EXAMPLE 14-2

Calculate the pH during the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

(a) At 24.50 mL added, $[H_3O^+]$ is very small and cannot be computed from stoichiometric considerations but can be obtained from $[OH^-]$

$$[OH^-] = c_{NaOH} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}}$$

$$= \frac{50.00 \times 0.0500 - 24.50 \times 0.100}{50.00 + 24.50} = 6.71 \times 10^{-4} \, M$$

$$[H_3O^+] = K_w/(6.71 \times 10^{-4}) = 1.00 \times 10^{-14}/(6.71 \times 10^{-4})$$

$$= 1.49 \times 10^{-11} \, M$$

$$pH = -\log(1.49 \times 10^{-11}) = 10.83$$

Curves for the titration of 0.0500 M and 0.00500 M NaOH with 0.1000 M and 0.0100 M HCl are shown in Figure 14-4. Indicator selection is based on the same considerations described for the titration of a strong acid with a strong base.
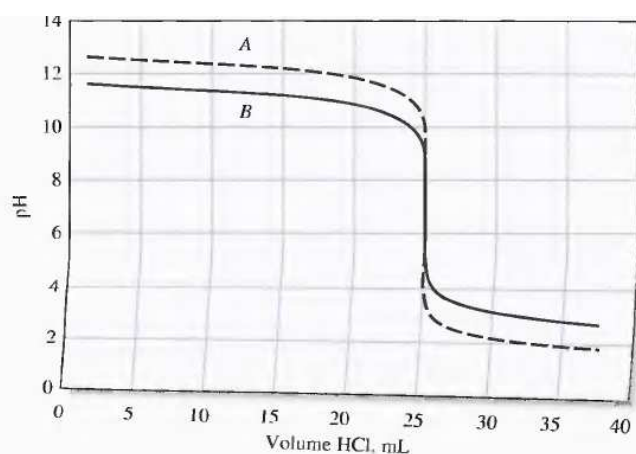
Figure 14-4   Titration curves for NaOH with HCl. Curve A: 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl. Curve B: 50.00 mL of 0.00500 M NaOH with 0.0100 M HCl.

14C TITRATION CURVES FOR WEAK ACIDS

Four distinctly different types of calculations are needed to derive a titration curve for a weak acid (or a weak base):

1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.
2. After various increments of titrant have been added (in quantities up to, but not including, an equivalent amount), the solution consists of a series of buffers. The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the residual concentrations of the weak acid or base.
3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.
4. Beyond the equivalence point, the excess of strong acid or base titrant represses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

EXAMPLE 14-3

Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid with 0.1000 M sodium hydroxide.

Initial pH
First, we must calculate the pH of a 0.1000 M solution of HOAc using Equation 9-22.

$$[H_3O^+] = \sqrt{K_a c_{HOAc}} = \sqrt{1.75 \times 10^{-5} \times 0.100} = 1.32 \times 10^{-3} \, M$$

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$

pH after Addition of 5.00 mL of Reagent
A buffer solution consisting of NaOAc and HOAc has now been produced. The analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00 \text{ mL} \times 0.100 \text{ M} - 5.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{4.500}{60.00} \text{ M}$$

$$c_{NaOAc} = \frac{5.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{0.500}{60.00} \text{ M}$$

Now for the 5.00-mL volume, we substitute the concentrations of HOAc and OAc⁻ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](0.500/\cancel{60.00})}{4.500/\cancel{60.00}} = 1.75 \times 10^{-5}$$

$$[H_3O^+] = 1.58 \times 10^{-4}\ M$$

$$pH = 3.80$$

Note that the total volume of solution is present in both numerator and denominator and thus cancels in the expression for $[H_3O^+]$. Calculations similar to this provide points on the curve throughout the buffer region. Data from these calculations are presented in column 2 of Table 14-3.

TABLE 14-3

Changes in pH during the Titration of a Weak Acid with a Strong Base

	pH	
Volume of NaOH, mL	50.00 mL of 0.1000 M HOAc with 0.1000 M NaOH	50.00 mL of 0.001000 M HOAc with 0.001000 M NaOH
0.00	2.88	3.91
10.00	4.16	4.30
25.00	4.76	4.80
40.00	5.36	5.38
49.00	6.45	6.46
49.90	7.46	7.47
50.00	8.73	7.73
50.10	10.00	8.09
51.00	11.00	9.00
60.00	11.96	9.96
70.00	12.22	10.25

pH after Addition of 25.00 mL of Reagent

As in the previous calculation, the analytical concentrations of the two constituents are

$$c_{HOAc} = \frac{50.00 \text{ mL} \times 0.100 \text{ M} - 25.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{2.500}{60.00} \text{ M}$$

$$c_{NaOAc} = \frac{25.00 \text{ mL} \times 0.100 \text{ M}}{60.00 \text{ mL}} = \frac{2.500}{60.00} \text{ M}$$

Now for the 25.00-mL volume, we substitute the concentrations of HOAc and OAc⁻ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[H_3O^+](2.500/60.00)}{2.500/60.00} = [H_3O^+] = 1.75 \times 10^{-5}$$

$$pH = pK_a = 4.76$$

At this point in the titration, both the analytical concentrations of the acid and conjugate base as well as the total volume of solution cancel in the expression for $[H_3O^+]$.

Equivalence Point pH

At the equivalence point, all the acetic acid has been converted to sodium acetate. The solution is therefore similar to one formed by dissolving that salt in water, and the pH calculation is identical to that shown in Example 9-10 (page 250) for a weak base. In the present example, the NaOAc concentration is 0.0500 M. Thus,

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$[OH^-] = [HOAc]$$

$$[OAc^-] = 0.0500 - [OH^-] \approx 0.0500$$

Substituting in the base dissociation-constant expression for OAc^- gives

$$\frac{[OH^-]^2}{0.0500} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$[OH^-] = \sqrt{0.0500 \times 5.71 \times 10^{-10}} = 5.34 \times 10^{-6} \text{ M}$$

$$pH = 14.00 - (-\log 5.34 \times 10^{-6}) = 8.73$$

pH after Addition of 50.01 mL of Base

After the addition of 50.01 mL of NaOH, both the excess base and the acetate ion are sources of hydroxide ion. The contribution from the acetate ion is small, however, because the excess of strong base represses the reaction of acetate with water. This fact becomes evident when we consider that the hydroxide ion concentration is only 5.35×10^{-6} at the equivalence point; once a tiny excess of

strong base is added, the contribution from the reaction of the acetate is even smaller. We then have

$$[OH^-] \approx c_{NaOH} = \frac{50.01 \text{ mL} \times 0.1000 \text{ M} - 50.00 \text{ mL} \times 0.1000 \text{ M}}{100.01 \text{ mL}}$$

$$= 1.00 \times 10^{-5} \text{ M}$$

$$pH = 14.00 - [-\log (1.00 \times 10^{-5})] = 9.00$$

Note that the titration curve for a weak acid with a strong base is identical to that for a strong acid with a strong base in the region slightly beyond the equivalence point.

Table 14-3 and Figure 14-5 compare the pH values calculated in this example with a more dilute titration. The effect of concentration is discussed in Section 14C-1.
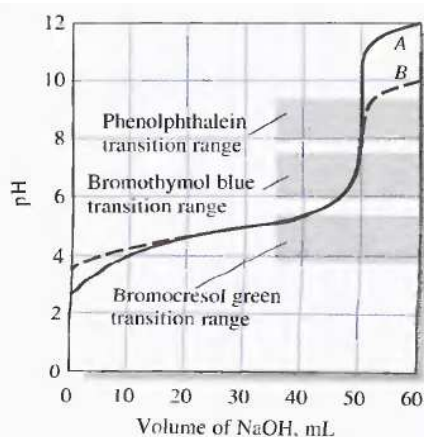
Figure 14-5 Curve for the titration of acetic acid with sodium hydroxide. Curve A: 0.1000 M acid with 0.1000 M base. Curve B: 0.001000 M acid with 0.001000 M base.

14D TITRATION CURVES FOR WEAK BASES

The calculations needed to draw the titration curve for a weak base are analogous to those for a weak acid.

EXAMPLE 14-4

A 50.00-mL aliquot of 0.0500 M NaCN is titrated with 0.1000 M HCl. The reaction is

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$$

Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.

(a) **0.00 mL of Reagent**
The pH of a solution of NaCN can be derived by the method shown in Example 9-10, page 250:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$$[OH^-] = [HCN]$$

$$[CN^-] = c_{NaCN} - [OH^-] \approx c_{NaCN} = 0.050 \text{ M}$$

Substitution into the dissociation-constant expression gives, after rearrangement,

$$[OH^-] = \sqrt{K_b c_{NaCN}} = \sqrt{1.61 \times 10^{-5} \times 0.0500} = 8.97 \times 10^{-4}$$

$$pH = 14.00 - (-\log 8.97 \times 10^{-4}) = 10.95$$

(b) **10.00 mL of Reagent**
Addition of acid produces a buffer with a composition given by

$$c_{NaCN} = \frac{50.00 \times 0.0500 - 10.00 \times 0.1000}{60.00} = \frac{1.500}{60.00} \text{ M}$$

$$c_{HCN} = \frac{10.00 \times 0.1000}{60.00} = \frac{1.000}{60.00} \text{ M}$$

These values are then substituted into the expression for the acid dissociation constant of HCN to give $[H_3O^+]$ directly (see Margin Note):

$$[H_3O^+] = \frac{6.2 \times 10^{-10} \times (1.000/60.00)}{1.500/60.00} = 4.13 \times 10^{-10}$$

$$pH = -\log(4.13 \times 10^{-10}) = 9.38$$

(c) 25.00 mL of Reagent

This volume corresponds to the equivalence point, where the principal solute species is the weak acid HCN. Thus,

$$c_{HCN} = \frac{25.00 \times 0.1000}{75.00} = 0.03333 \text{ M}$$

Applying Equation 9-22 gives

$$[H_3O^+] = \sqrt{K_a c_{HCN}} = \sqrt{6.2 \times 10^{-10} \times 0.03333} = 4.45 \times 10^{-6} \text{ M}$$

$$pH = -\log(4.45 \times 10^{-6}) = 5.34$$

(d) 26.00 mL of Reagent

The excess of strong acid now present represses the dissociation of the HCN to the point where its contribution to the pH is negligible. Thus,

$$[H_3O^+] = c_{HCl} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{76.00} = 1.32 \times 10^{-3} \text{ M}$$

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$

Figure 14-7 shows hypothetical titration curves for a series of weak bases of different strengths. The curves show that indicators with *acidic* transition ranges must be used for weak bases.
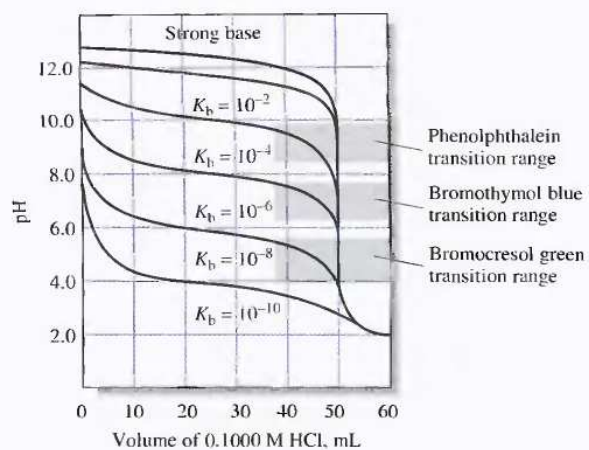
Figure 14-7 The effect of base strength (K_b) on titration curves. Each curve represents the titration of 50.00 mL of 0.1000 M base with 0.1000 M HCl.