Lacture-9

Titrations Based on Acid-Base Reactions

The earliest acid-base titrations involved the determination of the acidity or alkalinity of solutions, and the purity of carbonates and alkaline earth oxides. Various acid-base titration reactions, including a number of scenarios of base in the burette, acid in the reaction flask, and vice versa, as well as various monoprotic and polyprotic acids titrated with strong bases and various weak monobasic and polybasic bases titrated with strong acids.   A **monoprotic acid** is an acid that has only one hydrogen ion (or proton) to donate per formula. Examples are hydrochloric acid, HCl, a strong acid, and acetic acid, $HC_2H_3O_2$, a weak acid. A **polyprotic acid** is an acid that has two or more hydrogen ions to donate per formula. Examples include sulfuric acid, H_2SO_4, a **diprotic acid,** and phosphoric acid, H_3PO_4, a **triprotic** acid.

A **monobasic base** is one that will accept just one hydrogen ion per formula.Examples include sodium hydroxide, NaOH, a strong base; ammonium hydroxide, NH_4OH, a weak base; and sodium bicarbonate, $NaHCO_3$, a weak base. A **polybasic base** is one that will accept two or more hydrogen ions per formula. Examples include sodium carbonate, Na_2CO_3, a **dibasic base,** and sodium phosphate, Na_3PO_4, a **tribasic base.**

Acid-Base Titration Curves

In the overview to the titration we noted that the experimentally determined end point should coincide with the titration's equivalence point. For an acid-base titration, the equivalence point is characterized by a pH level that is a function of the acid-base strengths and concentrations of the analyte and titrant. The pH at the end point, however, may or may not correspond to the pH at the equivalence point. To understand the relationship between end points and equivalence points we must know how the pH changes during a titration. In this section we will learn how to construct titration curves for
several important types of acid-base titrations.

Titrating Strong Acids and Strong Bases

For our first titration curve let's consider the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. For the reaction of a strong base with a strong acid the only equilibrium reaction of importance is

$$H_3O^+(aq) + OH^-(aq) = 2H_2O(l)$$

The first task in constructing the titration curve is to calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point we know from reaction above that

Moles HCl = moles NaOH

$$M_a V_a = M_b V_b$$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point, therefore, is

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{(0.200 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. Initially the solution is 0.100 M in HCl, which, since HCl is a strong acid, means that the pH is

$$\text{pH} = -\log[H_3O^+] = -\log[HCl] = -\log(0.100) = 1.00$$

The equilibrium constant for reaction is $(K_w)^{-1}$, or 1.00×10^{14}. Since this is such a large value we can treat reaction as though it goes to completion. After adding 10.0 mL of NaOH, therefore, the concentration of excess HCl is

$$[HCl] = \frac{\text{moles excess HCl}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

$$= \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.050 \text{ M}$$

giving a pH of 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.

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = [H_3O^+]^2$$

$$[H_3O^+] = 1.00 \times 10^{-7} \text{ M}$$

Thus, the pH at the equivalence point is 7.00.

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

$$[OH^-] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b}$$

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

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

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13}$$

giving a pH of 12.10.

The table and the figure below show additional results for this titration curve.

Data for Titration of 50.00 mL of 0.100 M HCl with 0.0500 M NaOH

Volume (mL) of Titrant	pH
0.00	1.00
5.00	1.14
10.00	1.30
15.00	1.51
20.00	1.85
22.00	2.08
24.00	2.57
25.00	7.00
26.00	11.42
28.00	11.89
30.00	12.50
35.00	12.37
40.00	12.52
45.00	12.62
50.00	12.70
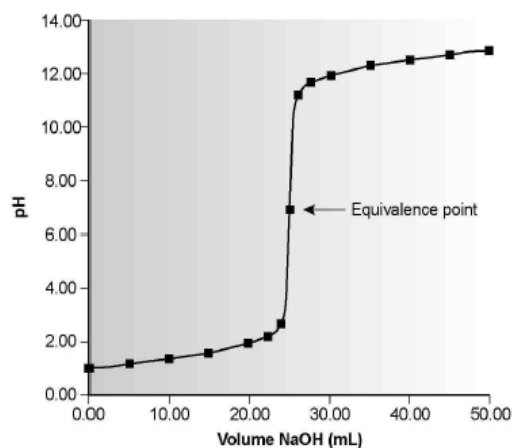
Calculating the titration curve for the titration of a strong base with a strong acid is handled in the same manner, except that the strong base is in excess before the equivalence point and the strong acid is in excess after the equivalence point.

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 0.100 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

$$\text{Moles } CH_3COOH = \text{Moles NaOH}$$

$$M_a V_a = M_b V_b$$

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 50.0 \text{ mL}$$

Before adding any NaOH the pH is that for a solution of 0.100 M acetic acid. Since acetic acid is a weak acid, we calculate the pH using this method

$$CH_3COOH(aq) + H_2O(l) = H_3O^+(aq) + CH_3COO^-(aq)$$
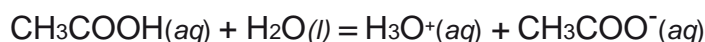
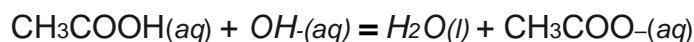$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [H_3O^+] = 1.32 \times 10^{-3}$$

We can use the following equation :

$$[H_3O^+] = \sqrt{K_a\, c(HA)}$$

At the beginning of the titration the pH is 2.88.
Adding NaOH converts a portion of the acetic acid to its conjugate base.

$$CH_3COOH(aq) + OH^-(aq) = H_2O(l) + CH_3COO^-(aq)$$

Any solution containing comparable amounts of a weak acid, HA, and its conjugate weak base, A$^-$, is a buffer. As we learned before, we can calculate the pH of a buffer using the Henderson-Hasselbalch equation.

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

The equilibrium constant for the above reaction is large $(K = K_a/K_w = 1.75 \times 10^9)$, so we can treat the reaction as one that goes to completion. Before the equivalence point, the concentration of unreacted acetic acid is

$$[CH_3COOH] = \frac{\text{moles unreacted } CH_3COOH}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

and the concentration of acetate is

$$[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH$_3$COOH and CH$_3$COO$^-$ are

$$(0.100\ M)(50.0\ mL) - (0.100\ M)(10.0\ mL)$$

$$[CH_3COOH] = \frac{\text{--}}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0667 \text{ M}$$

$$[CH_3COO^-] = \frac{(0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0167 \text{ M}$$

giving a pH of

$$pH = 4.76 + \log \frac{[0.0167]}{[0.0667]} = 4.16$$

A similar calculation shows that the pH after adding 20.0 mL of NaOH is 4.58.

At the equivalence point, the moles of acetic acid initially present and the moles of NaOH added are identical. Since their reaction effectively proceeds to completion, the predominate ion in solution is CH3COO-, which is a weak base. To calculate the pH we first determine the concentration of CH3COO--

$$[CH_3COO^-] = \frac{\text{moles } CH_3COOH}{\text{total volume}} = \frac{(0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 50.0 \text{ mL}} = 0.0500 \text{ M}$$

The pH is then calculated for a weak base.

$$CH_3COO^-(aq) + H_2O(l) = OH^-(aq) + CH_3COOH(aq)$$

$$[OH^-] = \sqrt{K_b \, c(B)}$$

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

The concentration of H3O+, therefore, is 1.87 × 10^{-9}, or a pH of 8.73.

After the equivalence point NaOH is present in excess, and the pH is determined in the same manner as in the titration of a strong acid with a strong base. For example, after adding 60.0 mL of NaOH, the concentration of OH$^-$ is

$$[OH] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b} = 0.00909 M$$

$$= \frac{(0.100 \text{ M})(60.0 \text{ mL}) - (0.100 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 60.0 \text{ mL}} = 0.0125 \text{ M}$$

giving a pH of 11.96. The table and figure below show additional results for this titration.

The calculations for the titration of a weak base with a strong acid are handled in a similar manner except that 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 the concentration of excess strong acid.

Volume of NaOH (mL)	pH
0.00	2.88
5.00	3.81
10.00	4.16
15.00	4.39
20.00	4.58
25.00	4.76
30.00	4.94
35.00	5.13
40.00	5.36
45.00	5.71
48.00	6.14
50.00	8.73
52.00	11.29
55.00	11.68
60.00	11.96
65.00	12.12
70.00	12.22
75.00	12.30
80.00	12.36
85.00	12.41
90.00	12.46
95.00	12.49
100.00	12.52
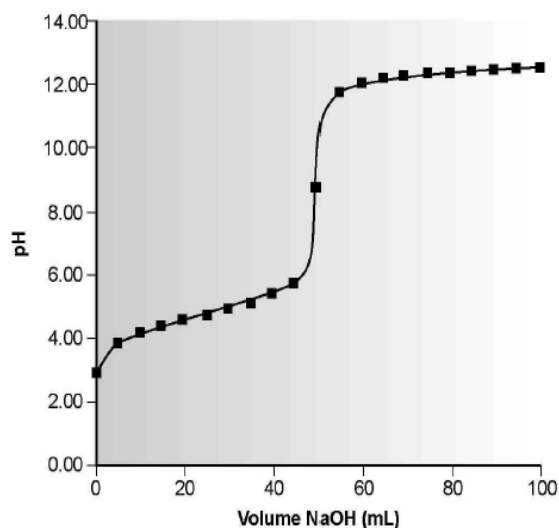
Data and titration curve for Titration of 50.0 mL of 0.100 M Acetic Acid with 0.100 M NaOH.

Method for finding the end point in acid-base titration
1- Finding the End Point with a Visual Indicator.
2- Finding the End Point by Monitoring pH.
3- Finding the End Point by Monitoring Temperature.