

General Certificate of Education

Chemistry (6421)

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2008 examination - January series

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(a) (i)
$$K_w = [H^+][OH^-]$$
 if wrong only score in (ii) and (iii) except if $[H_2O] = 1 * 1$

(ii)
$$2.34 \times 10^{-7}$$
 penalise 2.3×10^{-7} i.e. 2 sfs once in the question 1

(iii)
$$2.34 \times 10^{-7}$$
 conseq = (ii)

(iv) 5.48 to 5.50
$$\times 10^{-14}$$
 conseq = (ii) \times (iii) 1

*if [H₂O] = 1 can score for correct answer here

(b)
$$[H+] = \frac{10^{-14}}{0.136}$$
 (1) = 7.35 ×10⁻¹⁴ OR pOH = 0.87 1
pH = 13.13

Total 6

Question 2

(a) M1
$$K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]}$$
 if wrong, score max 1 for M3 from their $[H^+]$ 1

penalise round brackets once in the qu

M2
$$[H^+]$$
 = $\sqrt{(1.35 \times 10^{-5} \times 0.169)}$ (1) = 1.51 ×10⁻³ 1

If $\sqrt{\text{visible can score 2 for 5.64}}$

M3 pH =
$$2.82$$
 allow 1 for correct pH from their [H $^{+}$] 1

(b) (i)
$$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$$
 penalise 1 OR $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H_2O$ covalent Na

(ii) mol propanoic acid =
$$0.250 - 0.015 = 0.235$$
 penalise rounding to 1 mol propanoate ions = $0.190 + 0.015 = 0.205$ 2sfs once 1

(iii) M1
$$[H^{+}] = \frac{K_a \times [CH_3CH_2COOH]}{[CH_3CH_2COO^{-}]}$$
 correct rearrangement, as here or with their numbers even if x

$$\text{allow } \frac{\text{K}_{\text{a}} \times [\text{HA}]}{[\text{A}^{\text{-}}]}$$

$$\text{M2} = \frac{(1.35 \times 10^{-5}) (0.235)}{0.205} \quad \text{insertion of correct numbers} \quad 1$$

$$\text{here or in Ka expression}$$

$$\text{(= } 1.548 \times 10^{-5})$$

- (a) $K_c = \frac{[H_2]^3 [C_2 H_2]}{[CH_4]^2}$ if round brackets, penalise here but mark on if K_c wrong can score only M1 and conseq units
- (b) M1 dividing by volume if moles used instead of conc can score throughout shown only M3* (+ units M4); can score this in M2

M2
$$K_c = \frac{(\frac{0.28}{0.25})^3(\frac{0.12}{0.25})}{(\frac{0.44}{0.25})^2}$$

$$(= \frac{(1.12)^3(0.48)}{(1.76)^2})$$

- M3 = 0.218 or 0.22 * 1.36×10^{-2} if vol not used 1 allow 0.217 0.22
- $M4 ext{ mol}^2 ext{ dm}^{-6}$
- (c) to right or to product(s) or forwards 1
 Increase 1
- (d) to left or to reagent or backwards 1
 no effect 1
- (e) total no moles = 0.84 if CE, no second mark 1
- $\frac{0.12}{0.84} = 0.14(3)$ allow $\frac{1}{7}$
- (f) $0.143 \times 2.78 \times 10^4 = 3.97 \times 10^3$ (allow $3.89 4.00 \times 10^3 \& 2$ sfs i.e. 3.9 4.0) 1 conseq on (e): penalise wrong units
- (g) $mol H_2 = 2.1$ mark independently 1 $mol C_2H_2 = 0.7$

Total 14

1

(a) (i) A
$$C=C$$
 CH_3 must show C=C 1

(iii) E
$$CH_3CH_2COOH$$
 or $C_2H_5CO_2H$ 1

(iv) G
$$CH_3CH=CHCH_2CH_3CH_3$$
 $CH_3CH=CHCH(CH_3)_2$

H
$$H_{3C}$$
 $CH=CH_{2}$ allow $C_{2}H_{3}$ or $CHCH_{2}$ 1

(v) I
$$CH_3$$
 or $(CH_3)_2C(OH)C_2H_5$ 1 $H_3C-C-CH_2CH_3$ OH

J or
$$(CH_3)_3CCH_2OH$$
 1

 CH_3
 H_3C
 CH_2OH
 CH_3

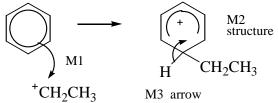
| (b) | (i) | 5 | 1 |
|------------|--------|--|--------|
| | (ii) | a singlet QWC b triplet QWC | 1 1 |
| | | Total | |
| Question 5 | | | |
| (a) | (i) | CH ₃ + COO H | 1 |
| | (ii) | H ₂ N-CH ₂ CH ₂ -COOH not H ₂ N-C ₂ H ₄ -COOH | 1 |
| | (iii) | ethan(e)-1,2-diamine allow ethylene diamine or 1,2-diaminoethane but penalise wrong numbers | 1 |
| | | butan(e)(-1,4-)dioic acid NOT dibutanoic acid | 1 |
| (b) | (i) | addition not additional | 1 |
| | (ii) | 3-methylpent-2-ene | 1 |
| (c) | (i) | HOCH ₂ CH ₂ OH HOOCCH ₂ CH ₂ COOH or CIOCCH ₂ CH ₂ COCI | 1 1 |
| | (ii) | HOCH₂CH₂COO ⁻ allow -COONa but not covalently bonded Na | 1 |
| (d) | (i) | van der Waals allow vdW or London forces or dispersion forces | 1 |
| | (ii) | dipole- dipole QWC Not temporary dipole- induced dipole | 1 |
| | | Total | 11 |
| Ques | tion 6 | all answers to 3 sfs penalise fewer once | |
| (a) | (i) | Expt 2 2.68 ×10 ⁻⁴ | 1 |
| | | Expt 3 $10.7(2) \times 10^{-4}$ | 1 |
| | | Expt 4 2.08 ×10 ⁻³ | 1 |
| | (ii) | $k = \frac{\text{rate}}{[X]^2} \text{ or } \frac{2.68 \times 10^{-4}}{(1.20 \times 10^{-3})^2}$ | 1 |
| | | = 186 | 1 |
| | | mol ⁻¹ dm ³ s ⁻¹ allow mol ⁻¹ dm ³ for misprint | 1 |

(b) increases (exponentially) allow straight line but not 1

Total 7

Question 7

(a) AlCl₃ or AlBr₃ FeCl₃ FeBr₃ 1 $CH_3CH_2CI + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^- \text{ ignore arrows unless wrong e.g. from lp on Al}$ $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl \text{ allow words if all reagents and products described correctly}$ electrophilic substitution 1



ethylbenzene ignore numbers allow phenylethane 1

phenylethene or poly(phenylethene) or styrene or poly(styrene) 1

or formula or repeating unit

9 marks

3

(b) nucleophilic substitution 1

N-ethylphenylamine or 1

N-phenylethylamine

6 marks

Total 15

(a) (nucleophilic) addition-elimination

$$C_6H_5$$
 C_6H_5
 C

NB Different from Qu 7b \rightarrow do not penalise M4 if Cl removes H⁺ 4

5 marks

1

NB There are four fragment ions in parts (b) and (c).

If these are written with a negative charge or with a radical dot they are all wrong, but if they are written with no charge at all, penalise the first two without + then allow the rest.

(b)
$$m/z$$
 105 C_6H_5CO or C_6H_5CO 1

m/z 77
$$C_6H_5^+$$
 or but not Wheland 1 horseshoe intermediate

$$C_6H_5COOCH_3^+$$
 \rightarrow $C_6H_5CO^+$ + OCH_3 allow dot anywhere 2 (1) (1) (for balanced equation)

4 marks

(c)
$$m/z$$
 43 CH_3CO^+ 1 1 V is $CH_3COOC_6H_5$ 1 1 m/z 91 $C_6H_5CH_2^+$ 0r CH_3 1

 \mathbf{W} is $HCOOCH_2C_6H_5$ $HCOOC_6H_4CH_3$ 1

4 marks

(d) (i) OH or acid or (absorption at) 2500-3000 cm⁻¹
 (present in acid not in ester)
 (ii) use of fingerprint region or (exact match with) known spectrum

2 marks

Total 15