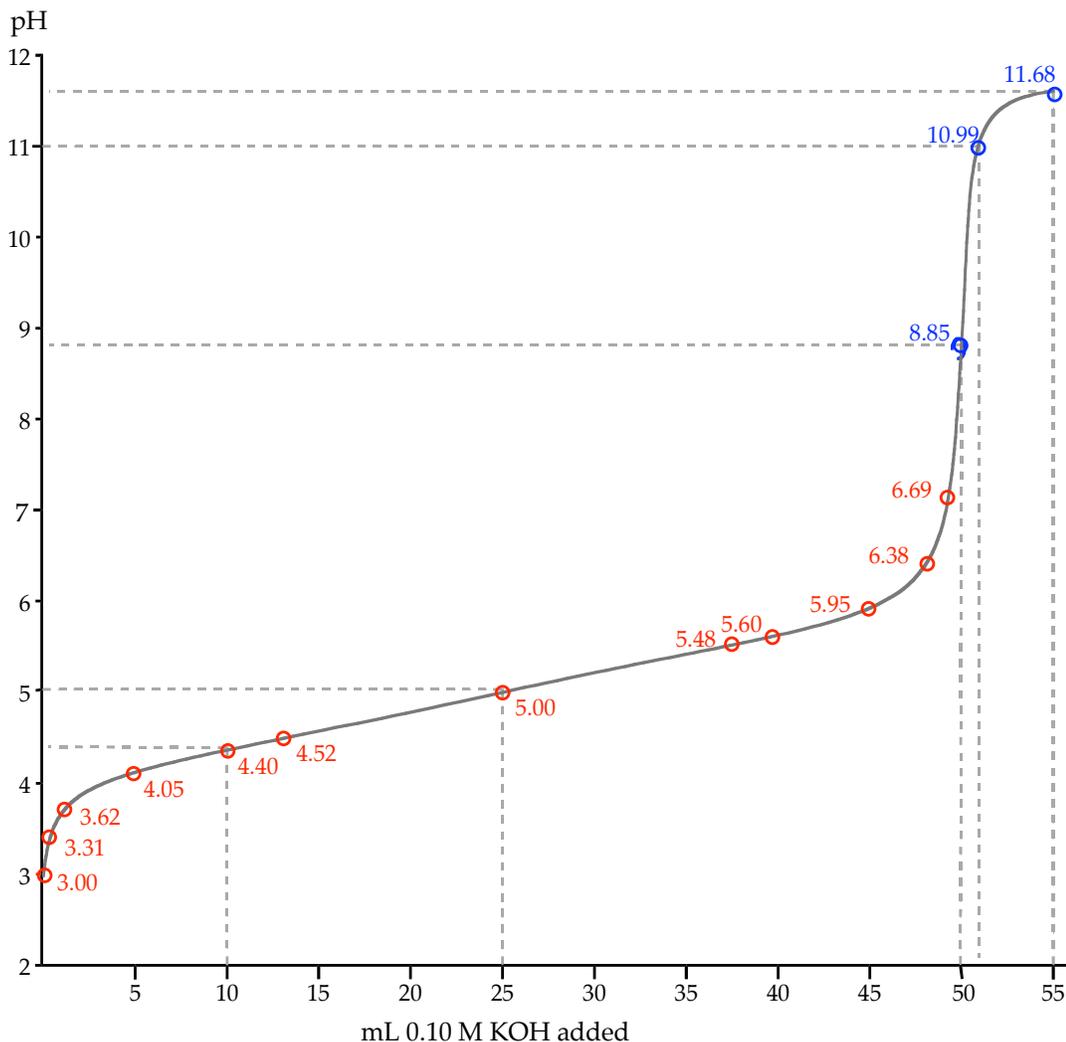


Plotting a Titration Curve

The points from Table 5.3 are represented in Figure 5-9 as circles. The curve is drawn to fit the circles. The shape of the curve for a weak acid is distinct. The buffer region is not perfectly flat, showing that pH changes slightly in the buffer region. The pH values at 1.00 mL and 2.00 mL are not exact, because the Henderson-Hasselbalch equation does not hold as well outside the $pK_a \pm 1$ range. Nevertheless, the values are close enough to generate a reasonable titration curve.

**Figure 5-9**

The titration curve should become familiar with enough examples. What makes curves useful is that they summarize a great deal of information. If you think of titration curves in terms of equivalents and regions, you can extract a substantial amount of information from them. For instance, when 21.27 mL of 0.1 M $KOH(aq)$ has been added, the pH is roughly 4.7 to 4.8. That range is small enough that an educated guess can be made on a multiple-choice question. We shall emphasize using titration curves in lieu of calculating the pH, when it comes to buffers and other mixtures.

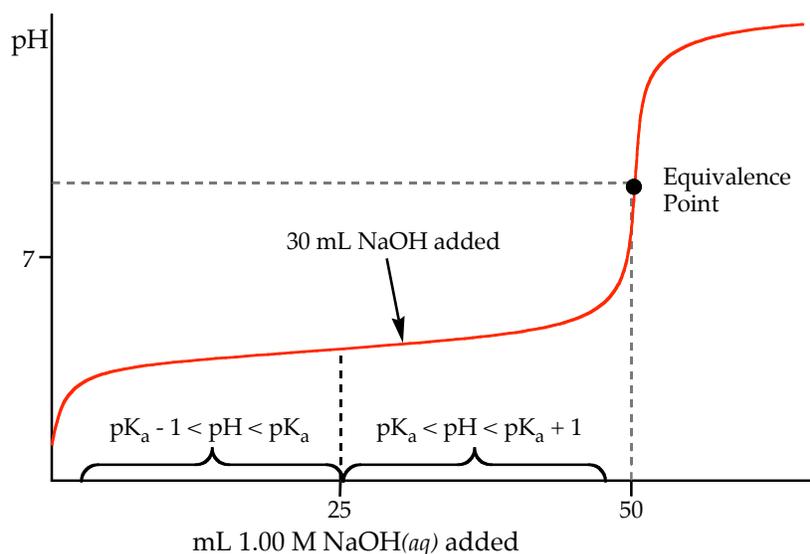
Example 5.11

What is the pH after 30 mL of 1.00 M NaOH(aq) has been added to 100 mL 0.50 M HOAc(aq)? HOAc has a $pK_a = 4.74$.

- A. 3.51
- B. 4.56
- C. 4.92
- D. 5.97

Solution

Because the strong base is twice as concentrated as the weak acid, only half the volume of strong base (relative to the weak acid) is required to reach the equivalence point. This means that 50 mL of 1.00 M NaOH fully neutralizes the 100 mL of 0.50 M HOAc. The halfway point of the titration is reached when exactly 25 mL of 1.00 M NaOH has been added. At the halfway point, the pH of the solution equals the pK_a of the weak acid. The additional 5 mL of strong base beyond the 25 mL to reach half way makes the pH of the solution slightly greater than the pK_a of the acid, 4.74. The best choice is answer C. The titration curve below shows a summary of the intuitive approach:



When 30 mL has been added, the mixture is just beyond the half-titrated point on the titration curve (as shown by the arrow). This makes the pH fall into the range of $pK_a < pH < pK_a + 1$, according to the titration curve. According to the Henderson-Hasselbalch equation, the pH equals the $pK_a + \log$ (conjugate base over acid). Past the half-titrated point, the concentration of the conjugate base exceeds the concentration of the acid, so the ratio of conjugate base to acid is greater than one. The log of a number greater than 1.0 is a positive value. When a positive value is added to the pK_a , the final value is greater than the pK_a , confirming that $pH > pK_a$. Questions of this type should be answered quickly, using either a titration curve or the Henderson-Hasselbalch equation in a purely conceptual manner.