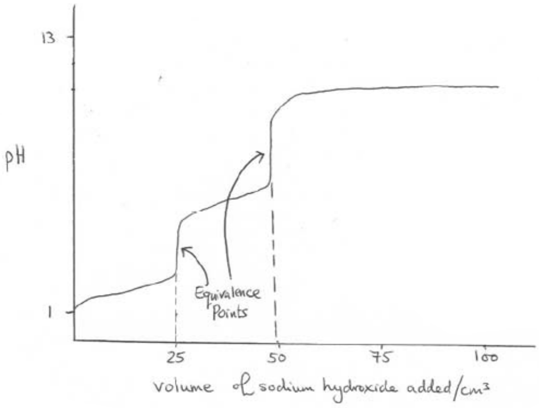
Question Number	Acceptable Answers	Reject	Mark
1(a)	(K_{a1} =) $\frac{[H_3O^+(aq)]\ [HS^-(aq)]}{[H_2S(aq)]}$ **(1)** (K_{a2} =) $\frac{[H_3O^+(aq)][\ S^{2-}(aq)]}{[HS^-(aq)]}$ Allow $H^+(aq)$ for $H_3O^+(aq)$ Ignore missing / incorrect state symbols **(1)**	$[H_3O^+]^2$ numerator $[H_3O^+]^2$ numerator	**(2)**

Question Number	Acceptable Answers	Reject	Mark
1(b)(i)	(H_2S + H_2O ⇌ H_3O^+ + HS^- Initially 0.100 0 0 At eqm 0.100 x x K_{a1} = $\frac{x^2}{0.100}$) **M1:** x^2 = 8.91 x 10^{-9} ($mol^2\ dm^{-6}$) **(1)** **M2:** (x = 9.4393 x 10^{-5}) $[HS^-]$ = 9.44 x 10^{-5} / 0.0000944 (mol dm^{-3}) For M2, answer must be to 3 sf **(1)** Correct answer without working scores (2)		**(2)**

Question Number	Acceptable Answers	Reject	Mark
1(b)(ii)	($[H^+]$ = ($\sqrt{8.91}$ x 10^{-9} =) 9.439 x 10^{-5}(mol dm^{-3})) pH = (-log 9.439 x 10^{-5}) = 4.0251/4.025 /4.03/4.0 TE on answer to (b)(i) provided pH <7	4/4.02	**(1)**

Question Number	Acceptable Answers	Reject	Mark
***1(b)(iii)**	**Any THREE from:** **Assumption 1** $[H_2S]_{equilibrium} = [H_2S]_{initial}$ OR The dissociation of H_2S is negligible OR 0.0000944 is **very** small compared to the initial concentration of H_2S/ 0.100 (hence a valid assumption) **Assumption 2** $[H_3O^+] = [HS^-]$ / $[H^+] = [HS^-]$ OR Ignore any H^+ from (the dissociation of) water / H^+ only from H_2S **Assumption 3** Ignored ionization of HS^- / HS^- doesn't (significantly) dissociate further OR K_{a2} very much smaller than K_{a1} **Assumption 4** Measurements at 298 K / standard **temperature** IGNORE References to the concentration of water References **just** to "standard conditions"		**(3)**

Question Number	Acceptable Answers	Reject	Mark
1(c)(i)	**M1:** General shape of an acid-base curve with the pH increasing and either one or two steep / vertical sections shown **NOTE** Penalise a pH range for a single vertical with a range of eight or more pH units (as this is the typical range for a strong monobasic acid with a strong base titration curve) **(1)** **M2:** Vertical / steep section at 25 cm^3 **(1)** **M3:** Vertical / steep section at 50 cm^3 **(1)** **M4:** Either equivalence point labelled anywhere on vertical section or x-axis **(1)** **M5:** Initial pH = 1.5 **and** a **recognisable** ‘plateau’ in the pH range of 12 to 13 **(1)** 		**(5)**

Question Number	Acceptable Answers	Reject	Mark
1(c)(ii)	The **pH** when 12.5 cm^3 of NaOH has been added OR the **pH** at “half-equivalence” (for the first equivalence point) **ALLOW** “**pH** at half neutralisation” Allow TE from an incorrect graph		**(1)**

Question Number	Acceptable Answers	Reject	Mark
2(a)(i)	$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$ (or →) ALLOW $H_2O(aq)$ Equation **(1)** states **(1)** ALLOW for 1 mark $HC_2O_4^-(aq) \rightleftharpoons C_2O_4^{2-}(aq) + H^+(aq)$ States mark is not stand alone but can be awarded if the equation has a minor error e.g. an incorrect charge		**2**

Question Number	Acceptable Answers	Reject	Mark
2(a)(ii)	$K_a = [C_2O_4^{2-}]\,[H_3O^+] / [HC_2O_4^-]$ OR $K_a = [C_2O_4^{2-}]\,[H^+] / [HC_2O_4^-]$ No TE on incorrect equation in (a)(i) Penalise incorrect charges in (i) and (ii) once only	$K_a =$ $[H^+]^2 / [HC_2O_4^-]$ $[H^+][A^-]/[HA]$	**1**

Question Number	Acceptable Answers	Reject	Mark
2 (a) (i	No TE on (a)(ii) $K_a = 10^{-4.28}$ OR 5.24807×10^{-5} (mol dm^{-3}) **(1)** $K_a = [H^+]^2 / [HC_2O_4^-]$ $K_a = [H^+]^2 / 0.050$ $[H^+] = \surd(0.05 \times 10^{-4.28}) = 1.61988 \times 10^{-3}$ (mol dm^{-3}) **(1)** TE on incorrect K_a value pH = −log 1.61988×10^{-3} = 2.7905 = 2.8 **(1)** For final mark TE on algebraic / arithmetical errors providing pH ≥ 1.3 Correct answer with no working scores 3 Ignore SF except 1 SF		**3**

Question Number	Acceptable Answers	Reject	Mark
2(b)(i)	IGNORE explanations **First mark:** $HC_2O_4^-$/hydrogenethanedioate ion ionization negligible ALLOW Acid for $HC_2O_4^-$ Slight / partial / incomplete / does not dissociate for negligible OR $[HC_2O_4^-]_{equilibrium} = [HC_2O_4^-]_{initial}$ / 0.050 (mol dm^{-3}) **(1)** **Second mark:** $[H^+]$ due to ionization of water negligible OR auto ionization of water negligible OR $[H^+]$ only due to ionization of $HC_2O_4^-$/acid OR $[C_2O_4^{2-}] = [H^+]$ **(1)** IGNORE references to temperature and to HA and A^- Penalize omission of [] in discussion once only	Use of $NaHC_2O_4$ for $HC_2O_4^-$ OR sodium hydrogen-ethanedioate for hydrogen-ethanedioate ion throughout this item	**2**

Question Number	Acceptable Answers	Reject	Mark
2(b)(ii)	Ethanedioic acid is a (much) stronger acid (than hydrogenethanedioate ion / sodium hydrogenethanedioate) OR Ethanedioic acid has a (much) smaller pK_a (than hydrogenethanedioate) OR Ionization / dissociation of ethanedioic acid is (much) greater (than hydrogenethanedioate) OR Reverse arguments **(1)** IGNORE $NaHC_2O_4$ ionization negligible Approximation of negligible ionization invalid / incorrect OR $[H_2C_2O_4]_{equilibrium}$ not equal to $[H_2C_2O_4]_{initial}$ **(1)** No TE on 18(a)(iii) IGNORE Second ionization occurs	Ethanedioic acid is a strong acid / fully dissociated Just ‘approximation invalid’	**2**

Question Number	Acceptable Answers	Reject	Mark
2(c)(i)	Start pH at 2.8 ALLOW 2—4 **(1)** Vertical section at 25 cm^3 within pH range 6-11 and 2.5-4 units long **(1)** end pH (approaching) value in range 12-13 (asymptotically) **(1)**	deviation from vertical maximum before final pH	**3**

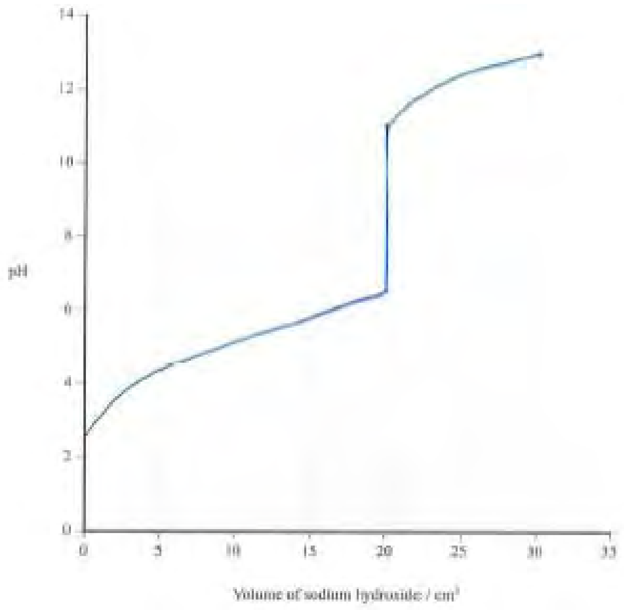
Question Number	Acceptable Answers	Reject	Mark
2(c)(ii)	**F mark:** Methyl yellow range = 2.9—4 and the phenolphthalein range = 8.2—10 ALLOW pK_{in} (methyl yellow) = 3.5 and pK_{in} (phenolphthalein) = 9.3 **(1)** **Second mark:** (The volumes are different) because ethanedioic acid is dibasic / diprotic / has two **replaceable / acidic** hydrogen atoms ALLOW dicarboxylic (acid) (therefore there are two stages to the neutralization) OR Methyl yellow range coincides with neutralization of first proton and phenolphthalein range coincides with neutralization of second proton **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
3 (a)(i)	*K*a = $[CH_3CO_2^-]$ $[H^+]/[CH_3CO_2H]$ OR *K*a = $[CH_3CO_2^-]$ $[H_3O^+]/[CH_3CO_2H]$ OR Use of $[CH_3COO^-]$ instead of $[CH_3CO_2^-]$ and $[CH_3COOH]$ instead of $[CH_3CO_2H]$ IGNORE state symbols even if wrong	Numerator as $[H^+]^2$ Expressions in terms of HA alone Round/curved brackets ‘()’ Any other carboxylic acid	**1**

Question Number	Acceptable Answers	Reject	Mark
3(a)(ii)	$1.7 \times 10^{-5} = [H^+]^2 / 0.5$ $[H^+] = \sqrt{1.7 \times 10^{-5} \times 0.5} / 2.915(476) \times 10^{-3}$ **(1)** pH = $(-\log[H^+])$ = 2.53529 OR = 2.54 OR = 2.5 **(1)** ALLOW TE for second mark from any hydrogen ion concentration as long as pH less than 7 Correct answer alone scores **(2)** ALLOW pH = 2.53 if $[H^+]$ is rounded to 2.92×10^{-3} IGNORE sf except 1	4.77 or 4.8 from using pH = -log Ka loses both marks	**2**

Question Number	Acceptable Answers	Reject	Mark
3(a)(iii)	20 (cm^3) IGNORE units OR 0.02 dm^3		**1**

Question Number	Acceptable Answers	Reject	Mark
3(a)(iv)	Moles of excess NaOH = 10/1000 x 0.50 = 5 x 10^{-3} **(1)** So [NaOH/OH^-] = 5 x 10^{-3} x 1000/50 = 0.10 mol dm^{-3} **(1)** EITHER Kw route: [H^+] x 0.1 = 1 x 10^{-14} **(1)** So pH = - log 1 x 10^{-14} / 0.1 = 13 **(1)** OR pOH route: pOH = 1 **(1)** So pH = (14 – 1) = 13 **(1)** ALLOW TE throughout Correct final answer scores **(4)**		**4**

Question Number	Acceptable Answers	Reject	Mark
3(a)(v)	Starting at pH 2-3 AND finishing at pH between 12 and 13.7 inclusive **(1)** Vertical section at 20 cm^3 **(1)** S-shaped curve, with gradual rise and vertical section within the pH range 5.5 and 11.5 and of 3 to 5 units in length **(1)** These are stand alone marks 		**3**

Question Number	Acceptable Answers	Reject	Mark
3(b)(i)	EITHER [base] = Ka [acid]/[H$^+$] Or [H+] = (10$^{-pH4.70}$) = 1.995 x 10^{-5} **(1)** [base] = 1.7 x 10^{-5} x 1/(1.995 x 10^{-5}) = 0.852 **(1)** moles base = 0.852 x 0.5 = 0.426 (mol) **(1)** mass base = 0.426 x 82 = 34.9 g **(1)** IGNORE sf except 1 Correct answer, with or without working **(4)** OR pH = p*K*a – log[acid]/[base] 4.70 = 4.8 – log [1/[base]] Log[1/[base]] = 0.1 **(1)** [base] = 0.794(328) (mol dm^{-3}) **(1)** So in 500 cm^3 Moles = 0.794 x 0.5 = 0.397 mol **(1)** Mass = 0.397 x 82 = 32.554/32.6 g **(1)** (ALLOW using p*K*a = 4.77)		**4**

Question Number	Acceptable Answers	Reject	Mark
3(b)(ii)	**First mark** Buffer has large amount/ excess/ reservoir of CH_3COOH (and CH_3COO^-) **(1)** **Second mark** OH^- ions added react with CH_3COOH OR $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$ OR $OH^- + H^+ \rightarrow H_2O$ **and** $CH_3COOH \rightarrow CH_3COO^-$ $+ \quad ^+$ OR Equations described in words **(1)** **Third mark** Ratio / values of $[CH_3COOH]$ to $[CH_3COO^-]$ remains (almost) unchanged **(1)** IGNORE concentration of hydrogen ions remains constant ALLOW answers in terms of HA and A^-		**3**

Question Number	Acceptable Answers	Reject	Mark
4 (a)	K_a = ($10^{-10.64}$) = **2.3×10^{-11}** / 2.2909×10^{-11} (mol dm^{-3}) Ignore sf except 1		**1**

Question Number	Acceptable Answers	Reject	Mark
4 (b)(i)	$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$ OR written as HCO_2^- and HCO_2H OR with H_3O^+ instead of H^+ Allow $K_a = \frac{[A^-][H^+]}{[HA]}$ if formula of HA and A^- given as HCOOH and $HCOO^-$	$K_a = \frac{[H^+]^2}{[HCOOH]}$ without also giving full expression	**1**

Question Number	Acceptable Answers	Reject	Mark
4 (b)(ii)	$1.6 \times 10^{-4} = \frac{[H^+]^2}{0.50}$ **(1)** $[H^+] = \sqrt{1.6 \times 10^{-4} \times 0.5}$ **(1)** (= $\sqrt{8 \times 10^{-5}}$ = 8.94×10^{-3}) pH = (2.048455) **= 2.05 / 2.0 (1)** Correct answer with no working **(3)** TE for third mark if $[H^+]$ calculated incorrectly No TE from incorrect K_a expression Ignore sf except 1	pH =2 pH =2.1	**3**

Question Number	Acceptable Answers	Reject	Mark
4 (b)(iii)	All H^+ comes from acid / none from water / $[H^+] = [HCOO^-]$ OR $[H^+] = [A^-]$ OR Dissociation of acid is negligible / very small OR $[HA]_{initial} = [HA]_{equilibrium}$	K_a is measured at 298K Just “dissociation of acid is partial”	**1**

Question Number	Acceptable Answers	Reject	Mark
4 (c)(i)	HCOOH $CH_3COOH_2^+$ both correct **(1)**		**1**

Question Number	Acceptable Answers	Reject	Mark
4 (c)(ii)	$(HIO + CH_3COOH \rightleftharpoons)\ H_2IO^+ + CH_3COO^-$ / $(HIO + CH_3COOH \rightleftharpoons)\ HIOH^+ + CH_3COO^-$ Ignore position of positive charges		**1**

Question Number	Acceptable Answers	Reject	Mark
4 (d)	(pH = 4.9) so $[H^+]$ = (1.2589254 x 10^{-5}) =**1.259 x 10^{-5} (1)** ($\frac{K_a}{[H^+]} = \frac{[HCOO^-]}{[HCOOH]}$ = $\frac{1.6 \times 10^{-4}}{1.259 \times 10^{-5}}$) **= 12.7 (:1) / 13(:1) ($HCOO^-$ per HCOOH or base:acid)** (12.709252 from unrounded $[H^+]$ 12.708499 from $[H^+]$ rounded to 1.259 x10^{-5} 12.3 from $[H^+]$ rounded to 1.3 x10^{-5}) TE from error in **$[H^+]$** **Allow 800:63** **(1)** **Correct answer scores 2** Accept (0.0786828) = **0.079 HCOOH per $HCOO^-$ for acid:base ratio** (0.0786874) = 0.079 from rounded pH **OR** $pK_a = -\log K_a = 3.79$ $3.79 = 4.9 - \log \frac{[base]}{[acid]}$ (1) $\log \frac{[base]}{[acid]} = 1.11$ $\frac{[base]}{[acid]}$ = (12.882496) = **12.9 (:1) (1)** **Correct answer scores 2** Accept **0.0776 / 0.078 HCOOH per $HCOO^-$ for acid:base ratio** (0.0776247) TE from error in pK_a Ignore sf except 1		**2**