

1. (a) The titration is a 1:1 reaction between a weak acid and a strong base.

(i) As acetic acid is a weak acid,  $[\text{H}_3\text{O}^+]$  must be calculated:

	$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{CH}_3\text{COO}^-$
initial	0.100		0	0
change	-x		+x	+x
final	$0.100 - x$		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{(0.100-x)}$$

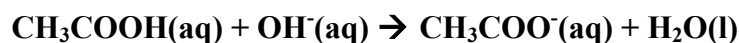
As  $\text{p}K_a = 4.76 = -\log_{10}K_a$ ,  $K_a = 10^{-4.76}$ . As  $K_a$  is very small,  $0.100 - x \sim 0.100$  and hence:

$$x^2 = 0.1 \times 10^{-4.76} \quad \text{or} \quad x = 0.00132 \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}[0.00132] = 2.88$$

(ii) Addition of the strong base  $\text{OH}^-(\text{aq})$  leads to the neutralization reaction:



The number of moles of  $\text{CH}_3\text{COO}^-$  is equal to the number of moles of  $\text{OH}^-(\text{aq})$  which have been added. The number of moles of  $\text{CH}_3\text{COOH}$  remaining is equal to the initial number of moles of  $\text{CH}_3\text{COOH}$  minus the number of moles of  $\text{OH}^-(\text{aq})$  which have been added.

Initially, there is 50.0 mL of 0.100 M  $\text{CH}_3\text{COOH}$  so

$$\begin{aligned} n(\text{CH}_3\text{COOH})_{\text{initial}} &= \text{concentration} \times \text{volume} \\ &= 0.100 \text{ M} \times 0.0500 \text{ L} = 0.00500 \text{ mol} \end{aligned}$$

25.0 mL of 0.100 M NaOH contains

$$\begin{aligned} n(\text{OH}^-)_{\text{added}} &= \text{concentration} \times \text{volume} \\ &= 0.100 \text{ M} \times 0.0250 \text{ L} = 0.00250 \text{ mol} \end{aligned}$$

Thus, after addition and the neutralization reaction, there are:

$$\begin{aligned} n(\text{CH}_3\text{COOH}) &= n(\text{CH}_3\text{COOH})_{\text{initial}} - n(\text{OH}^-)_{\text{added}} \\ &= (0.00500 - 0.00250) \text{ mol} = 0.00250 \text{ mol} \end{aligned}$$

$$n(\text{CH}_3\text{COO}^-) = n(\text{OH}^-)_{\text{added}} = 0.00250 \text{ mol}$$

These quantities are now in a solution with total volume (50.0 + 25.0) mL = 75.0 mL, so their concentrations are:

$$c(\text{CH}_3\text{COOH}) = n / V = 0.00250 \text{ mol} / 0.0750 \text{ L} = 0.0333 \text{ M}$$

$$c(\text{CH}_3\text{COO}^-) = n / V = 0.00250 \text{ mol} / 0.0750 \text{ L} = 0.0333 \text{ M}$$

Using the Henderson-Hasselbalch equation gives

$$\begin{aligned} \text{pH} &= \text{p}K_{\text{a}} + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \\ &= 4.76 + \log_{10} \left( \frac{0.0333 \text{ M}}{0.0333 \text{ M}} \right) = 4.76 \end{aligned}$$

At the  $\frac{1}{2}$  equivalence point, when the number of moles of base added is equal to  $\frac{1}{2}$  the number of moles of acid originally present, the pH is equal to the  $\text{p}K_{\text{a}}$ .

(iii) 45.0 mL of 0.100 M NaOH corresponds to

$$\begin{aligned} n(\text{OH}^-)_{\text{added}} &= \text{concentration} \times \text{volume} \\ &= 0.100 \text{ M} \times 0.0450 \text{ L} = 0.00450 \text{ mol} \end{aligned}$$

Thus, after addition and the neutralization reaction, there are:

$$\begin{aligned} n(\text{CH}_3\text{COOH}) &= n(\text{CH}_3\text{COOH})_{\text{initial}} - n(\text{OH}^-)_{\text{added}} \\ &= (0.00500 - 0.00450) \text{ mol} = 0.00050 \text{ mol} \end{aligned}$$

$$n(\text{CH}_3\text{COO}^-) = n(\text{OH}^-)_{\text{added}} = 0.00450 \text{ mol}$$

These quantities are now in a solution with total volume (50.0 + 45.0) mL = 95.0 mL, so their concentrations are:

$$c(\text{CH}_3\text{COOH}) = n / V = 0.00050 \text{ mol} / 0.0950 \text{ L} = 0.00526 \text{ M}$$

$$c(\text{CH}_3\text{COO}^-) = n / V = 0.00450 \text{ mol} / 0.0950 \text{ L} = 0.0474 \text{ M}$$

Using the Henderson-Hasselbalch equation gives

$$\text{pH} = 4.76 + \log_{10} \left( \frac{0.0474 \text{ M}}{0.00526 \text{ M}} \right) = 5.71$$

(iv) The addition of 50.0 mL of 0.100 M NaOH corresponds to the equivalence point as the number of moles of added base is equal to the number of moles of acid initially present. However, the pH is *not* equal to 7 for this point of the titration of a weak acid with a strong base.

50.0 mL of 0.100 M NaOH corresponds 0.00500 mol so whilst this leads to  $n(\text{CH}_3\text{COOH}) = 0.00$  mol, it also leads to  $n(\text{CH}_3\text{COO}^-) = 0.00500$  mol. A solution of a weak base has  $\text{pH} > 7$ .

As the total volume is  $(50.0 + 50.0)$  mL = 100.0 mL, the concentration of  $\text{CH}_3\text{COO}^-$  is:

$$c(\text{CH}_3\text{COO}^-) = n / V = 0.00500 \text{ mol} / 0.1000 \text{ L} = 0.05000 \text{ M}$$

The calculation of the pH now follows that in Q1(b) with the concentration of 0.05000 M:

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.05000 - x} = 9.24$$

As  $\text{p}K_b = 9.24$ ,  $K_b = 10^{-9.24}$ . Again,  $K_b$  is very small,  $0.05000 - x \sim 0.05000$  and hence:

$$x^2 = 0.0500 \times 10^{-9.24} \quad \text{or} \quad x = 5.36 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}[5.36 \times 10^{-6}] = 5.27$$

Finally,  $\text{pH} + \text{pOH} = 14$  so

$$\text{pH} = 14.0 - 5.27 = 8.73$$

- (v) Beyond the equivalence point, excess base is being added to a solution of a weak base and the pH is controlled by the excess amount of  $\text{OH}^-(\text{aq})$ . The calculation of the pH is then *exactly* the same as in Q3a (vi) from Problem Sheet 7.

55.0 mL of 0.100 M NaOH corresponds to 0.00550 mol. Of this, 0.00500 mol is used to react with the acid. The total volume is  $(0.050 + 0.055)$  L = 0.105 L. Hence

$$[\text{OH}^-(\text{aq})] = \frac{(0.00550 \text{ mol}) - (0.00500 \text{ mol})}{(0.105 \text{ L})} = 0.00476 \text{ M}$$

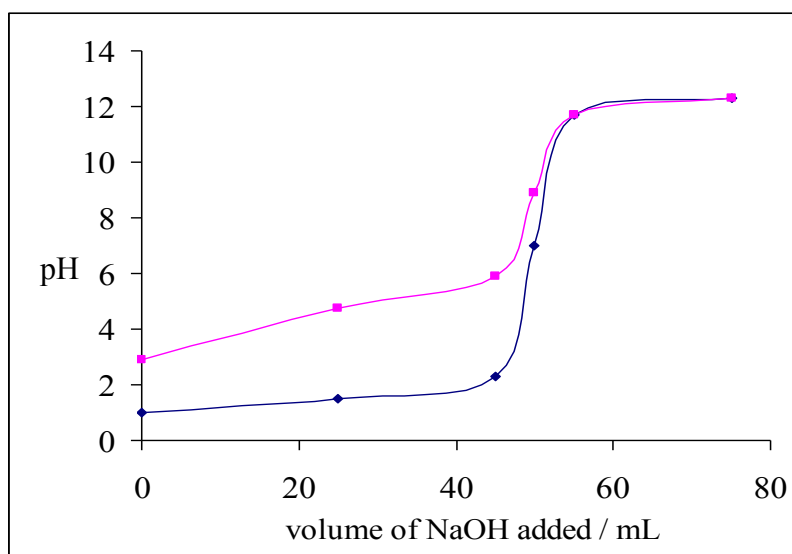
Hence,  $\text{pOH} = -\log_{10}(0.00476) = 2.32$  and  $\text{pH} = 14.00 - 2.32 = 11.7$ .

- (vi) 75.0 mL of 0.100 M NaOH corresponds to 0.00750 mol. Of this, 0.00500 mol is used to react with the acid and the total volume is  $(0.050 + 0.075)$  L = 0.125 L. Hence

$$[\text{OH}^-(\text{aq})] = \frac{(0.00750 \text{ mol}) - (0.00500 \text{ mol})}{(0.125 \text{ L})} = 0.0200 \text{ M}$$

Hence,  $\text{pOH} = -\log_{10}(0.0200) = 1.70$  and  $\text{pH} = 14.00 - 1.70 = 12.3$

- (b) Using these values, the pH curve for the titration can be constructed and is shown below (in pink).



- (c) The figure also includes the data from Q4 in Problem Sheet 7 for a strong acid / strong base titration (in blue).

For a weak acid / strong base titration:

- (i) The initial pH is higher. For a strong acid and a weak acid with the *same* concentration, the pH of the strong acid is lower.
- (ii) The pH at the  $\frac{1}{2}$  equivalence point is equal to the  $pK_a$  of the weak acid.
- (iii) At the equivalence point, the solution contains weak base and so the  $pH > 7$ .
- (iv) After the equivalence point, the pH is determined only the concentration of excess strong base and is thus the *same* for the two titrations.

2. The concentration of the acid that has dissociated at equilibrium can be calculated from the pH:

	HA	$\rightleftharpoons$	$H_3O^+$	$A^-$
initial	0.6		0	0
change	-x		+x	+x
final	$0.6 - x$		x	x

At equilibrium,  $[H_3O^+] = [H_3O^+]_{\text{from HA}} + [H_3O^+]_{\text{from water}}$ . As  $[H_3O^+]_{\text{from water}} \sim 10^{-7}$ , it can be assumed that the pH is due to the  $[H_3O^+]_{\text{from HA}}$ . Therefore:

$$pH = -\log_{10}[H_3O^+] \sim -\log[H_3O^+]_{\text{from HA}} = -\log x = 4.0$$

so

$$x = 10^{-4} \text{ M}$$

The initial concentration of HA is 0.6 so at equilibrium  $[\text{HA}] = 0.6 - 10^{-4} \sim 0.6 \text{ M}$ .  
The percentage dissociation is:

$$\frac{[\text{H}_3\text{O}^+]_{\text{from HA}}}{[\text{HA}]_{\text{equilibrium}}} = \frac{10^{-4}}{0.6} \times 100\% = \frac{10^{-4}}{0.6} \times 100\% = 0.017\%$$

3. (a) 0.2 M acetic acid

As acetic acid is a weak acid,  $[\text{H}_3\text{O}^+]$  must be calculated:

	$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{CH}_3\text{COO}^-$
initial	0.2		0	0
change	-x		+x	+x
final	$0.2 - x$		x	x

The equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.2 - x}$$

As  $\text{p}K_a = 4.76 = -\log_{10}K_a$  so  $K_a = 10^{-4.76}$ . As  $K_a$  is very small,  $0.2 - x \sim 0.2$  and hence:

$$x^2 = 0.2 \times 10^{-4.76} \quad \text{or} \quad x = 0.0019 \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}[0.0019] = 2.7$$

- (b) 0.2 M sodium acetate

As  $\text{CH}_3\text{COO}^-$  is a weak base,  $[\text{OH}^-]$  must be calculated in a similar way:

	$\text{CH}_3\text{COO}^-$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{OH}^-$	$\text{CH}_3\text{COOH}$
initial	0.2	large		0	0
change	-x	negligible		+x	+x
final	$0.2 - x$	large		x	x

The equilibrium constant  $K_b$  is given by:

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.2 - x}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

so

$$pK_b = 14.00 - 4.76 = 9.24$$

As  $pK_a = 4.76$ ,  $K_b = 10^{-9.24}$ . Again,  $K_b$  is very small,  $0.2 - x \sim 0.2$  and hence:

$$x^2 = 0.2 \times 10^{-9.24} \quad \text{or} \quad x = 0.00001 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$p\text{OH} = -\log_{10}[\text{OH}^-] = -\log_{10}[0.00001] = 5.0$$

Finally,  $\text{pH} + \text{pOH} = 14.0$  so

$$\text{pH} = 14.0 - 5.0 = 9.0$$

(c) A buffer that is 0.2 M in acetic acid and 0.2 M in sodium acetate

This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:

$$\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

As  $[\text{acetic acid}] = [\text{sodium acetate}]$ ,  $\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \log_{10}(1) = 0$  and so

$$\text{pH} = pK_a = 4.76$$

4. The Henderson-Hasselbalch equation can be used for this buffer:

$$\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

where  $[\text{base}] = [\text{KNO}_2]$  and  $[\text{acid}] = [\text{HNO}_2]$ . If  $K_a$  for  $\text{HNO}_2 = 4.00 \times 10^{-4} \text{ M}$ ,

$$pK_a = -\log_{10}(4.00 \times 10^{-4}) = 3.40$$

Hence,

$$\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 3.00 - 3.40 = -0.40$$

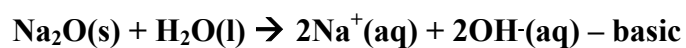
or

$$\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 10^{-0.40} = 0.40$$

As the concentrations of the acid and base are the same, the volume of base must be  $0.40 \times$  volume of acid. The volumes must add to give 1L:

**0.71 L of HNO<sub>2</sub> and 0.29 L of KNO<sub>2</sub>.**

5. (a) Na<sub>2</sub>O



(b) Cl<sub>2</sub>O<sub>7</sub>

