Chem Factsheet

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Buffers: Action and Calculations

To succeed in this topic you need to:
- understand definitions of Brønsted-Lowry acids and bases
- understand definitions of strong and weak acids and bases
- be able to calculate the pH of strong and weak acids and bases
- understand Le Chatelier's Principle
- be able to use the equation $pK_a = -\log_{10}K_a$

After working through this Factsheet you will:
- understand what a buffer solution does and how it does it
- be able to explain how to make a buffer solution
- be able to calculate the pH of buffer solutions

What does a buffer solution do?

Definition: A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added to it.

What this means is that, by adding a buffer solution to a mixture, the pH will stay roughly constant even when some acid or alkali is added to the mixture. This is useful in many experiments, especially many biological systems, where it can be vital to control the pH of an enzyme, for example.

What is a buffer solution made of?

Buffers can be acidic or alkaline. **Acid buffers** are made from a solution of a **weak** acid with a salt of same the weak acid. For example, an acid buffer could be made by mixing solutions of ethanoic acid (CH_3COOH, the weak acid) and sodium ethanoate (CH_3COONa, the salt). The pH of this solution would be below 7 (see below for how to calculate the pH of buffer solutions), so the buffer is acidic. **Alkali buffers** are made from a solution of a **weak** base with the salt of the same base. For example, you could mix ammonia solution (NH_3, the weak base) with ammonium chloride (NH_4Cl, the salt), and the pH of the resulting buffer solution would be above 7.

How do buffer solutions work?

Buffers work because they can absorb and release H^+ ions to maintain their pH. They do this by changing the position of equilibrium of the substances in solution.

Acid buffers

The weak acid (ethanoic acid, CH_3COOH) partially dissociates in solution (Equation 1), but the equilibrium lies a long way to the left because only a tiny percentage of acid dissociates:

Equation 1

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$

The salt (sodium ethanoate, CH_3COONa) dissociates completely in solution (Equation 2):

Equation 2

$$CH_3COONa\,(aq) \longrightarrow Na^+\,(aq) + CH_3COO^-\,(aq)$$

This means that this buffer solution contains relatively high concentrations of both CH_3COOH molecules and CH_3COO^- ions.

Note that we can use HA to represent any weak acid, which gives these **general equations**:

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$
$$NaA\,(aq) \longrightarrow Na^+\,(aq) + A^-\,(aq)$$

If an acid is added to the buffer, the concentration of H^+ ions increases. These extra H^+ ions combine with CH_3COO^- ions to make undissociated CH_3COOH (Equation 3), shifting the equilibrium in Equation 1 to the left. The concentration of H^+ ions (and therefore the pH) remains constant.

Equation 3

$$CH_3COO^-\,(aq) + H^+\,(aq) \longrightarrow CH_3COOH\,(aq)$$

If an alkali is added, the solution has to remove the extra OH^- ions. These combine with H^+ ions to make water (Equation 4). The equilibrium in Equation 1 will shift to the right to replace these used H^+ ions and again the pH will remain constant.

Equation 4

$$OH^-\,(aq) + H^+\,(aq) \longrightarrow H_2O\,(l)$$

Alkali buffers

Alkali buffers behave in similar ways to acid buffers, but there are subtle differences.

As with the acid buffer, the weak base (ammonia, NH_3, in this example) reacts with water to release ammonium ions (NH_4^+) and hydroxide ions (OH^-) (Equation 5), but the equilibrium lies a long way to the left because only a small percentage of ammonia dissociates:

Equation 5

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

Similarly, the salt (ammonium chloride, NH_4Cl) dissociates completely in solution (Equation 6):

Equation 6

$$NH_4Cl\,(aq) \longrightarrow NH_4^+\,(aq) + Cl^-\,(aq)$$

This means that this buffer solution contains relatively high concentrations of both NH_3 molecules and NH_4^+ ions.

Note that we can use B to represent any weak base, which gives these **general equations**:

$$B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH^-\,(aq)$$
$$BH^+Cl^-\,(aq) \longrightarrow BH^+\,(aq) + Cl^-\,(aq)$$

If acid is added, the concentration of H^+ ions will increase. These extra H^+ ions will combine with OH^- ions to make undissociated water (Equation 7). The equilibrium in Equation 5 will subsequently shift to the right to replace the OH^- ions.

Equation 7

$$H^+ (aq) + OH^- (aq) \longrightarrow H_2O (l)$$

If alkali is added, the solution has to remove the added OH^- ions. These react with NH_4^+ ions to make ammonia and water (Equation 8) and so the equilibrium in Equation 5 will shift to the left. Again the pH will remain constant.

Equation 8

$$OH^- (aq) + NH_4^+ (aq) \longrightarrow NH_3 (aq) + H_2O (l)$$

> ***Remember :*** *Don't forget that, with all buffer solutions, if a* ***large*** *amount of acid or alkali is added, then the pH will eventually change.*

Buffer Range

Buffers work effectively within a range of ±1 pH value of the pK_a of the weak acid (or the pK_b of the weak base). For example, ethanoic acid, the weak acid used in the example above, has a K_a of 1.76×10^{-5} moldm^{-3}. Its pK_a is therefore 4.75 (remember that $pK_a = -\log_{10}K_a$). The range of an ethanoic acid buffer is therefore from a pH of around 3.7 up to a pH of about 5.7.

Calculating the pH of a buffer solution

To calculate the pH of buffer solutions, you need to know:

- the amounts and concentrations of the weak acid (or base) and the salt in the buffer
- the K_a of the weak acid (or K_b of the weak base) – remember that this is a constant at a given temperature.

Example 1

A buffer solution was made containing 0.20 moldm^{-3} ethanoic acid and 0.25 moldm^{-3} sodium ethanoate. What is its pH? The K_a of ethanoic acid is 1.76×10^{-5} moldm^{-3}.

Step 1. Write an expression for K_a:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Step 2. Rearrange to give an expression for $[H_3O^+]$:

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Step 3. The salt is fully ionised in solution, so we can assume that $[CH_3COO^-]$ is equal to the concentration of the salt solution. So in this case $[CH_3COO^-] = 0.25$ moldm^{-3}.

Step 4. The weak acid is very slightly dissociated in solution, so we assume that $[CH_3COOH]$ is, in fact, equal to the concentration of acid in the buffer. In this case, then, $[CH_3COOH] = 0.20$ moldm^{-3}.

Step 5. Substitute the values into the equation:

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.76 \times 10^{-5} \times \frac{0.20}{0.25}$$

$$[H_3O^+] = 1.41 \times 10^{-5} \text{ moldm}^{-3}$$

Step 6. Calculate the pH:

$$pH = -\log_{10}[H^+] = -\log_{10}(1.41 \times 10^{-5}) = \underline{\mathbf{4.85}}$$

Example 2

A buffer solution was made by mixing 30.0 cm^3 of 2.0 moldm^{-3} ethanoic acid ($K_a = 1.76 \times 10^{-5}$ moldm^{-3}) with 35.0 cm^3 of 1.5 moldm^{-3} sodium ethanoate. What is its pH?

The first steps this time involve calculating the concentrations of the two liquids in the buffer solution.

Step 1. Calculate the number of moles of ethanoic acid in the solution:

$$\text{moles} = \text{concentration} \times \text{volume}$$
$$= 2.0 \times \frac{30.0}{1000} = 0.060 \text{ moles ethanoic acid}$$

Step 2. Calculate the number of moles of ethanoate ions in the solution:

$$\text{moles} = \text{concentration} \times \text{volume}$$
$$= 1.5 \times \frac{35.0}{1000} = 0.053 \text{ moles ethanoate ions}$$

The rest of the calculation follows the same route as Example 1:

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.76 \times 10^{-5} \times \frac{0.060/V_{tot}}{0.053/V_{tot}}$$

$$[H_3O^+] = 2.00 \times 10^{-5} \text{ moldm}^{-3}$$

$$pH = -\log_{10}[H^+] = -\log_{10}(2.00 \times 10^{-5}) = \underline{\mathbf{4.70}}$$

> **Note:** You don't need to calculate the actual concentrations of ethanoic acid and ethanoate ions, because the total volume of the solution (V_{tot}) cancels itself out in the equation.

Example 3

10.0 cm^3 of 0.10 moldm^{-3} hydrochloric acid was added to the buffer solution in Example 2. What is its new pH?

Adding hydrochloric acid to the buffer involves adding H^+ ions. The first step is to calculate how many moles of H^+ ions are added.

$$\text{moles} = \text{concentration} \times \text{volume}$$
$$= 0.10 \times \frac{10}{1000} = 0.001 \text{ moles } H^+ \text{ ions.}$$

These H^+ ions will react with 0.001 moles of CH_3COO^- ions to form 0.001 moles of CH_3COOH as shown in equation 9.

Equation 9

$$CH_3CHOO^- (aq) + H^+ (aq) \longrightarrow CH_3COOH (aq)$$

We need, therefore, to calculate new values of $[CH_3COO^-]$ and $[CH_3COOH]$.

New moles of CH_3COO^- ions = 0.053 – 0.001 = 0.052 moles.

New moles of CH_3COOH = 0.060 + 0.001 = 0.061 moles.

The rest of the calculation now follows the same route as before:

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.76 \times 10^{-5} \times \frac{0.061/V_{tot}}{0.052/V_{tot}}$$

$$[H_3O^+] = 2.07 \times 10^{-5} \text{ moldm}^{-3}$$

$$pH = -\log_{10}[H^+] = -\log_{10}(2.00 \times 10^{-5}) = \underline{\mathbf{4.68}}$$

You can see that, as expected, the addition of hydrochloric acid to this buffer solution has changed the pH only slightly.

Exam Hints:

1. Learn the definition of a buffer solution.
2. Practice writing equations to show how buffers work.
3. Remember that for a weak acid, [acid] is not equal to $[H^+]$.
4. Practice and take great care with the calculations; many students make mistakes with them.

Practice Questions

1. Given samples of the following solutions (all 0.20 $moldm^{-3}$), pick
   (a) a pair which could be mixed to make an acidic buffer, and
   (b) a pair which could be mixed to make an alkali buffer.

   Ammonia
   Ammonium nitrate
   Ethanoic acid
   Nitric acid
   Sodium hydroxide
   Sodium ethanoate
   Sodium nitrate
   Sulphuric acid

2. A buffer solution can be made by mixing solutions of propanoic acid (CH_3CH_2COOH) with sodium propanoate (CH_3CH_2COONa). Explain how this buffer maintains a constant pH when a small amount of hydrochloric acid is added.

3. Three buffer solutions contain ethanoic acid ($K_a = 1.76 \times 10^{-5}$ mol dm^{-3}) at a concentration of 0.15 $moldm^{-3}$. They also contain sodium ethanoate at concentrations of :
   (a) 0.10 $moldm^{-3}$
   (b) 0.25 $moldm^{-3}$ and
   (c) 0.50 $moldm^{-3}$.
   Calculate the pH values of the three solutions.

4. What is the pH of the buffer solution formed by mixing 25.0 cm^3 of 0.20 $moldm^{-3}$ sodium hydroxide with 25.0 cm^3 of 0.40 $moldm^{-3}$ ethanoic acid ($K_a = 1.76 \times 10^{-5}$ $moldm^{-3}$)?

5. A buffer solution was made by mixing 10.0 cm^3 of 0.025 mol dm^{-3} ethanoic acid ($K_a = 1.76 \times 10^{-5}$ mold m^{-3}) with 15.0 cm^3 of 0.025 mol dm^{-3} sodium ethanoate.

   A sample of 15 cm^3 0.010 $moldm^{-3}$ hydrochloric acid was added. Calculate the pH of the buffer solution (a) before, and (b) after the addition of the hydrochloric acid.

Answers

1. (a) acidic buffer: ethanoic acid and sodium ethanoate
   (b) alkali buffer: ammonia and ammonium nitrate

2. Propanoic acid is weak, so it only partially dissociates in solution. The equilibrium lies a long way to the left:

   $$CH_3CH_2COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CH_2COO^-\,(aq)$$

   The sodium propanoate salt ionises fully in solution:

   $$CH_3CH_2COONa\,(aq) \longrightarrow Na^+\,(aq) + CH_3CH_2COO^-\,(aq)$$

   This buffer solution therefore contains relatively high concentrations of both CH_3CH_2COOH molecules and $CH_3CH_2COO^-$ ions.

   When hydrochloric acid is added, the additional H^+ ions combine with $CH_3CH_2COO^-$ ions to make undissociated propanoic acid:

   $$CH_3CH_2COO^-\,(aq) + H^+\,(aq) \longrightarrow CH_3CH_2COOH\,(aq)$$

   The equilibrium shifts to the left and the concentration of H^+ ions (and therefore the pH) remains constant.

3. (a) 4.58, (b) 4.98, (c) 5.28.

4. 4.75. You first need to calculate the number of moles of NaOH $= 0.20 \times (25/1000) = 0.005$.
   Next, calculate the number of moles of CH_3COOH $= 0.4 \times (25/1000) = 0.010$.
   NaOH reacts with CH_3COOH to make sodium ethanoate and water:

   $$NaOH\,(aq) + CH_3COOH\,(aq) \rightarrow CH_3CH_2COONa\,(aq) + H_2O\,(l)$$

   0.005 moles of NaOH will make 0.005 moles of sodium ethanoate, leaving (0.010-0.005) = 0.005 moles of ethanoic acid unreacted.

   $$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.76 \times 10^{-5} \times \frac{0.005}{0.005}$$

   $$[H_3O^+] = 1.76 \times 10^{-5}\ moldm^{-3}$$

   $$pH = -\log_{10}[H^+] = 4.75$$

5. (a) 4.93, (b) 4.50.

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