Equilibria

Mark Scheme 2

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Rates, Equilibria & Further Organic Chemistry
Sub Topic	Equilibria
Booklet	Mark Scheme 2

Time Allowed: **66 minutes**

Score: **/55**

Percentage: **/100**

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

Question Number	Acceptable Answers	Reject	Mark
1(a) (i)	**1st mark: Identification of buffer** Any mention of buffer solution / buffering (region) **(1)** **2nd mark: Identification of species responsible for buffering action** ammonia/NH_3 **and** ammonium ions /NH_4^+ present (in significant concentrations) **OR** ammonia/NH_3 **and** ammonium chloride /NH_4Cl present (in significant concentrations) **OR** weak base **and** salt/conjugate acid present (in significant concentrations) **OR** B **and** BH^+ present (in significant concentrations) **Can be awarded from a correct equation** **(1)** **3rd mark: For mention of how this buffer works on addition of small amounts of H^+ ions** (relatively large concentration/reservoir of) ammonia molecules react with added hydrogen ions/ H^+ /(hydrochloric) acid **OR** (relatively large concentration /reservoir of weak) base reacts with added hydrogen ions / H^+ /(hydrochloric) acid **OR** $H^+ + NH_3 \rightarrow NH_4^+$ **Allow** reversible arrow **OR** Adding (hydrochloric) acid/H^+ /hydrogen ions has negligible effect on ratio $[NH_3]:[NH_4^+]$ **(1)** **Ignore** references to buffering action on addition of OH^- (not relevant here) **Ignore** general descriptions of buffer solution eg resists change in pH when small amounts of acid or alkali added	Acidic buffer Weak acid and its conjugate base HA and A^-	**3**

Question Number	Acceptable Answers	Mark
1(a) (ii)	**Note** – the equations $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$ score **all three marks** **Note** –the equation $NH_4^+ \rightarrow NH_3 + H^+$ scores 2 marks, but if (aq) state symbols are given, scores 3 marks **1st mark:** Ammonium ions /NH_4^+ present (at equivalence point) **OR** ammonium chloride/ammonium salt **(1)** **2nd mark** Ammonium (ions) / NH_4^+ react with water /hydrolysed by water /dissociate in water **Ignore** ammonium chloride reacts with water **(1)** **3rd mark** $NH_4^+ \rightarrow NH_3 + H^+$ **OR** $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ **Allow** $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$ **(1)** **Note if no other mark awarded** Just 'strong acid – weak base (titration)' / ammonium chloride is the salt of a strong acid and a weak base scores **(1)** only	**3**

Question Number	Acceptable Answers	Mark
1(a) (iii)	**If final answer is 1.6(2), with correct working or without working, award 4 marks** Mol of ammonia used = (25/1000 x 0.024) = $6x10^{-4}$ mol **and** Mol of acid added = (40/1000 x 0.054) = $2.16x10^{-3}$ **(1)** Mol of excess acid = $2.16x10^{-3} - 6x10^{-4}$ = $1.56x10^{-3}$ mol **(1)** $[H^+] = 1.56x10^{-3}/(65/1000) = 0.024$ mol dm^{-3} **(1)** $pH = -\log [H^+] = 1.6(2)$ **(1)** **Ignore** SF except 1 SF **Allow** TE for 2nd, 3rd marks **Allow** TE for 4th mark provided pH is less than 7 and it is based on some use of data in question **Alternative method for 1st and 2nd marks** Mol of ammonia used = (25/1000 x 0.024) = $6x10^{-4}$ mol **and** Volume of acid used = $\frac{6x10^{-4} \times 1000}{0.054}$ = 11.111 cm^3 **(1)** Volume of acid left = 40 – 11.111 = 28.889 cm^3 Mol of excess acid = $\frac{28.889 \times 0.054}{1000}$ = $1.56x10^{-3}$ mol **(1)**	**4**

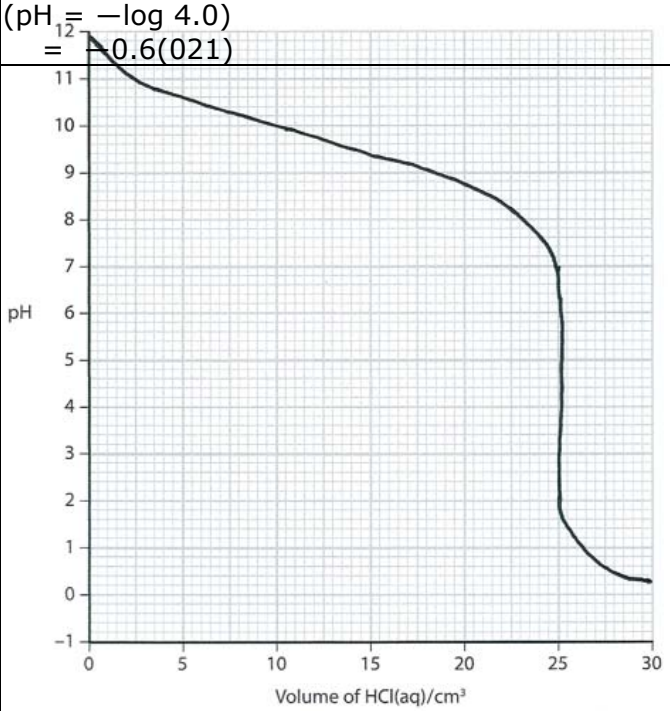
Question Number	Acceptable Answers	Reject	Mark
1(b)(i)	**ITHER** $[H^+]^2 = 5.5x10^{-13}$ or $[H^+] = \sqrt{5.5x10^{-13}}$ / $7.416x10^{-7}$ (mol dm^{-3}) **(1)** $pH = -\log\sqrt{5.5x10^{-13}}$ (= 6.12982 / 6.13) **(1)** **OR** $pK_w = 12.26$ **(1)** $pH = ½ pK_w$ (= 6.130) **(1)**	6.13 with no working	**2**

Question Number	Acceptable Answers	Reject	Mark
1(b) (ii)	Neutral **(1)** $[H^+]$ = $[OH^-]$ /equal amounts of H^+ and OH^- ions **OR** **Both** $[H^+]$and $[OH^-]$ have increased by the same amount **(1)**	Acidic or alkaline for both marks	**2**

Total for Question 1 = 14 marks

Question Number	Acceptable Answers	Reject	Mark
2(a)(i)	**IGNORE** sf except 1 **If answer is 8.485 x 10^{-3}** ($moldm^{-3}$), **award 2 marks** If not, $[OH^-(aq)] = \sqrt{(K_b\ [NH_3])}$ $= \sqrt{(1.8 \times 10^{-5} \times 4.0)}$ **(1)** $= 8.485 \times 10^{-3}$ ($mol\ dm^{-3}$) **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
2(a)(ii)	**IGNORE** sf except 1 **If answer is 11.9(3)/12, award 2 marks** If not, **EITHER – Method 1** $[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$ $= \frac{1 \times 10^{-14}}{8.485 \times 10^{-3}}$ **(1)** $= 1.179 \times 10^{-12}$ **ALLOW** ecf from their answer to (i) $pH = -\log 1.179 \times 10^{-12} = 11.9(3)$ **ALLOW** ecf from their answer for $[H^+]$ **(1)** **OR – Method 2** $pOH = -\log 8.485 \times 10^{-3} = 2.07$ **ALLOW** ecf from their answer to (i) **(1)** pH = (14 – 2.07 =) 11.9(3) **ALLOW** ecf from their answer to pOH **(1)**		**2**

Question No	Acceptable Answers	Mark
2(b)(i)	(pH = −log 4.0) = −0.6(021)	**1**
	 **First mark** graph starting at 11.9/ answer to a(ii), ± 1 small square, provided above 7 **(1)** **Second mark** buffering region to **25** cm^3 **ALLOW** any line showing a decrease in pH from 0 to 25 cm^3 of HCl added **(1)** **Third mark** straight **vertical** portion between 8 and 1, midpoint below 7 and between 2 and 7 pH units long **(1)** **Fourth mark** finishing at +0.5 to −0.8, with at least 27.5 cm^3 of HCl added **ALLOW** final pH as answer to (b)(i), within 1 pH unit, if pH is less than answer to (b)(i) or within 1 small square if pH is more than answer to (b)(i) **(1)** **ALLOW** If graph is drawn with aqueous ammonia added to hydrochloric acid, only the second and third marks are available for the correct vertical portion at 25cm^3	**4**

Question Number	Acceptable Answers	Reject	Mark
2(b)*(iii)	**First mark** any indicator from 4 to 10 or 12, 13 in the Data booklet – see end **ALLOW** ecf from the vertical portion on their graph **(1)** **Second mark** alkaline to acidic colour change for their stated indicator **ALLOW** acidic to alkaline colour change if their curve shows alkali added to acid **(1)** **Third mark** pH range (of indicator) is within the vertical section of the graph **OR** p*K*in (± 1) is in the vertical section of the graph **OR** p*K*in is nearest to the pH at the end/ equivalence point **ALLOW** indicator will change colour in the vertical section of the graph **ALLOW** Indicator will change colour at the end/ equivalence point **ALLOW** (because it is a) titration of a strong acid with a weak base **(1)**	universal indicator loses all 3 marks litmus loses first mark only	**3**

Question Number	Acceptable Answers	Mark
2(c)(i)	**IGNORE** sf except 1 **If answer is 3.84** (mol dm^{-3}), **award 3 marks** If not, number of moles of acid = $\frac{24.0 \times 4}{1000} = 0.096$ **(1)** **EITHER** number of moles ammonia = 0.096 **in 25 cm^3** **(1)** concentration of ammonia $= \frac{0.096 \times 1000}{25}$ = 3.84 (mol dm^{-3}) **(1)** **OR** number of moles ammonia = 0.288 **in 75 cm^3** **(1)** concentration of ammonia $= \frac{0.288 \times 1000}{75}$ = 3.84 (mol dm^{-3}) **(1)** **IGNORE** unit unless incorrect **ALLOW** ecf in both methods on their number of moles of ammonia	**3**

Question Number	Acceptable Answers	Mark
2(c)(ii)	**IGNORE** sf except 1 (concentration of ammonia in trichloromethane =) 0.16 (mol dm^{-3}) **ALLOW** ecf from their answer to (c)(i), provided it is less than 4.0 and given to 2 or more sf	**1**

Question Number	Acceptable Answers	Reject	Mark
2(c)(iii)	**Expression for *K*c and answer needed for the mark** $K_c = \frac{[NH_3(aq)]}{[NH_3(CHCl_3)]}$ **ALLOW** one state symbol missing $= \frac{3.84}{0.16}$ = 24(.0) **IGNORE** sf, including 1 sf, and units **ALLOW** ecf from answers to (c)(i) and (c)(ii)	K_c expressions without both state symbols	**1**

Question Number	Acceptable Answers	Reject	Mark
2(c)(iv)	(ammonia/ it is much more soluble in water) as can form **hydrogen bonds with water** **ALLOW** more/ stronger hydrogen bonds with water (than with trichloromethane) **IGNORE** answers based on polarity/ hydrophilic		**1**

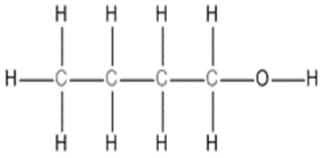
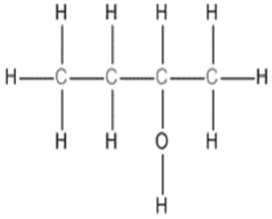
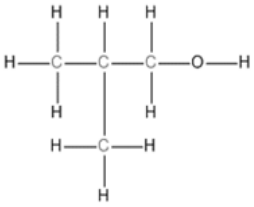
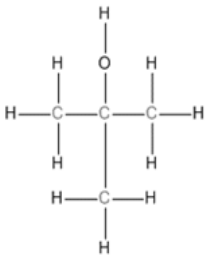
Total for Question 2 = 18 marks

Question Number	Acceptable Answers	Mark
3(a)(i)	(K_c =) $\frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$ **ALLOW** C_2H_5OH for ethanol **ALLOW** CH_3CO_2H for ethanoic acid **ALLOW** $CH_3CO_2CH_2CH_3$ / $CH_3CO_2C_2H_5$ /$CH_3COOC_2H_5$ for ethyl ethanoate **IGNORE** state symbols, even if incorrect	**(1)**

Question Number	Acceptable Answers	Mark
3(a)(ii)	**Stand alone marks** the enthalpy change is (very) small/close to zero **OR** reaction is slightly exothermic **(1)** therefore, (the magnitude of) $\Delta S_{surroundings}$ (= $-\Delta H/T$) **changes very little** **(1)** **IGNORE** $\Delta S_{surroundings}$ is positive/small/less/decreases ΔS_{total} / K_c changes very little (provided there is no change of state) **(1)** Ignore references to ΔS_{system}	**(3)**

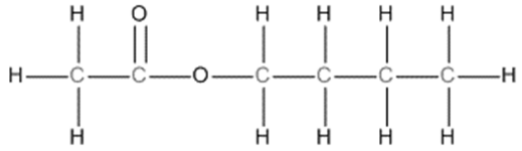
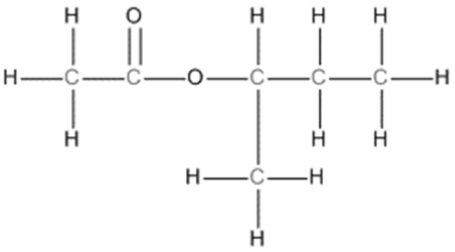
Question Number	Acceptable Answers	Reject	Mark
3(a)*(iii)	**If final answer is 5.1143/5.1, award 6 marks** If not, award marks as follows **Marks 1 and 2** If mol CH_3COOH left = 0.040 **(2)** Otherwise: mol NaOH/total mol of acid = 45.0 x 1.00/1000 = 0.045 **(1)** mol CH_3COOH left = mol NaOH/total mol of acid – 0.005 **(1)** **Marks 3 to 6** mol CH_3CH_2OH at eqm = 0.140 **(1)** mol $CH_3COOCH_2CH_3$ at eqm = 0.080 **(1)** mol H_2O at eqm = 0.358 **(1)** $K_c = \frac{0.080}{V} \times \frac{0.358}{V} \div \frac{0.040}{V} \times \frac{0.140}{V}$ $= 5.1143$ **(1)** **consequential** on their expression for K_c shown/used here and their numbers of moles **ALLOW** K_c expression without the Vs but **do not allow** this sixth mark if the moles are divided by a specific volume e.g. 45 to calculate the concentration **IGNORE** SF except 1 SF in final answer	any units	**(6)**

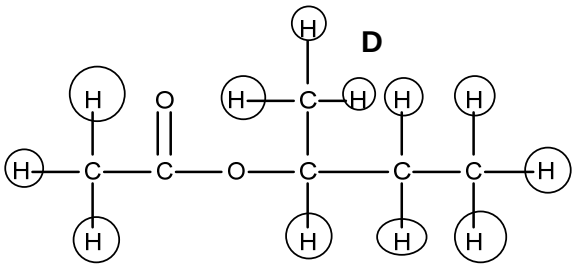
Question Number	Acceptable Answers	Mark
3(b)(i)	**EITHER** C : H : O mol $\frac{64.9}{12}$: $\frac{13.5}{1}$: $\frac{21.6}{16}$ = 5.408 : 13.5 : 1.35 **(1)** **=** 4.006 : 10 : 1 = 4 : 10 : 1 use of 74 to show molecular formula is $C_4H_{10}O$ eg M_r is (4x12)+(10x1)+16 =74 **(1)** **OR** C atoms = $\frac{64.9 \times 74}{100 \times 12} = 4$ H atoms = $\frac{13.5 \times 74}{100 \times 1} = 10$ O atoms = $\frac{21.6 \times 74}{100 \times 16} = 1$ This may be done in 2 steps eg C $\frac{64.9 \times 74}{100} = 48$ $\frac{48}{12} = 4$ All 3 correct scores **2** Any 2 correct scores **1** **OR** % C = $\frac{48 \times 100}{74} = 64.9$ % H = $\frac{10 \times 100}{74} = 13.5$ % O = $\frac{16 \times 100}{74} = 21.6$ All 3 correct scores **(2)** Any 2 correct scores **(1)**	**(2)**

Question Number	Acceptable Answers	Reject	Mark
3(b)(ii)	    Alcohols can be in any order **ALLOW** OH All **FOUR** correct scores **(2)** Two or three correct scores **(1)** **ALLOW all four** skeletal/structural/mixture of displayed and structural **(1)** **IGNORE** optical isomers of butan-2-ol	molecular formula OH-C.. on left of structure once only more than 1 H missing from a bond	**(2)**

Question Number	Acceptable Answers	Mark
3(b)(iii)	$CH_3C^+HOH/[CH_3CHOH]^+$ **ALLOW** $CH_3CHOH^+/^+CH_3CHOH$ **(1)** $^+CH_2CH_2OH/[CH_2CH_2OH]^+$ **ALLOW** $CH_2CH_2OH^+/C_2H_4OH^+$ **(1)** Only penalise missing + once. **Note:** If no structures given, allow 1 mark for $C_2H_5O^+$ but do not award the mark if $C_3H_9^+$ is given as well	**(2)**

Question Number	Acceptable Answers	Mark
3(b)(iv)	butan-1-ol and butan-2-ol **OR** structures **OR** identified by number from (b)(ii)	**(1)**

Question Number	Acceptable Answers	Reject	Mark
3(b)(v)	  **ALLOW** any unambiguous structures e.g. displayed, structural, skeletal or a combination of these, TE from (b)(iv)	C_4H_9 structures with more than 1 H missing from a bond	**(1)**

Question Number	Acceptable Answers	Mark
3(b)(vi)	No structure is given or an ester formed from a different alcohol eg propanol scores **(0)** **First mark - structure** **Correct structure** **(1)**  **B** **A** **C** **E** Protons can be labelled or circled and labelled **ALLOW** any unambiguous structure eg displayed, structural, skeletal or a combination of these. **Five peaks correct scores (2)** **Three or four peaks correct scores (1)** **Splitting** **Any two correct scores (2)** **No** splitting for peak B as there is no H attached to the adjacent carbon **OR** application of the (n+1) rule to peak **A** (which is a multiplet/sextet) **OR** application of the (n+1) rule to peak **C** (which is a multiplet/quintet) **OR** application of the (n+1) rule to peak **D** (which is a doublet) **OR** application of the (n+1) rule to peak **E** (which is a triplet) If ester has been formed from butan-1-ol, maximum 2 marks for identification of peaks **B**, **C** and **E** **and** 2 marks for correct splitting in any two of peaks **B**, **C** and **E** If ester has been formed from either of the other 2 alcohols, 1 ark for identification of peak **B**, 1 mark for explaining why there is no splitting in peak **B**	**(5)**

(Total for Question 3 = 23 marks)