

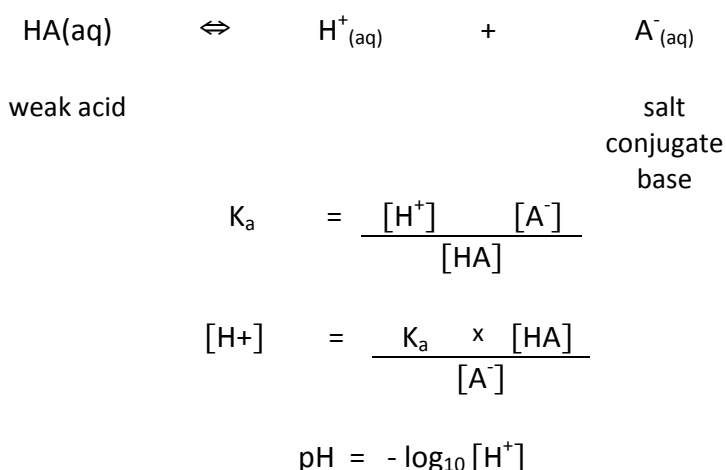
18.2.2 Calculating the pH of a BUFFER SOLUTION

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

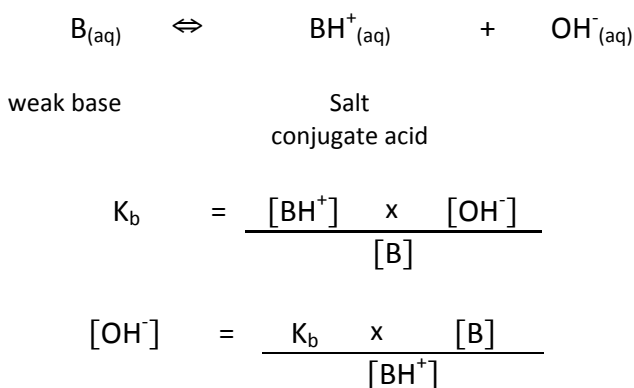
Generalized Equation:



Finding : $[OH^-]$ or K_b of a weak base/conjugate acid buffer

E.g. ammonia and ammonium chloride

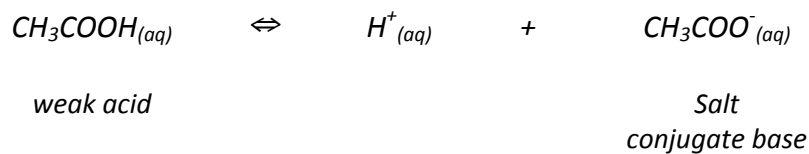
Generalized Equation:



Example 1

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

Answer



$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{CH}_3\text{COOH}] = 0.20 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COO}^-] = 0.050 \text{ mol dm}^{-3}$$

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

$$[\text{H}^+] = \frac{K_a \times \text{CH}_3\text{COOH}}{\text{CH}_3\text{COO}^-}$$

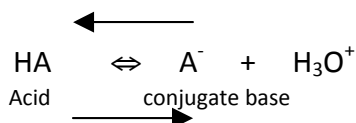
$$[\text{H}^+] = \frac{1.74 \times 10^{-5} \times 0.20}{0.050}$$

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

$$\begin{aligned}
 \text{pH} &= -\log_{10} [\text{H}^+] \\
 &= -\log_{10} 6.96 \times 10^{-5} \\
 &= 4.2 \quad (2\text{SF})
 \end{aligned}$$

Changing the pH of a buffer solution

For example a weak acid and conjugate base buffer



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

or

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 $[\text{H}_3\text{O}^+]$ to decrease 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.

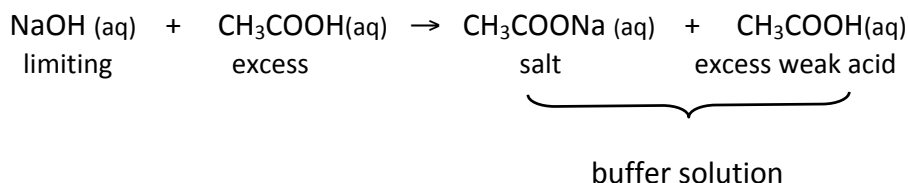
or

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

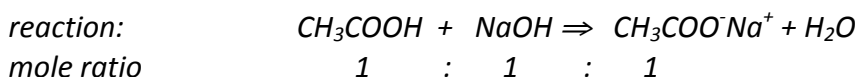
In practice, acidic buffers are often made by taking *equal concentrations* of a weak acid and a strong base. Excess weak acid is added to the base so that the resulting solution contains the salt, water and the unreacted weak acid.



Example 1

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

Answer

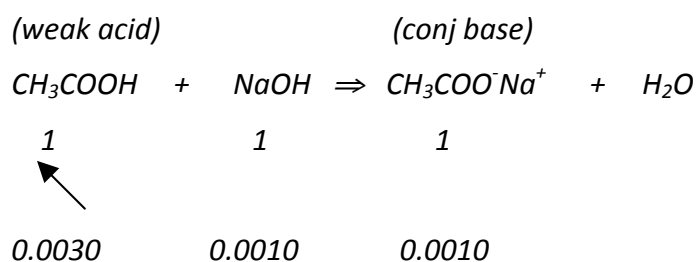


$$K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\begin{aligned}
 \text{actual moles CH}_3\text{COOH} &= c \times v \\
 &= 0.100 \times (30 / 1000) \\
 &= 0.0030 \text{ mol} \\
 &= 0.0030 \text{ mol dm}^{-3} \text{ (2SF)}
 \end{aligned}$$

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

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



(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:

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

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

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

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 200cm³ of 0.10 mol dm⁻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 50cm³ of ammonia solution of concentration 0.10 mol dm⁻³ and 50cm³ of hydrochloric acid solution of concentration 0.050 mol dm⁻³. $pK_b(\text{NH}_3) = 4.75$ [4]
4. (N05/H) Calculate the pH of a buffer solution containing 0.0500 mol dm⁻³ of ethanoic acid ($K_a = 1.74 \times 10^{-5}$) 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 dm³ of 2.0×10^{-2} mol dm⁻³ benzoic acid, ($K_a = 6.3 \times 10^{-5}$) 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 10cm³ of the solution to 100cm³
 - 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 cm³ of 0.100 mol dm⁻³ CH₃COOH is placed in a beaker and mixed with 20 cm³ 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 CH₃COOH = 1.74×10^{-5} mol dm⁻³) [4]

Answer to example 2

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

$$\text{moles CH}_3\text{COOH} = c \times v = 1.0 \times (100.0/1000) = 0.10 \text{ mol or } 0.10 \text{ mol dm}^{-3}$$

(weak acid)		(salt)	
$\text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COO}^-\text{Na}^+ + \text{H}_2\text{O}$			
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 ;

$$\text{b) } n(\text{CH}_3\text{COONa}) = m \div M = 0.25 \text{ g} \div 82.04 \text{ g mol}^{-1} = 0.0031 \text{ mol} ;$$

$$[\text{CH}_3\text{COONa}] = n \div v = 0.00305 \text{ mol} \div 200 \text{ cm}^3 = 0.015 \text{ mol dm}^{-3} ; (2\text{SF})$$

c)

From the data booklet $K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$

$$[\text{H}^+] = \frac{K_a \times \text{CH}_3\text{COOH}}{\text{CH}_3\text{COO}^-} ;$$

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

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

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

2. (M06/H)

weak base and its salt / weak base and strong acid ;

3. (M05/H)

Calculate the pH of a mixture of 50cm³ of ammonia solution of concentration 0.10 mol dm⁻³ and 50cm³ of hydrochloric acid solution of concentration 0.050 mol dm⁻³.
 $pK_b(\text{NH}_3) = 4.75$

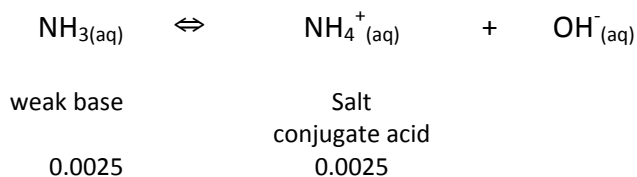
$$\begin{aligned} n(\text{HCl}) &= c \times v \\ &= 0.050 \times (50 / 1000) \\ &= 0.0025 \text{ mol} \\ &= 0.0025 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} n(\text{NH}_3) &= c \times v \\ &= 0.10 \times (50 / 1000) \\ &= 0.0050 \text{ mol} \\ &= 0.0050 \text{ mol dm}^{-3} ; \end{aligned}$$

NH_3 is in excess

$$n(\text{NH}_3) \text{ remaining} = 0.0050 - 0.0025 = 0.0025 \text{ mol} = 0.0025 \text{ mol dm}^{-3}$$

From mole ratio in the equation assume $[\text{NH}_4^+] = [\text{NH}_3] = 0.0025 \text{ mol dm}^{-3}$ because they are in a 1:1 mole ratio ;



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

$$K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3]}$$

$$[\text{OH}^-] = \frac{K_b \times [\text{NH}_3]}{[\text{NH}_4^+]}$$

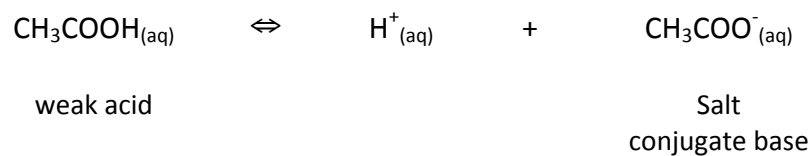
$$[\text{OH}^-] = \frac{1.78 \times 10^{-5} \times 0.0025}{0.0025}$$

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

$$pOH = 4.75$$

$$pH = 9.25 \text{ (allow 9.2 to 9.3) ;}$$

4. (N05/H)



$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{CH}_3\text{COOH}] = 0.0500 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COO}^-] = 0.100 \text{ mol dm}^{-3}$$

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

$$[\text{H}^+] = \frac{K_a \times \text{CH}_3\text{COOH}}{\text{CH}_3\text{COO}^-}$$

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

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

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

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

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

(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 ;

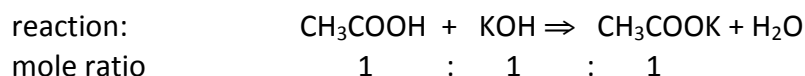
in equimolar amounts / so that $[\text{HCOOH}] = [\text{HCOONa}]$;

(from K_a expression) $\text{pH} = \text{p}K_a$;

9.

10. Will 30 cm³ of 0.100 mol dm⁻³ CH₃COOH & 10 cm³ of 0.100 mol dm⁻³ NaOH produce a buffer solution and if so what will be its pH?

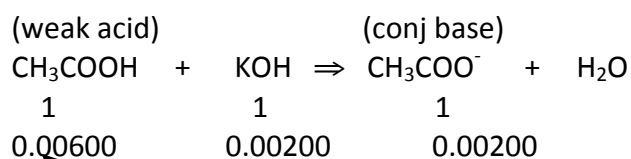
Answer



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

actual moles CH₃COOH = 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



(acid in excess by 0.00400 mole)

Therefore in this reaction you have 0.00600 – 0.00200 = 0.00400 mole of CH₃COOH 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:

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

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

$$\text{pH} = -\log [H^+] = -\log 3.48 \times 10^{-5} = 4.46 \quad (3\text{SF})$$