

6.6: pH Calculations for Acid–Base Titrations

Acid–Base Titration Curves

In this section we will learn how to calculate the pH of an analyte solution throughout the titration, and use these values to prepare a titration curve. We also will learn how to sketch a good approximation of any acid–base titration curve using a limited number of simple calculations.

Titration Strong Acids and Strong Bases

For our first titration curve, let's consider the titration of 50.0 mL of 0.100 M HCl using a titrant of 0.200 M NaOH. When a strong base and a strong acid react the only reaction of importance is



The first task is to calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point we know that

$$\text{moles } \text{H}_3\text{O}^+ = \text{moles } \text{OH}^- \quad (6.6.2)$$

The volume of NaOH needed to reach the equivalence point is

$$50.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \times \frac{1000 \text{ mL NaOH}}{0.200 \text{ mol NaOH}} = 25 \text{ mL NaOH} \quad (6.6.3)$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of unreacted HCl. At the start of the titration the solution is 0.100 M in HCl, which, because HCl is a strong acid, means the pH is

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

After adding 10.0 mL of NaOH the concentration of excess HCl is

$$\begin{aligned} [\text{HCl}] &= \frac{(\text{mol HCl})_{\text{initial}} - (\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b} \\ [\text{HCl}] &= \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0500 \text{ M} \end{aligned}$$

and the pH increases to 1.30.

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

$$\begin{aligned} K_w &= 1.00 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2 \\ [\text{H}_3\text{O}^+] &= 1.00 \times 10^{-7} \end{aligned}$$

Thus, the pH at the equivalence point is 7.00.

For volumes of NaOH greater than the equivalence point, the pH is determined by the concentration of excess OH^- . For example, after adding 30.0 mL of titrant the concentration of OH^- is

$$\begin{aligned} [\text{OH}^-] &= \frac{(\text{mol NaOH})_{\text{added}} - (\text{mol HCl})_{\text{initial}}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b} \\ [\text{OH}^-] &= \frac{(0.200 \text{ M})(30.0 \text{ mL}) - (0.100 \text{ M})(50.0 \text{ mL})}{30.0 \text{ mL} + 50.0 \text{ mL}} = 0.0125 \text{ M} \end{aligned}$$

To find the concentration of H_3O^+ we use the K_w expression

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13} \text{ M}$$

to find that the pH is 12.10. Table 6.6.1 and Figure 6.6.1 show additional results for this titration curve. You can use this same approach to calculate the titration curve for the titration of a strong base with a strong acid, except the strong base is in excess

before the equivalence point and the strong acid is in excess after the equivalence point.

Table 6.6.1 . Titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH

volume of NaOH (mL)	pH	volume of NaOH (mL)	pH
0.00	1.00	26.0	11.42
5.00	1.14	28.0	11.89
10.0	1.30	30.0	12.10
15.0	1.51	35.0	12.37
20.0	1.85	40.0	12.52
22.0	2.08	45.0	12.63
24.0	2.57	50.0	12.70
25.0	7.00		

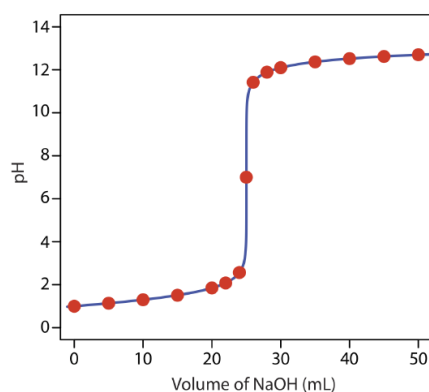


Figure 6.6.1 . Titration curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. The red points correspond to the data in Table 6.6.1 . The blue line shows the complete titration curve.

? Exercise 6.6.1

Construct a titration curve for the titration of 25.0 mL of 0.125 M NaOH with 0.0625 M HCl.

Answer

The volume of HCl needed to reach the equivalence point is

$$V_{eq} = V_a = \frac{M_b V_b}{M_a} = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{(0.0625 \text{ M})} = 50.0 \text{ mL}$$

Before the equivalence point, NaOH is present in excess and the pH is determined by the concentration of unreacted OH^- . For example, after adding 10.0 mL of HCl

$$[\text{OH}^-] = \frac{(0.125 \text{ M})(25.0 \text{ mL}) - (0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0714 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0714 \text{ M}} = 1.40 \times 10^{-13} \text{ M}$$

the pH is 12.85.

For the titration of a strong base with a strong acid the pH at the equivalence point is 7.00.

For volumes of HCl greater than the equivalence point, the pH is determined by the concentration of excess HCl. For example, after adding 70.0 mL of titrant the concentration of HCl is

$$[\text{HCl}] = \frac{(0.0625 \text{ M})(70.0 \text{ mL}) - (0.125 \text{ M})(25.0 \text{ mL})}{70.0 \text{ mL} + 25.0 \text{ mL}} = 0.0132 \text{ M}$$

giving a pH of 1.88. Some additional results are shown here.

volume of HCl (mL)	pH	volume of HCl (mL)	pH
0	13.10	60	2.13
10	12.85	70	1.88
20	12.62	80	1.75
30	12.36	90	1.66
40	11.98	100	1.60
50	7.00		

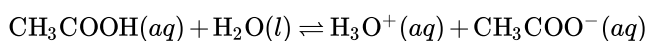
Titrating a Weak Acid with a Strong Base

For this example, let's consider the titration of 50.0 mL of 0.100 M acetic acid, CH_3COOH , with 0.200 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

$$\text{mol CH}_3\text{COOH} = \text{mol NaOH}$$

$$50.0 \text{ mL CH}_3\text{COOH} \times \frac{0.100 \text{ mol CH}_3\text{COOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol}} \times \frac{1000 \text{ mL NaOH}}{0.200 \text{ mol NaOH}} = 25.0 \text{ mL NaOH} \quad (6.6.4)$$

Before we begin the titration the pH is that for a solution of 0.100 M acetic acid. Because acetic acid is a weak acid, we calculate the pH using the acid equilibrium constant.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

finding that the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base, CH_3COO^- .



Because the equilibrium constant for reaction 6.6.5 is quite large

$$K = K_a / K_w = 1.75 \times 10^9$$

we can treat the reaction as if it goes to completion.

Any solution that contains comparable amounts of a weak acid, HA, and its conjugate weak base, A^- , is a buffer. We can calculate the pH of a buffer using the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Before the equivalence point the concentration of unreacted acetic acid is

$$[\text{CH}_3\text{COOH}] = \frac{(\text{mol CH}_3\text{COOH})_{\text{initial}} - (\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

and the concentration of acetate is

$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH_3COOH and CH_3COO^- are

$$[\text{CH}_3\text{COOH}] = \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0500 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{(0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0333 \text{ M}$$

which gives us a pH of

$$\text{pH} = 4.76 + \log \frac{0.0333 \text{ M}}{0.0500 \text{ M}} = 4.58$$

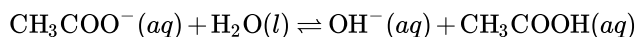
At the equivalence point the moles of acetic acid initially present and the moles of NaOH added are identical. Because their reaction effectively proceeds to completion, the predominate ion in solution is CH_3COO^- , which is a weak base. To calculate the pH we first determine the concentration of CH_3COO^-

$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{(0.200 \text{ M})(25.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}$$

Alternatively, we can calculate acetate's concentration using the initial moles of acetic acid; thus

$$[\text{CH}_3\text{COO}^-] = \frac{(\text{mol CH}_3\text{COOH})_{\text{initial}}}{\text{total volume}} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 0.0667 \text{ M}$$

Next, we calculate the pH of the weak base.



$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{(x)(x)}{0.0667 - x} = 5.71 \times 10^{-10}$$

$$x = [\text{OH}^-] = 6.17 \times 10^{-6} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{6.17 \times 10^{-6}} = 1.62 \times 10^{-9} \text{ M}$$

finding that the pH at the equivalence point is 8.79.

After the equivalence point, the titrant is in excess and the titration mixture is a dilute solution of NaOH. We can calculate the pH using the same strategy as in the titration of a strong acid with a strong base. For example, after adding 30.0 mL of NaOH the concentration of OH^- is

$$[\text{OH}^-] = \frac{(0.200 \text{ M})(30.0 \text{ mL}) - (0.100 \text{ M})(50.0 \text{ mL})}{30.0 \text{ mL} + 50.0 \text{ mL}} = 0.0125 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13} \text{ M}$$

giving a pH of 12.10. Table 6.6.2 and Figure 6.6.2 show additional results for this titration. You can use this same approach to calculate the titration curve for the titration of a weak base with a strong acid, except the initial pH is determined by the weak base, the pH at the equivalence point by its conjugate weak acid, and the pH after the equivalence point by excess strong acid.

Table 6.6.2 . Titration of 50.0 mL of 0.100 M Acetic Acid with 0.200 M NaOH

volume of HCl (mL)	pH	volume of HCl (mL)	pH
0.00	2.88	26.0	11.43

5.00	4.16	28.0	11.89
10.0	4.58	30.0	12.10
15.0	4.94	35.0	12.37
20.0	5.36	40.0	12.52
22.0	5.63	45.0	12.63
24.0	6.14	50.0	12.70
25.0	8.79		

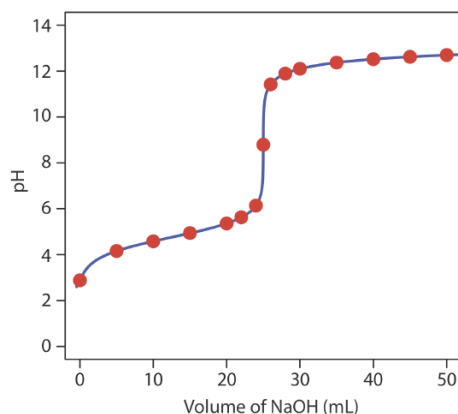


Figure 6.6.2 . Titration curve for the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH. The red points correspond to the data in Table 6.6.2 . The blue line shows the complete titration curve.

? Exercise 6.6.2

Construct a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl.

Answer

The volume of HCl needed to reach the equivalence point is

$$V_{aq} = V_a = \frac{M_b V_b}{M_a} = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{(0.0625 \text{ M})} = 50.0 \text{ mL}$$

Before adding HCl the pH is that for a solution of 0.100 M NH_3 .

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{(x)(x)}{0.125 - x} = 1.75 \times 10^{-5}$$

$$x = [\text{OH}^-] = 1.48 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{1.48 \times 10^{-3} \text{ M}} = 6.76 \times 10^{-12} \text{ M}$$

The pH at the beginning of the titration, therefore, is 11.17.

Before the equivalence point the pH is determined by an $\text{NH}_3/\text{NH}_4^+$ buffer. For example, after adding 10.0 mL of HCl

$$[\text{NH}_3] = \frac{(0.125 \text{ M})(25.0 \text{ mL}) - (0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0714 \text{ M}$$

$$[\text{NH}_4^+] = \frac{(0.0625 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0179 \text{ M}$$

$$\text{pH} = 9.244 + \log \frac{0.0714 \text{ M}}{0.0179 \text{ M}} = 9.84$$

At the equivalence point the predominate ion in solution is NH_4^+ . To calculate the pH we first determine the concentration of NH_4^+

$$[\text{NH}_4^+] = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{25.0 \text{ mL} + 50.0 \text{ mL}} = 0.0417 \text{ M}$$

and then calculate the pH

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.0417 - x} = 5.70 \times 10^{-10}$$

obtaining a value of 5.31.

After the equivalence point, the pH is determined by the excess HCl. For example, after adding 70.0 mL of HCl

$$[\text{HCl}] = \frac{(0.0625 \text{ M})(70.0 \text{ mL}) - (0.125 \text{ M})(25.0 \text{ mL})}{70.0 \text{ mL} + 25.0 \text{ mL}} = 0.0132 \text{ M}$$

and the pH is 1.88. Some additional results are shown here.

volume of HCl (mL)	pH	volume of HCl (mL)	pH
0	11.17	60	2.13
10	9.84	70	1.88
20	9.42	80	1.75
30	9.07	90	1.66
40	8.64	100	1.60
50	5.31		

We can extend this approach for calculating a weak acid–strong base titration curve to reactions that involve multiprotic acids or bases, and mixtures of acids or bases. As the complexity of the titration increases, however, the necessary calculations become more time consuming. Not surprisingly, a variety of algebraic and spreadsheet approaches are available to aid in constructing titration curves.

The following papers provide information on algebraic approaches to calculating titration curves: (a) Willis, C. J. *J. Chem. Educ.* **1981**, 58, 659–663; (b) Nakagawa, K. *J. Chem. Educ.* **1990**, 67, 673–676; (c) Gordus, A. A. *J. Chem. Educ.* **1991**, 68, 759–761; (d) de Levie, R. *J. Chem. Educ.* **1993**, 70, 209–217; (e) Chaston, S. *J. Chem. Educ.* **1993**, 70, 878–880; (f) de Levie, R. *Anal. Chem.* **1996**, 68, 585–590.

The following papers provide information on the use of spreadsheets to generate titration curves: (a) Currie, J. O.; Whiteley, R. V. *J. Chem. Educ.* **1991**, 68, 923–926; (b) Breneman, G. L.; Parker, O. J. *J. Chem. Educ.* **1992**, 69, 46–47; (c) Carter, D. R.; Frye, M. S.; Mattson, W. A. *J. Chem. Educ.* **1993**, 70, 67–71; (d) Freiser, H. *Concepts and Calculations in Analytical Chemistry*, CRC Press: Boca Raton, 1992.

Sketching an Acid–Base Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching an acid–base titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH to illustrate our approach. This is the same example that we used to develop the calculations for a weak acid–strong base titration curve. You can review the results of that calculation in [Table 6.6.2](#) and in [Figure 6.6.2](#).

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next we draw our axes, placing pH on the y-axis and the titrant's volume on the x-axis. To indicate the equivalence point volume, we draw a vertical line that intersects the x-axis at 25.0 mL of NaOH. Figure 6.6.3 a shows the first step in our sketch.

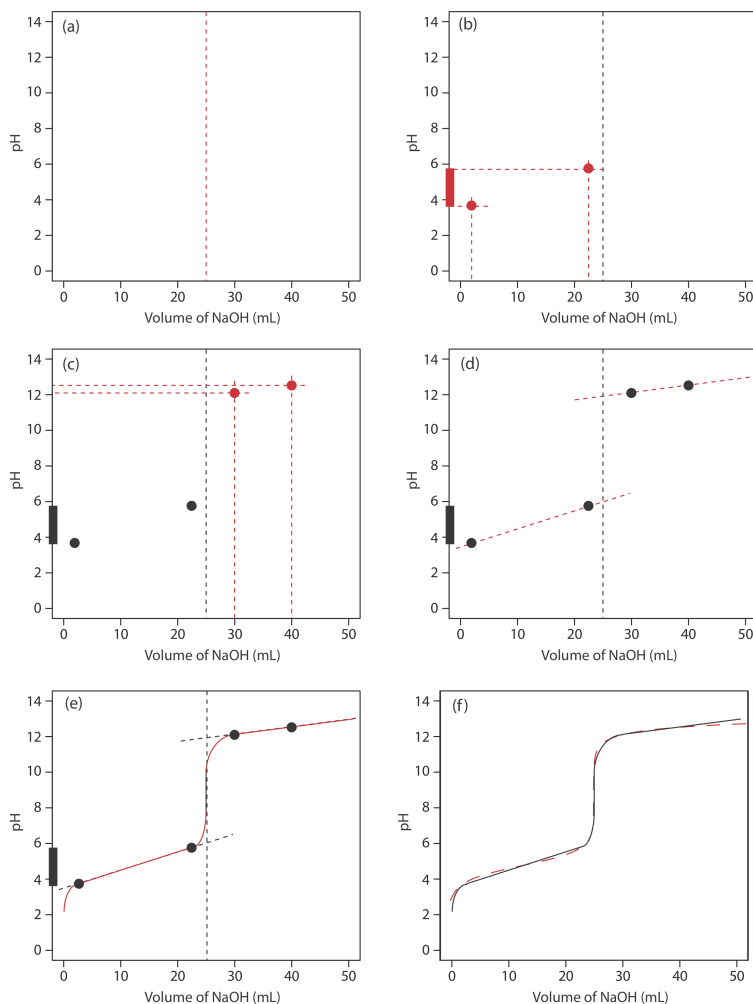


Figure 6.6.3 . Illustrations showing the steps used to sketch an approximate titration curve for the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Before the equivalence point the titrand's pH is determined by a buffer of acetic acid, CH_3COOH , and acetate, CH_3COO^- . Although we can calculate a buffer's pH using the Henderson–Hasselbalch equation, we can avoid this calculation by making a simple assumption. You may recall from [Chapter 6](#) that a buffer operates over a pH range that extends approximately ± 1 pH unit on either side of the weak acid's $\text{p}K_a$ value. The pH is at the lower end of this range, $\text{pH} = \text{p}K_a - 1$, when the weak acid's concentration is $10\times$ greater than that of its conjugate weak base. The buffer reaches its upper pH limit, $\text{pH} = \text{p}K_a + 1$, when the weak acid's concentration is $10\times$ smaller than that of its conjugate weak base. When we titrate a weak acid or a weak base, the buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

The actual values are 9.09% and 90.9%, but for our purpose, using 10% and 90% is more convenient; that is, after all, one advantage of an approximation!

Figure 6.6.3 b shows the second step in our sketch. First, we superimpose acetic acid's ladder diagram on the y-axis, including its buffer range, using its $\text{p}K_a$ value of 4.76. Next, we add two points, one for the pH at 10% of the equivalence point volume (a pH of

3.76 at 2.5 mL) and one for the pH at 90% of the equivalence point volume (a pH of 5.76 at 22.5 mL).

The third step is to add two points after the equivalence point. The pH after the equivalence point is fixed by the concentration of excess titrant, NaOH. Calculating the pH of a strong base is straightforward, as we saw earlier. Figure 6.6.3 c includes points (see Table 6.6.2) for the pH after adding 30.0 mL and after adding 40.0 mL of NaOH.

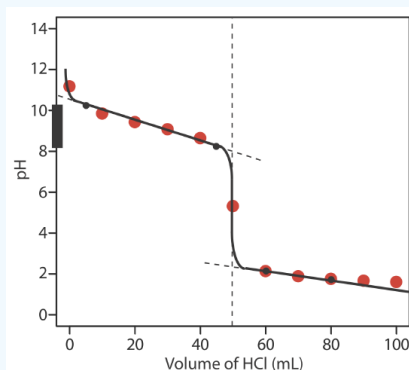
Next, we draw a straight line through each pair of points, extending each line through the vertical line that represents the equivalence point's volume (Figure 6.6.3 d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 6.6.3 e). A comparison of our sketch to the exact titration curve (Figure 6.6.3 f) shows that they are in close agreement.

? Exercise 6.6.3

Sketch a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl and compare to the result from Exercise 6.6.2 .

Answer

The figure below shows a sketch of the titration curve. The black dots and curve are the approximate sketch of the titration curve. The points in red are the calculations from Exercise 6.6.2 . The two black points before the equivalence point ($V_{\text{HCl}} = 5 \text{ mL}$, $\text{pH} = 10.24$ and $V_{\text{HCl}} = 45 \text{ mL}$, $\text{pH} = 8.24$) are plotted using the pK_a of 9.244 for NH_4^+ . The two black points after the equivalence point ($V_{\text{HCl}} = 60 \text{ mL}$, $\text{pH} = 2.13$ and $V_{\text{HCl}} = 80 \text{ mL}$, $\text{pH} = 1.75$) are from the answer to Exercise 6.6.2 .



As shown in the following example, we can adapt this approach to any acid–base titration, including those where exact calculations are more challenging, including the titration of polyprotic weak acids and bases, and the titration of mixtures of weak acids or weak bases.

✓ Example 6.6.1

Sketch titration curves for the following two systems: (a) the titration of 50.0 mL of 0.050 M H_2A , a diprotic weak acid with a pK_{a1} of 3 and a pK_{a2} of 7; and (b) the titration of a 50.0 mL mixture that contains 0.075 M HA, a weak acid with a pK_a of 3, and 0.025 M HB, a weak acid with a pK_a of 7. For both titrations, assume that the titrant is 0.10 M NaOH.

Solution

Figure 6.6.4 a shows the titration curve for H_2A , including the ladder diagram for H_2A on the y-axis, the two equivalence points at 25.0 mL and at 50.0 mL, two points before each equivalence point, two points after the last equivalence point, and the straight-lines used to sketch the final titration curve. Before the first equivalence point the pH is controlled by a buffer of H_2A and HA^- . An $\text{HA}^-/\text{A}^{2-}$ buffer controls the pH between the two equivalence points. After the second equivalence point the pH reflects the concentration of excess NaOH.

Figure 6.6.4 b shows the titration curve for the mixture of HA and HB. Again, there are two equivalence points; however, in this case the equivalence points are not equally spaced because the concentration of HA is greater than that for HB. Because HA is the stronger of the two weak acids it reacts first; thus, the pH before the first equivalence point is controlled by a buffer

of HA and A^- . Between the two equivalence points the pH reflects the titration of HB and is determined by a buffer of HB and B^- . After the second equivalence point excess NaOH determines the pH.

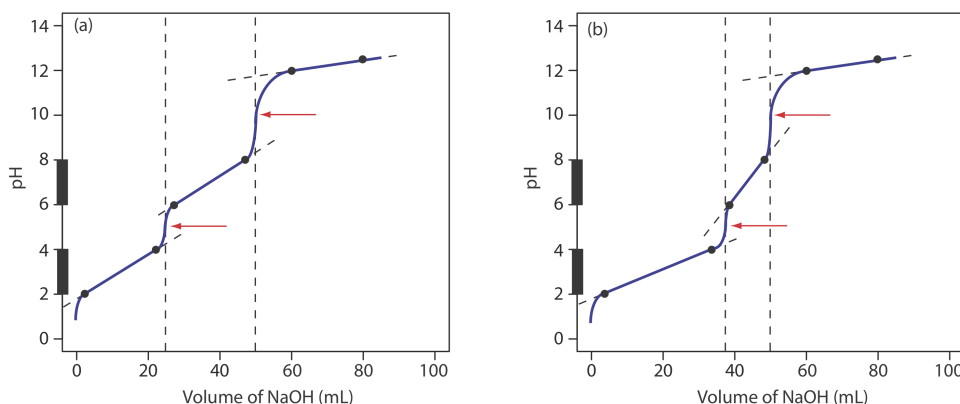


Figure 6.6.4 . Titration curves for Example 6.6.1 . The solid black dots show the points used to sketch the titration curves (shown in blue) and the red arrows show the locations of the equivalence points.

? Exercise 6.6.4

Sketch the titration curve for 50.0 mL of 0.050 M H_2A , a diprotic weak acid with a $\text{p}K_{\text{a}1}$ of 3 and a $\text{p}K_{\text{a}2}$ of 4, using 0.100 M NaOH as the titrant. The fact that $\text{p}K_{\text{a}2}$ falls within the buffer range of $\text{p}K_{\text{a}1}$ presents a challenge that you will need to consider.

Answer

The figure below shows a sketch of the titration curve. The titration curve has two equivalence points, one at 25.0 mL ($\text{H}_2\text{A} \rightarrow \text{HA}^-$) and one at 50.0 mL ($\text{HA}^- \rightarrow \text{A}^{2-}$). In sketching the curve, we plot two points before the first equivalence point using the $\text{p}K_{\text{a}1}$ of 3 for H_2A

$$V_{\text{HCl}} = 2.5 \text{ mL, pH} = 2 \text{ and } V_{\text{HCl}} = 22.5 \text{ mL, pH} = 4$$

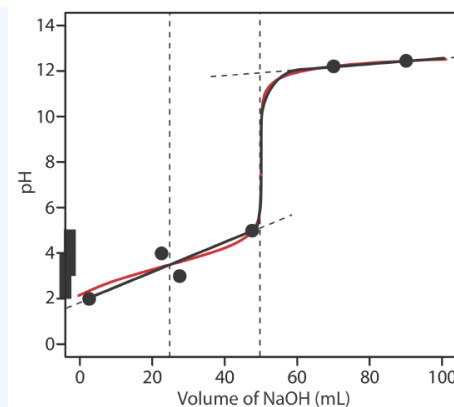
two points between the equivalence points using the $\text{p}K_{\text{a}2}$ of 5 for HA^-

$$V_{\text{HCl}} = 27.5 \text{ mL, pH} = 3, \text{ and } V_{\text{HCl}} = 47.5 \text{ mL, pH} = 5$$

and two points after the second equivalence point

$$V_{\text{HCl}} = 70 \text{ mL, pH} = 12.22 \text{ and } V_{\text{HCl}} = 90 \text{ mL, pH} = 12.46$$

Drawing a smooth curve through these points presents us with the following dilemma—the pH appears to increase as the titrant's volume approaches the first equivalence point and then appears to decrease as it passes through the first equivalence point. This is, of course, absurd; as we add NaOH the pH cannot decrease. Instead, we model the titration curve before the second equivalence point by drawing a straight line from the first point ($V_{\text{HCl}} = 2.5 \text{ mL, pH} = 2$) to the fourth point ($V_{\text{HCl}} = 47.5 \text{ mL, pH} = 5$), ignoring the second and third points. The results is a reasonable approximation of the exact titration curve.



Selecting and Evaluating the End Point

Earlier we made an important distinction between a titration's end point and its equivalence point. The difference between these two terms is important and deserves repeating. An equivalence point, which occurs when we react stoichiometrically equal amounts of the analyte and the titrant, is a theoretical not an experimental value. A titration's end point is an experimental result that represents our best estimate of the equivalence point. Any difference between a titration's equivalence point and its corresponding end point is a source of determinate error.

Where is the Equivalence Point?

Earlier we learned how to calculate the pH at the equivalence point for the titration of a strong acid with a strong base, and for the titration of a weak acid with a strong base. We also learned how to sketch a titration curve with only a minimum of calculations. Can we also locate the equivalence point without performing any calculations. The answer, as you might guess, often is yes!

For most acid–base titrations the inflection point—the point on a titration curve that has the greatest slope—very nearly coincides with the titration's equivalence point. The red arrows in Figure 6.6.4, for example, identify the equivalence points for the titration curves in Example 6.6.1. An inflection point actually precedes its corresponding equivalence point by a small amount, with the error approaching 0.1% for weak acids and weak bases with dissociation constants smaller than 10^{-9} , or for very dilute solutions [Meites, L.; Goldman, J. A. *Anal. Chim. Acta* **1963**, 29, 472–479].

The principal limitation of an inflection point is that it must be present and easy to identify. For some titrations the inflection point is missing or difficult to find. Figure 6.6.5, for example, demonstrates the affect of a weak acid's dissociation constant, K_a , on the shape of its titration curve. An inflection point is visible, even if barely so, for acid dissociation constants larger than 10^{-9} , but is missing when K_a is 10^{-11} .

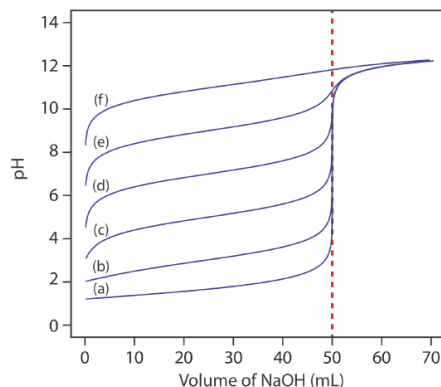
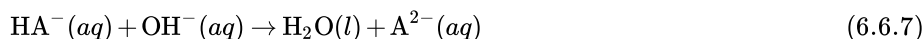
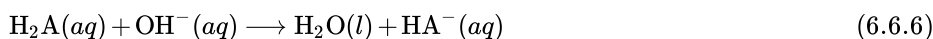


Figure 6.6.5 . Weak acid–strong base titration curves for the titration of 50.0 mL of 0.100 M HA with 0.100 M NaOH. The pK_a values for HA are (a) 1, (b) 3, (c) 5, (d) 7, (e) 9, and (f) 11. The dashed red line shows the equivalence point, which is 50.0 mL for all six analytes.

An inflection point also may be missing or difficult to see if the analyte is a multiprotic weak acid or weak base with successive dissociation constants that are similar in magnitude. To appreciate why this is true let's consider the titration of a diprotic weak acid, H_2A , with NaOH. During the titration the following two reactions occur.



To see two distinct inflection points, reaction 6.6.6 must essentially be complete before reaction 6.6.7 begins.

Figure 6.6.6 shows titration curves for three diprotic weak acids. The titration curve for maleic acid, for which K_{a1} is approximately $20000\times$ larger than K_{a2} , has two distinct inflection points. Malonic acid, on the other hand, has acid dissociation constants that differ by a factor of approximately 690. Although malonic acid's titration curve shows two inflection points, the first is not as distinct as the second. Finally, the titration curve for succinic acid, for which the two K_a values differ by a factor of only $27\times$, has only a single inflection point that corresponds to the neutralization of $\text{HC}_2\text{H}_4\text{O}_4^-$ to $\text{C}_2\text{H}_4\text{O}_4^{2-}$. In general, we can detect separate inflection points when successive acid dissociation constants differ by a factor of at least 500 (a ΔK_a of at least 2.7).

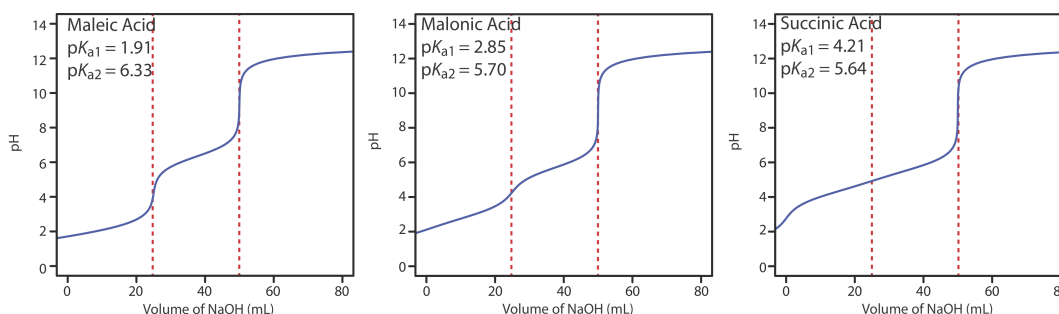


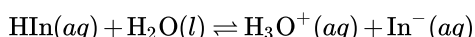
Figure 6.6.6 . Titration curves for the diprotic weak acids maleic acid, malonic acid, and succinic acid. Each titration curve is for 50.0 mL of 0.0500 M weak acid using 0.100 M NaOH as the titrant. Although each titration curve has equivalence points at 25.0 mL and 50.0 mL of NaOH (shown by the dashed red lines), the titration curve for succinic acid shows only one inflection point.

The same holds true for mixtures of weak acids or mixtures of weak bases. To detect separate inflection points when titrating a mixture of weak acids, their pK_a values must differ by at least a factor of 500.

Finding the End Point with an Indicator

One interesting group of weak acids and weak bases are organic dyes. Because an organic dye has at least one highly colored conjugate acid–base species, its titration results in a change in both its pH and its color. We can use this change in color to indicate the end point of a titration provided that it occurs at or near the titration's equivalence point.

As an example, let's consider an indicator for which the acid form, HIn , is yellow and the base form, In^- , is red. The color of the indicator's solution depends on the relative concentrations of HIn and In^- . To understand the relationship between pH and color we use the indicator's acid dissociation reaction



and its equilibrium constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad (6.6.8)$$

Taking the negative log of each side of Equation 6.6.8, and rearranging to solve for pH leaves us with an equation that relates the solution's pH to the relative concentrations of HIn and In^- .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad (6.6.9)$$

If we can detect HIn and In^- with equal ease, then the transition from yellow-to-red (or from red-to-yellow) reaches its midpoint, which is orange, when the concentrations of HIn and In^- are equal, or when the pH is equal to the indicator's pK_a . If the indicator's pK_a and the pH at the equivalence point are identical, then titrating until the indicator turns orange is a suitable end point. Unfortunately, we rarely know the exact pH at the equivalence point. In addition, determining when the concentrations of HIn and In^- are equal is difficult if the indicator's change in color is subtle.

We can establish the range of pHs over which the average analyst observes a change in the indicator's color by making two assumptions: that the indicator's color is yellow if the concentration of HIn is $10\times$ greater than that of In^- and that its color is red if the concentration of HIn is $10\times$ smaller than that of In^- . Substituting these inequalities into Equation 6.6.9

$$\text{pH} = \text{p}K_a + \log \frac{1}{10} = \text{p}K_a - 1$$

$$\text{pH} = \text{p}K_a + \log \frac{10}{1} = \text{p}K_a + 1$$

shows that the indicator changes color over a pH range that extends ± 1 unit on either side of its $\text{p}K_a$. As shown in Figure 6.6.7, the indicator is yellow when the pH is less than $\text{p}K_a - 1$ and it is red when the pH is greater than $\text{p}K_a + 1$. For pH values between $\text{p}K_a - 1$ and $\text{p}K_a + 1$ the indicator's color passes through various shades of orange. The properties of several common acid-base indicators are listed in Table 6.6.3.

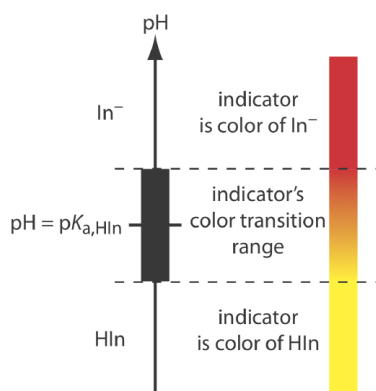


Figure 6.6.7. Diagram showing the relationship between pH and an indicator's color. The ladder diagram defines pH values where HIn and In^- are the predominate species. The indicator changes color when the pH is between $\text{p}K_a - 1$ and $\text{p}K_a + 1$.

Table 6.6.3. Properties of Selected Acid-Base Indicators

indicator	acid color	base color	pH range	$\text{p}K_a$
cresol red	red	yellow	0.2–1.8	—
thymol blue	red	yellow	1.2–2.8	1.7
bromothymol blue	yellow	blue	3.0–4.6	4.1
methyl orange	red	yellow	3.4–4.4	3.7
Congo red	blue	red	3.0–5.0	—
bromocresol green	yellow	blue	3.8–5.4	4.7
methyl red	red	yellow	4.2–6.3	5.0
bromocresol purple	yellow	purple	5.2–6.8	6.1
litmus	red	blue	5.0–8.0	—
bromothymol blue	yellow	blue	6.0–7.6	7.1
phenol red	yellow	blue	6.8–8.4	7.8
cresol red	yellow	red	7.2–8.8	8.2
thymol blue	yellow	red	8.0–9.6	8.9
phenolphthalein	colorless	red	8.3–10.0	9.6
alizarin yellow R	yellow	orange-red	10.1–12.0	—

You may wonder why an indicator's pH range, such as that for phenolphthalein, is not equally distributed around its $\text{p}K_a$ value. The explanation is simple. Figure 6.6.7 presents an idealized view in which our sensitivity to the indicator's two colors is

equal. For some indicators only the weak acid or the weak base is colored. For other indicators both the weak acid and the weak base are colored, but one form is easier to see. In either case, the indicator's pH range is skewed in the direction of the indicator's less colored form. Thus, phenolphthalein's pH range is skewed in the direction of its colorless form, shifting the pH range to values lower than those suggested by Figure 6.6.7 .

The relatively broad range of pHs over which an indicator changes color places additional limitations on its ability to signal a titration's end point. To minimize a determinate titration error, the indicator's entire pH range must fall within the rapid change in pH near the equivalence point. For example, in Figure 6.6.8 we see that phenolphthalein is an appropriate indicator for the titration of 50.0 mL of 0.050 M acetic acid with 0.10 M NaOH. Bromothymol blue, on the other hand, is an inappropriate indicator because its change in color begins well before the initial sharp rise in pH, and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining an inaccurate result, and the range of possible end point volumes increases the probability of obtaining imprecise results.

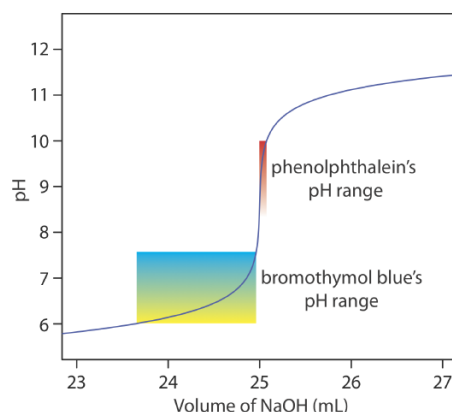


Figure 6.6.8 . Portion of the titration curve for 50.0 mL of 0.050 M CH_3COOH with 0.10 M NaOH, highlighting the region that contains the equivalence point. The end point transitions for the indicators phenolphthalein and bromothymol blue are superimposed on the titration curve.

? Exercise 6.6.5

Suggest a suitable indicator for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M NaOH. You constructed a titration curve for this titration in [Exercise 6.6.2](#) and [Exercise 6.6.3](#) .

Answer

The pH at the equivalence point is 5.31 (see [Exercise 6.6.2](#)) and the sharp part of the titration curve extends from a pH of approximately 7 to a pH of approximately 4. Of the indicators in [Table 6.6.3](#) , methyl red is the best choice because its pK_a value of 5.0 is closest to the equivalence point's pH and because the pH range of 4.2–6.3 for its change in color will not produce a significant titration error.

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