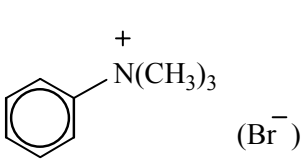
Sn or Fe/H_2SO_4 dil or neither not HNO_3

H_2/Ni not $NaBH_4$ $LiAlH_4$ Na/C_2H_5OH



C_6H_5 or $3H_2$ organic species (1) balanced (1) 2

(ii) nucleophilic substitution 1



Be lenient on position of + 1

5 marks

Total 11