25. Equilibria

25.1 Acids and bases

Paper 4

Marking Scheme

Q1.

(b)	**M1** $[H^+] = 10^{-12.2}$ **OR** 6.31×10^{-13} **M2** $[OH^-] = 0.0158$ mol dm^{-3} ecf **M3** $[Ba(OH)_2] = 0.01585 \div 2 = 7.92$ ecf **M4** mol of $Ba(OH)_2 = 0.00792 \div 4 = 1.98 \times 10^{-3}$ mass $Ba(OH)_2 = 0.339$ g ecf	**4**
(c)(i)	$K_{sp} = [Fe^{2+}][OH^-]^2$	**1**
(c)(ii)	**M1** $K_{sp} = 4 \times (5.85 \times 10^{-6})^3 = 8.01 \times 10^{-16}$ **M2** mol^3 dm^{-9}	**2**

Q2.

(f)	**M1** $HC_2O_4^- + H^+ \rightarrow H_2C_2O_4$ **M2** $HC_2O_4^- + OH^- \rightarrow C_2O_4^{2-} + H_2O$	**2**

Q3.

(a)(i)	species / molecules / pair that differ (by the presence or absence) of a H^+ ion / proton	**1**
(a)(ii)	$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$	**1**
(b)(i)	$K_a = \dfrac{[H^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$	**1**

(b)(ii)	**M1** $K_a = 10^{-4.82} = 1.51 \times 10^{-5}$ **OR** $[H^+] = 10^{-3.25} = 5.62 \times 10^{-4}$ **M2** $[HA] = (10^{-3.25})^2 \div 1.51 \times 10^{-5} = 0.021 / 0.0209 / 0.02089$ (mol dm^{-3}) ecf min 2sf	**2**
(c)(i)	**M1** a solution that resists / opposes / minimises changes in pH **M2** when small amounts of acid / H^+ and base / alkali / OH^- are added to it	**2**
(c)(ii)	Method 1 **M1** $[H^+] = 10^{-5.70}$ **OR** 2.00×10^{-6} **OR** 1.99526×10^{-6} **M2** moles $CH_3COONa = 0.400 \times 0.125 = 5.00 \times 10^{-2}$ moles $CH_3COOH_{eqm} = (5.00 \times 10^{-2} \times 2.00 \times 10^{-6}) \div 1.78 \times 10^{-5}$ **OR** 5.60×10^{-3} **M3** $[CH_3COOH]_{initial} = 5.60 \times 10^{-3} \times 1000 / 600$ $[CH_3COOH]_{initial} = 0.00933–0.00936$ (mol dm^{-3}) ecf min 2sf Method 2 **M1** $pK_a = -\log(1.78 \times 10^{-5})$ **OR** 4.75 **M2** $pH = pK_a + \log[B^-] / [HA]$ $5.7 = 4.75 + \log(0.05 / (0.6x))$ $0.95 = \log(0.05 / (0.6x))$ **M3** $10^{0.95} = (0.05 / (0.6x))$ $5.348x = 0.05$ x = 0.00935-0.00937 (mol dm^{-3}) ecf min 2sf	**3**

Q4.

(a)(i)	$[H^+] = 10^{-12.35}$ **OR** $[H^+] = 4.47 \times 10^{-13}$ $K_w / 4.47 \times 10^{-13}$ **OR** pOH = 1.65 $[OH^-] = 10^{-1.65}$	[1] [1] [1] [1]	2
(a)(ii)	$K_{sp} = (0.0112)(0.0224)^2$ **OR** $K_{sp} = [Ca^{2+}][OH^-]^2$ answer 5.62×10^{-6} $mol^3\,dm^{-9}$	[1] [1] [1]	3
(a)(iii)	white solid / white ppt **AND** pH between 7.01 and 12.34 common ion effect hydroxide removed by precipitation **OR** ppt is $Ca(OH)_2$	[1] [1] [1]	3
(a)(iv)	lattice energy and hydration energy greater for $CaSO_4$ **OR** lattice energy and hydration energy decrease down group hydration energy decreases more / is dominant factor enthalpy of solution is more endothermic for $BaSO_4$ **OR** is more endothermic down grp	 [1] [1] [1]	3
(b)(i)	$Ca + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2$	[1]	1
(b)(ii)	Pair 1: CH_3COOH and CH_3COO^- Pair 2: H_3O^+ and H_2O **OR** H_2O and OH^-	[1] [1]	2
(b)(iii)	$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	[1]	1
(b)(iv)	$[CH_3COO^-] = 0.788$, $[CH_3COOH] = 0.270$ $[H^+] = 5.96 \times 10^{-6}$ pH = 5.22	 [1] [1]	2
(b)(v)	$CH_3COO^- + H^+ \rightarrow CH_3COOH$ **OR** $Ca(CH_3COO)_2 + 2H^+ \rightarrow 2CH_3COOH + Ca^{2+}$ $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$	 [1] [1]	2

Q5.

(e)(i)	$pK_a = -\log K_a$ **AND** $pH = -\log [H^+]$	1
(e)(ii)	**M1** $[H^+] = \sqrt{0.120 \times 2.00 \times 10^{-4}} = 4.89(317) \times 10^{-3}$ **M2** pH = 2.31	2
(e)(iii)	% ionisation = $4.89 \times 10^{-3}/0.12 \times 100 = 4.1\%$	1

Q6.

(b)(i)	**M1** resists change in pH **M2** when a **small** amount of acid or alkali is added	2
(b)(ii)	**M1** $H_2NCH(CH_3)COOH + H^+ \rightarrow H_3N^+CH(CH_3)COOH$ **M2** $H_2NCH(CH_3)COOH + OH^- \rightarrow H_2NCH(CH_3)COO^- + H_2O$	2

Q7.

(e)(i)	(K_{sp} =) $[Ag^+]^2[SO_3^{2-}]$ [1]	1
(e)(ii)	x = $\sqrt[3]{1.5 \times 10^{-14}/4}$ = 1.55×10^{-5} (mol dm^{-3}) $[Ag^+]$ = $1.55 \times 10^{-5} \times 2$ = 3.11×10^{-5} (mol dm^{-3}) min 2sf ecf (e)(i)	1

Q8.

(a)	(K_w =)[H+][OH–] OR (K_w =)[H3O+][OH–] [1]	1
(b)(i)	M1: pH values 1.5 AND 12.5 [1] M2: conc of HC*l* = 10–1.5 = 0.0316 ecf [1] min 2sf	2
(b)(ii)	sodium chloride / NaC*l* AND 7 [1]	1
(b)(iii)	(mixture Y) 1 to 3 AND (mixture Z) 11 to 13 [1]	1
(c)(i)	H_2SO_4 > CH_3CCl_2COOH > CH_3CH_2COOH [1] u / c explanation • H_2SO_4 is fully dissociated / strong acid • CH_3CH_2COOH / CH_3CCl_2COOH are partly dissociated / weak acids • C*l* / chlorine is electron-withdrawing / electronegative • alkyl group (in CH3CH2COOH) is electron donating • stabilises / destabilises anion OR weakens / strengthens O-H bond (linked correctly) • correct reference to release of / donation of / form H+ / proton any two [1] any four [2]	3
(c)(ii)	• H_3O+ and H_2O • H_2SO_4 and HSO_4^- • HSO_4^- and SO_4^{2-} any one correct pair [1] all three correct pairs [2]	2

Q9.

(a)	resists pH change when small amount of acid or alkali is added [1]	1
(b)(i)	C_6H_5COOH + NaOH → $C_6H_5COO^-Na^+$ + H_2O [1]	1
(b)(ii)	$C_6H_5COO^-Na^+$ + HNO_3 → C_6H_5COOH + $NaNO_3$ [1]	1
(c)	$[H^+]$ = 7.08×10^{-5} [1] $[C_6H_5COOH]$ = 8.20×10^{-3} [1] $[C_6H_5COO^-Na^+]$ = 7.31×10^{-3} [1]	3
(d)	neutralisation is exothermic [1] All of the C_6H_5COOH has reacted **AND** excess KOH 1]	2
(e)(i)	If [X] = $[Mg^{2+}]$ = $[Mg(C_6H_5COO^-)_2]$ $4X^3$ = 1.76×10^{-7} so X = 3.53×10^{-3} [1] 0.940 g dm^{-3} [1]	2
(e)(ii)	lower than **AND** common ion effect [1]	1

Q10.

(c)	**M1** solubility of $BaSO_4$ $= \sqrt{1.08 \times 10^{-10}} = 1.04 \times 10^{-5}$ (mol dm^{-3}) **M2** $= 1.04 \times 10^{-5} \times 233.4 / 10 = 2.43 \times 10^{-4}$ (g per 100 cm^3 of solution) min 2sf	**2**

Q11.

(b)(i)	**M1** $K_{sp} = [Be^{2+}][OH^-]^2$ **M2** $mol^3\,dm^{-9}$ ecf	**2**
(b)(ii)	**M1** solubility of $Be(OH)_2 = 2.40 \times 10^{-6} / 43 = 5.58 \times 10^{-8}$ (mol dm^{-3}) ecf (b)(i) **M2** $K_{sp} = 4 \times (5.58 \times 10^{-8})^3 = 6.95 \times 10^{-22}$ ecf min 2sf	**2**

Q12.

(c)(i)	**M1** solution which resists changes in pH when opposes / resists change in pH **M2** when small amount of acid / H^+ or alkali / base / OH^- is added	**2**
(c)(ii)	**M1** (with acid) $HCO_3^- + H^+ \rightarrow H_2CO_3$ **OR** $HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$ **M2** (with alkali) $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$	**2**
(c)(iii)	**M1** $K_a = 10^{-6.35} = 4.47 \times 10^{-7}$ **M2** $[H^+] = 4.47 \times 10^{-7} / 14.1 = 3.17 \times 10^{-8}$ ecf **M3** pH = $-\log [H^+] = 7.5$ ecf from a calculated $[H^+]$ min 2sf	**3**

Q13.

(b)(i)	pH resists change when **small** amount of acid or base added	**1**
(b)(ii)	$CH_3CH_2CH_2COO^-$ / salt of butanoic acid / sodium butanoate **AND** NaOH	**1**
(c)(i)	$K_{sp} = [Al^{3+}][OH^-]^3$	**1**
(c)(ii)	$[OH^-] = 3 \times 2.47 \times 10^{-9}$ **OR** 7.41×10^{-9} [1] $K_{sp} = [2.47 \times 10^{-9}][7.41 \times 10^{-9}]^3$ $= \mathbf{1.01 \times 10^{-33}}$ min 2sf ecf from 1st mark [1] $mol^4\,dm^{-12}$ [1]	**3**

Q14.

(a)(i)	$27x^4 = 2 \times 10^{-39}$ $x = 9.28 \times 10^{-11}$ mol dm^{-3}	1
(a)(ii)	$[Fe^{3+}][0.02]^3 = 2 \times 10^{-39}$ [1] $[Fe^{3+}] = 2.5 \times 10^{-34}$ [1]	2
(a)(iii)	common ion (effect)	1
(b)(i)	two species that differ by one H^+ ion	1
(b)(ii)	HBrO BrO^- H_3O^+ H_2O	1
(b)(iii)	[acid] = 4×10^{-2} $[H^+]^2 = 8.0 \times 10^{-11}$ [1] pH = 5.05 [1]	2
(b)(iv)	8.70	1

Q15.

(d)	**M1:** $[OH^-] = 2 \times 0.12 = 0.24$ (mol dm^{-3}) $[H^+] = 1 \times 10^{-14}/0.24 = 4.17 \times 10^{-14}$ / pOH = –log(0.24) **OR** 0.62 **M2:** pH = –log[H$^+$] = 13.4 **OR** pH = 14 – 0.6 = 13.4	2

Q16.

(a)(i	$K_a = \frac{[H^+][Cl(CH_2)_3CO_2^-]}{[Cl(CH_2)_3CO_2H]}$ [1]	1
(a)(ii)	pK_a = – logK_a **OR** $K_a = 10^{-pKa}$ [1]	1
(a)(iii)	$[H^+] = 10^{-4.0}$ = **1×10^{-4}** [1]	1

(a)(iv)	• $[HCl] = 1 \times 10^{-4}$ ecf 2(a)(iii) • $K_a = 10^{-4.52} = 3.02 \times 10^{-5}$ • $[Cl(CH_2)_3CO_2H] = (1 \times 10^{-4})^2 / 3.02 \times 10^{-5}$ $= 3.3 \times 10^{-4}$ ecf • $\frac{[HCl]}{[Cl(CH_2)_3CO_2H]} = \frac{1\times10^{-4}}{3.3\times10^{-4}} = \mathbf{0.302}$ min 2sf ecf	2
(b)	M1 $[H^+] = 10^{-5}$ **OR** 1×10^{-5} $K_a = [H^+][A^-] / [HA]$ **OR** pH = pKa + log $[A^-] / [HA]$ • ✓ [1] M2 moles of $A^- = (1.35 \times 10^{-5})(5 / 74) / (1 \times 10^{-5})$ moles of A^- = 0.0912 [1] ecf M3 mass of sodium propanoate = 0.0912 × 96 = **8.76** [1] min 2sf ecf	3
(c)	all of the (sodium) **propanoate** (ion) has been protonated / converted to (propanoic) acid / neutralised [1] **H^+** is in excess / **H^+** is 0.1 mol dm^{-3} (from the H_2SO_4) [1]	2

Q17.

(c)(i)	1.0×10^{-9} [1] $mol^3\ dm^{-9}$ [1]	**2**
(c)(ii)	yellow precipitate / yellow solid / yellow crystals [1] common ion effect / K_{sp} has been exceeded [1]	**2**

Q18.

(a)	**M1** 2-chloropropanoic acid > 3-chloropropanoic acid > propanoic acid [1] **M2** $CH_3CHClCO_2H$ / $ClCH_2CH_2CO_2H$ (are more acidic) as they contain an electronegative C*l* atom so weaken O-H bond / stabilise carboxylate anion [1] **M3** $CH_3CHClCO_2H$ (is more acidic than $ClCH_2CH_2CO_2H$) as the C*l* atom is closer to CO_2H so weaken O-H bond more / stabilise carboxylate anion more [1]	**3**

(b)(i)	$K_{eq} = 4.07 \times 10^{-3} / 1.78 \times 10^{-4} =$ **22.9**	**1**
(b)(ii)	3rd box ticked [to the right] **AND** as the K_{eq} is greater than one ecf on K_{eq}	**1**
(b)(iii)	pK_a 1.23 $HO_2CCO_2H + H_2O \rightleftharpoons HO_2CCO_2^- + H_3O^+$ **OR** $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$ pK_a 4.19 $HO_2CCO_2^- + H_2O \rightleftharpoons {}^-O_2CCO_2^- + H_3O^+$ **OR** $HO_2CCO_2^- \rightleftharpoons {}^-O_2CCO_2^- + H^+$	**2**
(b)(iv)	pK_a = – logK_a	**1**

Q19.

(g)(i)	$K_w = [D^+][DO^-]$	**1**
(g)(ii)	**M1** $[D^+] = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8}$ **M2** pH = -log [D^+] = **7.4**(3) min 2sf	**2**

Q20.

(a)(i)	**M1** $K_{sp} = [Ag^+]^2[CO_3^{2-}]$ **M2** units = $mol^3\ dm^{-9}$	**2**
(a)(ii)	$x = \sqrt[3]{6.3 \times 10^{-12}/4} = 1.16 \times 10^{-4}$ ($mol\ dm^{-3}$) $[Ag^+] = 1.16 \times 10^{-4} \times 2 =$ **2.33×10^{-4}** ($mol\ dm^{-3}$) min 2sf	**1**
(a)(iii)	$6.3 \times 10^{-12} = [0.05]^2[CO_3^{2-}]$ $[CO_3^{2-}] =$ **2.52×10^{-9}** ($mol\ dm^{-3}$) min 2sf	**1**

Q21.

(a)	**M1** a solution that resists changes in pH **M2** when small amounts of acid and alkali are added to it	**2**
(b)(i)	$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$	**1**
(b)(ii)	**M1** $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ **M2** $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	**2**
(b)(iii)	**M1** moles NH_3(initial) = 0.25 x 0.80 = 0.200 **AND** moles HC*l* = 0.20 x 0.20 = 0.040 (= moles $NH_4^+{}_{eqm}$) **M2** moles $NH_{3(eqm)}$ = 0.20 – 0.04 = 0.160 $[H^+] = (5.6 \times 10^{-10} \times 0.04)/(0.16) = 1.4 \times 10^{-10}$ (mol dm^{-3}) ecf on M1 **M3** pH = $-\log(1.4 \times 10^{-10})$ = **9.85** ecf on M2 min 2sf	**3**

Q22.

(d)(i)	**M1** $K_{sp} = [Ca^{2+}][IO_3^-]^2$ **M2** units = $mol^3\ dm^{-9}$	**2**
(d)(ii)	$K_{sp} = 4 \times (5.6 \times 10^{-3})^3$ K_{sp} = **7.03 x 10^{-7}** 2sf min	**1**
(d)(iii)	**M1** $Ca(IO_3)_2$ **AND** as solubility of $Ca(IO_3)_2$ decreases **M2** due to common ion effect	**2**

Q23.

(e)	**M1** $[H^+] = 10^{-8.8} = 1.585 \times 10^{-9}$ **M2** $[In^-]/[HIn] = 5.0 \times 10^{-10}/1.585 \times 10^{-9} = 0.315$	**2**

Q24.

(a)(i)	(pH =) $-\log[H^+]$ OR $-\lg[H^+]$ [1] (K_w =) $[H^+][OH^-]$ [1]	**2**
(a)(ii)	$[H^+] = 1 \times 10^{-14} / 0.027 = 3.7037 \times 10^{-13}$ pH = $-\log(3.7037 \times 10^{-13})$= **12.4** [1] min 3sf	**1**
(b)	$[H^+] = \sqrt{3.72 \times 10^{-8} \times 0.010} = 1.9287 \times 10^{-5}$ pH = $-\log(1.9287 \times 10^{-5})$= **4.7** [1] min 2sf	**1**

Q25.

(a)	$[H^+][A^-] / [HA]$ [1]	**1**
(b)(i)	$[H^+] = 3.9 \times 10^{-5}$ [1] $K_a = 1.5 \times 10^{-6}$ [1]	**2**
(b)(ii)	5.82 [1]	**1**
(c)	$4 \times {}^3 = 1.1 \times 10^{-11}$ [1] $x = 1.4 \times 10^{-4}$ [1]	**2**

Q26.

(d)(i)	$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$	**1**
(d)(ii)	K_a of H_2SO_4 is larger than K_{a2}	**1**

(e)	**M1**: $[H^+] = 10^{-2.90} = 1.26 \times 10^{-3}$ **M2**: $K_a = [1.26 \times 10^{-3}]^2 / 0.025 =$ **6.3×10^{-5}** ($mol\ dm^{-3}$)	**2**

Q27.

(c)(i)	solubility = $\sqrt{5.0 \times 10^{-13}}$ = **7.1×10^{-7}** ($mol\ dm^{-3}$) [1] min 2sf	**1**
(c)(ii)	M1 (in conc. NH_3) $[NH_3]$ increases **and** equilibrium 2 shifts to the right [1] M2 $[Ag^+]$ decreases **and** equilibrium **1** shifts to the right [1]	**2**
(c)(iii)	$AgBr + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Br^-$ [1]	**1**
(c)(iv)	$K_{eq3} = K_{sp} \times K_{stab}$ [1] **ALLOW** $K_{eq3} = [Ag(NH_3)_2^+][Br^-]/[NH_3]^2$	**1**

Q28.

(b)(i)	$H_2NCH_2CO_2H$ + HCl → $Cl^-H_3N^+CH_2CO_2H$ [1] $H_2NCH_2CO_2H$ + $NaOH$ → $H_2NCH_2CO_2^-Na^+$ + H_2O [1]	2

(d)(i)	NH_3 (in ethanol) heat in a sealed tube [1] nucleophilic substitution [1]	2
(d)(ii)	acidity of Cl_3CCO_2H > $ClCH_2CO_2H$ > CH_3CO_2H [1] **any two of:** Cl is electronegative / electron withdrawing group **AND** Cl_3CCO_2H has more / 3 Cl groups [1] weakens O-H bond **so** more likely to ionise / dissociate **OR negative** charge on anion is more stabilised **OR** charge / electron density on COO^- decreases so anion is (more) stabilised [1] CH_3 is electron donating **so** O-H bond is stronger so less likely to ionise in CH_3CO_2H **OR** CH_3CO_2H has no -I group **so** O-H bond is stronger and less likely to ionise [1]	3

Q29.

(a)(i)	$K_{sp} = [Ag^+]^2[S^{2-}]$	1
(a)(ii)	• $[S^{2-}] = 1.16 \times 10^{-17}$ • $[Ag^+] = 2.32 \times 10^{-17}$ • K_{sp} = **$6.2(4) \times 10^{-51}$** minimum 2 sig. fig. correct answer scores 2 marks Award 1 mark for two points, award 2 marks for three points	2
(a)(iii)	**M1**: moles Ag_2S = 1 / 247.9 = 0.00403 moles [1] 2sf min **M2**: $1.16 \times 10^{-17} = 0.0040 / V$ so V = **3.5×10^{14}** (dm^3) [1] 2sf min ecf on M1 correct answer scores 2 marks	2
(b)(i)	**M1:** $[H^+] = \sqrt{2.0 \times 10^{-9} \times 0.20}$ $[H^+] = 2.0 \times 10^{-5}$ (1.9976×10^{-5}) **M2:** pH = **4.7** (4.699) minimum 2 sig. fig. min correct answer scores 2 marks	2

(b)(ii)	**M1: Both** equilibria correctly stated moles KOH = $0.005 \times 0.2 = 1 \times 10^{-3}$ moles HOBr(initial) = $0.020 \times 0.2 = 4 \times 10^{-3}$ moles HOBr(eqm) = $4 \times 10^{-3} - 1 \times 10^{-3}$ = **3×10^{-3}** moles BrO^-(eqm) = **1×10^{-3}** **M2:** ratio $[OBr^-]/[HOBr]$ = 1/3 $[H^+] = 3 \times 2.0 \times 10^{-9} = 6 \times 10^{-9}$ pH = **8.2(2)** correct answer scores 2 marks	2

Q30.

(a)(i)	1.3×10^{-5}	**1**
(a)(ii)	**M1:** K_a expression used correctly **and** $K_a = 5.5(3) \times 10^{-10}$ **M2:** $pK_a = 9.26$ Award 2 marks for correct answer	**2**
(b)(i)	$NH_3 + H^+ \rightarrow NH_4^+$	**1**
(b)(ii)	$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ **or** $H^+ + OH^- \rightarrow H_2O$ **and** reference to expression in Q shifting R	**1**
(c)(i)	quotes $K_w = 1 \times 10^{-14}$ or 1×10^{-1} $[H^+][OH^-]$ $[H^+] = 1 \times 10^{-7}$	**1**
(c)(ii)	**M1:** $[H^+] = 2.3 \times 10^{-7}$ (calculator value 2.290867×10^{-7}) **and** $K_w = [2.3 \times 10^{-7}]^2$ **M2:** $K_w = 5.2 \times 10^{-14}$ calculator 5.248074×10^{-14} Award 2 marks for correct answer	**2**