

CHEM1612 Answers to Problem Sheet 6

1. (a) 0.2 M acetic acid

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

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

$$\text{p}K_a + \text{p}K_b = 14.00$$

so

$$\text{p}K_b = 14.00 - 4.76 = 9.24$$

As  $pK_b = 9.24$ ,  $K_b = 10^{-9.24}$ . 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,  $\text{pH} + \text{pOH} = 14$  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

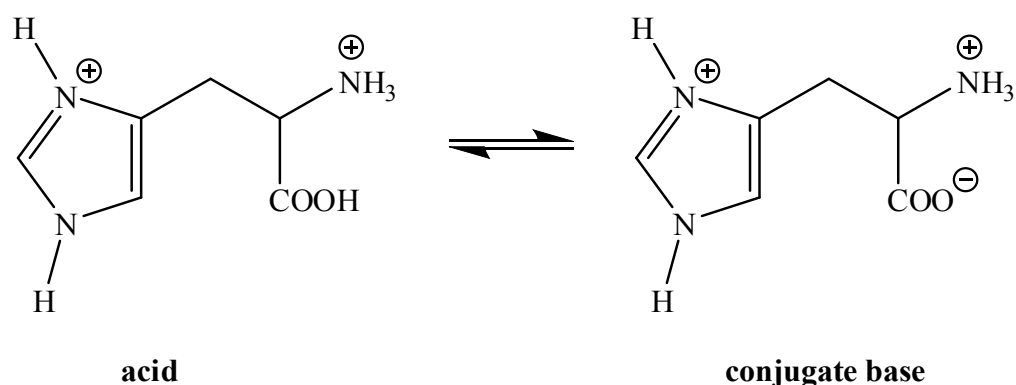
This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:

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

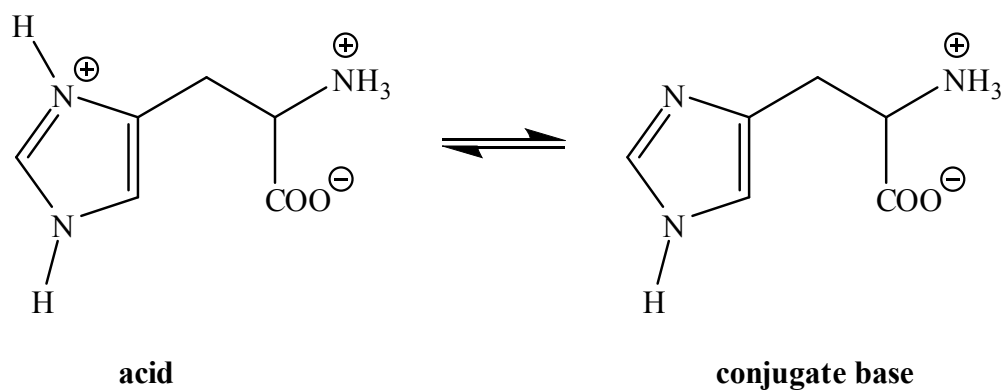
As  $[\text{acetic acid}] = [\text{sodium acetate}]$ ,  $\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \log_{10}(1) = 0$  and so

$$\text{pH} = \text{p}K_a = 4.76$$

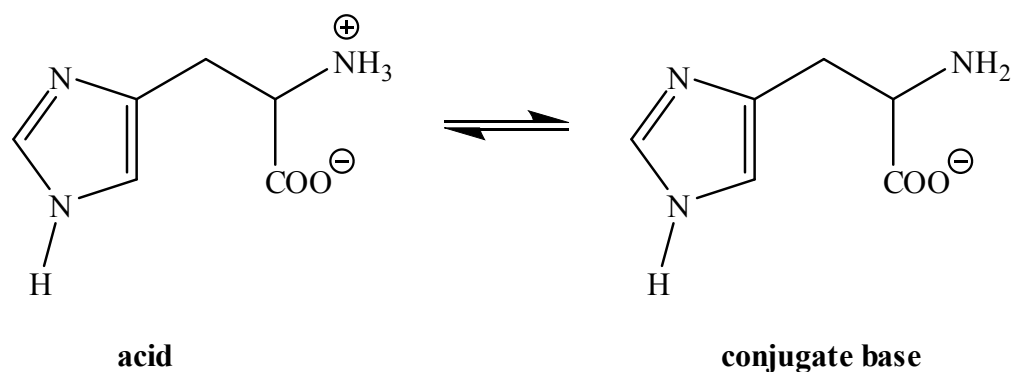
2. (a) As the  $\alpha$ -COOH group has the lowest  $\text{p}K_a$  value, it is the most acidic. At  $\text{pH} = 1.81$ , the  $\alpha$ -COOH group is in equilibrium with its conjugate base. The  $\text{p}K_a$  values of the imidazole N-H and the  $\alpha$ -NH<sub>3</sub><sup>+</sup> groups are higher than the pH value, both exist predominately in the protonated form at  $\text{pH} = 1.81$ .



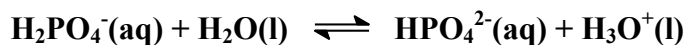
- (b) As  $\text{pH} = 6.05$  is higher than its  $\text{p}K_a$  value, the  $\alpha$ -COOH group will exist predominately in its conjugate base form. The  $\text{p}K_a$  value for the  $\alpha$ -NH<sub>3</sub><sup>+</sup> group is higher than the pH value so it will exist predominately in its protonated form. The ring N-H group will be in equilibrium with its conjugate base form.



- (c) As  $\text{pH} = 9.15$  is higher than their  $\text{p}K_a$  values, the  $\alpha\text{-COOH}$  and imidazole  $\text{N-H}$  groups will exist predominately in their conjugate base forms. The  $\alpha\text{-NH}_3$  group is in equilibrium with its conjugate base form.



3. The equilibrium of interest is:



where  $\text{H}_2\text{PO}_4^-$  is the acid and  $\text{HPO}_4^{2-}$  is the base. The Henderson-Hasselbalch equation can be used to calculate the required concentrations of each:

$$\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \text{ or } \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - \text{p}K_a$$

$$\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = (7.40 - 7.20) = 0.20$$

Hence,  $\left( \frac{[\text{base}]}{[\text{acid}]} \right) = 10^{0.20}$

Both the acid and base have initial concentrations of 0.10 M so the ratio of the volume of each required is:

$$\left( \frac{V_{\text{base}}}{V_{\text{acid}}} \right) = 10^{0.20} = 1.58$$

When the two solutions are added together, their total volume =  $V_{\text{base}} + V_{\text{acid}} = 1.0 \text{ L}$ .  
Hence,  $V_{\text{acid}} = 1.0 - V_{\text{base}}$

$$\left( \frac{V_{\text{base}}}{1.0 - V_{\text{base}}} \right) = 1.58 \text{ so } V_{\text{base}} = 0.61 \text{ L and } V_{\text{acid}} = 1.0 - V_{\text{base}} = 0.39 \text{ L}$$

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

	HA	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	A <sup>-</sup>
initial	0.6	large		0	0
change	-x	negligible		+x	+x
final	0.6 - x	large		x	x

At equilibrium,  $[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_{\text{from HA}} + [\text{H}_3\text{O}^+]_{\text{from water}}$ . As  $[\text{H}_3\text{O}^+]_{\text{from water}} \sim 10^{-7}$ , it can be assumed that the pH is due to the  $[\text{H}_3\text{O}^+]_{\text{from HA}}$ . Therefore:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \sim -\log[\text{H}_3\text{O}^+]_{\text{from HA}} = -\log x = 4.0$$

so

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

The initial concentration of HA is 0.6 M. The percentage dissociation is:

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

5. (a) The titration is a 1:1 reaction between a weak acid and a strong base.  
(i) Before addition of any base, the pH of the 0.100 M acetic solution follows the same method used in Q1(a).

Following the same steps (with a 0.100 M solution in place of a 0.2 M solution) gives the equilibrium constant  $K_a$  is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.1 - x}$$

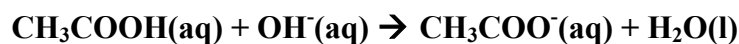
With the approximation that  $0.100 - x \sim 0.100$ ,

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

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  $\text{OH}^-$  (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  $\text{OH}^-$  (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

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

(Note: In fact one could have skipped the conversion of moles into concentration step, because the volume of solution is the same for  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  and it would just cancel out)

- (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:

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.05000 - x} = 10^{-9.24}$$

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 Q7(a)(v) from Problem Sheet 5.

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  $(0.050 + 0.055) \text{ L} = 0.105 \text{ L}$ . Hence

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

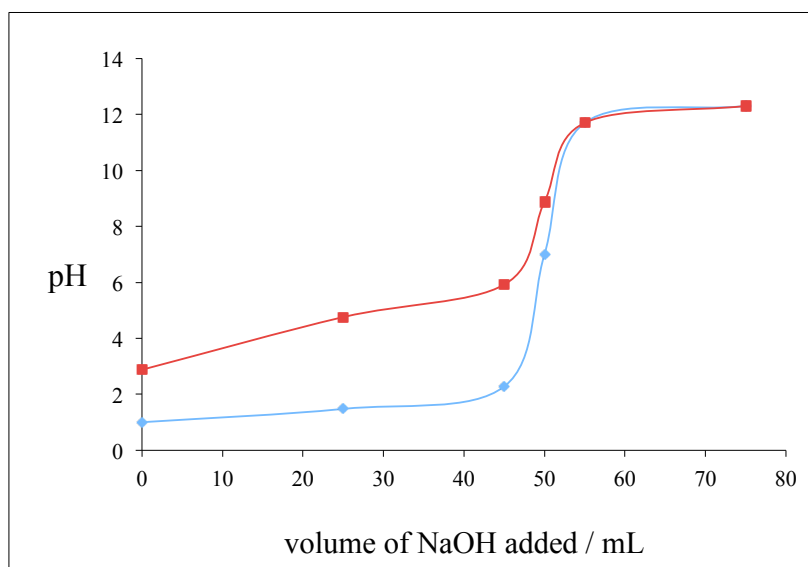
Hence,  $\text{pOH} = -\log_{10}(0.00476) = 2.32$  and  $\text{pH} = 14.00 - 2.32 = 11.7$ .

- (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  $(0.050 + 0.075) \text{ L} = 0.125 \text{ L}$ . 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 Q7 in Problem Sheet 5 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.