AQA

ASSESSMENT and
QUALIFICATIONS
ALLIANCE

General Certificate of Education

Chemistry 6421

CHM4　　　Further Physical and Organic Chemistry

Mark Scheme

2008 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.

CHM4

SECTION A

Question 1

(a) 1.42   pH to < or > 2dp penalised once per paper   (1)

(b) $[H^+] = 0.038/2$ or 0.019   (1)

   pH = 1.72   (1)

(c) (i) (only) partly or slightly   NOT "not completely ionised"]   (1)
         dissociated/ionised

         proton donor   (1)

   (ii) $$K_a = \frac{[H^+][X^-]}{[HX]}$$ Ignore use of HA etc   (1)

   (iii) $[H^+] = 10^{-3.48} = 3.3(1) \times 10^{-4}$ (1)

         $$K_a = \frac{[H^+]^2}{[HX]} \text{ here or in part(ii)} \quad \text{or} \quad \frac{(3.31 \times 10^{-4})^2}{0.063}$$ (1)

         $= 1.7(4) \times 10^{-6}$ (ignore units even if wrong)   (1)

(d) (i) 4.20 allow 4.19 – 4.21 (1)

(ii) mol NaOH $= 10.0 \times 10^{-3} \times 0.130 = 1.30 \times 10^{-3}$ or 0.0013 (M1)

mol HA left $= 0.055 - 0.0013 = 0.0537$ (M2)

mol A^- present $= 0.025 + 0.0013 = 0.0263$ (M3)

(M4)

$$[H^+] = \frac{Ka \ x \ [HA]}{[A^-]} \quad or \quad \frac{(2.87 \ x \ 10^{-5})(0.0537/V)}{(0.0263/V)} (= 5.86 \times 10^{-5})$$

If [HA] and [A] wrong way round - no further marks

pH $= 4.23$ (M5)

The essential part of this calculation is the subtraction/addition of 1.30×10^{-3} moles

- If no subtraction/addition at all - max 1 for M1

- If one subtraction/addition missing or chemically wrong – lose M2 or M3 and next mark gained = max 3 (see * below)

If subtraction/addition reversed - max 2 for M1 and M5 ([H$^+$] = 6.82×10^{-5}) pH = 4.17

$0.0537/0.110 = 0.488$ $0.0263/0.110 = 0.239$

$* \quad \dfrac{(2.87 \ x \ 10^{-5})(0.0550/V)}{(0.0263/V)} = 6.00 \times 10^{-5}$ pH = 4.22

$* \quad \dfrac{(2.87 \ x \ 10^{-5})(0.0537/V)}{(0.0250/V)} = 6.16 \times 10^{-5}$ pH = 4.21

Total 15 marks

Question 2

(a) order wrt **A** = 2 (1)

order wrt **B** = 1 (1)

(b) (i) (rate =) k [**C**][**D**]^2 (1)

(ii) (1)
$$k = \frac{1.45 \times 10^{-4}}{(2.50 \times 10^{-2})(6.65 \times 10^{-2})^2} \quad \text{NOT} \quad \frac{\text{rate}}{[\text{C}][\text{D}]^2}$$
(1)

= 1.3(1) (1)

$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$ allow units conseq to wrong rate equation in (b)(i)

Total 6 marks

Question 3

(a) (i)   pp = mole fraction × total pressure   (1)

          or pp hydrazine = 0.22 × 150

              = 33 (kPa) ignore units even if wrong   (NB **2** marks for 33)   (1)

     (ii)   pp N_2 + pp H_2 = 150 – 33 = 117   Or mol fn N_2 + mol fn H_2 = 0.78   (1)

          pp N_2 = ⅓ ×117 = 39   pp N_2 = 0.26 × 150 = 39   (1)

          pp H_2 = ⅔ ×117 = 78   pp H_2 = 0.52 × 150 = 78   (1)

          conseq on (i) but must show working

          Allow one for pp H_2 = 2 × pp N_2

          also allow one for pp H_2 if you can see that their answer has been achieved
          by subtracting (their ppN_2H_4 + their pp N_2) from 150

(b) (i)

     $$K_p = \frac{P_{N_2} \times P^2_{H_2}}{P_{N_2H_4}}$$

                                                Penalise [ ] but mark on

                                                if K_p wrong, no marks for calc   (1)

     (ii)

     $$K_p = \frac{27 \times 48^2}{75}$$

                                                If numbers reversed, score units mark
                                                only
                                                                                                            (1)

          = 829 or 830   (or   829 or 830 ×10^6 tied to Pa below)   (1)

          kPa^2 or conseq on their wrong K_p in (b)(i)   (1)

(c) equm moves to <u>fewer</u> (gas) <u>moles</u>   (not just to LHS)   (1)

     to counter increase P or to reduce P   (1)

                                                                                              Total 11 marks

Question 4

(a) Condensation or addition-elimination   (1)
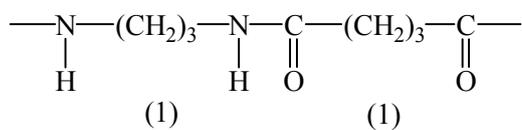
—N—(CH$_2$)$_3$—N—C—(CH$_2$)$_3$—C—   Penalise missing ties in polymers   (2)
  | | ‖   ‖   once per question
  H   H   O   O
      (1)   (1)   Allow CONH and COHN

Must have both C chains and an attempt at a peptide link to score at all, then -1 per error

OOC-(CH$_2$)$_3$-COO   counts as 1 mistake

(b) (i)   H$_2$C═CH
                |
                O
                |
                C═O   allow –OCOCH$_3$ and -O$_2$CCH$_3$
                | (1)
                CH$_3$

    (ii)   —CH$_2$—CH—   (1)
                    |
                    OH

(c) (i)

$$H_2N-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{CH_2OH}{|}}{\overset{\overset{H}{|}}{C}}-COOH$$

(1)

penalise –COONH- again

$$H_2N-\underset{\underset{CH_2OH}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-COOH$$

(1)

penalise polymer both times

(ii)

$$\overset{+}{H_3N}-\underset{\underset{CH_2OH}{|}}{\overset{\overset{H}{|}}{C}}-COO^-$$

(1)

(iii)

$$H_2N-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-COOCH_3 \qquad \text{or } -\overset{+}{N}H_3$$

(1)

(iv)

(2)
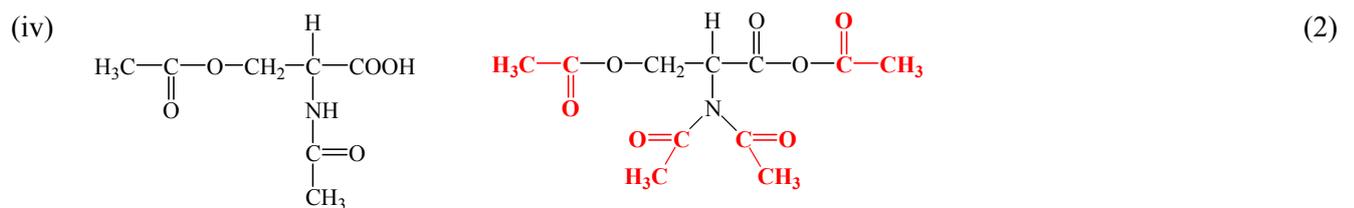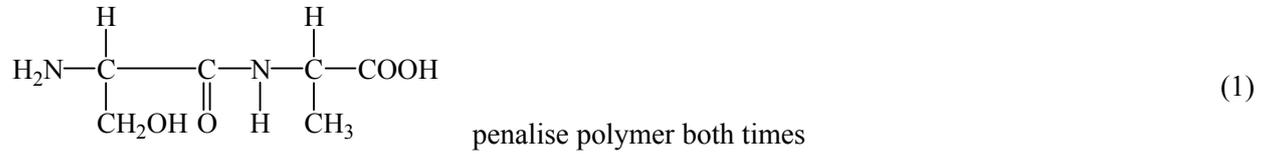
CH$_3$CO can in theory be attached in 4 places as shown in above (RHS)

max 2 marks for any two attachments

If three attachments +2-1 =1 mark;   if four attachments +2-2 = 0 marks

Total 11 marks

Question 5

(a) (i)   electrophilic addition   (1)

(ii) CH_3-CH=CH-CH_3 must show C=C   (1)

(b) nucleophilic substitution   (1)

M3 for structure

M4 for arrow

(4)
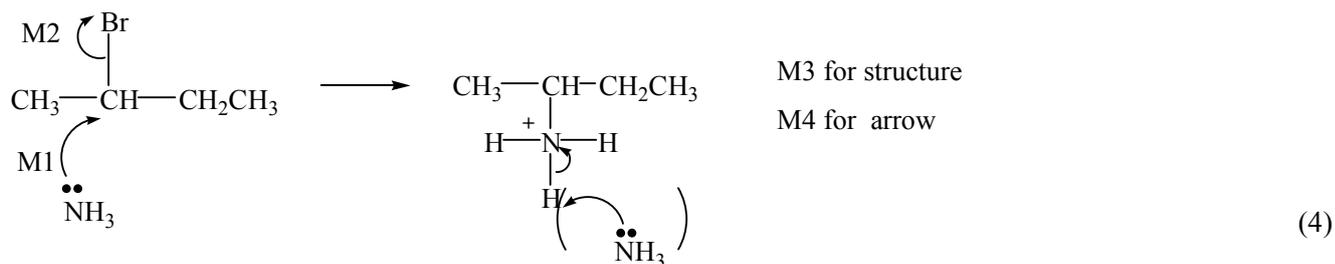
Allow SN1   lose M4 if :Br⁻ used to remove H⁺

(c) (i) C_4H_9Br → $C_4H_{11}N$ (1)

$M_r = 137$ $M_r = 73$ (both Mr values) or   10/137   (= 0.0730)

0.0730 × 73 (= 5.33)   (1)

53.4% = 0.534 × 5.33   = 2.85 g (allow rounding)   (1)

(ii)   further substitution   or **G** reacts with F   or further reaction   or II/III   (1)
       etc amines formed   NOT just "other products formed"

(d) 4   (1)

a doublet or 2   (1)

b triplet or 3   (1)

(e) (i)   (1)

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH_2$$

(ii) $CH_3-\underset{\underset{H}{|}}{N}-CH(CH_3)_2$ (1)

(iii) $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_2CH_3$ or C_2H_5 (1)

Total 17 marks

Question 6

(a) $CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2COOH + HCl$ (1)

allow molecular formulae $C_3H_5OCl + H_2O \rightarrow C_3H_6O_2 + HCl$

Penalise CH_3COCl once in the question

(nucleophilic) addition-elimination (1)

M3 for structure

M4 for 3 arrows and lone pair
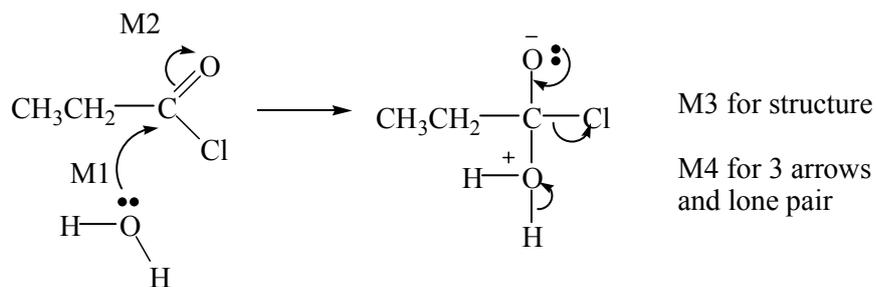
Allow M1 only for attack of water on acylium ion   but not M2 separately (4)

Total 6 marks

(b)

$$CH_3CH_2COCl \longrightarrow \text{benzene} - C(=O) - CH_2CH_3 + HCl$$

(1)

allow $C_6H_6 + C_3H_5OCl \longrightarrow C_9H_{10}O + HCl$

$AlCl_3$ allow $AlBr_3$ $FeCl_3$ $FeBr_3$ (1)

(1)

$$CH_3CH_2COCl + AlCl_3 \longrightarrow CH_3CH_2\overset{+}{C}O + AlCl_4^- \qquad \text{equ (1)}$$
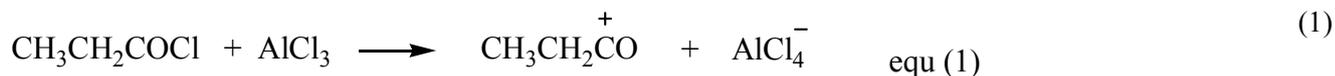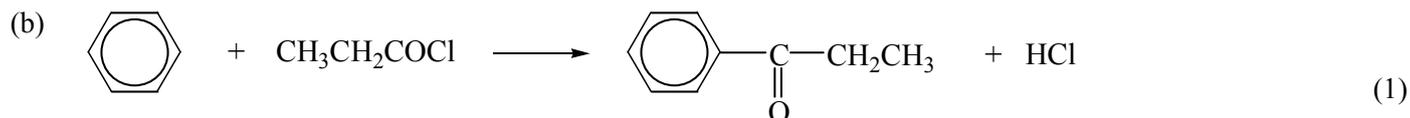
Ignore arrows except if from Al

Be lenient on position of + in equation

$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$ (1)

electrophilic substitution (1)

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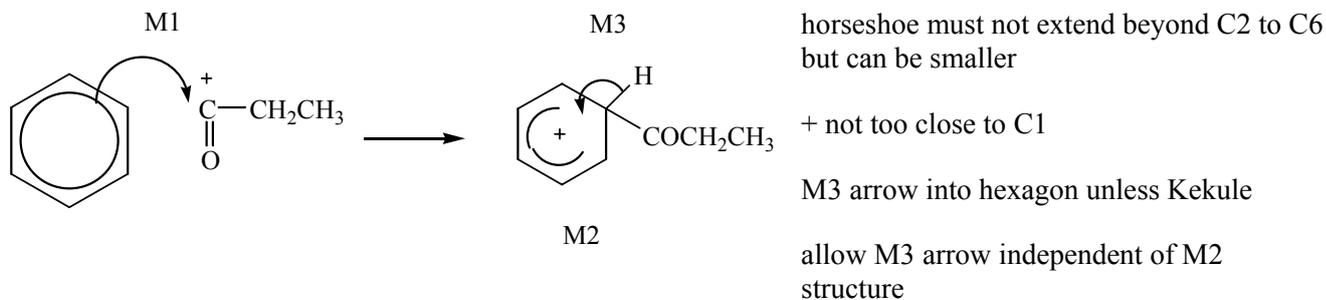
M1 arrow from within hexagon to C or to + on C

+ must be on C of RCO in mechanism

(3)

(8 marks)

Total 14 marks

Question 7

(a) 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 for one test;   if either reagent wrong - no marks at all

For "no reaction" allow "nothing"   **Wrong reagent is CE = zero**

(i)	reagent	Br_2 **not Br_2/uv**	$KMnO_4$ / acidified or H^+			(1)
	P	no reaction	no reaction or stays purple			(1)
	Q	bromine decolourised	colourless or brown			(1)

(ii)	reagent	Na_2CO_3/ $NaHCO_3$	UI	PCl_5 PCl_3	Suitable	(1)
		named carbonate	litmus	$SOCl_2$	metal	
	R	no reaction	No reaction	No reaction	No reaction	(1)
	S	effervescence or CO_2 or dissolves	red	fumes	effervescence or H_2 or dissolves	(1)

Alternate:

(ii)	reagent	Bradys or 2,4,dnph	I_2/NaOH or NaOCl/KI	named alcohol /acid (catalyst)	(1)
	R	Orange/yellow ppt	Yellow ppt	No reaction	(1)
	S	No reaction	No reaction	Smell	(1)

(iii)	reagent	$K_2Cr_2O_7$ / acidified or H^+	$KMnO_4$/ acidified or H^+	(1)
	T	turns green	colourless or brown	(1)
	U	no reaction stays orange	no reaction stays purple	(1)

(9 marks)

(b)

$$H_3C-\underset{\underset{+}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \quad \text{or} \quad (CH_3)_3C^+ \quad \text{allow } [\quad]^+$$

(1)

$[(CH_3)_3CCH_2OH]^{+\bullet} \rightarrow (CH_3)_3C^+ + {}^{\bullet}CH_2OH \text{ or } {}^{\bullet}CH_3O$ (allow dot anywhere)

(2)

or $[C_5H_{12}O]^{+\bullet}$ (1) or $C_4H_9^+$ (1) for radical

(3 marks)

(c) $CDCl_3$ or CCl_4 or D_2O or C_6D_6 (1)
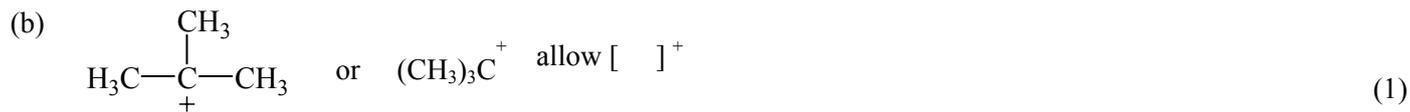
V ethanoic anhydride (1)

W dimethylethan(e)dioate (ignore numbers) (1)

V has peak at $\delta = 2.1\text{-}2.6$ (and **W** doesn't) **or**

W has peak at $\delta = 3.7 – 4.1$ (and **V** doesn't) (1)

Allow δ for **W** is higher than δ for **V** or peak for **W** is further to left etc

but if use numbers both must be correct.

(4 marks)

Total 16 marks