# Solutions and Complex-Ion Equilibria

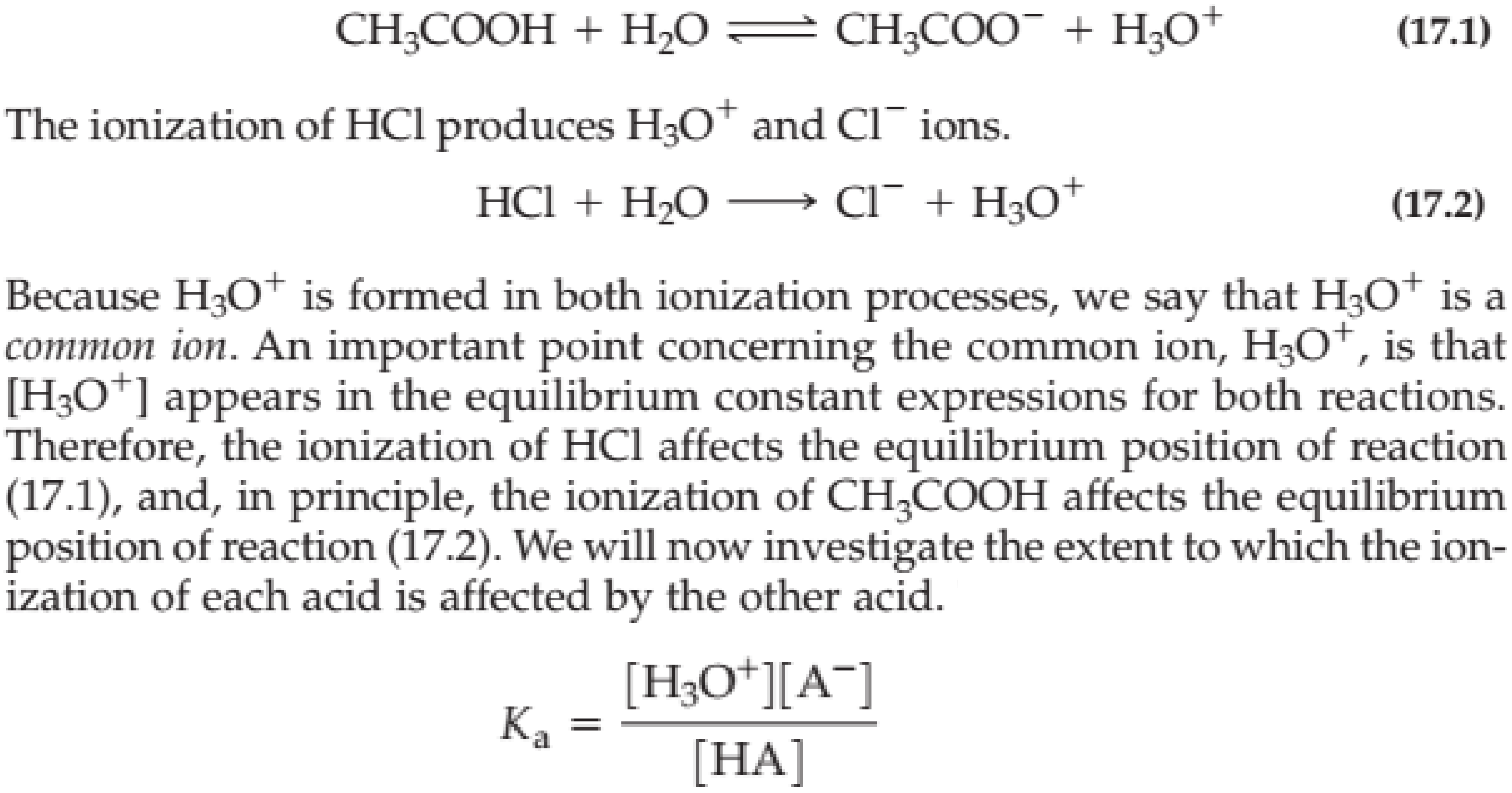
References : 1.General Chemistry- principles and modern applications (Petrucci, Herring, Madura, Bissonnette).
2. Chemistry_10th_Edition_Raymond_Chang

In this section, we will consider the acid-base properties of a solution with two dissolved solutes that contain the same ion (cation or anion), called the common ion. The presence of a common ion suppresses the ionization of a weak acid or a weak base.

## The Common Ion Effect:

### Solutions of Weak Acids and Strong Acids

Consider a solution that is at the same time 0.100 M $CH_3COOH$ and 0.100 M HCl. We can write separate equations for the ionizations of the acids, one weak and the other strong. The ionization of $CH_3COOH$ produces and $CH_3COO^-$ ions:



$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad (17.1)$$

The ionization of HCl produces $H_3O^+$ and $Cl^-$ ions.

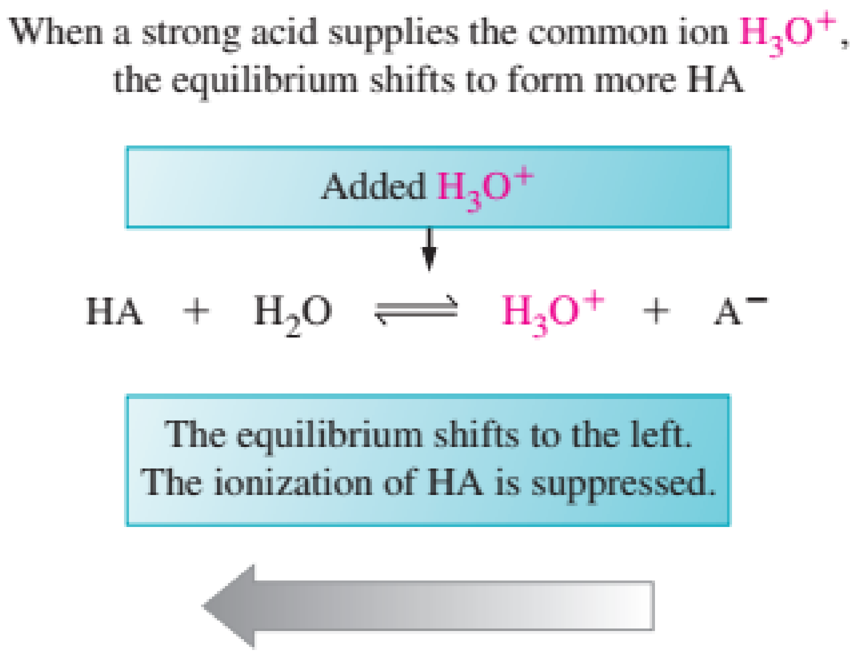
$$HCl + H_2O \longrightarrow Cl^- + H_3O^+ \qquad (17.2)$$

Because $H_3O^+$ is formed in both ionization processes, we say that $H_3O^+$ is a *common ion*. An important point concerning the common ion, $H_3O^+$, is that $[H_3O^+]$ appears in the equilibrium constant expressions for both reactions. Therefore, the ionization of HCl affects the equilibrium position of reaction (17.1), and, in principle, the ionization of $CH_3COOH$ affects the equilibrium position of reaction (17.2). We will now investigate the extent to which the ionization of each acid is affected by the other acid.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Example illustrates that the ionization of a weak acid is significantly suppressed by the presence (or addition) of a strong acid. It is also the case that the ionization of a weak base is significantly suppressed by the presence or addition of a strong base. These statements can be justified by applying Le Châtelier's principle. Let's first consider a solution of a weak acid, HA, that has reached equilibrium. The effect of adding strong acid is illustrated below.

For a solution of a weak base, B, that has reached equilibrium, the effect of adding a strong base can be described similarly.

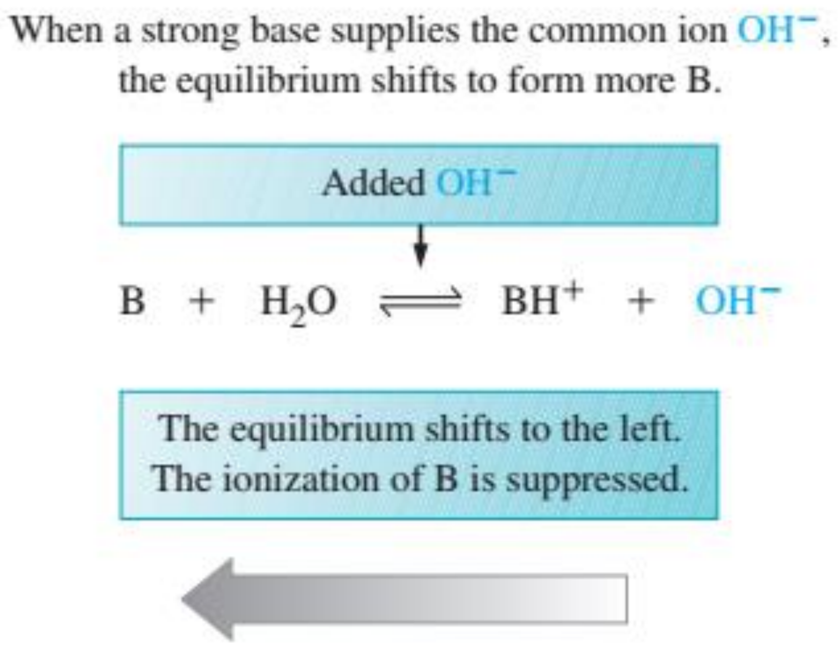


When a strong acid supplies the common ion $H_3O^+$, the equilibrium shifts to form more HA

Added $H_3O^+$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium shifts to the left.
The ionization of HA is suppressed.



When a strong base supplies the common ion $OH^-$, the equilibrium shifts to form more B.

Added $OH^-$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

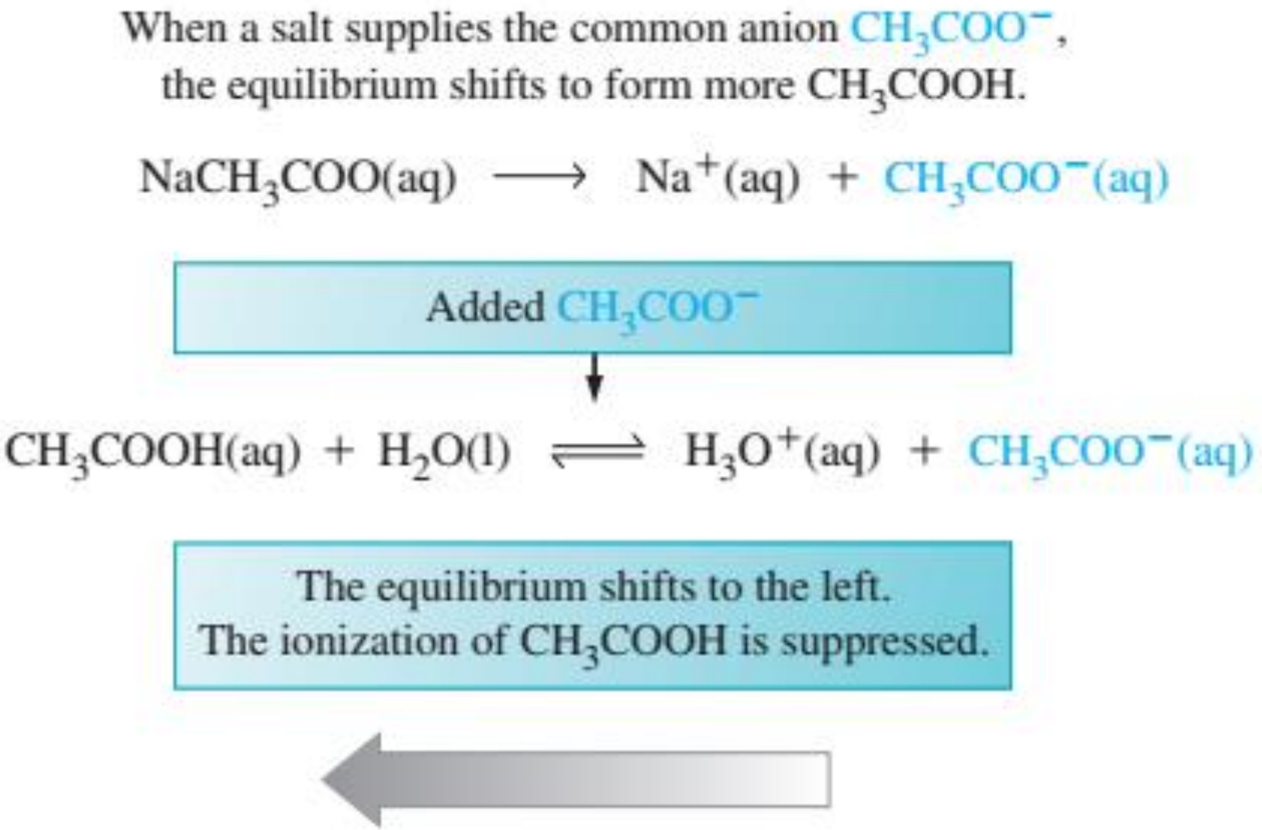
The equilibrium shifts to the left.
The ionization of B is suppressed.

## Solutions of Weak Acids and Their Salts

If sodium acetate and acetic acid are dissolved in the same solution, for example, they both dissociate and ionize to produce $CH_3COO^-$ ions:

$$CH_3COONa(s) \xrightarrow{H_2O} CH_3COO^-(aq) + Na^+(aq)$$
$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$CH_3COONa$ is a strong electrolyte, so it dissociates completely in solution, but $CH_3COOH$, a weak acid, ionizes only slightly. According to Le Châtelier’s principle, the addition of $CH_3COO^-$ ions from $CH_3COONa$ to a solution of $CH_3COOH$ will suppress the ionization of $CH_3COOH$ (that is, shift the equilibrium from right to left), thereby decreasing the hydrogen ion concentration. Thus, a solution containing both $CH_3COOH$ and $CH_3COONa$ will be less acidic than a solution containing only $CH_3COOH$ at the same concentration. The shift in equilibrium of the acetic acid ionization is caused by the acetate ions from the salt. $CH_3COO^-$ is the common ion because it is supplied by both $CH_3COOH$ and $CH_3COONa$.



When a salt supplies the common anion $CH_3COO^-$, the equilibrium shifts to form more $CH_3COOH$.

$$NaCH_3COO(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$

Added $CH_3COO^-$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

The equilibrium shifts to the left.
The ionization of $CH_3COOH$ is suppressed.

The common ion effect is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance. The common ion effect plays an important role in determining the pH of a solution. Here we will study the common ion effect as it relates to the pH of a solution. Keep in mind that despite its distinctive name, the common ion effect is simply a special case of Le Châtelier’s principle.

The ionization of a weak electrolyte is suppressed by the addition of an ion that is the product of the ionization and is known as the common-ion effect.

## Buffer Solutions

A buffer solution is a solution of (1) a weak acid or a weak base and (2) its salt; both components must be present. The solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base. Buffers are very important to chemical and biological systems.

The pH in the human body varies greatly from one fluid to another; for example, the pH of blood is about 7.4, whereas the gastric juice in our stomachs has a pH of about 1.5. These pH values, which are crucial for proper enzyme function and the balance of osmotic pressure, are maintained by buffers in most cases.

A buffer solution must contain a relatively large concentration of acid to react with any $OH^-$ ions that are added to it, and it must contain a similar concentration of base to react with any added $H^+$ ions. Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair, for example, a weak acid and its conjugate base (supplied by a salt) or a weak base and its conjugate acid (supplied by a salt).

A simple buffer solution can be prepared by adding comparable molar amounts of acetic acid ($CH_3COOH$) and its salt sodium acetate ($CH_3COONa$) to water. The equilibrium concentrations of both the acid and the conjugate base (from $CH_3COONa$) are assumed to be the same as the starting concentrations. A solution containing these two substances has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociates completely in water:

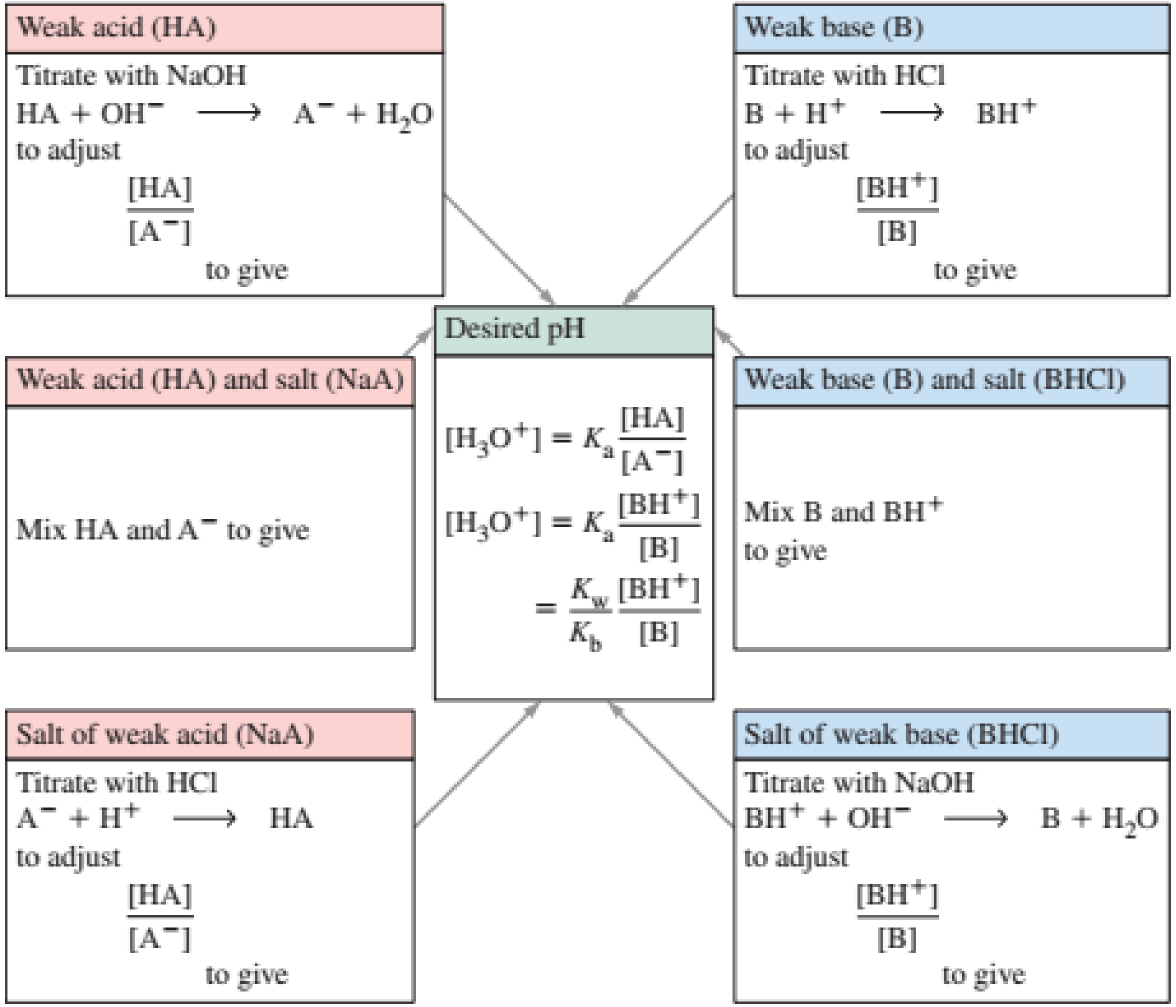
$$\mathrm{CH_3COONa}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3COO^-}(aq) + \mathrm{Na^+}(aq)$$

If a base is added to the buffer system, the OH ions will be neutralized by the acid in the buffer:

$$\mathrm{CH_3COOH}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l)$$

If an acid is added, the $H^+$ ions will be consumed by the conjugate base in the buffer,

$$\mathrm{CH_3COO^-}(aq) + \mathrm{H^+}(aq) \longrightarrow \mathrm{CH_3COOH}(aq)$$



▲ FIGURE 17-5

**Six methods for preparing buffer solutions**

Depending on the pH range required and the type of experiment the buffer is to be used for, either a weak acid or a weak base can be used to prepare a buffer solution.

## An Equation for Buffer Solutions: The Henderson–Hasselbalch Equation

For buffer calculations, it is often useful to describe a buffer solution by means of an equation known as the Henderson–Hasselbalch equation. Biochemists and molecular biologists commonly use this equation. To derive this variation of the ionization constant expression, let's consider a mixture of a hypothetical weak acid, HA and its salt, NaA. We start with the familiar expressions

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

and rearrange the right side of the Ka expression to obtain

$$K_a = [H_3O^+] \times \frac{[A^-]}{[HA]}$$

Next, we take the *negative logarithm* of each side of this equation.

$$-\log K_a = -\log[H_3O^+] - \log\frac{[A^-]}{[HA]}$$

Now, recall that $pH = -\log[H_3O^+]$ and that $pK_a = -\log K_a$, which gives

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

Solve for pH by rearranging the equation.

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$A^-$ is the conjugate base of the weak acid HA, so we can write the more general equation (17.7), the Henderson–Hasselbalch equation.

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]} \qquad \textbf{(17.7)}$$

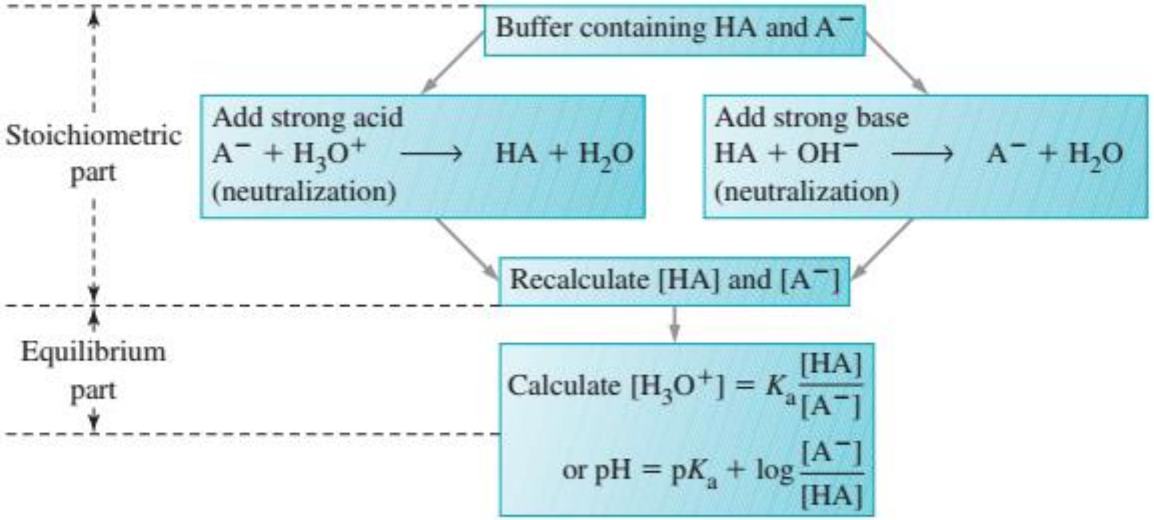
$$pH = pK_a + \log\frac{[\text{conjugate base}]_{\text{initial}}}{[\text{acid}]_{\text{initial}}}$$

## Calculating pH Changes in Buffer Solutions

To calculate how the pH of a buffer solution changes when small amounts of a strong acid or base are added, we must first use stoichiometric principles to establish how much of one buffer component is consumed and how much of the other component is produced. Then the new concentrations of weak acid (or weak base) and its salt can be used to calculate the pH of the buffer solution. Essentially, this problem is solved in two steps.

First, we assume that the neutralization reaction proceeds to completion and determine new stoichiometric concentrations.

Then these new stoichiometric concentrations are substituted into the equilibrium constant expression and the expression is solved for which is converted to pH. This method is applied in Example 17-6 and illustrated in Figure 17-6.



▲ FIGURE 17-6

**Calculation of the new pH of a buffer after strong acid or base is added**

The stoichiometric and equilibrium parts of the calculation are indicated. This scheme can also be applied to the conjugate acid–base pair $BH^+/B$, where B is a base.

**Buffer capacity** refers to the amount of acid or base that a buffer can neutralize before its pH changes appreciably. In general, the maximum buffer capacity exists when the concentrations of a weak acid and its conjugate base are kept *large* and *approximately equal to each other*.