Section 7.1

1	pН	$H = -log_{10} [H^+(aq)] \text{ or } pH = -log_{10} [H_3O^+]$		
	[H3	$[_{3}O^{+}][OH^{-}] = 10^{-14}$		
	a	$pH = -log_{10} 0.001 = 3$		
	b	$pH = -log_{10} 0.00624 = 2.20$		
	c	$[H_3O^+] = 2 \times [H_2SO_4] = 2 \times (2.34 \times 10^{-5}) = 4.68 \times 10^{-5}$		
		$pH = -\log_{10} \left(4.68 \times 10^{-5} \right) = 4.33$		
	d	NaOH is a base, so must find $[H_3O^+]$ first:		
		$[H_3O^+] = \frac{10^{-14}}{6.5 \times 10^{-2}} = 1.54 \times 10^{-13}$		
		$pH = -log_{10}(1.54 \times 10^{-13}) = 12.8 = 13 (2 \text{ sig. figs})$		
	e	$[H_3O^+] = \frac{10^{-14}}{3.5 \times 10^{-3}} = 2.86 \times 10^{-12}$		
		$pH = -log_{10} (2.86 \times 10^{-12}) = 11.5 = 12 (2 \text{ sig. figs})$		
	f	$[OH^{-}] = 2 \times [Ba(OH)_2] = 2 \times (5.0 \times 10^{-4}) = 1.0 \times 10^{-3}$		
		$[H_3O^+] = \frac{10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}$		
		$pH = -log_{10} 1.0 \times 10^{-11} = 11$		
2	рO	$H = -\log_{10} [OH^{-}]$		
	a	$pOH = -\log_{10} 1.5 \times 10^{-6} = 5.8$		
	b	$[OH^{-}] = \frac{10^{-14}}{[H_3O^{+}]} = \frac{10^{-14}}{0.00245} = 4.08 \times 10^{-12}$		
		$pOH = -\log_{10} 4.08 \times 10^{-12} = 11.4$		
	c	$[H_3O^+] = 2 \times [H_2SO_4] = 2 \times (9.05 \times 10^{-5}) = 1.81 \times 10^{-4}$		
		$[OH^{-}] = \frac{10^{-14}}{1.81 \times 10^{-4}} = 5.52 \times 10^{-11}$		
		$pOH = -\log_{10} 5.52 \times 10^{-11} = 10.3$		
	d	$[OH^{-}] = 2 \times [Ca(OH)_{2}] = 2 \times 0.15 = 0.30$		
		$pOH = -log_{10} 0.30 = 0.52$		
3	[H	$(aq)] = 10^{-pH}$		
	pН	+ pOH = 14		
	a	$[H^{+}(aq)] = 10^{-2.5} = 0.0032 \text{ mol } dm^{-3}$		

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b
$$[H^{+}(aq)] = 10^{-1.75} = 0.0178 \text{ mol } dm^{-3}$$

c $pH = 14 - pOH = 14 - 2.2 = 11.8$
 $[H^{+}(aq)] = 10^{-11.8} = 1.58 \times 10^{-12} \text{ mol } dm^{-3}$
d $pH = 14 - 3.5 = 10.5$
 $[H^{+}(aq)] = 10^{-10.5} = 3.16 \times 10^{-11} \text{ mol } dm^{-3}$
4 $[H^{+}(aq)] = \frac{n}{V} = \frac{0.225}{1.50} = 0.15 \text{ mol } dm^{-3}$
 $pH = -log_{10} 0.15 = 0.82$
5 a $c_1V_1 = c_2V_2$
 $c_2 = \frac{c_1V_1}{V_2} = \frac{1.35 \times 85.0}{600} = 0.191 \text{ mol } dm^{-3}$
 $pH = -log_{10} 0.191 = 0.718$
b Note that final volume = 15 + 265 = 280 cm^3
 $c_2 = \frac{c_1V_1}{V_2} = \frac{8.00 \times 15.0}{280} = 0.429 \text{ mol } dm^{-3}$
 $pH = -log_{10} 0.429 = 0.368$
6 $n(KOH) = \frac{m}{M} = \frac{3.73}{39.10 + 16.00 + 1.01} = 0.0665 \text{ mol}$
 $[OH^-] = [KOH] = \frac{n}{V} = \frac{0.0665}{0.250} = 0.266 \text{ mol } dm^{-3}$
 $[H^+(aq)] = \frac{10^{-14}}{0.266} = 3.76 \times 10^{-14}$
 $pH = -log_{10} 3.76 \times 10^{-14} = 13.4$
7 $HCl(aq) + LiOH(aq) \rightarrow LiCl(aq) + H_2O(1)$
 $n(HCl) = cV = 0.117 \times 0.085 = 9.945 \times 10^{-3} \text{ mol}$
 $n(LiOH) = n(HCl)$, so LiOH will be in excess
 $n(LiOH)$ in excess = 0.0129 - 9.945 \times 10^{-3} = 0.00296 \text{ mol}
 $[OH^-] = \frac{n}{V} = \frac{0.00296}{0.085 + 0.135} = 0.0135 \text{ mol } dm^{-3}$
 $[H^+(aq)] = \frac{10^{-14}}{0.0135} = 7.43 \times 10^{-13}$

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8

- Both solutions are alkaline $n(\text{NaOH}) = cV = 0.00334 \times 0.3400 = 1.1356 \times 10^{-3} \text{ mol}$ $n(\text{KOH}) = cV = 8.45 \times 10^{-4} \times 0.265 = 2.23925 \times 10^{-4} \text{ mol}$ $n(\text{OH}^-) = n(\text{NaOH}) + n(\text{KOH}) = 1.1356 \times 10^{-3} + 2.23925 \times 10^{-4} = 1.36 \times 10^{-3} \text{ mol}$ $p\text{OH} = -\log_{10} [\text{OH}^-] = -\log_{10} \frac{1.36 \times 10^{-3}}{0.605} = -\log_{10} 2.25 \times 10^{-3} = 2.65$ pH = 14 - 2.65 = 11.35 = 11.4 (3 sig. figs)pH decreases as temperature increases. (See table 7.1.1 p. 199 of the Higher Level coursebook.)
- 9 pH decreases as temperature increases. (See table 7.1.1 p. 199 of the Higher Level coursebook.)As the water cooled back to 25°C, the pH would increase from about 6 to 7.
- **10 a i** From the graph: pH at 20° C = 7.08 [H⁺(aq)] at 20° C = $10^{-7.08}$ = 8.32×10^{-8} mol dm⁻³
 - ii From the graph: pH at $35^{\circ}C = 6.85$ [H⁺(aq)] at $35^{\circ}C = 10^{-6.85} = 1.41 \times 10^{-7} \text{ mol dm}^{-3}$ [OH⁻(aq)] at $35^{\circ}C = [\text{H}^+(\text{aq})] = 1.41 \times 10^{-7} \text{ mol dm}^{-3}$
 - iii From the graph: pH at $45^{\circ}C = 6.70$

$$[H_{3}O^{+}] \text{ at } 45^{\circ}C = 10^{-6.70} = 1.995 \times 10^{-7} \text{ mol dm}^{-3}$$
$$[OH^{-}(aq)] \text{ at } 45^{\circ}C = [H^{+}(aq)] = 1.995 \times 10^{-7} \text{ mol dm}^{-3}$$
$$K_{w} = [OH^{-}(aq)][H^{+}(aq)] = 1.995 \times 10^{-7} \times 1.995 \times 10^{-7}$$
$$= 3.98 \times 10^{-14} \text{ mol}^{2} \text{ dm}^{-6}$$

b The self-ionization of water is endothermic, since the value of K_w increases as the temperature increases.

Section 7.2

1 a i $HCOOH(1) + H_2O(1) \Leftrightarrow H_3O^+(aq) + HCOO^-(aq)$

$$\mathbf{ii} \quad K_{\mathrm{a}} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{HCOO}^{-}]}{[\mathrm{HCOOH}]}$$

b i
$$HOBr(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + OBr^-(aq)$$

$$\mathbf{ii} \quad K_{\mathrm{a}} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{OBr}^{-}]}{[\mathrm{HOBr}]}$$

c i
$$HSO_4^{-}(aq) + H_2O(l) \Leftrightarrow H_3O^{+}(aq) + SO_4^{2-}(aq)$$

ii
$$K_{a} = \frac{[H_{3}O^{+}][SO_{4}^{2-}]}{[HSO_{4}^{-}]}$$

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2 a i
$$CH_3CH_2NH_2(aq) + H_2O(l) \Leftrightarrow OH^-(aq) + CH_3CH_2NH_3^+(aq)$$

ii
$$K_{\rm b} = \frac{[\rm OH^-][\rm CH_3\rm CH_2\rm NH_3^+]}{[\rm CH_3\rm CH_2\rm NH_2]}$$

b i
$$(CH_3)_3N(aq) + H_2O(1) \Leftrightarrow OH^-(aq) + (CH_3)_3NH^+(aq)$$

ii
$$K_{\rm b} = \frac{[\rm OH^-][(\rm CH_3)_3\rm NH^+]}{[(\rm CH_3)_3\rm N]}$$

c i
$$C_6H_5NH_2(aq) + H_2O(l) \Leftrightarrow OH^-(aq) + C_6H_5NH_3^+(aq)$$

ii
$$K_{\rm b} = \frac{[OH^-][C_6H_5NH_3^+]}{[C_6H_5NH_2]}$$

3
$$pK_a = -\log_{10} K_a; K_a = 10^{-pK_a}$$

Monoprotic acid	$K_{\rm a}$ (mol dm ⁻³)	р <i>К</i> а	
Phenylethanoic acid	4.90×10^{-5}	4.31	
Boric acid	5.75 × 10 ⁻¹⁰	9.24	
Bromoethanoic acid	1.26 × 10 ^{−3}	2.90	
Pentanoic acid	1.38×10^{-5}	4.86	

4
$$pK_b = -\log_{10} K_b$$
; $K_b = 10^{-pK_b}$

Base	K _b (mol dm⁻³)	р <i>К</i> ь	
Ammonia	1.78 × 10 ^{−5}	4.75	
Methylamine	4.37×10^{-4}	3.36	
Diethylamine	8.51 × 10 ⁻⁴	3.07	
Phenylamine	4.17×10^{-10}	9.38	

5 $HCN(l) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CN^-(aq)$

$$K_{a} = \frac{[H_{3}O^{+}][CN^{-}]}{[HCN]}$$

$$6.0 \times 10^{-10} = \frac{[H_{3}O^{+}][CN^{-}]}{0.50}$$

$$[H_{3}O^{+}]^{2} = 6.0 \times 10^{-10} \times 0.50$$

$$[H_{3}O^{+}] = \sqrt{6.0 \times 10^{-10} \times 0.50}$$

$$= 1.73 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} 1.73 \times 10^{-5} = 4.76$$

6 a
$$K_{\rm a} = 10^{-{\rm p}K_{\rm a}}$$

 $K_{\rm a}(\rm CH_3COOH) = 10^{-4.76} = 1.74 \times 10^{-5}$

$$CH_3COOH(l) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CH_3COO^-(aq)$$

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 $K_{a} = \frac{[H_{3}O^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]}$ $1.74 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{0.524}$ $[H_3O^+]^2 = 1.74 \times 10^{-5} \times 0.524$ $[H_3O^+] = \sqrt{7.4 \times 10^{-5} \times 0.524}$ $= 3.02 \times 10^{-3} \text{ mol dm}^{-3}$ $pH = -log_{10} 3.02 \times 10^{-3} = 2.52$ $K_{a}(C_{4}H_{9}COOH) = 10^{-4.86} = 1.38 \times 10^{-5}$ b $C_4H_9COOH(1) + H_2O(1) \Leftrightarrow H_3O^+(aq) + C_4H_9COO^-(aq)$ $K_{a} = \frac{[H_{3}O^{+}][C_{4}H_{9}COO^{-}]}{[C_{4}H_{9}COOH]}$ $1.38 \times 10^{-5} = \frac{[H_3O^+][C_4H_9COO^-]}{8.25 \times 10^{-3}}$ $[H_3O^+]^2 = 1.38 \times 10^{-5} \times (8.25 \times 10^{-3})$ $[H_3O^+] = \sqrt{1.38 \times 10^{-5} \times 8.25 \times 10^{-3}}$ $= 3.37 \times 10^{-4} \text{ mol dm}^{-3}$ $pH = -log_{10} 3.37 \times 10^{-4} = 3.47$ **c** $n(\text{HCOOH}) = \frac{m}{M} = \frac{8.05}{46.03} = 0.175 \text{ mol}$ $[\text{HCOOH}] = \frac{n}{V} = \frac{0.175}{0.200} = 0.875 \text{ mol dm}^{-3}$ $K_{a}(\text{HCOOH}) = 10^{-3.75} = 1.78 \times 10^{-4}$ $HCOOH(1) + H_2O(1) \Leftrightarrow H_3O^+(aq) + HCOO^-(aq)$ $K_{\rm a} = \frac{[\rm H_3O^+][\rm HCOO^-]}{[\rm HCOOH]}$ $1.78 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{0.875}$ $[H_3O^+]^2 = 1.78 \times 10^{-4} \times 0.875$ $[H_3O^+] = \sqrt{1.78 \times 10^{-4} \times 0.875}$ $= 0.0125 \text{ mol dm}^{-3}$ $pH = -log_{10} 0.0125 = 1.90$

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7 a K_{\rm b} = 10^{-pK_{\rm b}}
            K_{\rm b}(\rm NH_3) = 10^{-4.75} = 1.78 \times 10^{-5}
            NH_3(aq) + H_2O(1) \Leftrightarrow OH^-(aq) + NH_4^+(aq)
            K_{\rm b} = \frac{[{\rm OH}^-][{\rm NH}_4^+]}{[{\rm NH}_3]}
            1.78 \times 10^{-5} = \frac{[OH^-][NH_4^+]}{0.123}
            [OH^{-}]^{2} = 1.78 \times 10^{-5} \times 0.123
            [OH^{-}] = \sqrt{1.78 \times 10^{-5} \times 0.123}
                  = 1.48 \times 10^{-3}
            i pOH = -log_{10} 1.48 \times 10^{-3} = 2.83
            ii pH = 14.00 - 2.83 = 11.17 = 11.2 (to 3 sig. figs)
          K_{\rm b}({\rm CH_2NH_2}) = 10^{-3.36} = 4.37 \times 10^{-4}
      b
            CH_2NH_2(aq) + H_2O(1) \Leftrightarrow OH^-(aq) + CH_2NH_3^+(aq)
            K_{\rm b} = \frac{[\rm OH^{-}][\rm CH_2\rm NH_3^{+}]}{[\rm CH_2\rm NH_2]}
            4.37 \times 10^{-4} = \frac{[OH^{-}][CH_2NH_3^{+}]}{4.25 \times 10^{-4}}
            [OH^{-}]^{2} = 4.37 \times 10^{-4} \times (4.25 \times 10^{-4})
            [OH^{-}] = \sqrt{4.37 \times 10^{-4} \times 4.25 \times 10^{-4}}
                      =4.31 \times 10^{-4}
                  pOH = -log_{10} 4.31 \times 10^{-4} = 3.37
            i
            ii pH = 14.00 - 3.37 = 10.63 = 10.6 (to 3 sig. figs)
8
           i Conjugate base of HCOOH is HCOO<sup>-</sup>.
     a
            ii pK_a + pK_b = pK_w
                  At 298 K, pK_{\rm b}(\rm HCOO^{-}) = 14 - 3.75 = 10.25.
           i Conjugate base of C_2H_5COOH is C_2H_5COO^-
      b
            ii At 298 pK_b(C_2H_5COO^-) = 14 - 4.87 = 9.13.
```

c i Conjugate base of
$$CH_2CICOOH$$
 is CH_2CICOO^- .

ii At 298 K, $pK_b(CH_2ClCOO^-) = 14 - 2.86 = 11.14$.

9 The larger the pK_a value, the weaker the acid; so, of the three acids listed, propanoic acid, C_2H_5COOH , is the weakest.

Order of acid strength from strongest to weakest: $CH_2CICOOH > HCOOH > C_2H_5COOH$

10 a NH₄⁺(aq) + H₂O(1) → H₃O⁺(aq) + NH₃(aq)
b
$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

[H₃O⁺] = 10^{-pH} = 10^{-5.32} = 4.79 × 10⁻⁶
 $K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$
= $\frac{(4.79 \times 10^{-6})^2}{0.040}$
= 5.73 × 10⁻¹⁰ mol dm⁻³

Section 7.3

- **1 a** A buffer solution is a solution containing a mixture of solutes and resists changes in pH when a small amount of an acid or a base is added.
 - **b** This buffer solution contains NH_3 and NH_4^+ .
 - i When a small amount of HCl is added, the pH initially *decreases*. The weak base, NH₃, reacts with the added H⁺ ions, causing the pH to increase to a value that is close to its original value.

 $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

Including the spectator ions this could be written as:

 $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

ii When a small amount of NaOH is added, the pH initially *increases* due to the reaction between $OH^{-}(aq)$ and $H^{+}(aq): OH^{-}(aq) + H^{+}(aq) \rightarrow H_2O(1)$

The conjugate acid, NH_4^+ , dissociates to supply $H^+(aq)$ ions and *decrease* the pH to its original value: $NH_4^+(aq) \rightarrow H^+(aq) + NH_3$ (aq)

Overall this could be written as: $NH_4^+(aq) + NaOH \rightarrow NH_3(aq) + H_2O(l) + Na^+(aq)$

- 2 a An acid buffer solution is made up of a weak acid and the conjugate base of the weak acid.
 - **b** Two compounds that could be used to prepare an acid buffer solution are ethanoic acid and sodium hydroxide.
- **3** To prepare a buffer solution using 50 cm³ of solution containing 0.20 mol of ammonia, HCl could be used. 50 cm³ of solution could be used, containing 0.10 mol of HCl. This would create 100 cm^3 of solution with 0.10 mol of NH₃ and 0.10 mol of NH₄Cl.

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- 4 An acidic buffer is made up of a weak acid and its conjugate base; a basic buffer is made up of a weak base and its conjugate acid.
- 5 Buffers are used in the human body to maintain a constant pH. For example, hemoglobin acts as a buffer to help control the pH of the blood and allows carbon dioxide to return in the bloodstream to the lungs without upsetting the pH of the blood.
- 6 $pK_a(\text{propanoic acid}) = -\log_{10}(1.35 \times 10^{-5}) = 4.87$

```
pH(buffer) = pK_a + \log_{10} \frac{[salt]}{[acid]}

= 4.87 + \log_{10} \frac{0.12}{0.045}

= 4.87 + 0.43

= 5.30

7 pOH(buffer) = pK_b + \log_{10} \frac{[salt]}{[base]}

= 4.75 + \log_{10} \frac{0.20}{0.10}

= 4.75 + 0.30

= 5.05

pH = K_w - pOH

= 14 - 5.05

= 8.95
```

8 $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

 $n(\text{HCl}) = 0.10 \times 0.050 = 0.0050 \text{ mol}$

 $n(NH_3) = 0.10 \times 0.050 = 0.0050 \text{ mol}$

The resulting solution would be fully neutralized. It would only contain NH_4Cl . There would be no NH_3 to complete the buffer solution.

9 HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H₂O(l)

 $n(\text{HCOOH}) = 0.10 \times 0.075 = 0.0075 \text{ mol}$

 $n(\text{NaOH}) = 0.050 \times 0.075 = 0.00375 \text{ mol}$

HCOOH is in excess.

n(HCOONa) = n(NaOH) = 0.0075 mol

n(HCOOH) remaining = 0.0075 - 0.00375 = 0.00375 mol

Total volume of solution = 150 cm^3

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$$[\text{HCOONa}] = [\text{HCOOH}] = \frac{0.00375}{0.150} = 0.025 \text{ mol dm}^{-3}$$

$$p\text{H(buffer)} = pK_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 3.75 + \log_{10} \frac{0.025}{0.025}$$

$$= 3.75 + 0 = 3.75$$
10 $\text{pH} = pK_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$

$$5.0 = 4.76 + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$$

$$\log_{10} \frac{[\text{salt}]}{[\text{acid}]} = 0.24$$

$$\frac{[\text{salt}]}{[\text{acid}]} = 10^{0.24}$$

$$\frac{[\text{salt}]}{[\text{acid}]} = 1.74$$

0 00077

To make a buffer solution of pH = 5.0 using ethanoic acid and sodium ethanoate, the concentration of the anion, sodium ethanoate, will need to be 1.74 times that of the ethanoic acid. For example, the buffer could be made up of a 0.10 mol dm⁻³ solution of ethanoic acid and a 0.174 mol dm⁻³ solution of sodium ethanoate.

Section 7.4

1 $n(\text{NaOH}) = cV = 0.200 \times 0.02460 = 0.00492 \text{ mol}$ $n(\text{CH}_3\text{COOH}) = n(\text{NaOH})$ $n(\text{CH}_3\text{COOH}) \text{ in } 100.0 \text{ cm}^3 \text{ solution} = n(\text{CH}_3\text{COOH}) \times \frac{100.0}{20.00} = 0.00492 \times 5 = 0.0246$ $c(\text{CH}_3\text{COOH}) \text{ in vinegar} = \frac{n}{V} = \frac{0.0246}{0.2000} = 1.23 \text{ mol dm}^{-3}$ 2 $n(\text{HCl}) = cV = 0.112 \times 0.02103 = 0.00236 \text{ mol}$ $n(\text{Na}_3\text{PO}_4) = \frac{1}{2}n(\text{HCl}) = 0.00118 \text{ mol}$ $c(\text{Na}_3\text{PO}_4) = \frac{n}{2} = \frac{0.00118}{0.2010} = 0.236 \text{ mol dm}^{-3}$

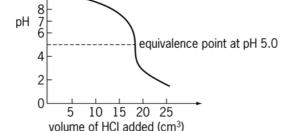
$$c(\text{Na}_3\text{PO}_4) = \frac{n}{V} = \frac{0.00118}{0.00500} = 0.236 \text{ mol dm}^{-2}$$

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3 $n(\text{NaOH}) = cV = 0.0832 \times 0.01962 = 0.001632 \text{ mol}$ $n(\text{C}_6\text{H}_8\text{O}_6) = n(\text{NaOH})$ $m(\text{C}_6\text{H}_8\text{O}_6) = n \times M = 0.001632 \times 176.14 = 0.287 \text{ g}$ $\% \text{ C}_6\text{H}_8\text{O}_6 = \frac{0 \cdot 287}{0 \cdot 300} \times \frac{100}{1} = 95.8\%$ 4 **a** HCl(aq) + NH₃(aq) \rightarrow NH₄Cl(aq) $n(\text{NH}_3) = n(\text{HCl}) = 0.100 \times 0.0180 = 0.00180 \text{ mol}$ **b**, **c** 14^{+}_{12} $p_{\text{H}} \frac{8}{7}_{1}^{+}_{12}$



d The solution has a pH of approximately 5 at the equivalence point. This is because one of the products of the reaction is NH_4^+ , which is a weak acid. It reacts with water according to

 $NH_4^+(aq) + H_2O(1) \rightarrow NH_3(aq) + H_3O^+(aq)$, producing an acidic solution.

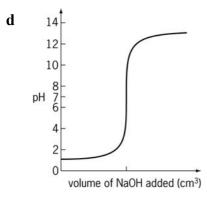
5 a The equivalence point would be at pH = 7.

b
$$n(\text{NaOH}) = 0.12 \times 0.015 = 0.0018 \text{ mol}$$

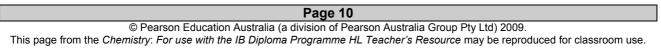
n(HCl) = n(NaOH) = 0.0018 mol

$$c(\text{HCl}) = \frac{n}{V} = \frac{0.0018}{0.02000} = 0.090 \text{ mol dm}^{-3}$$

c
$$pH = -log_{10}[H^+(aq)] = -log_{10}0.090 = 1.0$$



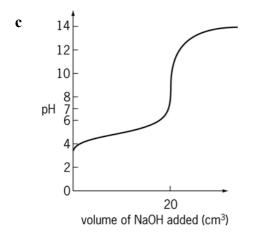
e When the HCl was half-neutralized 7.5 cm^3 of NaOH would have been added.



- 6 NaOH(aq) + CH₃COOH(aq) \rightarrow CH₃COONa(aq) + H₂O(l)
 - **a** $n(CH_3COOH) = 0.00850 \times 0.0200 = 1.7 \times 10^{-4} \text{ mol}$ n(NaOH) to neutralize CH₃COOH = $1.7 \times 10^{-4} \text{ mol}$

$$V(\text{NaOH}) = \frac{1.7 \times 10^{-4}}{0.0100} = 0.017 \text{ dm}^3 = 17 \text{ cm}^3$$

b The pH at the equivalence point will be greater than 7. Possibly between 8 and 9.



- 7 a Curve Y represents the experiment using the HCl solution.
 - **b** The pH at the start of each curve is different because the $[H^+(aq)]$ is different for each acid.
 - **c** The pH values at the equivalence points are different because the pH of the two salt solutions formed in the neutralization reactions are different. The product of the reaction between NaOH and CH₃COOH is a weak base, the ethanoate ion, CH₃COO⁻, whereas the product of the reaction between NaOH and HCl is NaCl, a neutral salt.
 - **d** pH at half-neutralization point = $pK_a(acid)$ pH of ethanoic acid at half-neutralization point ≈ 5 , so $pK_a(CH_3COOH) \approx 5$.
 - e The concentration of the two acids is stated in the question as being the same.

n(NaOH) that reacts with 25.00 cm³ HCl = $0.100 \times 0.020 = 0.0020$ mol

n(HCl) = n(NaOH) = 0.0020 mol

$$[CH_3COOH] = [HC1] = \frac{0.0020}{0.025} = 0.080 \text{ mol } \text{dm}^{-3}$$

8 A direct titration involves the reaction of an acid with a base or vice versa. It involves just one step in which the second solution is added until all of the first solution has reacted, at which point the titration is complete.

A back titration involves adding a measured excess of reagent to the sample being analysed. A reaction occurs completely and usually quickly, and an amount of unreacted reagent remains in the solution. This unreacted amount is then determined by direct titration.

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```
9 n(\text{NaOH}) \text{ added} = cV = 0.120 \times 0.02500 = 3.00 \times 10^{-3} \text{ mol}

n(\text{HCl}) = cV = 0.100 \times 0.01613 = 1.613 \times 10^{-3} \text{ mol}

n(\text{NaOH}) \text{ unreacted} = n(\text{HCl}) = 1.613 \times 10^{-3} \text{ mol}

n(\text{NaOH}) \text{ reacting with fertilizer} = 3.00 \times 10^{-3} - 1.613 \times 10^{-3} = 1.387 \times 10^{-3} \text{ mol}

n(\text{NH}_4^+) = n(\text{NaOH}) \text{ reacting} = 1.387 \times 10^{-3}

m(\text{NH}_4^+) = n \times M = (1.387 \times 10^{-3}) \times 18.05 = 0.0250 \text{ g}

\% \text{ NH}_4^+ = \frac{0.0250}{0.104} \times \frac{100}{1} = 24.1\%
```

Section 7.5

- 1 a $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$
 - **b** NaOH(aq) + HCOOH(aq) \rightarrow HCOONa(aq) + H₂O(1)
 - c $HNO_3(aq) + NH_3(aq) \rightarrow NH_4NO_3(aq)$
 - **d** $CH_3COOH(aq) + CH_3NH_2(aq) \rightarrow CH_3COOCH_3NH_3(aq)$
- **2 a** pH = 7
 - **b** pH = 8–9
 - **c** pH = 4-5
- 3 The salt formed by the reaction of a strong acid with a weak base forms an aqueous solution with pH < 7, because the salt is made up of a cation that is the conjugate acid of the weak base and an anion that has no acid–base properties. The conjugate acid ion, BH^+ , can react with water (undergo hydrolysis):

 $BH^+(aq) + H_2O(1) \Leftrightarrow H_3O^+(aq) + B(aq)$. This solution is acidic.

- 4 The order of the salts from most acidic to least acidic is $Al(NO_3)_3 > MgSO_4$, $NaCl > KHCO_3$.
- 5 The Fe^{3+} ion is a small highly charged ion which attracts water molecules to itself in solution. The complex of water and Fe^{3+} is then able to donate H^+ ions, thereby producing an acidic solution.

 $[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \Leftrightarrow [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^{+}(aq), K_a = 6 \times 10^{-3} \text{ mol dm}^{-3}$

In comparison, the Na⁺ ion in NaCl is not sufficiently small or highly charged to attract water molecules, so NaCl does not affect the pH of a solution.

- 6 a HNO₃(aq) + KOH(aq) (any strong acid and strong base)
 - **b** $HNO_3(aq) + NH_3(aq)$ (any strong acid and weak base)
 - **c** HCOOH(aq) + KOH(aq) (any weak acid and strong base)

Section 7.6

- 1 The equivalence point of a titration is the point at which the two reactants have reacted in their correct stoichiometric amounts; the endpoint of a titration is the point at which the indicator changes colour.
- 2 In order to act as an acid–base indicator, a compound needs to be a weak acid and to exhibit distinctly different colours in its acid and conjugate base forms.
- **3 a** At pH = 3, bromocresol green will be yellow.
 - **b** At pH = 4.7, bromocresol green will be green.
 - **c** At pH = 9, bromocresol green will be blue.
- 4 The pK_a of an indicator is equal to the pH of the midpoint over which the indicator changes colour. The range of the colour change is about one pH unit on either side of the pK_a .
- 5 a equivalence point at pH = 7: phenol red or bromothymol blue indicator
 - **b** equivalence point at pH = 8-9: phenolphthalein indicator
 - **c** equivalence point at pH = 4-5: methyl red indicator
- 6 The titration of a weak acid with a weak base does not have a distinct endpoint that may be indicated by an acid-base indicator. Its titration curve does not have a vertical section with a width of 2 pH units, so no indicator will change colour dramatically when a small volume of alkali is added. A pH meter is more suitable for plotting the titration curve and hence determining the equivalence point as the midpoint of the section in which the most dramatic change in pH occurs.
- 7 The Henderson equation: $pH = pK_{in} \log_{10} \frac{[HIn]}{[In^-]}$

When [HIn] = [In⁻], $\log_{10} \frac{[HIn]}{[In^-]} = 0$, so $pH = pK_{in}$

8 The titration of ethanoic acid with sodium hydroxide follows the equation:

 $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

The conjugate base CH₃COO⁻ reacts with water to form an alkali solution:

 $\rm CH_3\rm COO^-(aq) + \rm H_2\rm O(l) \rightarrow \rm CH_3\rm COOH + \rm OH^-(aq)$

so the pH at the equivalence point of this titration is greater than 7. Since the pH range over which methyl orange changes colour is pH = 3.1-4.4, this indicator would not be at all suitable to show the equivalence point of this reaction.

9 At pH = 5, the solution will be blue if the indicator is bromophenol blue, because this pH is above pK_a of the indicator, and yellow if the indicator is bromothymol blue, because this pH is below its pK_a .

10
$$K_a = \frac{[Cr^-][H_3O^+]}{[HCr]} = 5.01 \times 10^{-9}$$

a When pH = 4, $[H_3O^+] = 10^{-4} \text{ mol dm}^{-3}$
so $\frac{[Cr^-] \times 10^{-4}}{[HCr]} = 5.01 \times 10^{-9}$
and $\frac{[Cr^-]}{[HCr]} = 5.01 \times 10^{-5}$
 $[HCr] >> [Cr^-] \text{ so the indicator will be yellow (the acid colour).}$
b When pH = 13, $[H_3O^+] = 10^{-13} \text{ mol dm}^{-3}$
so $\frac{[Cr^-] \times 10^{-13}}{[HCr]} = 5.01 \times 10^{-9}$

and
$$\frac{[Cr^-]}{[HCr]} = 5.01 \times 10^4$$

 $[Cr^-] >> [HCr]$ so the indicator will be red (the basic colour).

c When pH = 8.3,
$$[H_3O^+] = 10^{-8.3} \text{ mol dm}^{-3}$$

so $\frac{[Cr^-] \times 10^{-8.3}}{[MO_3]} = 5.01 \times 10^{-9}$

$$[HCr] = 5.01 \times 10$$

and $\frac{[Cr^{-}]}{[HCr]} = 1$

 $[HCr] = [Cr^{-}]$ so the indicator will be orange since $pH = pK_a$.

Chapter 7 Review questions

- **1 a** $pH = -log_{10} 0.0010 = 3$
 - **b** $pH = -log_{10} (2 \times 5.83 \times 10^{-3}) = 1.93$
 - c pOH = $-\log_{10} 8.52 \times 10^{-6} = 5.07$ pH = 14 - 5.07 = 8.93
 - **d** $pOH = -log_{10} (2 \times 7.73 \times 10^{-9}) = 7.81$ pH = 14 - 7.81 = 6.19
- **2 a** $[H_3O^+] = 10^{-2.25} = 5.62 \times 10^{-3} \text{ mol } \text{dm}^{-3}$
 - **b** $[H_3O^+] = 10^1 = 10 \text{ mol } dm^{-3}$

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3
$$c_1 V_1 = c_2 V_2$$

 $c_2 = \frac{c_1 V_1}{V_2} = \frac{10.0 \times 0.250}{3.00} = 0.833 \text{ mol dm}^{-3}$
pH = $-\log_{10} 0.833 = 0.0792$

4
$$n(\text{NaOH}) = \frac{m}{M} = \frac{9.35}{(22.99 + 16.00 + 1.01)} = 0.234 \text{ mol}$$

$$[OH^{-}] = [NaOH] = \frac{n}{V} = \frac{0.234}{0.400} = 0.584 \text{ mol dm}^{-3}$$

$$[\mathrm{H}^{+}(\mathrm{aq})] = \frac{10^{-14}}{0.584} = 1.71 \times 10^{-14}$$

$$pH = -\log_{10} 1.71 \times 10^{-14} = 13.8$$

5 $[H_3O^+]$ when pH = 2 is $10^{-2} = 0.0100$ mol dm⁻³

$$c_1 V_1 = c_2 V_2$$

 $V_2 = \frac{c_1 V_1}{c_2} = \frac{14.0 \times 0.00500}{0.0100} = 7.00 \text{ dm}^3$

Since 5 cm^3 is already present, 6.995 dm^3 needs to be added. (Significant figures have been ignored to give the answer.)

6 a
$$HCN(aq) + H_2O(l) \Leftrightarrow CN^{-}(aq) + H_3O^{+}(aq)$$

$$K_{\rm a} = \frac{[\rm CN^-][\rm H_3O^+]}{[\rm HCN]}$$

b $C_2H_5COOH(aq) + H_2O(l) \Leftrightarrow C_2H_5COO^{-}(aq) + H_3O^{+}(aq)$

$$K_{\rm a} = \frac{[\rm C_2H_5COO^-][\rm H_3O^+]}{[\rm C_2H_5COOH]}$$

c $HNO_2(aq) + H_2O(l) \Leftrightarrow NO_2^{-}(aq) + H_3O^{+}(aq)$

$$K_{\rm a} = \frac{[\rm NO_2^{-}][\rm H_3O^{+}]}{[\rm HNO_2]}$$

7 $K_{a}(C_{6}H_{5}OH) = 1.05 \times 10^{-10}$ $C_{6}H_{5}OH(l) + H_{2}O(l) \Leftrightarrow H_{3}O^{+}(aq) + C_{6}H_{5}O^{-}(aq)$

$$K_{a} = \frac{[H_{3}O^{+}][C_{6}H_{5}O^{-}]}{[C_{6}H_{5}OH]}$$
$$1.05 \times 10^{-10} = \frac{[H_{3}O^{+}][C_{6}H_{5}COO^{-}]}{3.5 \times 10^{-3}}$$

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$$[H_{3}O^{+}]^{2} = 1.05 \times 10^{-10} \times (3.5 \times 10^{-3})$$

$$[H_{3}O^{+}] = \sqrt{1.05 \times 10^{-10} \times 3.5 \times 10^{-3}}$$

$$= 6.06 \times 10^{-7} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} 6.06 \times 10^{-7} = 6.21$$

$$K_{a}(C_{6}H_{5}COOH) = 10^{-4.20} = 6.31 \times 10^{-5}$$

8
$$K_{a}(C_{6}H_{5}COOH) = 10^{-4.20} = 6.31 \times 1$$

 $C_{6}H_{5}COOH(l) + H_{2}O(l) \Leftrightarrow H_{3}O^{+}(aq) + C_{6}H_{5}COO^{-}(aq)$

$$K_{a} = \frac{[H_{3}O^{+}][C_{6}H_{5}COO^{-}]}{[C_{6}H_{5}COOH]}$$

$$6.31 \times 10^{-5} = \frac{[H_{3}O^{+}][C_{6}H_{5}COO^{-}]}{0.020}$$

$$[H_{3}O^{+}]^{2} = 6.31 \times 10^{-5} \times 0.02$$

$$[H_{3}O^{+}] = \sqrt{6.31 \times 10^{-5} \times 0.02}$$

$$= 1.12 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} 1.12 \times 10^{-3} = 2.95$$

9
$$[H_3O^+] = 10^{-pH} = 10^{-2.22} = 0.00603$$

$$K_{a} = \frac{[H_{3}O^{+}][NO_{2}^{-}]}{[HNO_{2}]}$$
$$= \frac{[H_{3}O^{+}]^{2}}{[HNO_{2}]}$$
$$= \frac{0.00603^{2}}{0.050} = 7.26 \times 10^{-4} \text{ mol dm}^{-3}$$

10 a $CH_3CH_2NH_2(aq) + H_2O(l) \Leftrightarrow OH^-(aq) + CH_3CH_2NH_3^+(aq)$

b
$$K_{b} = \frac{[OH^{-}][CH_{3}CH_{2}NH_{3}^{+}]}{[CH_{3}CH_{2}NH_{2}]}$$

c $pK_{a} + pK_{1} = pK_{a}$

c
$$pK_a + pK_b = pK_w$$

At 298 K, $pK_a(CH_3CH_2NH_3^+) = 14 - 3.27 = 10.73$.

11 a
$$CH_3(CH_2)_2COO^{-}(aq) + H_2O(l) \Leftrightarrow OH^{-}(aq) + CH_3(CH_2)_2COOH(aq)$$

b
$$K_{\rm b} = \frac{[OH^-][CH_3(CH_2)_2COOH]}{[CH_3(CH_2)_2COO^-]}$$

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С

$$pK_{a} + pK_{b} = pK_{w}$$
At 298 K, $pK_{a}(CH_{3}(CH_{2})_{2}COOH) = 14 - 9.18 = 4.82$

$$K_{a}(CH_{3}(CH_{2})_{2}COOH) = 10^{-4.82} = 1.51 \times 10^{-5}$$

$$K_{a} = \frac{[H_{3}O^{+}][CH_{3}(CH_{2})_{2}COO^{-}]}{[CH_{3}(CH_{2})_{2}COOH]}$$

$$1.51 \times 10^{-5} = \frac{[H_{3}O^{+}][CH_{3}(CH_{2})_{2}COO^{-}]}{0.050}$$

$$[H_{3}O^{+}]^{2} = 1.51 \times 10^{-5} \times 0.050$$

$$[H_{3}O^{+}] = \sqrt{1.51 \times 10^{-5} \times 0.050}$$

$$= 8.70 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} 8.70 \times 10^{-4} = 3.06$$

- **12** a The term *half-neutralized* refers to the point in a titration when the amount of base that has been added is equal to half the amount that is required to neutralize the acid.
 - **b** Because [acid] = [salt] in a half-neutralized solution $pH = pK_a$, so pH = 4.76 (pK_a of ethanoic acid) and $[H^+(aq)] = 10^{-4.76} = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$
 - **c** When a small amount of a base is added to the buffer solution, the pH initially *increases*, as $H^+(aq)$ is removed from the solution by reaction with $OH^-(aq)$.

 $OH^{-}(aq) + H^{+}(aq) \rightarrow H_2O(l)$

The weak acid dissociates to increase $[H^+(aq)]$ and hence to decrease the pH to a value that is close to its original value.

 $CH_3COOH(aq) \rightarrow H^+(aq) + CH_3COO^-(aq)$

- **13** a To form a basic buffer solution, a weak base such as NH₃ and the salt of the weak base such as NH₄Cl can be added to water. Alternately, the weak base and a strong acid can be added to water, but the quantity of acid must be such that the weak base is in excess.
 - **b** When a small amount of an acid is added to the buffer solution, the pH initially *decreases*. The weak base, NH₃, reacts with the added H⁺ ions, causing the pH to increase and to be restored to close to its original value.

 $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

14 HCl and NH₃ react according to the equation:

 $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

 $n(\text{HCl}) = 0.10 \times 0.050 = 0.0050 \text{ mol}$

 $n(NH_3) = 0.20 \times 0.050 = 0.010 \text{ mol}$, so NH₃ is in excess

 $n(NH_4Cl)$ produced = n(HCl) = 0.0050 mol

 $n(NH_3)$ in excess = 0.010 - 0.0050 = 0.0050 mol

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This solution has 0.0050 mol of NH₃ and 0.0050 mol of NH₄Cl (a weak base and the salt of its conjugate acid) in it, so it can act as a buffer.

 $pOH(buffer) = pK_b + \log \frac{[salt]}{[acid]}$ =4.75+0pH = 14 - 4.75= 9.25

15 a At the equivalence point the species present are $NaNO_3$ and H_2O . i

- ii pH at the equivalence point = 7.
- iii A suitable indicator would be phenol red.
- i At the equivalence point only NH₄Cl is present. b
 - ii pH at the equivalence point < 7.
 - iii A suitable indicator would be methyl red.
- At the equivalence point the species present are CH₃COOK and H₂O. i С
 - ii pH at the equivalence point > 7.
 - iii A suitable indicator would be phenolphthalein.
- The two species being reacted together in this titration are a weak acid and a strong base. 16 a
 - pH of the acid solution = 2.8. b
 - 28 cm^3 of the base is added to reach the equivalence point. С
 - pH at the equivalence point $\cong 8$. d
 - Phenol red could be used as an indicator to detect the equivalence point of this titration. e

17 a
$$H_2S(aq) + H_2O(l) \rightarrow HS^{-}(aq) + H_3O^{+}(aq)$$

b
$$n(H_2S) = \frac{m}{M} = \frac{3.4}{34.08} = 0.10 \text{ mol}$$

 $c(H_2S) = \frac{n}{V} = \frac{0.10}{1.0} = 0.10 \text{ mol } \text{dm}^{-3}$
c $K_a = \frac{[H_3O^+][HS^-]}{[H_2S]}$

$$[H_2S]$$

$$9.88 \times 10^{-8} = \frac{[H_3O^+][HS^-]}{0.10}$$
$$[H_3O^+]^2 = 9.88 \times 10^{-8} \times 0.10$$
$$[H_3O^+] = \sqrt{9.88 \times 10^{-8} \times 0.10} = 9.94 \times 10^{-5} \text{ mol dm}^{-3}$$
$$pH = -\log_{10} 9.94 \times 10^{-5} = 4.00$$

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- **d i** A buffer solution maintains a constant pH when small amounts of an acid or base are added.
 - **ii** When a small amount of acid is added to the buffer solution, the pH initially *decreases*. The conjugate base ions, A⁻, react with the added H⁺ ions, causing the pH to increase again to close to the original value.

 $A^{-}(aq) + H^{+}(aq) \rightarrow HA(aq)$

18 a $HIn(aq) \Leftrightarrow H^{+}(aq) + In^{-}(aq)$

b The acid form and the conjugate base form of an indicator are distinctly different colours. During an acid–base reaction, the indicator either gains H⁺ ions from the acid that is being added or loses H⁺ ions to the base that is being added. In doing so it changes from its acid form to its base form or vice versa and hence changes colour.

19 a
$$K_a = \frac{[H_3O^+][Me^-]}{[HMe]}$$

b pH of endpoint of an indicator = pK_a of the indicator.

 $pK_a = -\log_{10} K_a = -\log_{10} 2.0 \times 10^{-4} = 3.70 = pH$

- **20** a Phenol red will be yellow in acid solution. (All In⁻ will have gained an H⁺ to form HIn.)
 - **b** The lowest pH of a solution that would appear a strong red colour would be approximately 1 pH unit higher than the pK_a since the colour begins to change at that point. The pH would be approximately 8.9. It is possible that it may still appear red for at least half a pH unit more.

Chapter 7 Test

Question	Answer	Explanation	
1	В	A buffer solution may be obtained if you add a small amount of strong acid to a base. In all other possibilities the amount of strong acid is equal to or greater than the amount of base.	
2	D	The stronger the acid, the lower the pK_a . Thus, in order of increasing acid strength we have 4.87 (W), 4.86 (Y), 4.85 (Z) and 4.82 (X).	
3	С	The equation given here is the equation for an acid. Therefore we require the K_a for this reaction. $K_a \times K_b = K_w$; therefore $K_a = \frac{K_w}{K_b}$	
4	А	The highest pH at the equivalence point will be for a strong base and a weak acid.	
5	A	The lowest pH will occur with a solution that is acidic. Sodium nitrate and potassium chloride are both neutral as they are formed from a strong acid and a strong base. Sodium ethanoate will be slightly basic as it is a combination of a weak acid with a strong base.	

Part A: Multiple-choice questions

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Question	Answer	Explanation	
6	С	The ideal situation is for the indicator to change colour at a pH that is as close as	
		possible to the pH of the equivalence point. If we use a strong base and a weak	
		acid, the pH at the equivalence point will be above 7 and so phenolphthalein could	
		be used as its pK_a is 9.3.	
7	А	Pure water is neutral at all temperatures, but pH varies with temperature. As it is an	
		endothermic reaction, as temperature is increased, K_c will also increase. Since	
		there is now more product, $[H^+]$ increases, therefore pH decreases.	
8	В	Just as the lower the pH the stronger the acid, the lower the pK_a the stronger the	
		acid. The lowest p K_a value is 3.	
9	А	$[H^+] \times [OH^-] = 10^{-14}$, thus pH + pOH = 14	
10	В	A pH greater than 7 will be one that forms a basic solution. A basic solution forms	
		with a combination of a weak acid with a strong base. (Potassium from KOH and	
		carbonate from H ₂ CO ₃ .)	

Key words that are fundamental to the answer are shown in **bold**.

Part B: Short-answer questions

- **1 a** $HIn(aq) \Leftrightarrow H^{+}(aq) + In^{-}(aq)$
 - **b i** Since this is an equilibrium, the indicator will turn yellow as the equilibrium shifts to the left, in order to remove the added $H^+(aq)$.

(1 mark)

(1 mark)

ii At the equivalence point of a titration, the indicator will be green, as both HIn(aq) and In⁻(aq) are present and the combination of yellow and blue will give green.

(2 marks)

(1 mark)

(2 marks)

2 a
$$pK_a = 3.75$$
, therefore $K_a = 10^{-3.75} = 1.78 \times 10^{-4}$

b Methanoic acid is a weak acid as there is a small K_{a} .

c
$$HCOOH \Leftrightarrow H^+ + HCOO^-$$

 $K_{a} = \frac{[H^{+}][HCOO^{-}]}{[HCOOH]}$ Let $[H^{+}] = x$, therefore $HCOO^{-} = x$ Thus, $K_{a} = \frac{x^{2}}{0.010}$

$$x^2 = 1.78 \times 10^{-4} \times 0.010 = 1.78 \times 10^{-6}$$

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 $x = 1.33 \times 10^{-3}$ mol dm⁻³ = [H⁺] pH = $-\log_{10} (1.33 \times 10^{-3}) = 2.88$ The assumption is that x << 0.010.

(4 marks)

(2 marks)

(3 marks)

- **3** a A buffer solution is one that **resists changes in pH** when **small** amounts of acid or alkali are added.
 - **b** $M_{\rm r}$ of sodium ethanoate = **82** $n(\text{sodium ethanoate}) = \frac{0.25}{82} = 0.0030 \text{ mol}$ $[\text{CH}_3\text{COO}^-] = \frac{0.0030}{0.2} = 0.015 \text{ mol dm}^{-3}$
 - **c** $CH_3COOH \Leftrightarrow H^+ + CH_3COO^-$

$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]}$$
$$[H^{+}] = \frac{10^{-4.76} \times 0.10}{0.015} = 1.159 \times 10^{-4}$$
$$pH = -\log_{10}(1.159 \times 10^{-4}) = 3.94$$

Part C: Data-based question

a $pH = -log_{10}[H^+] = -log_{10}(0.25) = 0.60$ No K_a is given because **HCl is a strong acid**; that is, it is **completely dissociated**.

(2 marks)

(3 marks)

b $CH_3COOH \Leftrightarrow H^+ + CH_3COO^-$

$$0.25 - x \times x$$

$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

$$K_{a} = \frac{x^{2}}{(0.25 - x)}$$

$$1.8 \times 10^{-5} = \frac{x^{2}}{0.25}$$

$$x^{2} = 1.8 \times 10^{-5} \times 0.25 = 4.5 \times 10^{-6}$$

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 $[\mathbf{H}^+] = 2.12 \times 10^{-3}$ $\mathbf{pH} = -\log_{10} (2.12 \times 10^{-3}) = 2.67$ The assumptions are $- [\mathbf{H}^+] = [\mathbf{CH}_3\mathbf{COO}^-]$ OR $[\mathbf{CH}_3\mathbf{COO}^-] \iff [\mathbf{CH}_3\mathbf{COOH}]$; that is, $\ll 0.25$

(4 marks)

(1 mark)

(2 marks)

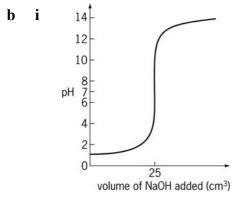
(1 mark)

- **c i** A buffer solution is intended to maintain a constant pH upon the addition of **small** amounts of acid or base.
 - **ii** Fewer moles of solution C (NaOH) should be mixed with solution B (CH₃COOH) so the final solution contains both CH₃COOH and CH₃COO⁻.

d
$$pK_b = -\log_{10} K_b = -\log_{10} (1.8 \times 10^{-5}) = 4.74$$

Part D: Extended-response question

- **a i** 4.8–4.9 as this is the pH at the half the equivalence point.
 - (2 marks)
 ii Phenolphthalein is a suitable indicator as the pK_{in} value or pH range of the indicator is within the vertical part of the graph. A colour change occurs as pH changes rapidly near the equivalence point.
 - (2 marks)



It is important to show that the initial pH = 1, the vertical region is from about pH = 3-10 and the final pH = 12-13.

(3 marks)

ii Similarities: the final pH is the same in both because NaOH is used, same volume of NaOH is required to reach the equivalence point (25 cm³ alkali needed)

Differences: initial pH = 1 because $[H^+] = 0.1 \text{ mol } dm^{-3}$, pH at equivalence point is different, the vertical region is longer

(4 marks)

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