Buffers

Consider the acetic acid/acetate equilibrium:

$$HC_2H_3O_{2\ (aq)} \leftrightarrow C_2H_3O_2^-{}_{(aq)} + H^+{}_{(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

$[C_2H_3O_2^-]$ is small because the equilibrium lies to the left. $[C_2H_3O_2^-]$ can be increased by adding an acetate salt which dissolves completely (e.g., sodium acetate):

$$NaC_2H_3O_{2\ (s)} \rightarrow Na^+{}_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

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 $[H^+]$ of the solution will depend on the ratio of the acid to the anion.

Consider the K_a expression for the acetic acid ionization:

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Solving for $[H^+]$,

$$[H^+] = \frac{K_a[HC_2H_3O_2]}{[C_2H_3O_2^-]}$$

Notice that $[H^+]$ 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 $[HC_2H_3O_2] = [C_2H_3O_2^-] = 1.0$ M (large!)

Equilibrium: $HC_2H_3O_{2\ (aq)} \leftrightarrow C_2H_3O_2^-{}_{(aq)} + H^+{}_{(aq)}$
Stress: Add H^+.
Effect: The equilibrium will shift to the left to relieve the stress. $[C_2H_3O_2^-]$ decreases; $[HC_2H_3O_2]$ 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. $[H^+]$ decreases, and the equilibrium shifts right to compensate. $[HC_2H_3O_2]$ decreases; $[C_2H_3O_2^-]$ 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 NH_3/NH_4^+ alkaline buffer:

Equilibrium: $NH_{3\ (aq)} + H_2O_{\ (\ell)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_b = 1.8 \times 10^{-5}$
Stress: Add H^+.
Effect: Water is formed with the OH^-. $[OH^-]$ decreases. The equilibrium shifts right, $[NH_3]$ decreases and $[NH_4^+]$ increases.

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Stress: Add OH^-.
Effect: $[OH^-]$ increases. The equilibrium shifts left. $[NH_4^+]$ decreases; $[NH_3]$ increases.

EXERCISES

A. 1) What is the pH of an acetic acid/acetate buffer made from a mixture of 1.00 M $NaC_2H_3O_2$ and 1.00 M $HC_2H_3O_2$?

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* <u>*all*</u> *the* H^+ *up and recalculate* $[HC_2H_3O_2]$ *and* $[C_2H_3O_2^-]$.]

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 $NH_4C\ell$ solution.

1) Determine $[NH_3]$.

2) Determine $[NH_4^+]$.

3) Using the equilibrium equation, derive an expression for $[OH^-]$.

4) Determine $[OH^-]$.

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 an 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) $[OH^-] = \frac{K_b \cdot [NH_3]}{[NH_4^+]}$, $K_b = 1.8 \times 10^{-5}$ (4) 2.4×10^{-5} M (5) 9.4 (6) 9.2 (*$[OH^-] = 1.6364\ldots \times 10^{-5}$*)

C. (1) pH goes down; it becomes more acidic. (2) pH goes up; it becomes more basic.