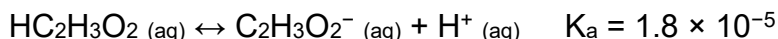


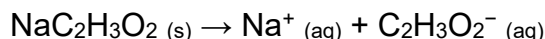


Buffers

Consider the acetic acid/acetate equilibrium:



$[\text{C}_2\text{H}_3\text{O}_2^-]$ is small because the equilibrium lies to the left. $[\text{C}_2\text{H}_3\text{O}_2^-]$ can be increased by adding an acetate salt which dissolves completely (e.g., sodium acetate):



A **buffer** can be formed by combining a weak acid of known concentration with a known concentration of the salt (anion) of that acid. Thus the $[\text{H}^+]$ of the solution will depend on the ratio of the acid to the anion.

Consider the K_a expression for the acetic acid ionization:

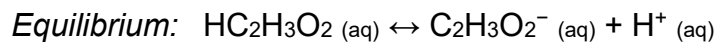
$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Solving for $[\text{H}^+]$,

$$[\text{H}^+] = \frac{K_a[\text{HC}_2\text{H}_3\text{O}_2]}{[\text{C}_2\text{H}_3\text{O}_2^-]}$$

Notice that $[\text{H}^+]$ only changes as the ratio of concentrations changes.

Let's examine the effect of adding acid or base to a buffer solution. Given a buffer where $[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-] = 1.0 \text{ M}$ (large!)



Stress: Add H^+ .

Effect: The equilibrium will shift to the left to relieve the stress. $[\text{C}_2\text{H}_3\text{O}_2^-]$ decreases; $[\text{HC}_2\text{H}_3\text{O}_2]$ increases. Those concentrations were initially large, so their ratio stays much the same. Therefore pH is only slightly affected.

Stress: Add OH^- .

Effect: The added OH^- reacts with the H^+ to form water. $[\text{H}^+]$ decreases, and the equilibrium shifts right to compensate. $[\text{HC}_2\text{H}_3\text{O}_2]$ decreases; $[\text{C}_2\text{H}_3\text{O}_2^-]$ increases. Again, those concentrations were initially large, so their ratio remains essentially the same. The pH is only slightly affected.

A buffer can also be formed by combining a weak base with the salt (cation) of that base. Consider the $\text{NH}_3/\text{NH}_4^+$ alkaline buffer:



Stress: Add H^+ .

Effect: Water is formed with the OH^- . $[\text{OH}^-]$ decreases. The equilibrium shifts right, $[\text{NH}_3]$ decreases and $[\text{NH}_4^+]$ increases.



Stress: Add OH^- .
Effect: $[\text{OH}^-]$ increases. The equilibrium shifts left. $[\text{NH}_4^+]$ decreases; $[\text{NH}_3]$ increases.

EXERCISES

- A. 1) What is the pH of an acetic acid/acetate buffer made from a mixture of 1.00 M $\text{NaC}_2\text{H}_3\text{O}_2$ and 1.00 M $\text{HC}_2\text{H}_3\text{O}_2$?
2) 0.20 mol HCl is added to 1.00 L of the buffer. In which direction will the equilibrium shift?
3) How are the concentrations of acetic acid and acetate affected by the HCl ?
4) What is the new pH after adding the HCl ? [*Hint: Assume the shift uses all the H^+ up and recalculate $[\text{HC}_2\text{H}_3\text{O}_2]$ and $[\text{C}_2\text{H}_3\text{O}_2^-]$.]*
5) 0.20 mol NaOH is added to 1.00 L of the original buffer from (1), *not* (4)! Which way will the equilibrium shift?
6) How are the concentrations of acetic acid and acetate affected by the NaOH ?
7) What is the new pH after adding the NaOH ?
- B. An alkaline buffer was prepared by mixing 200 mL of a 0.60 M NH_3 solution and 300 mL of a 0.30 M NH_4Cl solution.
1) Determine $[\text{NH}_3]$.
2) Determine $[\text{NH}_4^+]$.
3) Using the equilibrium equation, derive an expression for $[\text{OH}^-]$.
4) Determine $[\text{OH}^-]$.
5) Determine the pH of the buffer.
6) Determine the pH after 0.020 mol H^+ is added.
- C. 1) What is the effect on the pH when an acid is added to a buffer?
2) What is the effect on the pH when a base is added to a buffer?

SOLUTIONS

- A. (1) 4.74 (2) to the left (3) acid increases; salt decreases (4) 4.57 (5) to the right (6) acid decreases; salt increases (7) 4.92
B. (1) 0.24 M (2) 0.18 M (3) $[\text{OH}^-] = \frac{K_b \cdot [\text{NH}_3]}{[\text{NH}_4^+]}$, $K_b = 1.8 \times 10^{-5}$ (4) 2.4×10^{-5} M (5) 9.4 (6) 9.2 ($[\text{OH}^-] = 1.6364 \dots \times 10^{-5}$)
C. (1) pH goes down; it becomes more acidic. (2) pH goes up; it becomes more basic.

