

The background of the slide features a light blue, semi-transparent image of laboratory glassware. On the left, a burette is visible, and on the right, a flask is shown. The overall aesthetic is clean and scientific.

Chapter 14

Principles of Neutralization Titrations

- Neutralization titrations are widely used to determine the amounts of acids and bases and to monitor the progress of reactions that produce or consume hydrogen ions.
- This chapter explores the principles of acid/base titrations. In addition, we investigate titration curves that are plots of pH vs. volume of titrant, and present several examples of pH calculations.

14 A Solutions and indicators for acid/base titrations

Neutralization titrations depend on a chemical reaction of the analyte with a standard reagent. There are several different types of acid/base titrations.

1. The titration of a strong acid, such as hydrochloric or sulfuric acid, with a strong base, such as sodium hydroxide.
 2. The titration of a weak acid, such as acetic or lactic acid, with a strong base.
 3. The titration of a weak base, such as sodium cyanide or sodium salicylate, with a strong acid.
- In all titrations, we must have a method of determining the point of chemical equivalence
 - Typically, a chemical indicator or an instrumental method is used to locate the end point, which we hope is very close to the equivalence point. Our discussion focuses on the types of standard solutions and the chemical indicators that are used for neutralization titrations

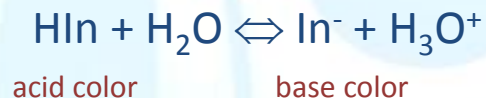
Standard Solutions

- The standard reagents used in acid/base titrations are always strong acids or strong bases, such as *HCl*, *HClO₄*, *H₂SO₄*, *NaOH*, and *KOH*.
- Weak acids and bases are never used as standard reagents because they react incompletely with analytes.
- Standard solutions of acids are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid.
- Nitric acid is seldom used because its oxidizing properties offer the potential for undesirable side reactions.
- Hot concentrated perchloric and sulfuric acids are potent oxidizing agents and are very hazardous.

Acid/Base Indicators

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form.

For example, the behavior of an acid-type indicator, HIn:



The equilibrium for a base-type indicator, In:



The equilibrium-constant expression for the dissociation of an acid-type indicator is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \qquad \text{Rearranging leads to} \qquad [\text{H}_3\text{O}^+] = K_a \cdot \frac{[\text{HIn}]}{[\text{In}^-]}$$

We see then that the hydronium ion is proportional to the ratio of the concentration of the acid form to the concentration of the base form of the indicator, which in turn controls the color of the solution.

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In⁻, particularly when the ratio [HIn]/[In⁻] is greater than about 10 or smaller than about 0.1.

HIn, exhibits its pure acid color when

$$[\text{HIn}]/[\text{In}^-] \geq 10/1$$

and its base color when

$$[\text{HIn}]/[\text{In}^-] \leq 1/10$$

Therefore, the range of hydronium ion concentrations needed for the indicator to change color can be estimated.

For full acid color, $[\text{H}_3\text{O}^+] = 10K_a$

and for the full base color, $[\text{H}_3\text{O}^+] = 0.1K_a$

To obtain the indicator pH range, we take the negative logarithms of the two expressions:

$$\text{pH (acid color)} = -\log(10K_a) = \text{p}K_a + 1$$

$$\text{pH (basic color)} = -\log(0.1K_a) = \text{p}K_a - 1$$

$$\text{Indicator pH range} = \text{p}K_a \pm 1$$

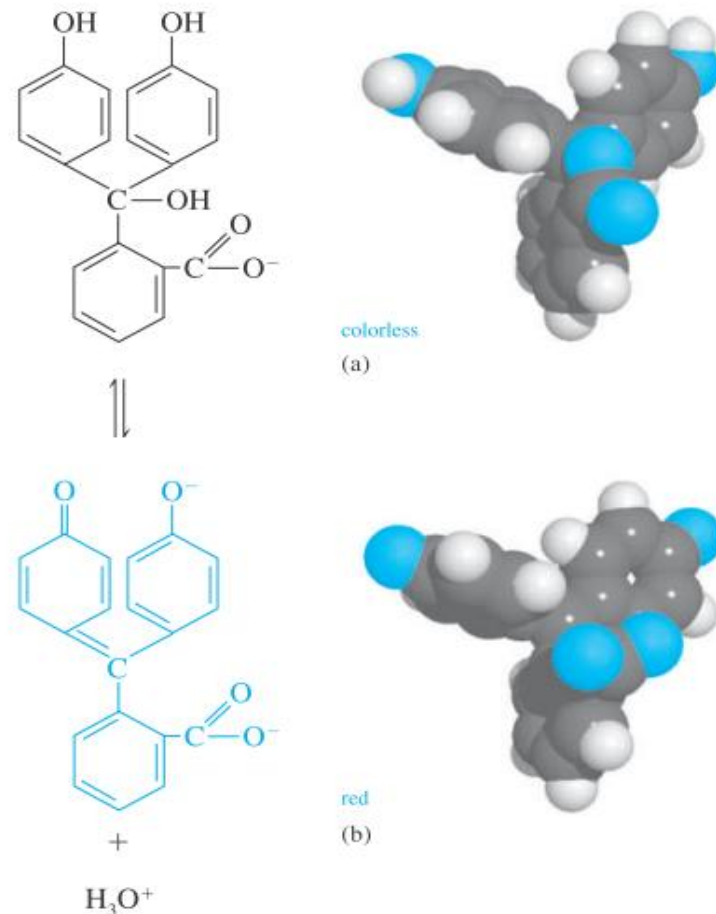


Figure 14-1 Color change and molecular modes for phenolphthalein. (a) Acidic form b) Basic form.

an indicator with an acid dissociation constant of 10^{-5} ($\text{p}K_a=5$) typically shows a complete color change when the pH of the solution in which it is dissolved changes from 4 to 6

Titration Errors with Acid/Base Indicators

There are two types of titration error in acid/base titrations:

Determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point.

It can usually be minimized by choosing the indicator carefully or by making a blank correction.

Indeterminate error that originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator.

The magnitude of this error depends on the change in pH per milliliter of reagent at—the equivalence point, on the concentration of the indicator, and on the sensitivity of the eye to the two indicator colors.

Variables That Influence the Behavior of Indicators

The pH interval over which a given indicator exhibits a color change is influenced by

- * temperature,
- * the ionic strength of the medium, and
- * the presence of organic solvents and colloidal particles.

Some of these effects can cause the transition range to shift by one or more pH units.

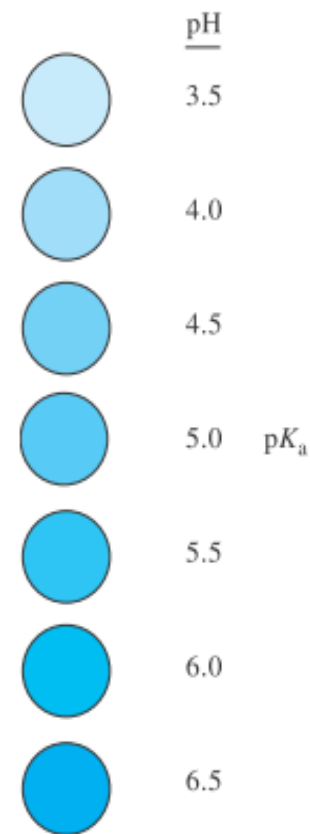


Figure 14-2 Indicator color as a function of pH (pK_a 5.0).

The Common Acid/Base Indicators

TABLE 14-1

Some Important Acid/Base Indicators

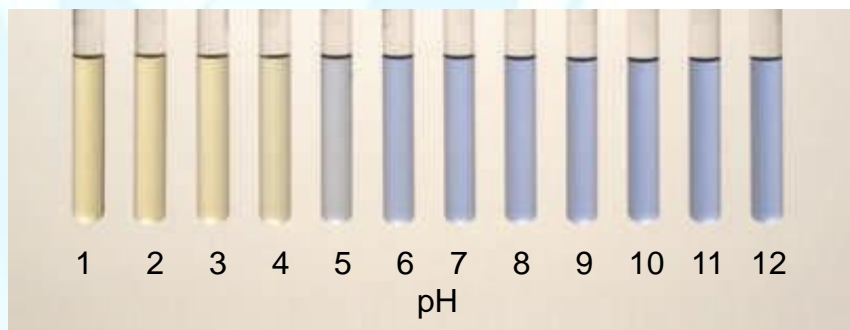
Common Name	Transition Range, pH	pK_a^*	Color Change [†]	Indicator Type [‡]
Thymol blue	1.2–2.8	1.65§	R – Y	1
	8.0–9.6	8.96§	Y – B	
Methyl yellow	2.9–4.0		R – Y	2
Methyl orange	3.1–4.4	3.46§	R – O	2
Bromocresol green	3.8–5.4	4.66§	Y – B	1
Methyl red	4.2–6.3	5.00§	R – Y	2
Bromocresol purple	5.2–6.8	6.12§	Y – P	1
Bromothymol blue	6.2–7.6	7.10§	Y – B	1
Phenol red	6.8–8.4	7.81§	Y – R	1
Cresol purple	7.6–9.2		Y – P	1
Phenolphthalein	8.3–10.0		C – R	1
Thymolphthalein	9.3–10.5		C – B	1
Alizarin yellow GG	10–12		C – Y	2

*At ionic strength of 0.1.

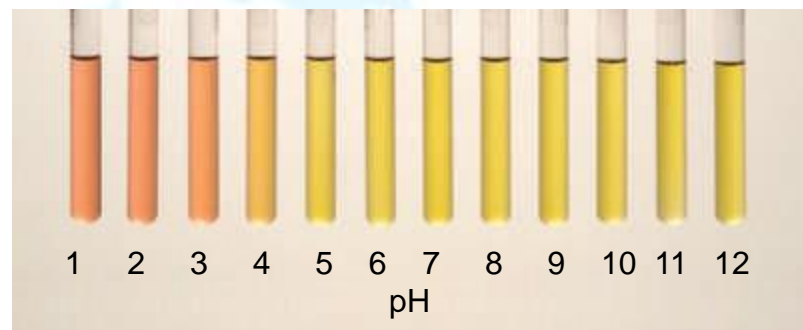
[†]B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

[‡](1) Acid type: $\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^-$; (2) Base type: $\text{In} + \text{H}_2\text{O} \rightleftharpoons \text{InH}^+ + \text{OH}^-$

[§]For the reaction $\text{InH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}$



Bromocresol green (3.8–5.4)



Methyl orange (3.2–4.4)

14 B Titration of strong acids and bases

The hydronium ions in an aqueous solution of a strong acid have two sources:

- (1) the reaction of the acid with water and
- (2) the dissociation of water itself.

In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that from the solvent (mostly water). For a solution of HCl with a concentration greater than about 10^{-6} M:

$$[\text{H}_3\text{O}^+] = c_{\text{HCL}} + [\text{OH}^-] \approx c_{\text{HCL}}$$

where $[\text{OH}^-]$ represents the contribution of hydronium ions from the dissociation of water.

For a solution of a strong base, such as sodium hydroxide:

$$[\text{OH}^-] = c_{\text{NAOH}} + [\text{H}_3\text{O}^+] \approx c_{\text{NAOH}}$$

14B-1 Titrating a Strong Acid with a Strong Base

Three types of calculations must be done to construct the hypothetical curve for titrating a solution of a strong acid with a strong base.

- (1) Preequivalence; compute the concentration of the acid from its starting concentration and the amount of base added.
- (2) Equivalence: the hydronium ion concentration can be calculated directly from the ion-product constant for water, K_w .
- (3) Postequivalence: the analytical concentration of the excess base is computed, and the hydroxide ion concentration is assumed to be equal to or a multiple of the analytical concentration.

Converting hydroxide concentration to pH can be developed by taking the negative logarithm of both sides of the ion-product constant expression for water. Thus,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$-\log K_w = -\log [\text{H}_3\text{O}^+][\text{OH}^-] = -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-]$$

$$\text{p}K_w = \text{pH} + \text{pOH}$$

At the equivalence point, the solution is neutral, and $\text{pH} = \text{pOH} = 7.00$, at 25C.

Beyond the equivalence point, we first calculate pOH and then pH.
Remember that $\text{pH} = \text{p}K_w - \text{pOH}$.
At 25C, $\text{pH} = 14.00 - \text{pOH}$.

EXAMPLE 14-1

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH at 25°C.

Initial Point

Before any base is added, the solution is 0.0500 M in H_3O^+ , and

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 0.0500 = 1.30$$

After Addition of 10.00 mL of Reagent

The hydronium ion concentration is decreased as a result of both reaction with the base and dilution. So, the remaining HCl concentration, c_{HCl} , is

$$\begin{aligned}c_{\text{HCl}} &= \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}} \\&= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}} \\&= \frac{(50.00 \text{ mL} \times 0.0500 \text{ M}) - (10.00 \text{ mL} \times 0.1000 \text{ M})}{50.00 \text{ mL} + 10.00 \text{ mL}} \\&= \frac{(2.500 \text{ mmol} - 1.00 \text{ mmol})}{60.00 \text{ mL}} = 2.50 \times 10^{-2} \text{ M}\end{aligned}$$

$$[\text{H}_3\text{O}^+] = 2.50 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.50 \times 10^{-2}) = 1.602 \approx 1.60$$

Note that we usually compute pH to two decimal places in titration curve calculations. We calculate additional points defining the curve in the region before the equivalence point in the same way. The results of these calculations are shown in the second column of [Table 14-2](#).

TABLE 14-2

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

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

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After Addition of 25.00 mL of Reagent: The Equivalence Point

At the equivalence point, neither HCl nor NaOH is in excess, and so, the concentrations of hydronium and hydroxide are equal. At this point, the concentration of the ion-product constant for water is

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.00$$

After Addition of 25.10 mL of Reagent

The solution now contains an excess of NaOH.

The equilibrium concentration of hydroxide ion is

$$[\text{OH}^-] = c_{\text{NaOH}} = 1.33 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.33 \times 10^{-4}) = 3.88$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.88 = 10.12$$

Additional values beyond the equivalence point are calculated in the same way. The results of these computations are shown in the last three rows of Table 14-2.

$$\begin{aligned}
 c_{\text{NaOH}} &= \frac{\text{no. mmol NaOH added} - \text{original no. of mmoles HCl}}{\text{total volume soln}} \\
 &= \frac{25.10 \times 0.1000 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}
 \end{aligned}$$

The Effect of Concentration

The effects of reagent and analyte concentration on the neutralization titration curves for strong acids are shown.

Choosing an Indicator

The selection of an indicator is not critical when the reagent concentration is approximately 0.1 M.

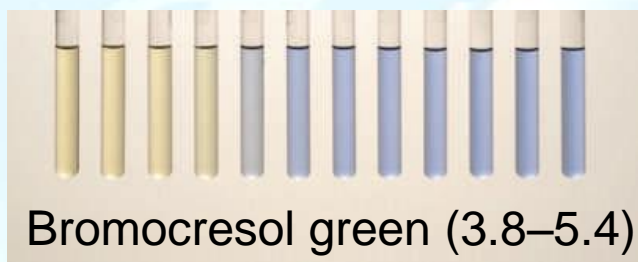
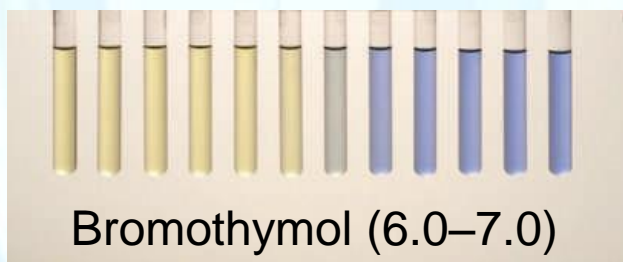


TABLE 14-2

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

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

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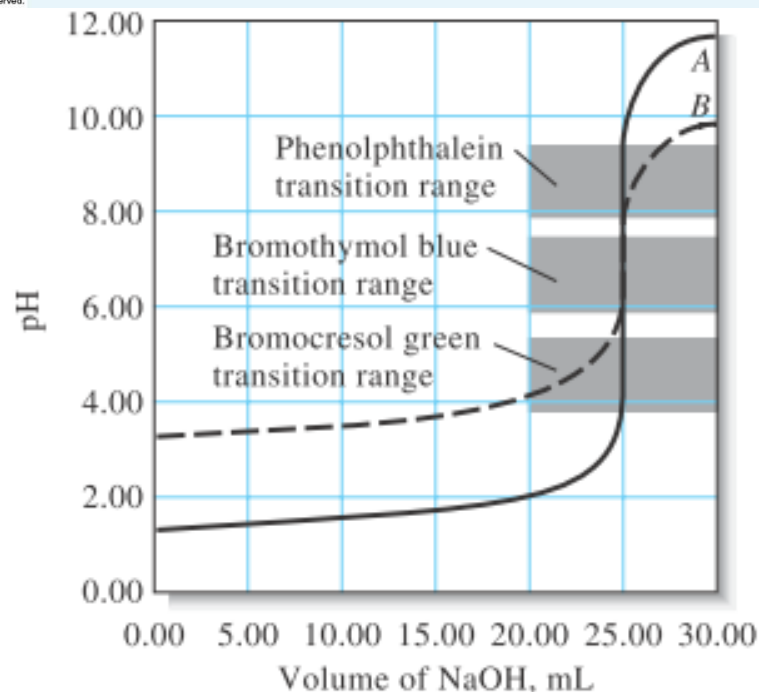


Figure 14-3 Titration curves for HCl with NaOH.

Curve A: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH.

Curve B: 50.00 mL of 0.000500 M HCl with 0.00100 M NaOH.

Titrating a Strong Base with a Strong Acid

Titration curves for strong bases are calculated in a similar way to those for strong acids.

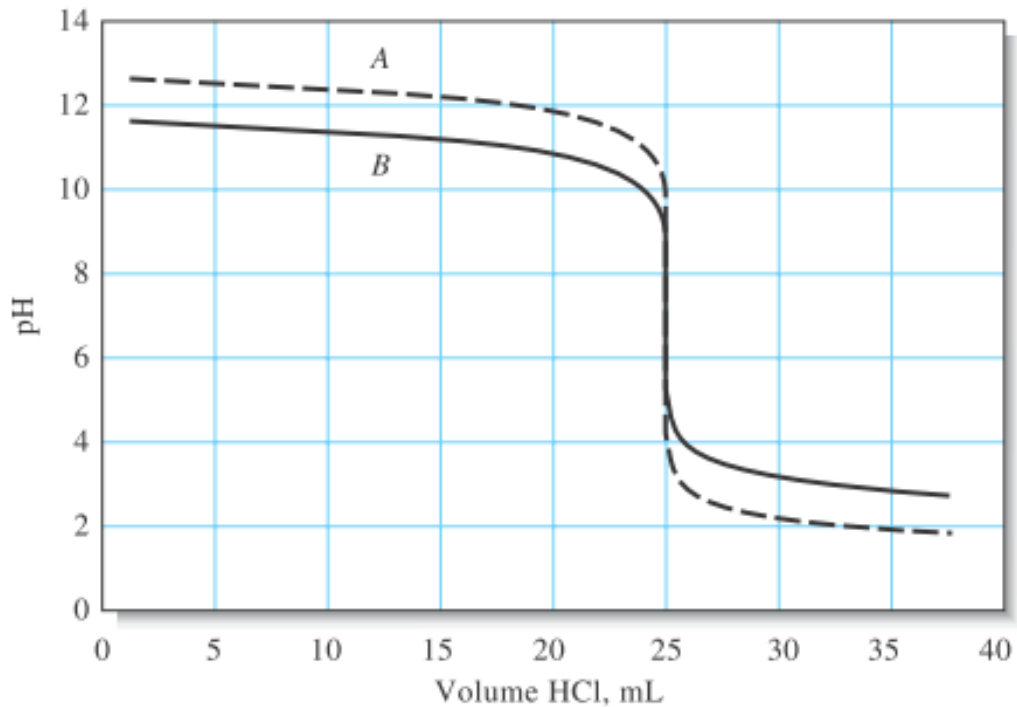


Figure 14- 4 Titration curves for NaOH with HCl.

EXAMPLE 14-2

Calculate the pH during the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl at 25°C after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

Solution

(a) At 24.50 mL added, $[\text{H}_3\text{O}^+]$ is very small and cannot be computed from stoichiometric considerations but can be obtained from $[\text{OH}^-]$:

$$\begin{aligned}[\text{OH}^-] &= c_{\text{NaOH}} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}} \\ &= \frac{50.00 \times 0.0500 - 24.50 \times 0.1000}{50.00 + 24.50} = 6.71 \times 10^{-4} \text{ M}\end{aligned}$$

$$\begin{aligned}[\text{H}_3\text{O}^+] &= K_w / (6.71 \times 10^{-4}) = 1.00 \times 10^{-14} / (6.71 \times 10^{-4}) \\ &= 1.49 \times 10^{-11} \text{ M}\end{aligned}$$

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

(b) 25.00 mL added is the

$$\begin{aligned}[\text{H}_3\text{O}^+] &= \sqrt{\dots} \\ \text{pH} &= -\log \dots\end{aligned}$$

(c) At 25.50 mL added

$$\begin{aligned}[\text{H}_3\text{O}^+] &= c_{\text{HCl}} = \frac{25.50 \times 0.1000 - 50.00 \times 0.0500}{75.50} \\ &= 6.62 \times 10^{-4} \text{ M} \\ \text{pH} &= -\log(6.62 \times 10^{-4}) = 3.18\end{aligned}$$

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](#). We use the same criteria described for the

14 C Titration curves for weak acids

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

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 (up to, but not including, the equivalence point), 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 concentrations of the weak acid or base that remains.

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 suppresses 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 (HOAc) with 0.1000 M sodium hydroxide at 25°C.

Initial pH

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

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_{\text{HOAc}}} = \sqrt{1.75 \times 10^{-5} \times 0.1000} = 1.32 \times 10^{-3} \text{ M}$$

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

pH after Addition of 10.00 mL of Reagent

A buffer solution consisting of NaOAc and HOAc has now been produced. The analytical concentrations of the two constituents are

$$c_{\text{HOAc}} = \frac{50.00 \text{ mL} \times 0.1000 \text{ M} - 10.00 \text{ mL} \times 0.1000 \text{ M}}{60.00 \text{ mL}} = \frac{4.000}{60.00} \text{ M}$$

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

Now, for the 10.00 mL volume, we substitute the concentrations of HOAc and OAc⁻ into the dissociation-constant expression for acetic acid and obtain

$$K_a = \frac{[\text{H}_3\text{O}^+](1.000/60.00)}{4.00/60.00} = 1.75 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = 7.00 \times 10^{-5}$$

$$\text{pH} = 4.15$$

TABLE 14-3

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

Volume of NaOH, mL	pH	
	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	4.15	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

$$c_{\text{HOAc}} = \frac{50.00 \text{ mL} \times 0.1000 \text{ M} - 25.00 \text{ mL} \times 0.1000 \text{ M}}{75.00 \text{ mL}} = \frac{2.500}{75.00} \text{ M}$$

$$c_{\text{NaOAc}} = \frac{25.00 \text{ mL} \times 0.1000 \text{ M}}{75.00 \text{ mL}} = \frac{2.500}{75.00} \text{ M}$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+](2.500/75.00)}{2.500/75.00} = 1.75 \times 10^{-5}$$

$$\text{pH} = \text{p}K_a = -\log(1.75 \times 10^{-5}) = 4.76$$

At this half-titration point, the analytical concentrations of the acid and conjugate

➤ The analytical concentrations of acid and conjugate base are identical when an acid has been half neutralized.

➤ The buffer capacities of each of the solutions are at a maximum at this point and these points, often called the half-titration points.

➤ At the half-titration point in a weak-acid titration,

$$[\text{H}_3\text{O}^+] = K_a \text{ and } \text{pH} = \text{p}K_a$$

Determining Dissociation Constants of Weak Acids and Bases

The dissociation constants of weak acids or weak bases are often determined by monitoring the pH of the solution while the acid or base is being titrated. A pH meter with a glass pH electrode is used for the measurements. The titration is recorded from the initial pH until after the end point. The pH at one-half the end point volume is then obtained and used to obtain the dissociation

Equivalence-point pH

At the equivalence point, all of the acetic acid has been converted to sodium acetate. The solution is, therefore, similar to one formed by dissolving NaOAc in water, and the pH calculation is identical to that shown in Example 9-10 (page 218) for a weak base. In the present example, the NaOAc concentration is

$$c_{\text{NaOAc}} = \frac{50.00 \text{ mL} \times 0.1000 \text{ M}}{100.00 \text{ mL}} = 0.0500 \text{ M}$$

Thus,



$$[\text{OH}^-] = [\text{HOAc}]$$

$$[\text{OAc}^-] = 0.0500 - [\text{OH}^-] \approx 0.0500$$

Substituting these quantities into the base dissociation-constant expression for OAc^- gives

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

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

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

pH After Addition of 50.10 mL of Base

After the addition of 50.10 mL of NaOH, the excess base and the acetate ion are both sources of hydroxide ion. The contribution from the acetate ion is small, however, because the excess of strong base suppresses the reaction of acetate with water. This fact becomes evident when we consider that the hydroxide ion concentration is only 5.34×10^{-6} M 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 have then

$$\begin{aligned}[\text{OH}^-] = c_{\text{NaOH}} &= \frac{50.10 \text{ mL} \times 0.1000 \text{ M} - 50.00 \text{ mL} \times 0.1000 \text{ M}}{100.10 \text{ mL}} \\ &= 9.99 \times 10^{-5} \text{ M} \\ \text{pH} &= 14.00 - [-\log(9.99 \times 10^{-5})] = 10.00\end{aligned}$$

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

Table 14-3 and **Figure 14-5** compares the pH values calculated in this example with a more dilute titration. In a dilute solution, some of the assumptions made in this example do not hold. The effect of concentration is discussed further in Section 14C-1.

14C-1 The Effect of Concentration

- The initial pH values are higher and the equivalence-point pH is lower for the more dilute solution (Curve B).
- At intermediate titrant volumes, however, the pH values differ only slightly because of the buffering action of the acetic acid/sodium acetate system that is present in this region.

14C-3 Choosing an Indicator:

- ✓ Figure 14-5 illustrates that bromocresol green is totally unsuited for titration of 0.1000 M acetic acid.
- ✓ Bromothymol blue does not work either because its full color change occurs over a range of titrant volume from about 47 mL to 50 mL of 0.1000 M base.
- ✓ On the other hand, an indicator exhibiting a color change in the basic region, such as phenolphthalein, provides a sharp end point with a minimal titration error.
- ✓ The end-point pH change associated with the titration of 0.001000 M acetic acid (curve B) is so small that there is likely to be a significant titration error regardless of indicator.
- ✓ However, using an indicator with a transition range between that of phenolphthalein and that of bromothymol blue in conjunction with a suitable color comparison standard makes it possible to establish the end point in this titration with decent precision (a few percent

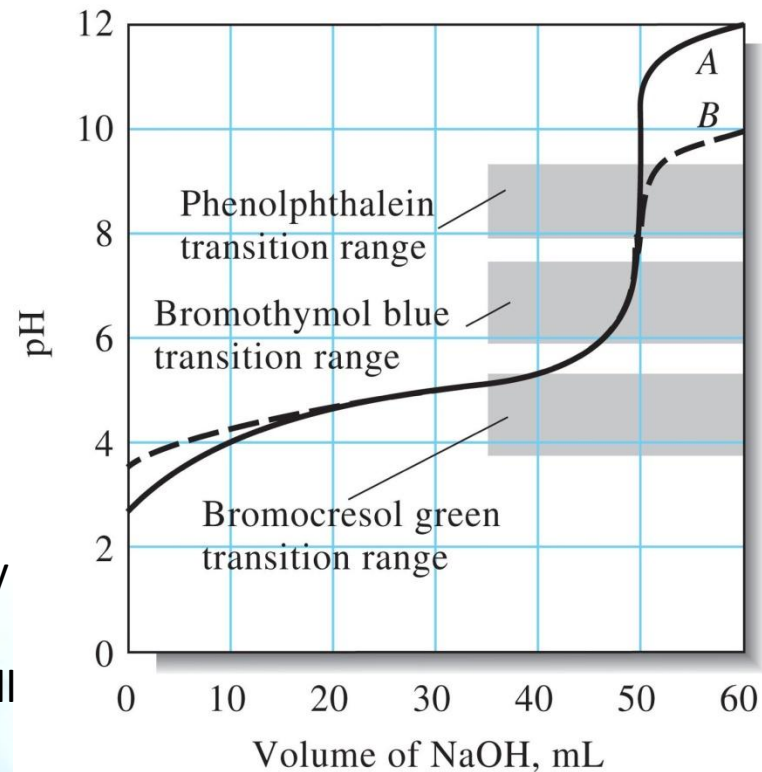


Figure 14-5 Curve for the titration of acetic acid with sodium hydroxide. Curve A: 0.1000 M acid with 0.1000 M base. Curve B: 0.001000 M acid with 0.001000 M base.

The Effect of Reaction Completeness

- Titration curves for 0.1000 M solutions of acids with different dissociation constants are shown.
- The pH change in the equivalence point region becomes smaller as the acid becomes weaker.

14C-3 Choosing an Indicator: The Feasibility of Titration

- Figures 14-5 and 14-6 show that the choice of indicator is more limited for the titration of a weak acid than for the titration of a strong acid.

- Figure 14-6 illustrates that similar problems occur as the strength of the acid being titrated decreases. A precision on the order of ± 2 ppt can be achieved by titrating a 0.1000 M solution of an acid with a dissociation constant of 10^{-8} if a suitable color comparison standard is available. With more concentrated solutions, weaker acids can be titrated with reasonable precision.

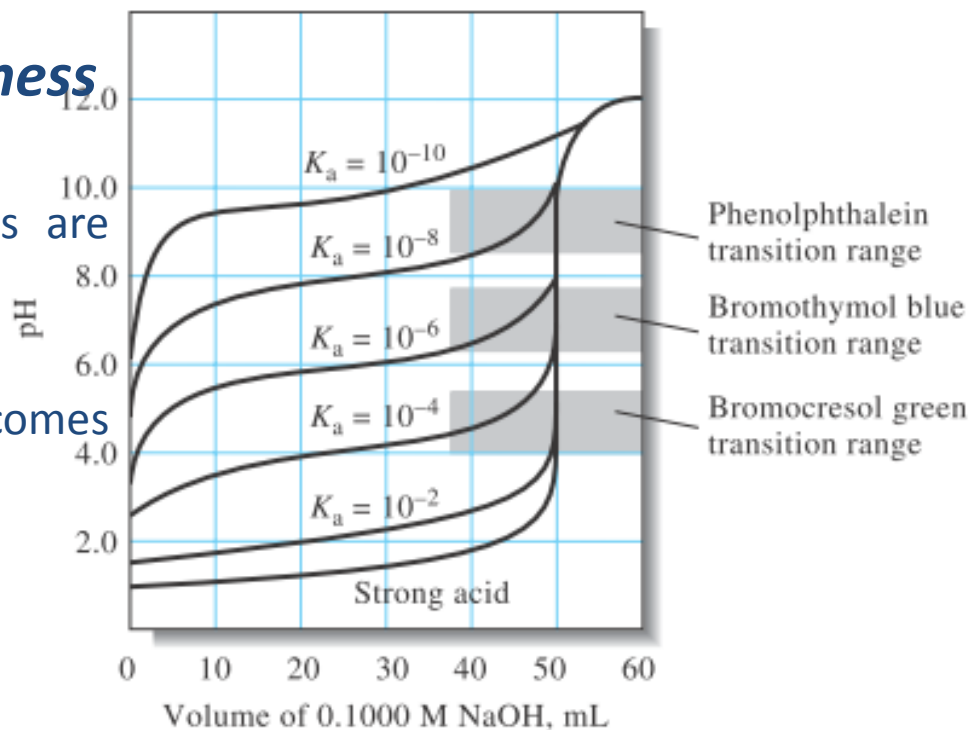


Figure 14-6 The effect of acid strength (dissociation constant) on titration curves.

14D Titration curves for weak bases

EXAMPLE 14-4

A 50.00-mL aliquot of 0.0500 M NaCN (K_a for HCN = 6.2×10^{-10}) is titrated with 0.1000 M HCl. The reaction is



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

Solution

(a) 0.00 mL of Reagent

The pH of a solution of NaCN can be calculated by the method in Example 9-10, page 218:



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

$$[\text{OH}^-] = [\text{HCN}]$$

$$[\text{CN}^-] = c_{\text{NaCN}} - [\text{OH}^-] \approx c_{\text{NaCN}} = 0.0500 \text{ M}$$

Substituting into the dissociation-constant expression gives, after rearranging,

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

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

(b) 10.00 mL of Reagent

Addition of acid produces a buffer with a composition given by

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

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

These values are then substituted into the expression for the acid dissociation constant of HCN to give $[\text{H}_3\text{O}^+]$ directly (see margin note):

$$[\text{H}_3\text{O}^+] = \frac{6.2 \times 10^{-10} \times (1.000/60.00)}{1.500/60.00} = 4.13 \times 10^{-10} \text{ M}$$

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

(c) 25.00 mL of Reagent

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

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

Applying Equation 9-22 Gives

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_{\text{HCN}}} = \sqrt{6.2 \times 10^{-10} \times 0.03333} = 4.55 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log(4.55 \times 10^{-6}) = 5.34$$

(d) 26.00 mL of Reagent

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

$$[\text{H}_3\text{O}^+] = c_{\text{HCl}} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{76.00} = 1.32 \times 10^{-3} \text{ M}$$

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

The curves show that indicators with mostly acidic transition ranges must be used for weak bases.

* When you titrate a weak base, use an indicator with a mostly acidic transition range.

* When titrating a weak acid, use an indicator with a mostly basic transition range.

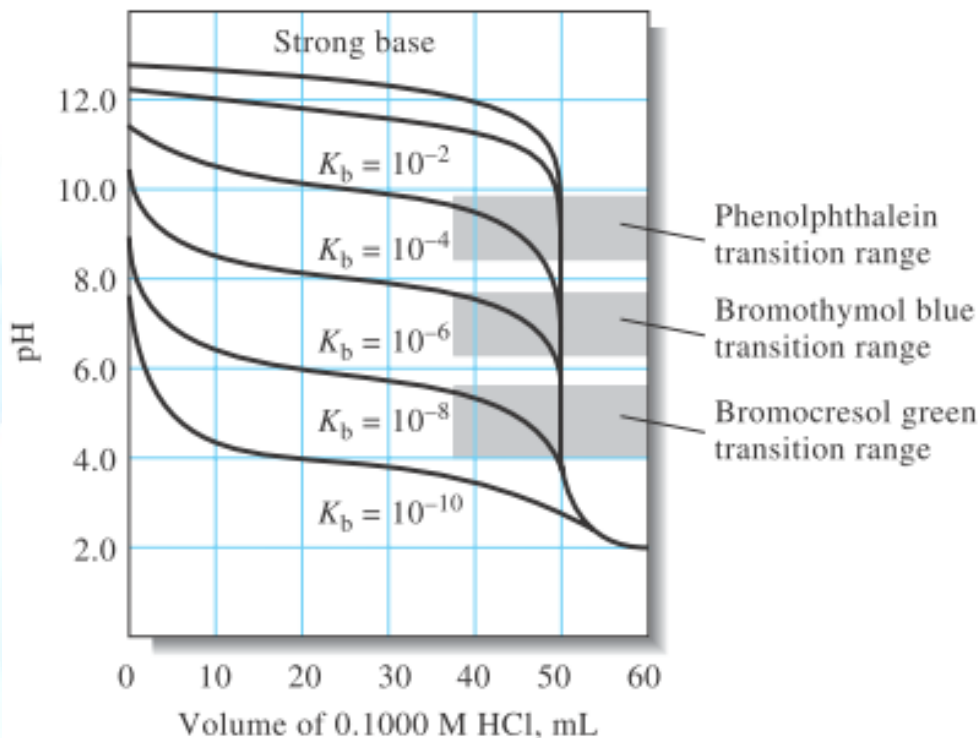
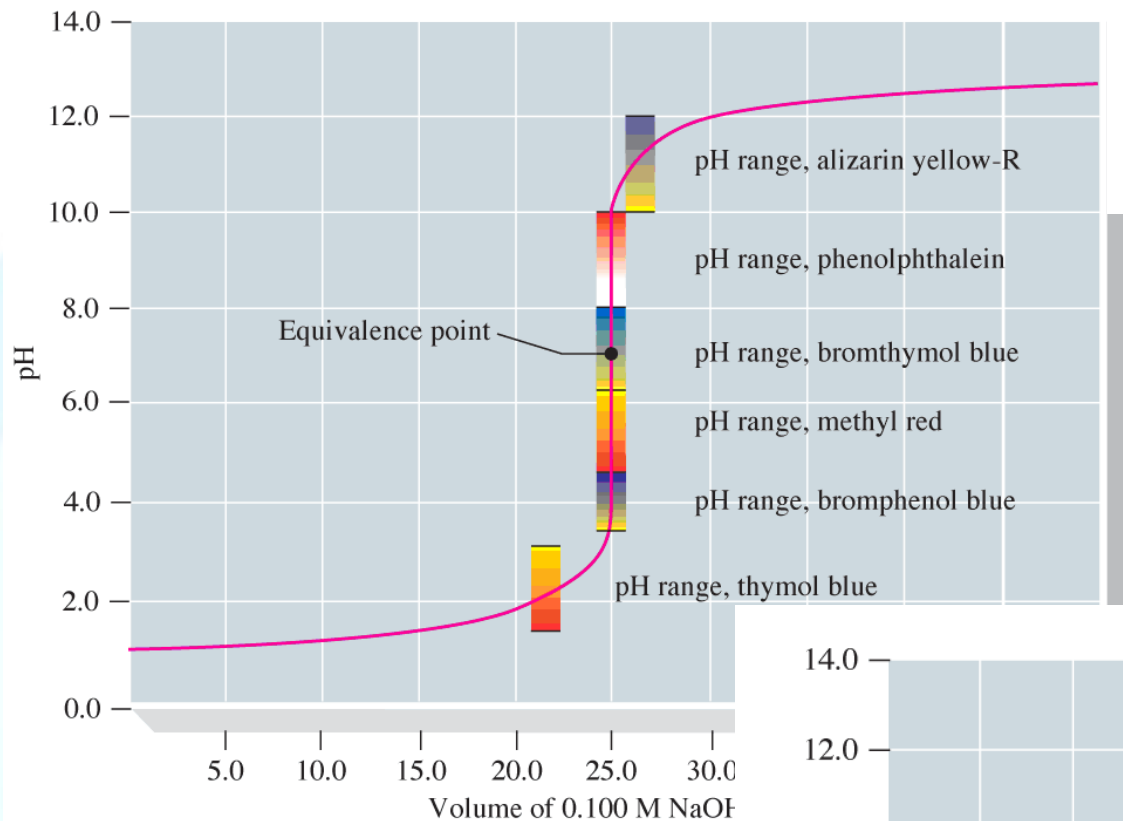
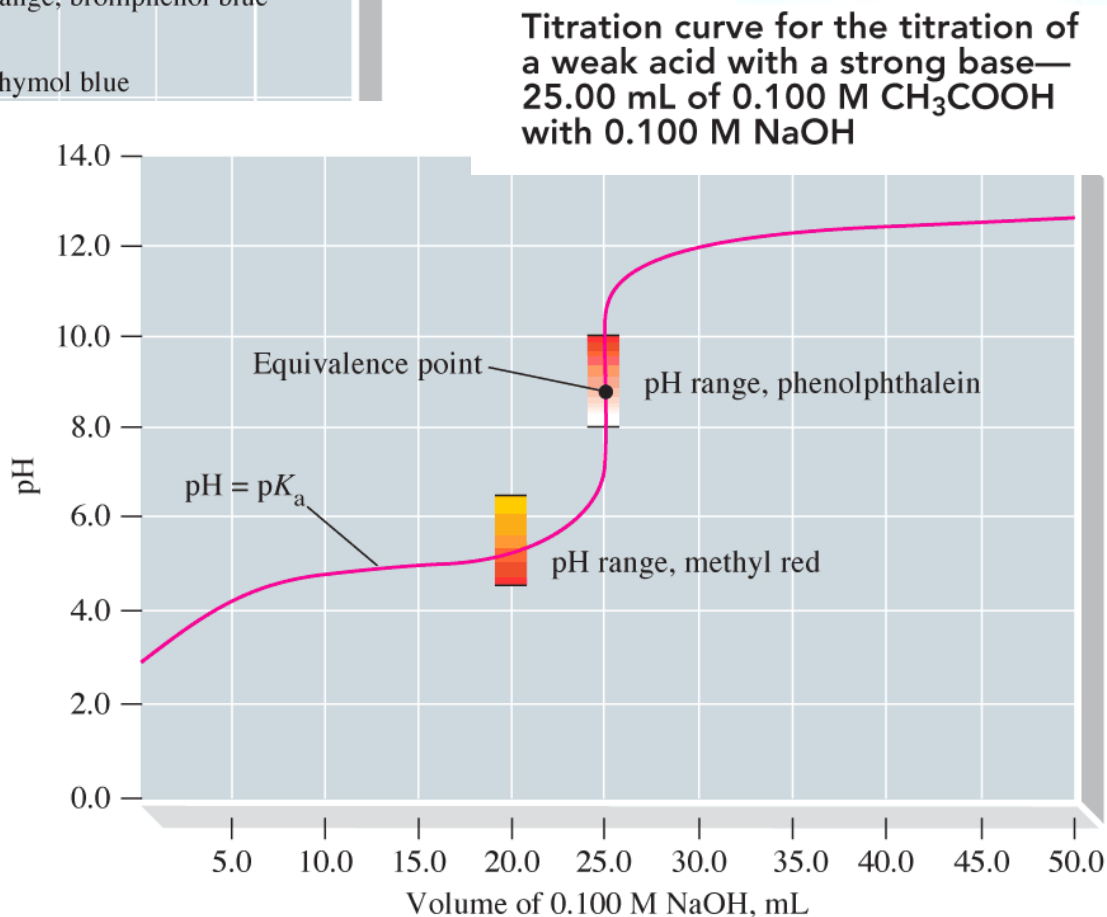


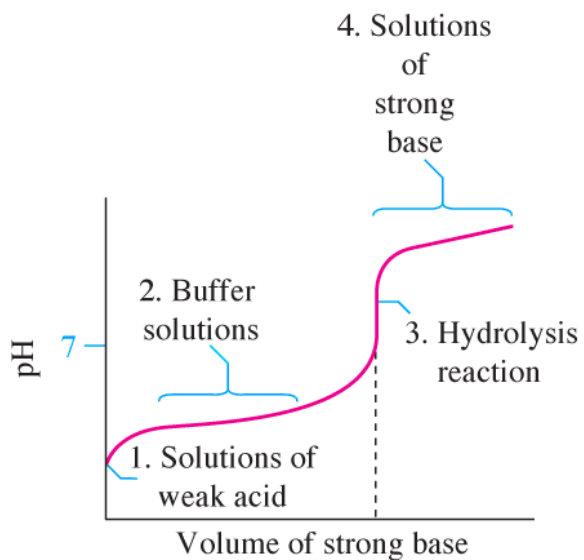
Figure 14-7 Hypothetical titration curves for a series of weak bases of different strengths. Each curve represents the titration of 50.00 mL of 0.1000 M base with 0.1000 M HCl



Titration curve for the titration of a strong acid with a strong base—25.00 mL of 0.100 M HCl with 0.100 M NaOH

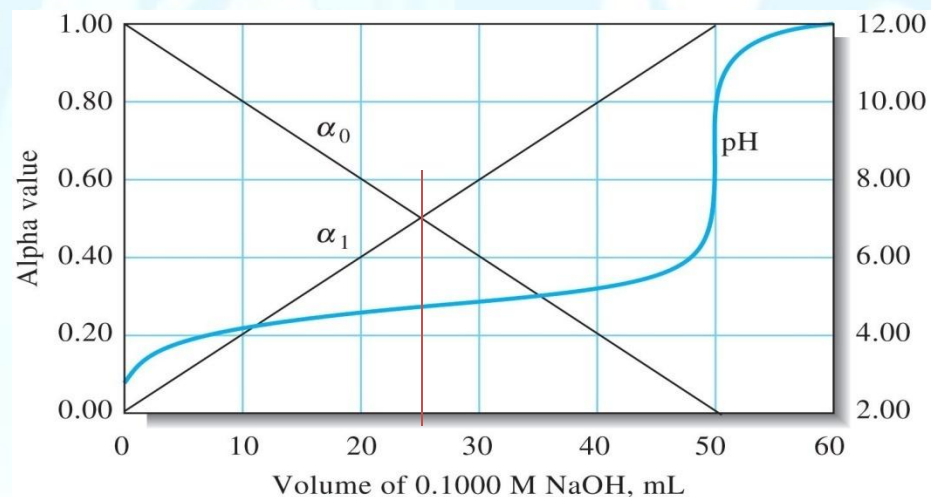


Titration curve for the titration of a weak acid with a strong base—25.00 mL of 0.100 M CH₃COOH with 0.100 M NaOH



14 E The composition of solutions during acid/base titrations

The changes in composition that occur while a solution of a weak acid or a weak base is being titrated can be visualized by plotting the relative equilibrium concentration α_0 of the weak acid as well as the relative equilibrium concentration of the conjugate base α_1 as functions of the pH of the solution.



- ✓ The straight lines show the change in relative amounts of HOAc (α_0) and OAc⁻ (α_1) during the titration of 50.00 mL of 0.1000 M acetic acid.
- ✓ The curved line is the titration curve for the system.

* Note that at the beginning of the titration α_0 is nearly 1 (0.987) meaning that 98.7% of the acetate containing species is present as HOAc and only 1.3% is present as OAc⁻.

* At the equivalence point, α_0 decreases to 1.1×10^{-4} , and α_1 approaches 1.

* Thus, only about 0.011% of the acetate containing species is HOAc. Notice that, at the half-titration point (25.00 mL), α_0 and α_1 are both 0.5.

* For polyprotic acids (see Chapter 15), the alpha values are very useful in illustrating the changes in solution composition during titrations

Figure 14-8 Plots of relative amounts of acetic acid and acetate ion during a titration.

Feature 14-6 Locating Titration End Points from pH Measurements

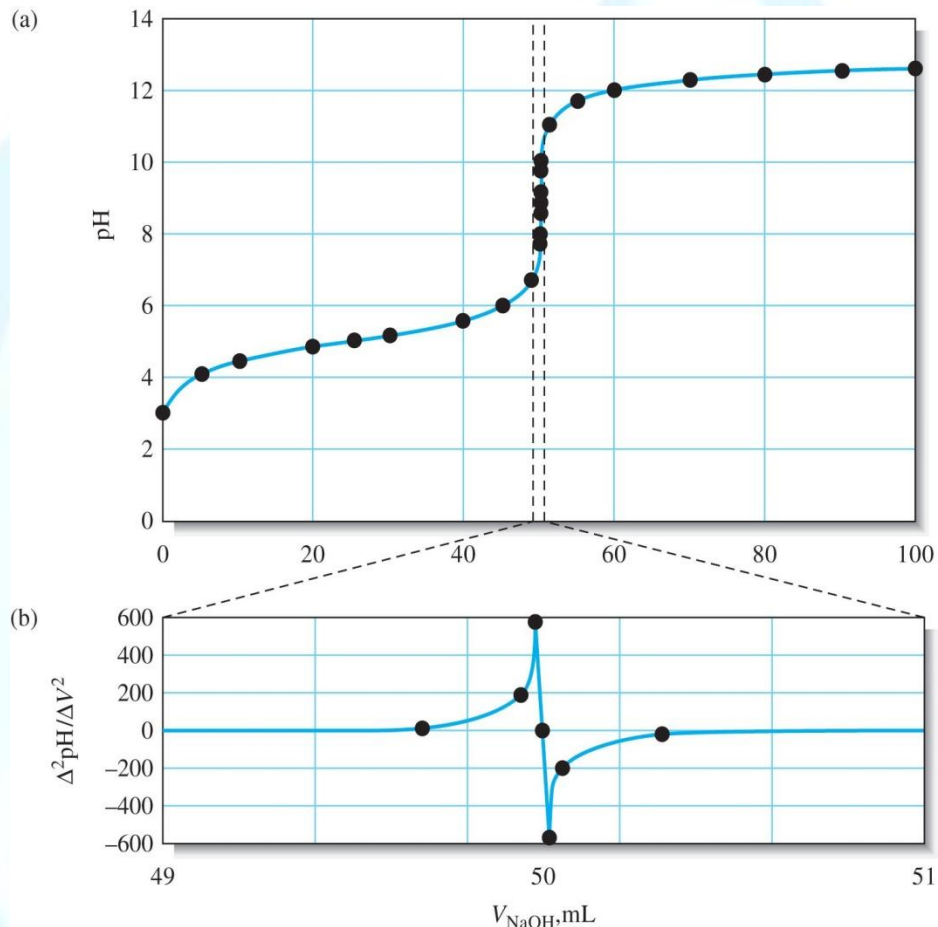


Figure 14F-4 In (a), the titration curve of 50.00 mL of 0.1000 M weak acid with 0.1000 M NaOH is shown as collected by a pH meter.

In (b), the second derivative is shown on an expanded scale. Note that the second derivative crosses zero at the end point. This can be used to locate the end point

- The end point can be taken as the inflection point of the titration curve.
- With a sigmoid-shaped titration curve, the inflection point is the steepest part of the titration curve where the pH change with respect to volume is a maximum.
- This point can be estimated visually from the plot or we can use calculus to find the first and second derivatives of the titration curve.
- The first derivative, which is approximately $\Delta \text{pH} / \Delta V$, is the slope of the titration curve. It goes from nearly zero far before the end point to a maximum at the end point back to zero far beyond the end point.
- We can differentiate the curve a second time to locate the maximum of the first derivative since the slope of the first derivative changes dramatically from a large positive value to a large negative value as we pass through the maximum in the first derivative curve.
- This is the basis for locating the end point by

The Gran plot:

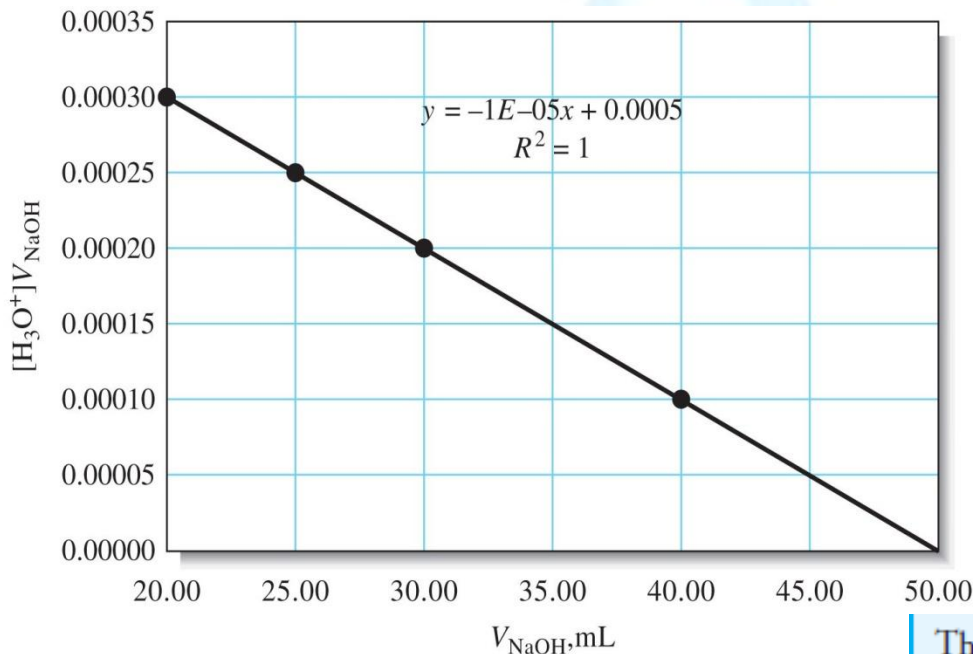


Figure 14F-5 Gran plot for the titration of 50.00 mL of 0.1000 M weak acid ($K_a=1.00 \times 10^{-5}$) with 0.1000 M NaOH. The least-squares equation for the line is given in the figure.

This method can decrease the tedium of making many measurements after dispensing tiny volumes of titrant in the end point region.

- The Gran plot is an alternative method for locating the end point in a titration.
- In this method, a linear plot is produced that can reveal both the acid dissociation constant and the volume of base required to reach the end point.
- Unlike the normal titration curve and derivative curves, which find the end point only from data located in the end point region, the Gran plot uses data far away from the end point.

The concentration of H_3O^+ can be found from the equilibrium con

$$[\text{H}_3\text{O}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]} = \frac{K_a(V_{\text{eq}} - V_{\text{NaOH}})}{V_{\text{NaOH}}}$$

Multiplying both sides by V_{NaOH} gives,

$$[\text{H}_3\text{O}^+]V_{\text{NaOH}} = K_aV_{\text{eq}} - K_aV_{\text{NaOH}}$$



A plot of the left-hand side of this equation versus the volume of titrant, V_{NaOH} , should yield a straight line with a slope of $-K_a$ and an intercept of K_aV_{eq}

QUESTIONS AND PROBLEMS

- *14-1. Why does the typical acid/base indicator exhibit its color change over a range of about 2 pH units?
- 14-2. What factors affect end-point sharpness in an acid/base titration?
- *14-3. Consider curves for the titration of 0.10 M NaOH and 0.010 M NH_3 with 0.10 M HCl.
- Briefly account for the differences between curves for the two titrations.
 - In what respect will the two curves be indistinguishable?
- 14-4. Why are the standard reagents used in neutralization titrations generally strong acids and bases rather than weak acids and bases?
- *14-5. What variables can cause the pH range of an indicator to shift?
- 14-6. Which solute would provide the sharper end point in a titration with 0.10 M HCl:
- 0.10 M NaOCl or 0.10 M hydroxylamine?
 - 0.10 M NH_3 or 0.10 M sodium phenolate?
 - 0.10 M methylamine or 0.10 M hydroxylamine?
 - 0.10 M hydrazine or 0.10 M NaCN?
- 14-7. Which solute would provide the sharper end point in a titration with 0.10 M NaOH:
- 0.10 M nitrous acid or 0.10 M iodic acid?
 - 0.10 M anilinium hydrochloride ($\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$) or 0.10 M benzoic acid?
 - 0.10 M hypochlorous acid or 0.10 M pyruvic acid?
 - 0.10 M salicylic acid or 0.10 M acetic acid?
- 14-8. Before glass electrodes and pH meters became widely used, pH was often determined by measuring the concentration of the acid and base forms of the indicator colorimetrically (see Chapter 26 for details). If bromothymol blue is introduced into a solution and the concentration ratio of acid to base form is found to be 1.29, what is the pH of the solution?
- *14-9. The procedure described in Problem 14-8 was used to determine pH with methyl orange as the indicator. The concentration ratio of the acid to base form of the indicator was 1.84. Calculate the pH of the solution.
- 14-10. Values for K_w at 0, 50, and 100°C are 1.14×10^{-15} , 5.47×10^{-14} , and 4.9×10^{-13} , respectively. Calculate the pH for a neutral solution at each of these
- 14-11. Using the data in Problem 14-10, calculate pK_w at
- 0°C.
 - 50°C.
 - 100°C.
- 14-12. Using the data in Problem 14-10, calculate the pH of a 1.00×10^{-2} M NaOH solution at
- 0°C.
 - 50°C.
 - 100°C.
- *14-13. What is the pH of an aqueous solution that is 3.00% HCl by mass and has a density of 1.015 g/mL?
- 14-14. Calculate the pH of a solution that contains 2.00% (w/w) NaOH and has a density of 1.022 g/mL.
- *14-15. What is the pH of a solution that is 2.00×10^{-8} M in NaOH? (Hint: In such a dilute solution you must take into account the contribution of H_2O to the hydroxide ion concentration.)
- 14-16. What is the pH of a 2.00×10^{-8} M HCl solution (see hint in Problem 14-15)?
- *14-17. What is the pH of the solution that results when 0.093 g of $\text{Mg}(\text{OH})_2$ is mixed with
- 75.0 mL of 0.0500 M HCl?
 - 100.0 mL of 0.0500 M HCl?
 - 15.0 mL of 0.0500 M HCl?
 - 30.0 mL of 0.0500 M MgCl_2 ?
- 14-18. Calculate the pH of the solution that results when mixing 20.0 mL of 0.1750 M HCl with 25.0 mL of
- distilled water.
 - 0.132 M AgNO_3 .
 - 0.132 M NaOH.
 - 0.132 M NH_3 .
 - 0.232 M NaOH.
- *14-19. Calculate the hydronium ion concentration and pH of a solution that is 0.0500 M in HCl
- neglecting activities.
 - using activities (see Chapter 10).
- 14-20. Calculate the hydroxide ion concentration and the pH of a 0.0167 M $\text{Ba}(\text{OH})_2$ solution
- neglecting activities.
 - using activities (see Chapter 10).
- *14-21. Calculate the pH of an aqueous solution that is
- 1.00×10^{-1} M in HOCl.
 - 1.00×10^{-2} M in HOCl.

- 14-22. Calculate the pH of a solution that is
 (a) 1.00×10^{-1} M NaOCl.
 (b) 1.00×10^{-2} M NaOCl.
 (c) 1.00×10^{-4} M NaOCl.
- *14-23. Calculate the pH of an ammonia solution that is
 (a) 1.00×10^{-1} M NH_3 .
 (b) 1.00×10^{-2} M NH_3 .
 (c) 1.00×10^{-4} M NH_3 .
- 14-24. Calculate the pH of a solution that is
 (a) 1.00×10^{-1} M NH_4Cl .
 (b) 1.00×10^{-2} M NH_4Cl .
 (c) 1.00×10^{-4} M NH_4Cl .
- *14-25. Calculate the pH of a solution in which the concentration of piperidine is
 (a) 1.00×10^{-1} M.
 (b) 1.00×10^{-2} M.
 (c) 1.00×10^{-4} M.
- 14-26. Calculate the pH of a solution that is
 (a) 1.00×10^{-1} M sulfamic acid.
 (b) 1.00×10^{-2} M sulfamic acid.
 (c) 1.00×10^{-4} M sulfamic acid.
- *14-27. Calculate the pH of a solution prepared by
 (a) dissolving 36.5 g of lactic acid in water and diluting to 500 mL.
 (b) diluting 25.0 mL of the solution in (a) to 250 mL.
 (c) diluting 10.0 mL of the solution in (b) to 1.00 L.
- 14-28. Calculate the pH of a solution prepared by
 (a) dissolving 2.13 g of picric acid, $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$ (229.11 g/mol), in 100 mL of water.
 (b) diluting 10.0 mL of the solution in (a) to 100 mL.
 (c) diluting 10.0 mL of the solution in (b) to 1.00 L.
- *14-29. Calculate the pH of the solution that results when 20.0 mL of 0.1750 M formic acid is
 (a) diluted to 45.0 mL with distilled water.
 (b) mixed with 25.0 mL of 0.140 M NaOH solution.
 (c) mixed with 25.0 mL of 0.200 M NaOH solution.
 (d) mixed with 25.0 mL of 0.200 M sodium formate solution.
- 14-30. Calculate the pH of the solution that results when 40.0 mL of 0.1250 M NH_3 is
 (a) diluted to 20.0 mL with distilled water.
 (b) mixed with 20.0 mL of 0.250 M HCl solution.
 (c) mixed with 20.0 mL of 0.300 M HCl solution.
 (d) mixed with 20.0 mL of 0.200 M NH_4Cl solution.
 (e) mixed with 20.0 mL of 0.100 M HCl solution.
- *14-31. A solution is 0.0500 M in NH_4Cl and 0.0300 M in NH_3 . Calculate its OH^- concentration and its pH
 (a) neglecting activities.
 (b) taking activities into account.
- 14-32. What is the pH of a solution that is
 (a) prepared by dissolving 7.85 g of lactic acid (90.08 g/mol) and 10.09 g of sodium lactate (112.06 g/mol) in 500 mL of water.
 (b) prepared by dissolving 7.85 g of lactic acid (90.08 g/mol) and 10.09 g of sodium lactate (112.06 g/mol) in 500 mL of water.
 (c) prepared by dissolving 3.00 g of salicylic acid, $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ (138.12 g/mol), in 50.0 mL of 0.1130 M NaOH and diluting to 500.0 mL?
 (d) 0.0100 M in picric acid and 0.100 M in sodium picrate?
- (c) prepared by dissolving 3.00 g of salicylic acid, $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ (138.12 g/mol), in 50.0 mL of 0.1130 M NaOH and diluting to 500.0 mL?
 (d) 0.0100 M in picric acid and 0.100 M in sodium picrate?
- *14-33. What is the pH of a solution that is
 (a) prepared by dissolving 3.30 g of $(\text{NH}_4)_2\text{SO}_4$ in water, adding 125.0 mL of 0.1011 M NaOH, and diluting to 500.0 mL?
 (b) 0.120 M in piperidine and 0.010 M in its chloride salt?
 (c) 0.050 M in ethylamine and 0.167 M in its chloride salt?
 (d) prepared by dissolving 2.32 g of aniline (93.13 g/mol) in 100 mL of 0.0200 M HCl and diluting to 250.0 mL?
- 14-34. Calculate the change in pH that occurs in each of the solutions listed below as a result of a tenfold dilution with water. Round calculated values for pH to three figures to the right of the decimal point.
 *(a) H_2O .
 (b) 0.0500 M HCl.
 *(c) 0.0500 M NaOH.
 (d) 0.0500 M CH_3COOH .
 *(e) 0.0500 M CH_3COONa .
 (f) 0.0500 M CH_3COOH + 0.0500 M CH_3COONa .
 *(g) 0.500 M CH_3COOH + 0.500 M CH_3COONa .
- *14-35. Calculate the change in pH that occurs when 1.00 mmol of a strong acid is added to 100 mL of the solutions listed in Problem 14-34.
- 14-36. Calculate the change in pH that occurs when 1.00 mmol of a strong base is added to 100 mL of the solutions listed in Problem 14-34. Calculate values to three decimal places.
- 14-37. Calculate the change in pH to three decimal places that occurs when 0.50 mmol of a strong acid is added to 100 mL of
 (a) 0.0200 M lactic acid + 0.0800 M sodium lactate.
 *(b) 0.0800 M lactic acid + 0.0200 M sodium lactate.
 (c) 0.0500 M lactic acid + 0.0500 M sodium lactate.
- 14-38. A 50.00-mL aliquot of 0.1000 M NaOH is titrated with 0.1000 M HCl. Calculate the pH of the solution after the addition of 0.00, 10.00, 25.00, 40.00, 45.00, 49.00, 50.00, 51.00, 55.00, and 60.00 mL of acid and prepare a titration curve from the data.
- *14-39. In a titration of 50.00 mL of 0.05000 M formic acid with 0.1000 M KOH, the titration error must be smaller than 0.05 mL. What indicator can be chosen to realize this goal?
- 14-40. In a titration of 50.00 mL of 0.1000 M ethylamine with 0.1000 M HClO_4 , the titration error must be smaller than 0.05 mL. What indicator can be chosen to realize this goal?
- 14-41. Calculate the pH after addition of 0.00, 5.00, 15.00, 25.00, 40.00, 45.00, 49.00, 50.00, 51.00, 55.00, and 60.00 mL of 0.1000 M NaOH in the titration of 50.00 mL of
 *(a) 0.1000 M HNO_2 .
 (b) 0.1000 M pyridinium chloride.
 *(c) 0.1000 M lactic acid.
- 14-42. Calculate the pH after addition of 0.00, 5.00, 15.00, 25.00, 40.00, 45.00, 49.00, 50.00, 51.00, 55.00, and 60.00 mL of 0.1000 M HCl in the titration of 50.00 mL of
 (a) 0.1000 M ammonia.
 (b) 0.1000 M hydrazine.
 (c) 0.1000 M sodium cyanide.
- 14-43. Calculate the pH after addition of 0.00, 5.00, 15.00, 25.00, 40.00, 49.00, 50.00, 51.00, 55.00, and 60.00 mL of reagent in the titration of 50.0 mL of
 *(a) 0.01000 M chloroacetic acid with 0.01000 M NaOH.
 (b) 0.1000 M anilinium chloride with 0.1000 M NaOH.
 *(c) 0.1000 M hypochlorous acid with 0.1000 M NaOH.
 (d) 0.1000 M hydroxylamine with 0.1000 M HCl. Construct titration curves from the data.

Homework (Due 20/03/2018)

Chapter 14, Questions and Problems

14-1, 14-3, 14-6, 14-8, 14-10, 14-12, 14-15, 14-16, 14-18, 14-21,
14-22, 14-23, 14-24, 14-27, 14-30, 14-32, 14-41(c), 14-42(a),
14-43(d)

End of Chapter 14