Pearson

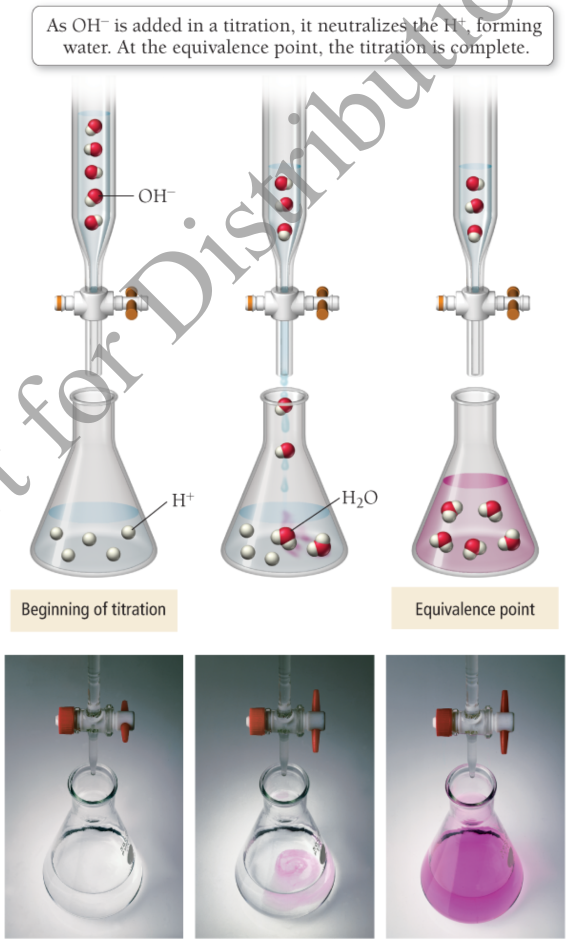
17.4: Titrations and pH Curves

Key Concept Video **The Titration of a Weak Acid with a Strong Base**

We first examined acid–base titrations in Section 8.7. In a typical **acid–base titration**, a basic (or acidic) solution of unknown concentration reacts with an acidic (or basic) solution of known concentration. The known solution is slowly added to the unknown one, while the pH is monitored with either a pH meter or an **indicator** (a substance whose color depends on the pH). As the acid and base combine, they neutralize each other. At the **equivalence point**—the point in the titration when the number of moles of base is stoichiometrically equal to the number of moles of acid—the titration is complete. When the equivalence point is reached, neither reactant is in excess and the number of moles of the reactants is related by the reaction stoichiometry (Figure 17.5).

Figure 17.5 **Acid–Base Titration**

The solution in the flask contains the indicator phenolthalein, which produces the color change at or near the equivalence point.

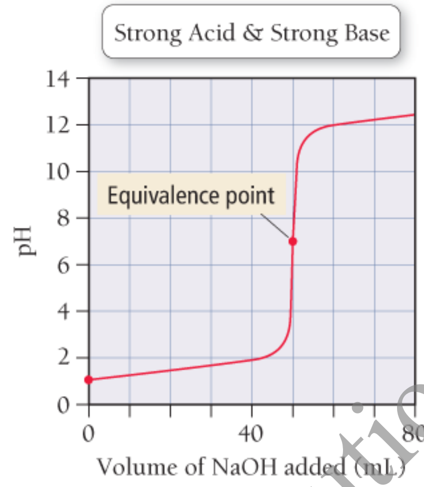

As OH^- is added in a titration, it neutralizes the H^+, forming water. At the equivalence point, the titration is complete.

> The equivalence point is so named because the number of moles of acid and base are stoichiometrically equivalent at this point.

In this section, we examine acid–base titrations more closely, concentrating on the pH changes that occur during the titration. A plot of the pH of the solution during a titration is a *titration curve* or *pH curve*. Figure 17.6 is a pH curve for the titration of HCl with NaOH Before any base is added to the solution, the pH is low (as expected for a solution of HCl). As the NaOH is added, the solution becomes less acidic because the NaOH begins to neutralize the HCl. The point of inflection in the middle of the curve is the equivalence point. Notice that the pH changes very quickly near the equivalence point (small amounts of added base cause large changes in pH). Beyond the equivalence point, the solution is basic because the HCl has been completely neutralized and excess base is being added to the solution. The exact shape of the pH curve depends on several factors, including the strength of the acid or base being titrated. Let’s consider several combinations individually.

Figure 17.6 Titration Curve: Strong Acid + Strong Base

This curve represents the titration of 50.0 mL of 0.100 M HCl with 0.100 M NaOH.



The Titration of a Strong Acid with a Strong Base

Consider the titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH. We begin by calculating the volume of base required to reach the equivalence point, and then we determine the pH at several points during the titration.

Volume of NaOH Required to Reach the Equivalence Point

During the titration, the added sodium hydroxide neutralizes the hydrochloric acid:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{H_2O}(l) + \mathrm{NaCl}(aq)$$

The equivalence point is reached when the number of moles of base added equals the number of moles of acid initially in solution. We calculate the amount of acid initially in solution from its volume and its concentration:

$$\text{initial mol HCl} = 0.0250\ \mathrm{L} \times \frac{0.100\ \mathrm{mol}}{1\ \mathrm{L}} = 0.00250\ \mathrm{mol\ HCl}$$

The amount of NaOH that must be added is 0.00250 mol NaOH. We calculate the volume of NaOH required from its concentration:

$$\text{volume NaOH solution} = 0.00250\ \mathrm{mol} \times \frac{1\ \mathrm{L}}{0.100\ \mathrm{mol}} = 0.0250\ \mathrm{L}$$

The equivalence point is reached when 25.0 mL of NaOH has been added. In this case, the concentrations of both solutions are identical, so the volume of NaOH solution required to reach the equivalence point is equal to the volume of the HCl solution that is being titrated.

Initial pH (before Adding Any Base)

The initial pH of the solution is simply the pH of a 0.100 M HCl solution. Since HCl is a strong acid, the concentration of H_3O^+ is also 0.100 M and the pH is 1.00:

$$\begin{aligned} pH &= -\log\left[H_3O^+\right] \\ &= -\log(0.100) \\ &= 1.00 \end{aligned}$$

pH after Adding 5.00 mL NaOH

As NaOH is added to the solution, it neutralizes H_3O^+:

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2\,H_2O(l)$$

We calculate the amount of H_3O^+ at any given point (before the equivalence point) by using the reaction stoichiometry—1 mol of NaOH neutralizes 1 mol of H_3O^+ The initial number of moles of H_3O^+ (as we just calculated) is 0.00250 mol. We calculate the number of moles of NaOH added at 5.00 mL by multiplying the added volume (in L) by the concentration of the NaOH solution:

$$\text{mol NaOH added} = 0.00500\text{ L} \times \frac{0.100\text{ mol}}{1\text{ L}} = 0.000500\text{ mol NaOH}$$

The addition of OH^- causes the amount of H^+ to decrease as shown in the following table:

	$OH^-(aq)$ +	$H_3O^+(aq) \longrightarrow$	$2\,H_2O(l)$
Before addition	≈0.00 mol	0.00250 mol	
Addition	0.000500 mol	—	
After addition	≈0.00 mol	0.00200 mol	

We calculate the H_3O^+ concentration by dividing the number of moles of H_3O^+ remaining by the *total volume* (initial volume plus added volume):

$$[H_3O^+] = \frac{0.00200\text{ mol }H_3O^+}{\underbrace{0.0250\text{ L}}_{\text{Initial volume}} + \underbrace{0.00500\text{ L}}_{\text{Added volume}}} = 0.0667\text{ M}$$

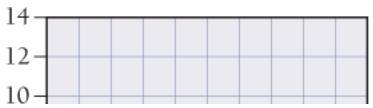
The pH is therefore 1.18.

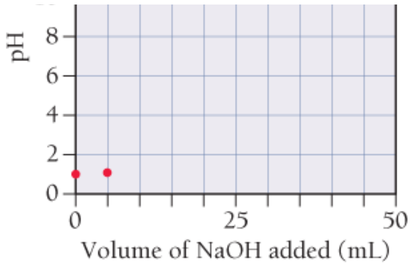
$$\begin{aligned} pH &= -\log 0.0667 \\ &= 1.18 \end{aligned}$$

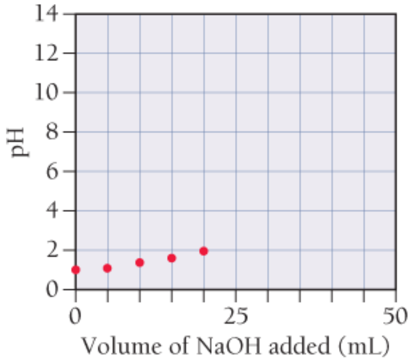
pH Values after Adding 10.0, 15.0, and 20.0 mL NaOH

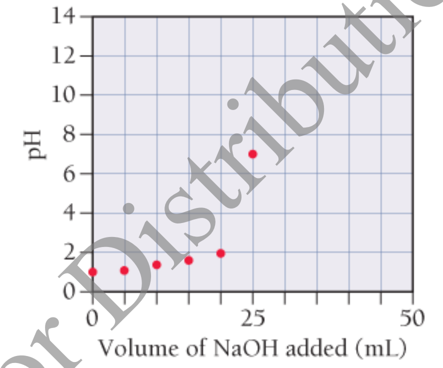
As more NaOH is added, it further neutralizes the H_3O^+ in the solution. We calculate the pH at each of these points in the same way that we calculated the pH at the 5.00 mL point. The results are tabulated as follows:

Volume (mL)	pH
10.0	1.37
15.0	1.60
20.0	1.95









pH after Adding 25.0 mL NaOH (Equivalence Point)

The pH at the equivalence point of a strong acid–strong base titration is always 7.00 (at 25 °C). At the equivalence point, the strong base has completely neutralized the strong acid. The only source of hydronium ions then is the ionization of water. The $[H_3O^+]$ at 25 °C from the ionization of water is 1.00×10^{-7} and the pH is 7.00.

pH after Adding 30.00 mL NaOH

As NaOH is added beyond the equivalence point, it becomes the excess reagent. We calculate the amount of OH^- at any given point (past the equivalence point) by subtracting the initial amount of H_3O^+ from the amount of OH^- added. The number of moles of OH^- added at 30.00 mL is:

$$\text{mol OH}^- \text{added} = 0.0300 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.00300 \text{ mol OH}^-$$

The number of moles of OH^- remaining after neutralization is shown in the following table:

	$OH^-(aq)$ +	$H_3O^+(aq)$	$\longrightarrow 2\,H_2O(l)$
Before addition	≈0.00 mol	0.00250 mol	

Addition	0.00300 mol	—	
After addition	0.00050 mol	0.00 mol	

We calculate the OH^- concentration by dividing the number of moles of OH^- remaining by the *total volume* (initial volume plus added volume):

$$\left[OH^-\right] = \frac{0.000500 \text{ mol } OH^-}{0.0250\text{L} + 0.0300\text{L}} = 0.00909 \text{ M}$$

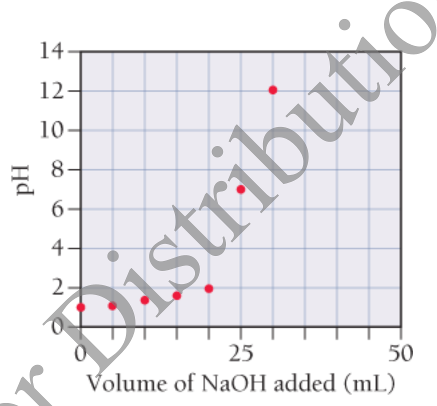
We can then calculate the $\left[H_3O^+\right]$ and pH:

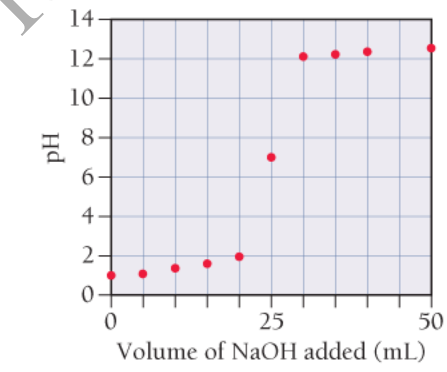
$$\left[H_3O^+\right]\left[OH^-\right] = 10^{-14}$$

$$\begin{aligned}\left[H_3O^+\right] &= \frac{10^{-14}}{\left[OH^-\right]} = \frac{10^{-14}}{0.00909} \\ &= 1.10 \times 10^{-12}\text{M} \\ \text{pH} &= -\log\left(1.10 \times 10^{-12}\right) \\ &= 11.96\end{aligned}$$

pH Values after Adding 35.0, 40.0, and 50.0 mL NaOH

As more NaOH is added, it further increases the basicity of the solution. We calculate the pH at each of these points in the same way that we calculated the pH at the 30.00 mL point. We tabulate the results as follows:



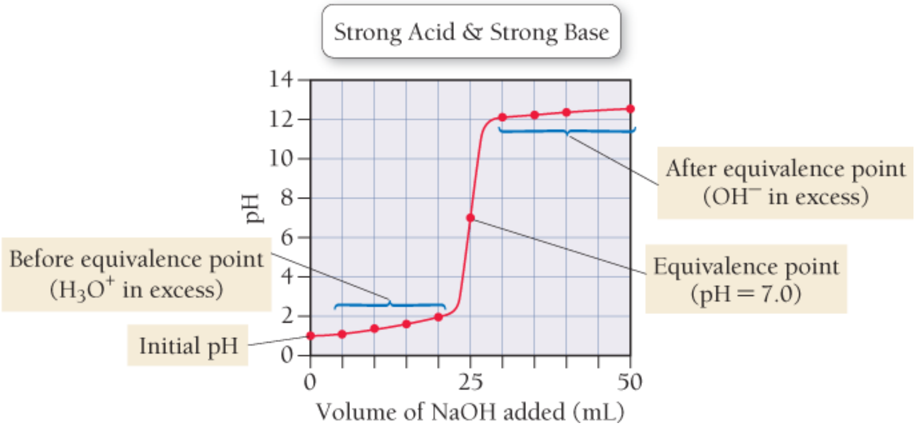


Volume (mL)	pH
35.0	12.22
40.0	12.36
50.0	12.52

The Overall pH Curve

The Overall pH Curve

The overall pH curve for the titration of a strong acid with a strong base has the characteristic S-shape we just plotted. The overall curve is as follows:



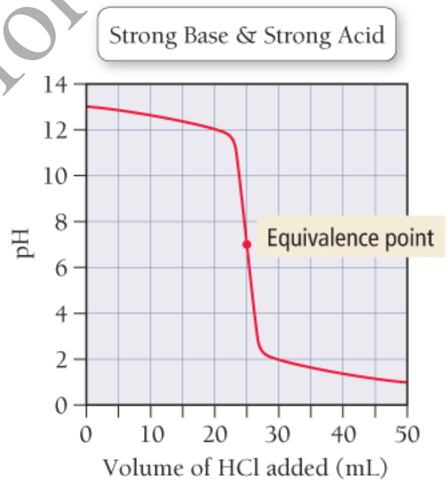
Summarizing the Titration of a Strong Acid with a Strong Base:

- The initial pH is the pH of the strong acid solution to be titrated.
- Before the equivalence point, H_3O^+ is in excess. Calculate the $[H_3O^+]$ by subtracting the number of moles of added OH^- from the initial number of moles of H_3O^+ and dividing by the *total* volume.
- At the equivalence point, neither reactant is in excess and the pH = 7.00.
- Beyond the equivalence point, OH^- is in excess. Calculate the $[OH^-]$ by subtracting the initial number of moles of H_3O^+ from the number of moles of added OH^- and dividing by the *total* volume.

The pH curve for the titration of a strong base with a strong acid is shown in Figure 17.7. Calculating the points along this curve is very similar to calculating the points along the pH curve for the titration of a strong acid with a strong base. The primary difference is that the curve starts basic and then becomes acidic after the equivalence point (instead of vice versa).

Figure 17.7 **Titration Curve: Strong Base + Strong Acid**

This curve represents the titration of 25.0 mL of 0.100 M NaOH with 0.100 M HCl.



Example 17.6 Strong Base–Strong Acid Titration pH Curve

A 50.0-mL sample of 0.200 M sodium hydroxide is titrated with 0.200 M nitric acid. Calculate the pH:

a. after adding 30.00 mL of HNO_3

b. at the equivalence point

SOLUTION

a. Begin by calculating the initial amount of NaOH (in moles) from the volume and molarity of the NaOH solution. Because NaOH is a strong base, it dissociates completely, so the amount of OH^- is equal to the amount of NaOH.

$$\begin{aligned}\text{moles NaOH} &= 0.0500\text{ L} \times \frac{0.200\text{ mol}}{1\text{ L}} \\ &= 0.0100\text{ mol} \\ \text{moles OH}^- &= 0.0100\text{ mol}\end{aligned}$$

Calculate the amount of HNO_3 (in moles) added at 30.0 mL from the molarity of the HNO_3 solution.

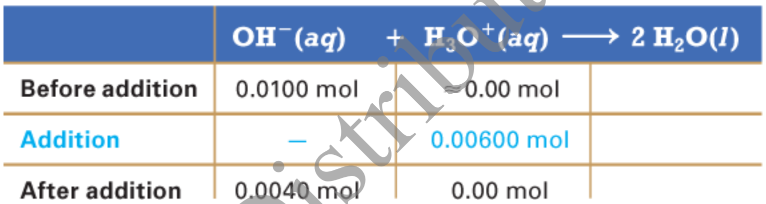
As HNO_3 is added to the solution, it neutralizes some of the OH^- Calculate the number of moles of OH^- remaining by setting up a table based on the neutralization reaction that shows the amount of OH^- before the addition, the amount of H_3O^+ added, and the amounts left after the addition.

Calculate the OH^- concentration by dividing the amount of OH^- remaining by the *total volume* (initial volume plus added volume).

Calculate the pOH from $\left[OH^-\right]$

Calculate the pH from the pOH using the equation $\text{pH}+\text{pOH} = 14$.

$$\begin{aligned}\text{moles HNO}_3\text{ added} &= 0.0300\text{L} \times \frac{0.200\text{ mol}}{1\text{L}} \\ &= 0.00600\text{ mol HNO}_3\end{aligned}$$



	$OH^-(aq)$	$+\ H_3O^+(aq)$	$\longrightarrow 2\ H_2O(l)$
Before addition	0.0100 mol	≈0.00 mol	
Addition	—	0.00600 mol	
After addition	0.0040 mol	0.00 mol	

$$\begin{aligned}\left[OH^-\right] &= \frac{0.0040\text{ mol}}{0.0500\text{L}+0.0300\text{L}} \\ &= 0.0500\text{M} \\ \text{pOH} &= -\log(0.0500) \\ &= 1.30 \\ \text{pH} &= 14 - \text{pOH} \\ &= 14 - 1.30 \\ &= 12.70\end{aligned}$$

b. At the equivalence point, the strong base has completely neutralized the strong acid. The $\left[H_3O^+\right]$ at 25 °C from the ionization of water is 1.00×10^{-7} M and the pH is therefore 7.00.

pH = 7.00

FOR PRACTICE 17.6 Calculate the pH in the titration in Example 17.6 after the addition of 60.0 mL of 0.200 M HNO_3

Interactive Worked Example 17.6 **Strong Acid–Strong Base Titration pH Curve**

Conceptual Connection 17.6 **Titration Equivalence Point**

The Titration of a Weak Acid with a Strong Base

Let's consider the titration of 25.0 mL of 0.100 M $HCHO_2$ with 0.100 M NaOH:

$$NaOH(aq) + HCHO_2(aq) \rightarrow H_2O(l) + NaCHO_2(aq)$$

The concentrations and the volumes here are identical to those in our previous titration, in which we calculated the pH curve for the titration of a *strong* acid with a strong base. The only difference is that $HCHO_2$ is a *weak* acid rather than a strong one. We begin by calculating the volume required to reach the equivalence point of the titration.

Volume of NaOH Required to Reach the Equivalence Point

From the stoichiometry of the equation, we can see that the equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in solution:

$$\text{initial mol HCHO}_2 = 0.0250\ \text{L} \times \frac{0.100\ \text{mol}}{1\ \text{L}} = 0.00250\ \text{mol HCHO}_2$$

The amount of NaOH that must be added is 0.00250 mol NaOH. The volume of NaOH required is therefore:

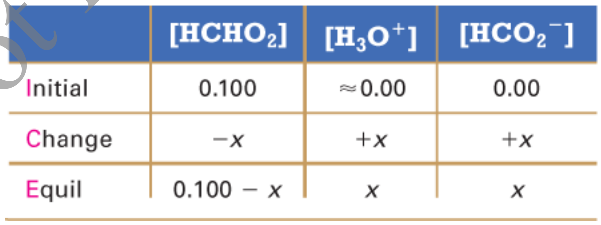
$$\text{volume NaOH solution} = 0.0250\ \text{mol} \times \frac{1\text{L}}{0.100\ \text{mol}} = 0.0250\ \text{NaOH solution}$$

The equivalence point occurs when 25.0 mL of base has been added. Notice that the volume of NaOH required to reach the equivalence point for this weak acid is identical to that required for a strong acid. *The volume at the equivalence point in an acid–base titration does not depend on whether the acid being titrated is a strong acid or a weak acid; it depends only on the amount (in moles) of acid present in solution before the titration begins, the stoichiometry of the reaction, and the concentration of the added base.*

Initial pH (before Adding Any Base)

The initial pH of the solution is the pH of a 0.100 M $HCHO_2$ solution. Since $HCHO_2$ is a weak acid, we calculate the concentration of H_3O^+ and the pH by doing an equilibrium problem for the ionization of $HCHO_2$ The procedure for solving weak acid ionization problems is demonstrated in Examples 16.5 and 16.6. We show a highly condensed calculation here K_a for $HCHO_2$ is 1.8×10^{-4}):

$$HCHO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$$



	$[HCHO_2]$	$[H_3O^+]$	$[HCO_2^-]$
Initial	0.100	≈0.00	0.00
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]}$$

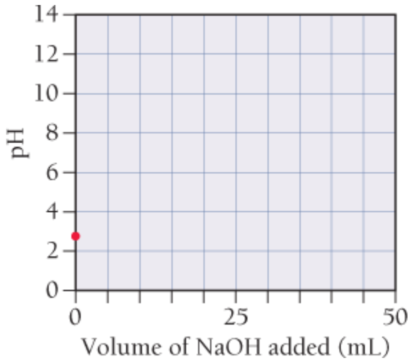
$$= \frac{x^2}{0.100 - x} (x \text{ is small})$$

$$1.8 \times 10^{-4} = \frac{x^2}{0.100}$$

$$x = 4.24 \times 10^{-3}$$

Therefore, $[H_3O^+] = 4.24 \times 10^{-3}\text{M}$

$$\begin{aligned} \text{pH} &= -\log(4.24 \times 10^{-3}) \\ &= 2.37 \end{aligned}$$



Notice that the pH is initially at a higher value (less acidic) than it is for a strong acid of the same concentration, as we would expect because the acid is weak.

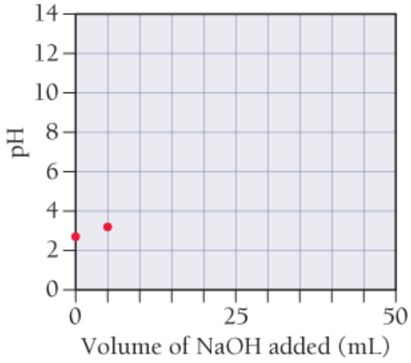
pH after Adding 5.00 mL NaOH

When we titrate a *weak acid* with a strong base, the added NaOH *converts a stoichiometric amount of the acid into its conjugate base*. As we calculated previously, 5.00 mL of the 0.100 M NaOH solution contains 0.000500 mol OH^- When the 0.000500 mol of OH^- is added to the weak acid solution, the OH^- reacts stoichiometrically with $HCHO_2$ causing the amount of $HCHO_2$ to *decrease* by 0.000500 mol and the amount of CHO_2^- to *increase* by 0.000500 mol. This is very similar to what happens when we add strong base to a buffer, and it is summarized in the following table:

	$OH^-(aq)$ +	$HCHO_2(aq) \longrightarrow$	$H_2O(l)$ +	$CHO_2^-(aq)$
Before addition	≈0.00 mol	0.00250 mol	—	0.00 mol
Addition	0.000500 mol	—	—	—
After addition	≈0.00 mol	0.00200 mol	—	0.000500 mol

Notice that, after the addition, the solution contains significant amounts of both an acid $(HCHO_2)$ and its conjugate base (CHO_2^-)—*the solution is now a buffer*. To calculate the pH of a buffer (when the *x is small* approximation applies as it does here), we can use the Henderson–Hasselbalch equation and pK_a for $HCHO_2$ (which is 3.74):

$$\begin{aligned} pH &= pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \\ &= 3.74 + \log\frac{0.000500}{0.002000} \\ &= 3.74 - 0.60 \\ &= 3.14 \end{aligned}$$

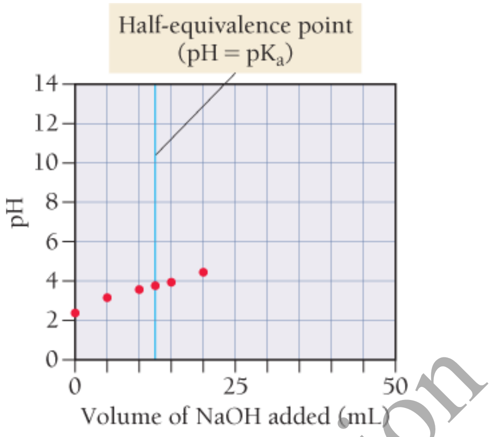


pH Values after Adding 10.0, 12.5, 15.0, and 20.0 mL NaOH

As more NaOH is added, it converts more $HCHO_2$ into CHO_2^-. We calculate the relative amounts of $HCHO_2$ and

CHO_2 at each of these volumes using the reaction stoichiometry and then calculate the pH of the resulting buffer using the Henderson–Hasselbalch equation (as we did for the pH at 5.00 mL). The amounts of $HCHO_2$ and CHO_2^- (after addition of the OH^- at each volume and the corresponding pH values are tabulated as follows:

Volume (mL)	mol $HCHO_2$	mol CHO_2^-	pH
10.0	0.00150	0.00100	3.56
12.5	0.00125	0.00125	3.74
15.0	0.00100	0.00150	3.92
20.0	0.00050	0.00200	4.34



As the titration proceeds, more of the $HCHO_2$ is converted to the conjugate base $\left(CHO_2^-\right)$ Notice that an added NaOH volume of 12.5 mL corresponds to one-half of the equivalence point. At this volume, half of the initial amount of $HCHO_2$ has been converted to CHO_2^- resulting in *equal amounts of weak acid and conjugate base.* For any buffer in which the amounts of weak acid and conjugate base are equal, $pH = pK_a$:

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

If [base] = [acid], then [base]/[acid] = 1.

$$\begin{aligned} pH &= pK_a + \log 1 \\ &= pK_a + 0 \\ &= pK_a \end{aligned}$$

> Since $pH = pK_a$ halfway to the equivalence point, we can use titrations to determine the pK_a of an acid.

pH after Adding 25.0 mL NaOH (Equivalence Point)

At the equivalence point, 0.00250 mol of OH^- have been added, and therefore all of the $HCHO_2$ has been converted into its conjugate base $\left(CHO_2^-\right)$ as summarized in the following table:

	$OH^-(aq)$ +	$HCHO_2(aq) \longrightarrow$	$H_2O(l)$ +	$CHO_2^-(aq)$
Before addition	≈0.00 mol	0.00250 mol	—	0.00 mol
Addition	0.00250 mol	—	—	—
After addition	≈0.00 mol	0.00 mol	—	0.00250 mol

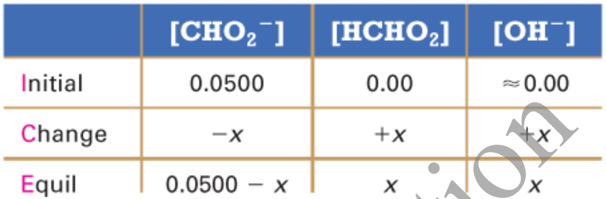
The solution is no longer a buffer (it no longer contains significant amounts of both a weak acid and its conjugate base). Instead, the solution contains an ion $\left(CHO_2^-\right)$ acting as a weak base. We demonstrated how to conjugate base). Instead, the solution contains an ion (CHO_2^-) acting as a weak base. We demonstrated how to calculate the pH of solutions such as this in Section 16.9 (see Example 16.14) by solving an equilibrium problem involving the ionization of water by the weak base (CHO_2^-):

$$CHO_2^-(aq) + H_2O(l) \rightleftharpoons HCHO_2(aq) + OH^-(aq)$$

We calculate the initial concentration of CHO_2^- for the equilibrium problem by dividing the number of moles of CHO_2^- (0.00250 mol) by the *total* volume at the equivalence point (initial volume plus added volume):

$$[CHO_2^-] = \frac{\overset{\text{Moles } CHO_2^- \text{ at equivalence point}}{0.00250\text{ mol}}}{\underset{\text{Initial volume}}{0.0250\text{ L}} + \underset{\text{Added volume at equivalence point}}{0.0250\text{ L}}} = 0.0500\text{ M}$$

We then proceed to solve the equilibrium problem as shown in condensed form here:



	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
Initial	0.0500	0.00	≈0.00
Change	$-x$	$+x$	$+x$
Equil	$0.0500 - x$	x	x

Before substituting into the expression for K_b we find the value of K_b from K_a for formic acid $K_a = 1.8 \times 10^{-4}$ and K_w:

$$K_a \times K_b = K_w$$

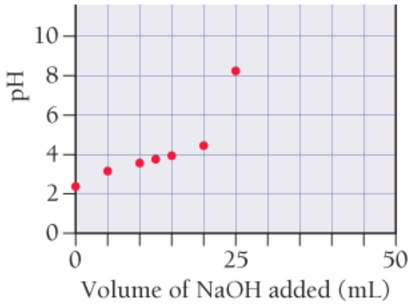
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

Then we substitute the equilibrium concentrations from the previous table into the expression for K_b:

$$\begin{aligned} K_b &= \frac{[HCHO_2][OH^-]}{[CHO_2^-]} \\ &= \frac{x^2}{0.0500 - x} (x \text{ is small}) \\ 5.6 \times 10^{-11} &= \frac{x^2}{0.0500} \\ x &= 1.7 \times 10^{-6} \end{aligned}$$

Remember that x represents the concentration of the hydroxide ion. We calculate $[H_3O^+]$ and pH:

$$\begin{aligned} [OH^-] &= 1.7 \times 10^{-6} M \\ [H_3O^+][OH^-] &= K_w = 1.0 \times 10^{-14} \\ [H_3O^+](1.7 \times 10^{-6}) &= 1.0 \times 10^{-14} \\ [H_3O^+] &= 5.9 \times 10^{-9} M \\ pH &= -\log[H_3O^+] \\ &= -\log(5.9 \times 10^{-9}) \\ &= 8.23 \end{aligned}$$



Notice that the pH at the equivalence point is *not* neutral but basic. *The titration of a weak acid by a strong base always has a basic equivalence point* because, at the equivalence point, all of the acid has been converted into its conjugate base, resulting in a weakly basic solution.

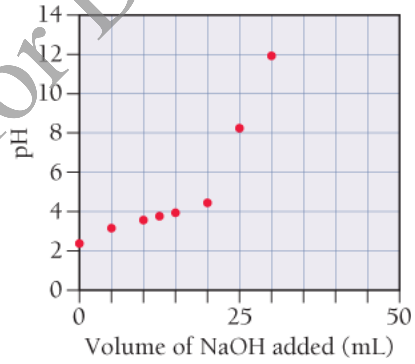
pH after Adding 30.00 mL NaOH

At this point in the titration, 0.00300 mol of OH^- have been added. NaOH has thus become the excess reagent as shown in the following table:

	$OH^-(aq)$ +	$HCHO_2(aq)$ ⟶	$H_2O(l)$ +	$CHO_2^-(aq)$
Before addition	≈0.00 mol	0.00250 mol	—	0.00 mol
Addition	0.00300 mol	—	—	—
After addition	0.00050 mol	≈0.00 mol	—	0.00250 mol

The solution is now a mixture of a strong base (NaOH) and a weak base $\left(CHO_2^-\right)$. The strong base completely overwhelms the weak base, and we can calculate the pH by considering the strong base alone (as we did for the titration of a strong acid and a strong base). We calculate the OH^- concentration by dividing the amount of OH^- remaining by the *total volume* (initial volume plus added volume):

$$\left[OH^-\right] = \frac{0.00050\text{ mol }OH^-}{0.0250L + 0.0300L} = 0.0091M$$



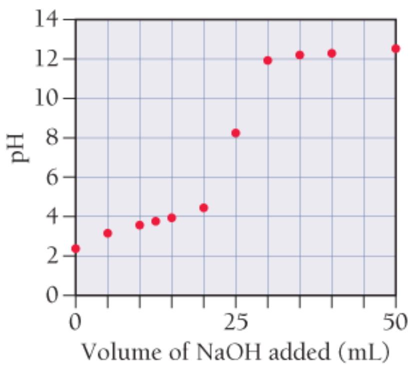
We then calculate the $\left[H_3O^+\right]$ and pH:

$$\begin{aligned}\left[H_3O^+\right]\left[OH^-\right] &= 1.0 \times 10^{-14}\\ \left[H_3O^+\right] &= \frac{1.0\times10^{-14}}{\left[OH^-\right]} = \frac{1.0\times10^{-14}}{0.0091} = 1.10 \times 10^{-12}M\\ pH &= -\log\left(1.10 \times 10^{-12}\right)\\ &= 11.96\end{aligned}$$

pH Values after Adding 35.0, 40.0, and 50.0 mL NaOH

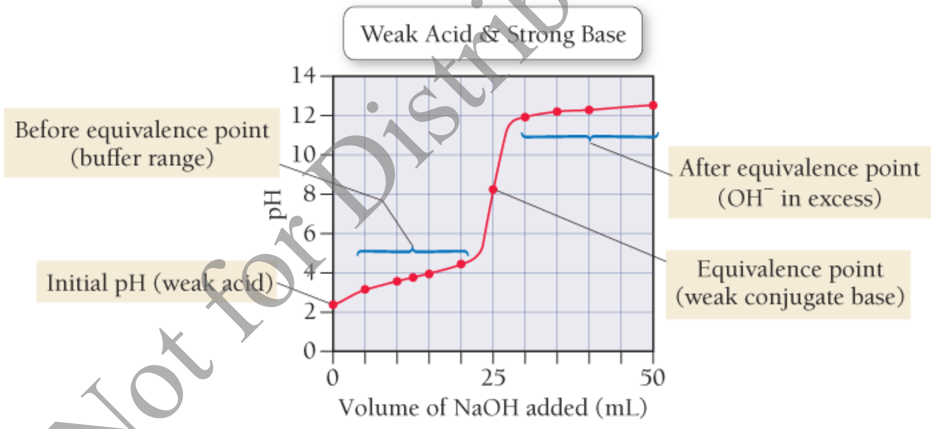
As more NaOH is added, the basicity of the solution increases further. We calculate the pH at each of these volumes in the same way we calculated the pH at 30.00 mL of added NaOH. The results are tabulated as follows:

Volume (mL)	pH
35.0	12.22
40.0	12.36
50.0	12.52



The Overall pH Curve

The overall pH curve for the titration of a weak acid with a strong base has a characteristic S-shape similar to that for the titration of a strong acid with a strong base. The primary difference is that the equivalence point pH is basic (not neutral). Notice that calculating the pH in different regions throughout the titration involves working different kinds of acid–base problems, all of which we have encountered before.



Summarizing Titration of a Weak Acid with a Strong Base:

- The initial pH is that of the weak acid solution to be titrated. Calculate the pH by working an equilibrium problem (similar to Examples 16.5 and 16.6) using the concentration of the weak acid as the initial concentration.
- Between the initial pH and the equivalence point, the solution becomes a buffer. Use the reaction stoichiometry to calculate the amounts of each buffer component and then use the Henderson–Hasselbalch equation to calculate the pH (as in Example 17.3).
- Halfway to the equivalence point, the buffer components are exactly equal and $\mathrm{pH} = \mathrm{p}K_a$.
- At the equivalence point, the acid has all been converted into its conjugate base. Calculate the pH by working an equilibrium problem for the ionization of water by the ion acting as a weak base (similar to Example 16.14). (Calculate the concentration of the ion acting as a weak base by dividing the number of moles of the ion by the total volume at the equivalence point.)
- Beyond the equivalence point, $\mathrm{OH^-}$ is in excess. Ignore the weak base and calculate the $[\mathrm{OH^-}]$ by subtracting the initial number of moles of the weak acid from the number of moles of added $\mathrm{OH^-}$ and

dividing by the *total* volume.

Example 17.7 Weak Acid–Strong Base Titration pH Curve

A 40.0-mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate:

a. the volume required to reach the equivalence point
b. the pH after adding 5.00 mL of KOH
c. the pH at one-half the equivalence point

SOLUTION

a. The equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in the solution. Begin by calculating the amount (in moles) of acid initially in the solution. The amount (in moles) of KOH that must be added is equal to the amount of the weak acid.

$$\begin{aligned} \text{mol } HNO_2 &= 0.0400 \text{ L} \times \frac{0.100\text{mol}}{\text{L}} \\ &= 4.00 \times 10^{-3}\text{mol} \\ \text{mol KOH required} &= 4.00 \times 10^{-3}\text{mol} \end{aligned}$$

Calculate the volume of KOH required from the number of moles of KOH and the molarity.

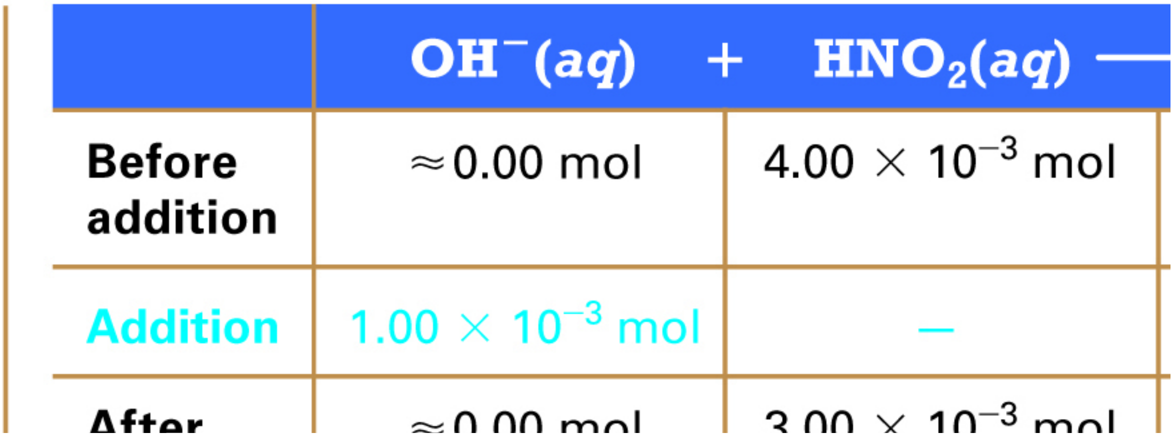
$$\begin{aligned} \text{Volume KOH solution} &= 4.00 \times 10^{-3}\text{mol} \times \frac{1\text{L}}{0.200\text{ mol}} \\ &= 0.0200 \text{ L KOH solution} \\ &= 20.0 \text{ mL KOH solution} \end{aligned}$$

b. Use the concentration of the KOH solution to calculate the amount (in moles) of OH^- in 5.00 mL of the solution.

Prepare a table showing the amounts of HNO_2 and NO_2^- before and after the addition of 5.00 mL KOH. The addition of the KOH stoichiometrically reduces the concentration of HNO_2 and increases the concentration of NO_2^-.

Since the solution now contains significant amounts of a weak acid and its conjugate base, use the Henderson–Hasselbalch equation and pK_a for HNO_2 (which is 3.34) to calculate the pH of the solution.

$$\begin{aligned} \text{mol } OH^- &= 5.00 \times 10^{-3} \cancel{\text{L}} \times \frac{0.200 \text{ mol}}{1 \cancel{\text{L}}} \\ &= 1.00 \times 10^{-3} \text{ mol } OH^- \end{aligned}$$



	$OH^-(aq)$ +	$HNO_2(aq)$ —
Before addition	≈0.00 mol	4.00×10^{-3} mol
Addition	1.00×10^{-3} mol	—
After	≈0.00 mol	3.00×10^{-3} mol

addition

$$\begin{aligned} pH &= pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \\ &= 3.34 + \log\frac{1.00\times10^{-3}}{3.00\times10^{-3}} \\ &= 3.34 - 0.48 = 2.86 \end{aligned}$$

c. At one-half the equivalence point, the amount of added base is exactly half the initial amount of acid. The base converts exactly half of the HNO_2 into NO_2^-, resulting in equal amounts of the weak acid and its conjugate base. The pH is therefore equal to pK_a.

	$OH^-(aq)$ +	$HNO_2(aq)$ ⟶	$H_2O(l)$ +	$NO_2^-(aq)$
Before addition	≈0.00 mol	4.00×10^{-3} mol	—	0.00 mol
Addition	2.00×10^{-3} mol	—	—	—
After addition	≈0.00 mol	2.00×10^{-3} mol	—	2.00×10^{-3} mol

$$\begin{aligned} pH &= pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \\ &= 3.34 + \log\frac{2.00\times10^{-3}}{2.00\times10^{-3}} \\ &= 3.34 + 0 = 3.34 \end{aligned}$$

FOR PRACTICE 17.7 Determine the pH at the equivalence point for the titration of HNO_2 and KOH in Example 17.7.

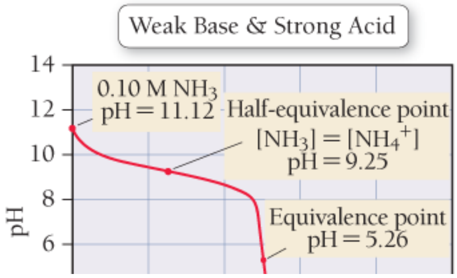
Interactive Worked Example 17.7 **Weak Acid–Strong Base Titration pH Curve**

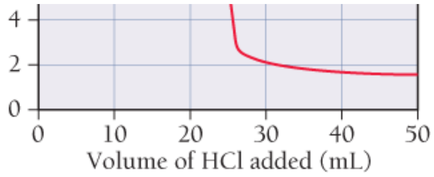
The Titration of a Weak Base with a Strong Acid

Figure 17.8 is the pH curve for the titration of a weak base with a strong acid. Calculating the points along this curve is very similar to calculating the points along the pH curve for the titration of a weak acid with a strong base (which we just did). The primary differences are that the curve starts basic and has an acidic equivalence point. We calculate the pH in the buffer region using $pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$ where the pK_a corresponds to the conjugate acid of the base being titrated.

Figure 17.8 **Titration Curve: Weak Base + Strong Acid**

This curve represents the titration of 25.0 mL of 0.100 M NH_3 with 0.100 M HCl.





Conceptual Connection 17.7 Weak Acid–Strong Base Titration

Conceptual Connection 17.8 The Half-Equivalence Point

The Titration of a Polyprotic Acid

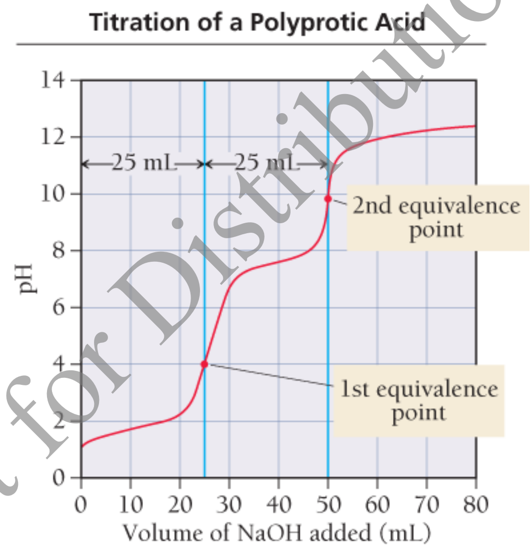
When a diprotic acid is titrated with a strong base, if K_{a_1} and K_{a_2} are sufficiently different, the pH curve has two equivalence points. For example, Figure 17.9 shows the pH curve for the titration of sulfurous acid $\left(H_2SO_3\right)$ with sodium hydroxide. Recall from Section 16.10 that sulfurous acid ionizes in two steps as follows:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \quad K_{a_1} = 1.6 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \quad K_{a_2} = 6.4 \times 10^{-8}$$

Figure 17.9 Titration Curve: Diprotic Acid + Strong Base

This curve represents the titration of 25.0 mL of 0.100 M H_2SO_3 with 0.100 M NaOH.



The first equivalence point in the titration curve represents the titration of the first proton while the second equivalence point represents the titration of the second proton. Notice that the volume required to reach the first equivalence point is identical to the volume required to reach the second one because the number of moles of H_2SO_3 in the first step determines the number of moles of HSO_3^- in the second step.

Conceptual Connection 17.9 Acid–Base Titrations

Indicators: pH-Dependent Colors

We can monitor the pH of a titration with either a pH meter or an indicator. The direct monitoring of pH with a meter yields data like the pH curves we have examined previously, allowing determination of the equivalence point from the pH curve itself, as shown in Figure 17.10. With an indicator, we rely on the point where the indicator changes color—called the **endpoint**—to determine the equivalence point, as shown in Figure 17.11.

With the correct indicator, the endpoint of the titration (indicated by the color change) occurs at the equivalence point (when the amount of acid equals the amount of base).

Figure 17.10 Monitoring pH during a Titration

A pH meter monitors pH during titration. The inflection point in the resulting pH curve signifies the equivalence point.

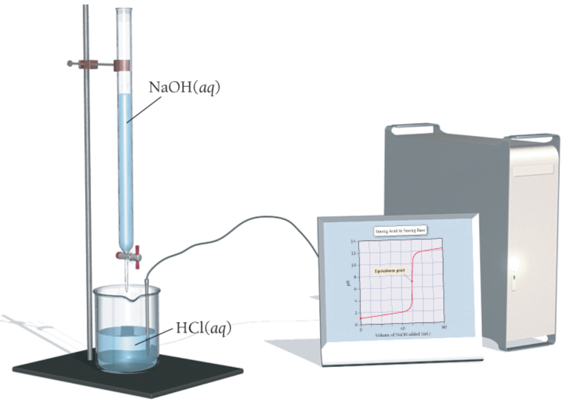
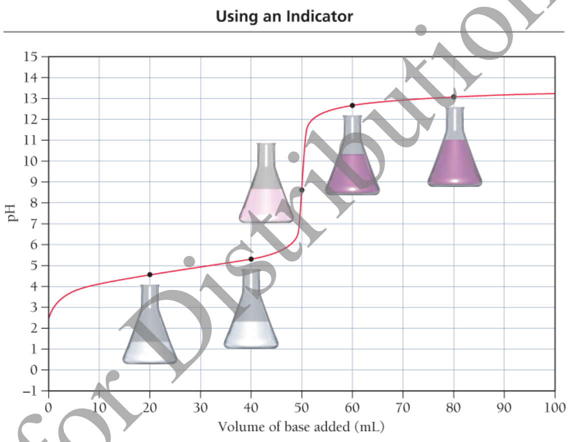


Figure 17.11 Monitoring Color Change during a Titration

Titration of 50.0 mL of 0.100 M $HC_2H_3O_2$ with 0.100 M NaOH. The endpoint of a titration is signaled by a color change in an appropriate indicator (in this case, phenolphthalein).

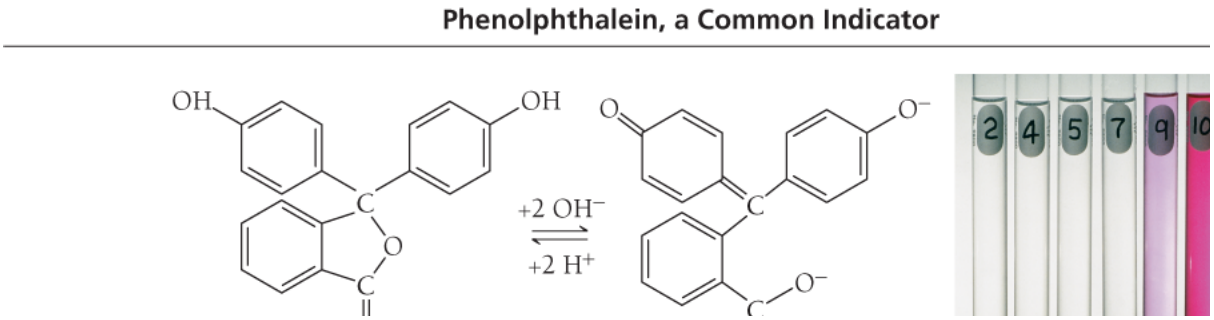


An indicator is itself a weak organic acid that is a different color than its conjugate base. For example, phenolphthalein (the structure of which is shown in Figure 17.12) is a common indicator whose acid form is colorless and conjugate base form is pink. If we let HIn represent the acid form of a generic indicator and In^- the conjugate base form, we have the following equilibrium:

$$HIn(aq)_{\text{color 1}} + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)_{\text{color 2}}$$

Figure 17.12 Phenolphthalein

Phenolphthalein, a weakly acidic compound, is colorless. Its conjugate base is pink.



Acidic - Colorless
Basic - Pink

Because its color is intense, only a small amount of indicator is required—an amount that will not affect the pH of the solution or the equivalence point of the neutralization reaction. When the $\left[H_3O^+\right]$ changes during the titration, the equilibrium shifts in response. At low pH, the $\left[H_3O^+\right]$ is high and the equilibrium lies far to the left, resulting in a solution of color 1. As the titration proceeds, the $\left[H_3O^+\right]$ decreases, shifting the equilibrium to the right. Since the pH change is large near the equivalence point of the titration, there is a large change in $\left[H_3O^+\right]$ near the equivalence point. Provided that the correct indicator is chosen, there is also a correspondingly significant change in color. For the titration of a strong acid with a strong base, one drop of the base near the endpoint is usually enough to change the indicator from color 1 to color 2.

The color of a solution containing an indicator depends on the relative concentrations of HIn and In^- As a useful guideline, we can assume the following:

- If $\frac{\left[\mathrm{In}^-\right]}{[\mathrm{HIn}]} = 1$, the indicator solution will be intermediate in color.
- If $\frac{\left[\mathrm{In}^-\right]}{[\mathrm{HIn}]} > 10$, the indicator solution will be the color of In^-.
- If $\frac{\left[\mathrm{In}^-\right]}{[\mathrm{HIn}]} < 0.1$, the indicator solution will be the color of HIn.

From the Henderson–Hasselbalch equation, we can derive an expression for the ratio of $\left[\mathrm{In}^-\right]/[\mathrm{HIn}]$:

$$\begin{aligned}\mathrm{pH} &= \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}\\ &= \mathrm{p}K_a + \log\frac{\left[\mathrm{In}^-\right]}{[\mathrm{HIn}]}\\ \log\frac{\left[\mathrm{In}^-\right]}{[\mathrm{HIn}]} &= \mathrm{pH} - \mathrm{p}K_a\\ \frac{\left[\mathrm{In}^-\right]}{[\mathrm{HIn}]} &= 10^{\left(\mathrm{pH}-\mathrm{p}K_a\right)}\end{aligned}$$

Consider the following three pH values relative to $\mathrm{p}K_a$ and the corresponding colors of the indicator solution:

pH (relative to $\mathrm{p}K_a$)	$[\mathrm{In}^-]/[\mathrm{HIn}]$ ratio	Color of Indicator Solution
$\mathrm{pH} = \mathrm{p}K_a$	$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = 10^0 = 1$	Intermediate Color
$\mathrm{pH} = \mathrm{p}K_a + 1$	$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = 10^1 = 10$	Color of In^-
$\mathrm{pH} = \mathrm{p}K_a - 1$	$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = 10^{-1} = 0.10$	Color of HIn

When the pH of the solution equals the $\mathrm{p}K_a$ of the indicator, the solution will have an intermediate color. When the pH is 1 unit (or more) above $\mathrm{p}K_a$ the indicator will be the color of In^-, and when the pH is 1 unit (or more) below $\mathrm{p}K_a$ the indicator will be the color of HIn. As we can see, the indicator changes color within a range of two pH units centered at $\mathrm{p}K_a$ (Figure 17.13). Table 17.1 shows various indicators and their colors as a function of pH.

Figure 17.13 Indicator Color Change

An indicator (in this case, methyl red) generally changes color within a range of two pH units. (The pH for each solution is marked on its test tube.)

Indicator Color Change: Methyl Red

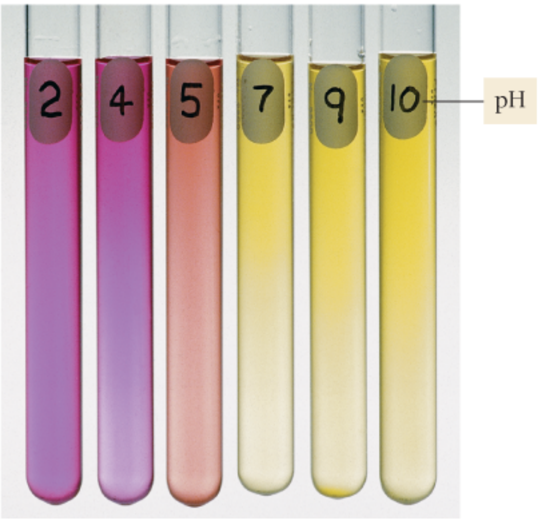
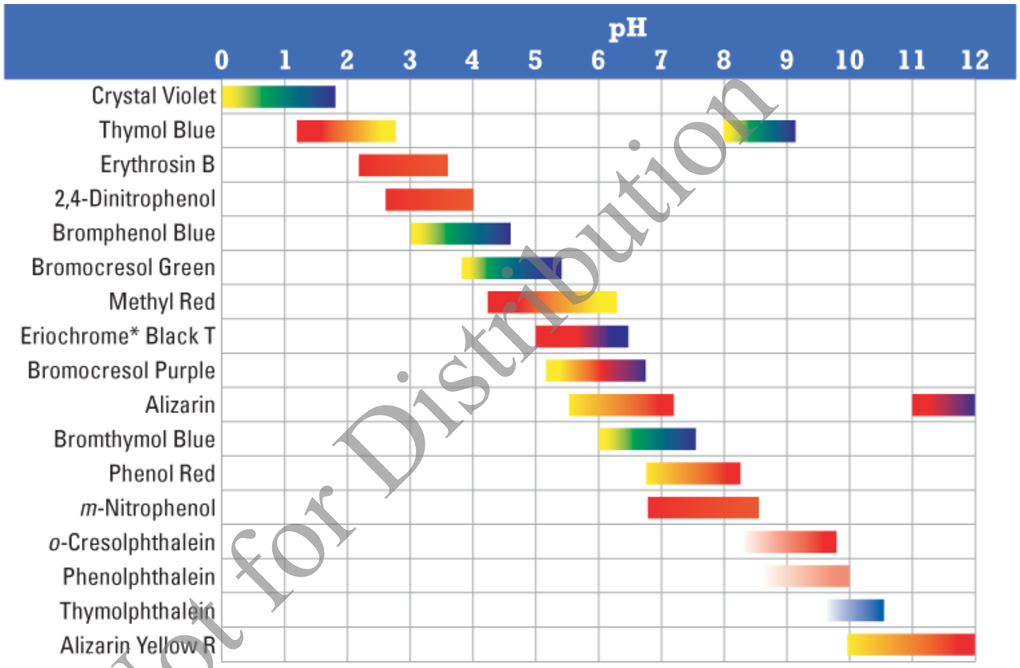


Table 17.1 **Ranges of Color Changes for Several Acid–Base Indicators**



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