18.2.2 Calculating the pH of a BUFFER SOLUTION

A **buffer solution** will resist changes in pH when a small amount of a strong acid or base is added.

Finding : $[H^+]$, pH and K_a of a weak acid/conjugate base buffer
E.g. ethanoic acid and sodium ethanoate

Generalized Equation:

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

weak acid — salt conjugate base

$$K_a = \frac{[H^+] \quad [A^-]}{[HA]}$$

$$[H+] = \frac{K_a \times [HA]}{[A^-]}$$

$$pH = -\log_{10}[H^+]$$

Finding : $[OH^-]$ or K_b of a weak base/conjugate acid buffer
E.g. ammonia and ammonium chloride

Generalized Equation:

$$B_{(aq)} \Leftrightarrow BH^+_{(aq)} + OH^-_{(aq)}$$

weak base — Salt conjugate acid

$$K_b = \frac{[BH^+] \times [OH^-]}{[B]}$$

$$[OH^-] = \frac{K_b \times [B]}{[BH^+]}$$

Example 1
Solid sodium ethanoate is added to 0.20 mol dm^{-3} ethanoic acid until the concentration of the salt is 0.050 mol dm^{-3}. Given that the K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3}. Calculate the pH of the buffer solution formed.

Answer

$$CH_3COOH_{(aq)} \quad \Leftrightarrow \quad H^+_{(aq)} \quad + \quad CH_3COO^-_{(aq)}$$

weak acid — *Salt conjugate base*

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

$[CH_3COOH] = 0.20 \text{ mol dm}^{-3}$

$[CH_3COO^-] = 0.050 \text{ mol dm}^{-3}$

$K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$

$$[H+] = \frac{K_a \times CH_3COOH}{CH_3COO^-}$$

$$[H+] = \frac{1.74 \times 10^{-5} \times 0.20}{0.050}$$

$$[H+] = 6.96 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} [H^+]$$

$$= -\log_{10} 6.96 \times 10^{-5}$$

$$= 4.2 \quad (2SF)$$

Changing the pH of a buffer solution

For example a weak acid and conjugate base buffer

$$\underset{\text{Acid}}{HA} \quad \Leftrightarrow \quad \underset{\text{conjugate base}}{A^-} \quad + \quad H_3O^+$$

1. If you add more salt (conjugate base) the buffer solution becomes more basic & pH will increase / become closer to 14.

   <u>or</u>

   If you add more of the salt (conjugate base) according to Le Chateliers principle the position of equilibrium will shift in the reverse (right) direction to oppose the change causing $[H_3O^+]$ to decreases and the pH to increase / get closer to 14.

2. If you add more acid, HA, the buffer solution becomes more acidic, the pH will decrease / become closer to 1.

<u>or</u>

If you add more acid, according to Le Chateliers principle the position of equilibrium will shift in the reverse (right) direction to oppose change. The $[H_3O^+]$ increases, pH decreases / gets closer to 1.

3. If you dilute the buffer by adding distilled water it will have no effect on the pH. The position of equilibrium is not altered.

Predicting whether a solution will be a buffer & calculating its pH

In practice, acidic buffers are often made by taking *equal concentrations* of a weak acid and a strong base. Excess weak acid is added to the base so that the resulting solution contains the salt, water and the unreacted weak acid.

$$\underset{\text{limiting}}{NaOH\,(aq)} + \underset{\text{excess}}{CH_3COOH(aq)} \rightarrow \underbrace{\underset{\text{salt}}{CH_3COONa\,(aq)} + \underset{\text{excess weak acid}}{CH_3COOH(aq)}}_{\text{buffer solution}}$$

Example 1
Will 30 cm^3 of 0.100 mol dm^{-3} CH_3COOH & 10 cm^3 of 0.100 mol dm^{-3} NaOH produce a buffer solution and if so what will be its pH?

Answer

reaction: $CH_3COOH + NaOH \Rightarrow CH_3COO^-Na^+ + H_2O$
mole ratio 1 : 1 : 1

$Ka = 1.74 \times 10^{-5}$ mol dm^{-3}

actual moles CH_3COOH $= c \times v$
$= 0.100 \times (30 / 1000)$
$= 0.0030$ mol
$= 0.0030$ mol dm^{-3} (2SF)

(10cm^3 and 30cm^3 are measured values so 2SF since they have an ± precision of 1 cm^3)

actual moles NaOH $= c \times v$
$= 0.100 \times (10 /1000)$
$= 0.0010$ mol
$= 0.0010$ mol dm^{-3} (2SF)

(weak acid) *(conj base)*

$$CH_3COOH \quad + \quad NaOH \quad \Rightarrow \quad CH_3COO^-Na^+ \quad + \quad H_2O$$

$$1 \qquad\qquad 1 \qquad\qquad 1$$

$$0.0030 \qquad 0.0010 \qquad 0.0010$$

(acid in excess by 0.00200 mol)

Therefore in this reaction you have 0.0030 – 0.0010 = 0.0020 mol of CH_3COOH left over after neutralization. This reaction will therefore make a buffer from the excess acid and its salt (conjugate base).

To find the pH of the buffer:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

$$[H^+] \quad = \quad \frac{K_a\ [HA]}{[A-]} \quad = \quad \frac{1.74 \times 10^{-5} \times 0.0020}{0.0010} \quad = \quad 3.5 \times 10^{-5}\ mol\ dm^{-3}\ \ (2SF)$$

$$pH = -\log [\,H^+\,] = -\log 3.5 \times 10^{-5} = 4.5 \quad (2SF)$$

Example 2

Will 200 cm^3 of 1.0 mol dm^{-3} NaOH and 100 cm^3 of 1.0 mol dm^{-3} ethanoic acid make a buffer?

18.2.2 Questions

1. (M03/H) A buffer solution can be made by dissolving 0.25g of sodium ethanoate in $200cm^3$ of 0.10 $moldm^{-3}$ ethanoic acid. Assume that the change in weight is negligible.
   a) Define the term buffer solution *[2]*
   b) Calculate the concentration of the sodium ethanoate. *[3]*
   c) Calculate the pH of the resulting buffer solution by using the information in table 16 of the data booklet. *[3]*

2. (M06/H) Identify two substances that can be added to water to form a basic buffer. *[2]*

3. (M05/H) Calculate the pH of a mixture of $50cm^3$ of ammonia solution of concentration 0.10 $moldm^{-3}$ and $50cm^3$ of hydrochloric acid solution of concentration 0.050 mol dm^{-3}. pK_b (NH_3) = 4.75 *[4]*

4. (N05/H) Calculate the pH of a buffer solution containing 0.0500 $moldm^{-3}$ of ethanoic acid (Ka = 1.74×10^{-5}) and 0.100 mol dm^{-3} of sodium ethanoate. *[3]*

5. (N03/H) Explain how you would prepare a buffer solution of pH 3.75 starting with methanoic acid. *[3]*

6. N02/H(1) A buffer solution contains equal concentrations of X^- (aq) and HX (aq). The K_a value for X^- (aq) is 1.0×10^{-10}. What is the pH of the buffer? *[1]*

7 N02/H(2) Calculate the pH of a buffer solution containing 7.2g of sodium benzoate in 1.0 dm^3 of 2.0×10^{-2} mol dm^{-3} benzoic acid, (K_a = 6.3×10^{-5}) stating any assumptions that you have made. *[6]*

8. (M98/H(1) A buffer solution that contains ethanoic acid and sodium ethanoate has a pH=4.0. How could the pH of this solution be changed to 5.0?
   A. Dilute $10cm^3$ of the solution to $100cm^3$
   B. Add more sodium ethanoate
   C. Add more ethanoic acid
   D. Add equal moles of ethanoic acid and sodium ethanoate

9. M01/H(2) 60 cm^3 of 0.100 mol dm^{-3} CH_3COOH is placed in a beaker and mixed with 20 cm^3 of 0.100 mol dm^{-3} KOH.
   a) Explain, with the help of an equation, how the solution formed acts as a buffer solution when a small quantity of acid is added to it. *[2]*
   b) Calculate the pH of the buffer solution. (K_a of CH_3COOH = 1.74×10^{-5} mol dm^{-3}) *[4]*

Answer to example 2

moles NaOH = c x v = 1.0 x (200.0/1000) = 0.20 mol or 0.20 mol dm^{-3}

moles CH_3COOH = c x v = 1.0 x (100.0/1000) = 0.10 mol or 0.10 mol dm^{-3}

(weak acid)		(salt)
$CH_3COOH + NaOH \Rightarrow CH_3COO^-Na^+ + H_2O$		
1	1	1
0.10	0.20	

This solution will not produce a buffer because the weak acid, CH_3COOH is the limiting reagent. All of it will be used up in the reaction and so there will be none available to form a buffer with the salt, CH_3COONa.

Answers

1. (M03/H)

a) a solution that resists changes in pH / maintains a nearly constant pH ;
when small amounts of acid or alkali are added ;

b) n (CH_3COONa) = m ÷ M = 0.25 g ÷ 82. 04 $gmol^{-1}$ = 0.0031 mol ;

[CH_3COONa] = n ÷ v = 0.00305 mol ÷ 200 cm^3 = 0.015 mol dm^{-3} ; (2SF)

c)
From the data booklet K_a (CH_3COOH) = 1.74 x 10^{-5}

$$[H+] = \frac{K_a \times CH_3COOH}{CH_3COO^-} \;;$$

$$[H+] = \frac{1.74 \times 10^{-5} \times 0.10}{0.015}$$

$$[H+] = 1.159 \times 10^{-4} \text{ mol dm}^{-3} \;;$$

$$\begin{aligned} pH &= -\log_{10}[H^+] \\ &= -\log_{10} 1.159 \times 10^{-4} \\ &= 3.9 \;;\; (2SF) \end{aligned}$$

2. (M06/H)
weak base and its salt / weak base and strong acid ;

3. (M05/H)

Calculate the pH of a mixture of $50cm^3$ of ammonia solution of concentration 0.10 $moldm^{-3}$ and $50cm^3$ of hydrochloric acid solution of concentration 0.050 mol dm^{-3}.
pK_b (NH_3) = 4.75

n (HCl) = c x v
= 0.050 x (50 / 1000)
= 0.0025 mol
= 0.0025 mol dm^{-3}

n(NH_3)= c x v
= 0.10 x (50 /1000)
= 0.0050 mol
= 0.0050 mol dm^{-3} ;

NH_3 is in excess

n(NH_3) remaining = 0.0050 – 0.0025 = 0.0025 mol = 0.0025 mol dm^{-3}

From mole ratio in the equation assume $[NH_4^+] = [NH_3]$ = 0.0025 mol dm^{-3} because they are in a 1:1 mole ratio ;

$$NH_{3(aq)} \Leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

weak base	Salt conjugate acid
0.0025	0.0025

$K_b = 10^{-pKb} = 10^{-4.75} = 1.78 \times 10^{-5}$

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_3]}$$

$$[OH^-] = \frac{K_b \times [NH_3]}{[NH_4^+]}$$

$$[OH^-] = \frac{1.78 \times 10^{-5} \times 0.0025}{0.0025}$$

$[OH^-] = 1.78 \times 10^{-5}$ $moldm^{-3}$;

pOH = 4.75

pH = 9.25 (allow 9.2 to 9.3) ;

4. (N05/H)

$$CH_3COOH_{(aq)} \Leftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$$

weak acid — Salt conjugate base

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

$[CH_3COOH] = 0.0500 \text{ mol dm}^{-3}$

$[CH_3COO^-] = 0.100 \text{ mol dm}^{-3}$

$K_a = 1.74 \times 10^{-5}$

$$[H+] = \frac{K_a \times CH_3COOH}{CH_3COO^-} \ ;$$

$$[H+] = \frac{1.74 \times 10^{-5} \times 0.0500}{0.100}$$

$$[H+] = 8.70 \times 10^{-6} \text{ mol dm}^{-3} \ ;$$

$$pH = -\log_{10}[H^+]$$

$$= -\log_{10} 8.70 \times 10^{-6}$$

$$= 5.06 \ ; \ \text{(3SF)}$$

(accept answer in the range 5.0 to 5.1)

5. (N03/H)

to methanoic acid - add strong base / NaOH / salt of methanoic acid / HCOONa ;

in equimolar amounts / so that [HCOOH] = [HCOONa] ;

(from Ka expression) pH = pK_a ;

9.

10. Will 30 cm^3 of 0.100 mol dm^{-3} CH_3COOH & 10 cm^3 of 0.100 mol dm^{-3} NaOH produce a buffer solution and if so what will be its pH?

Answer

reaction: $CH_3COOH + KOH \Rightarrow CH_3COOK + H_2O$

mole ratio 1 : 1 : 1

Ka = 1.74 x 10^{-5} mol dm^{-3}

actual moles CH_3COOH = c x v
= 0.100 x (60 / 1000)
= 0.00600 mol
= 0.00600 mol dm^{-3}

actual moles KOH = c x v
= 0.100 x (20 /1000)
= 0.00200 mol
= 0.00200 mol dm^{-3}

(weak acid)				(conj base)		
CH_3COOH	+	KOH	$\Rightarrow$	CH_3COO^-	+	H_2O
1		1		1		
0.00600		0.00200		0.00200		

(acid in excess by 0.00400 mole)

Therefore in this reaction you have 0.00600 – 0.00200 = 0.00400 mole of CH_3COOH left over after neutralization. This reaction will therefore make a buffer from the excess acid and its salt (conjugate base).

To find the pH of the buffer:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

$$[H^+] = \frac{K_a\ [HA]}{[A-]} = \frac{1.74 \times 10^{-5} \times 0.00400}{0.00200} = 3.48 \times 10^{-5} \text{ mol dm}^{-3}$$

pH = -log [H^+] = - log 3.48 x 10^{-5} = 4.46 (3SF)