

Chapter 3:

Titrimetric Methods

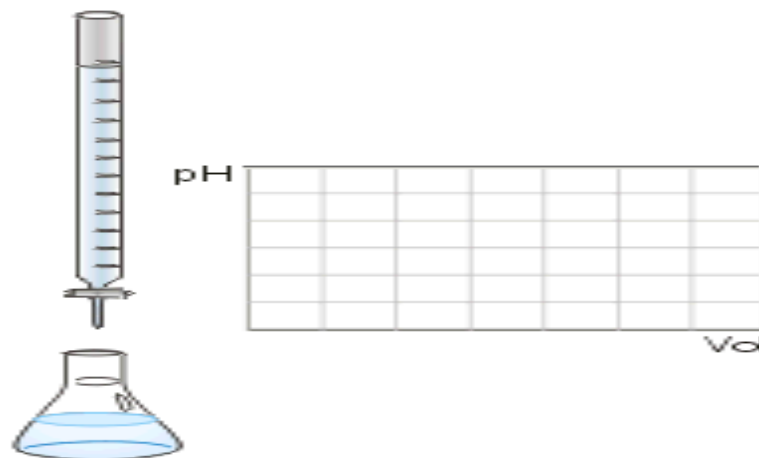
Assist.prof. Dr.
Nashwan H. Ali
Applied science
Samarra University

Chapter 3

Titrimetric Methods

Titration is widely used in analytical chemistry to determine acids, bases, oxidants, reductants, metal ions, proteins, and many other species. Titrations are based on a reaction between the analyte and a standard reagent known as the titrant. The reaction is of known and reproducible stoichiometry. The volume, or the mass, of the titrant needed to react essentially completely with the analyte is determined and used to obtain the quantity of analyte. A volume-based titration is shown in this figure, in which the standard solution is added from a buret, and the reaction occurs in the Erlenmeyer flask.

In some titrations, known as coulometric titrations, the quantity of charge needed to completely consume the analyte is obtained. In any titration, the point of chemical equivalence, experimentally called the end point, is signaled by an indicator color change or a change in an instrumental response.



SOME TERMS USED IN VOLUMETRIC TITRIMETRY

A standard solution (or a standard titrant) is a reagent of known concentration that is used to carry out a titrimetric analysis. A titration is performed by slowly adding a standard solution from a buret or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete. The volume or mass of reagent needed to complete the titration is determined from the difference between the initial and final readings. A volumetric titration process is depicted in Figure 3-1

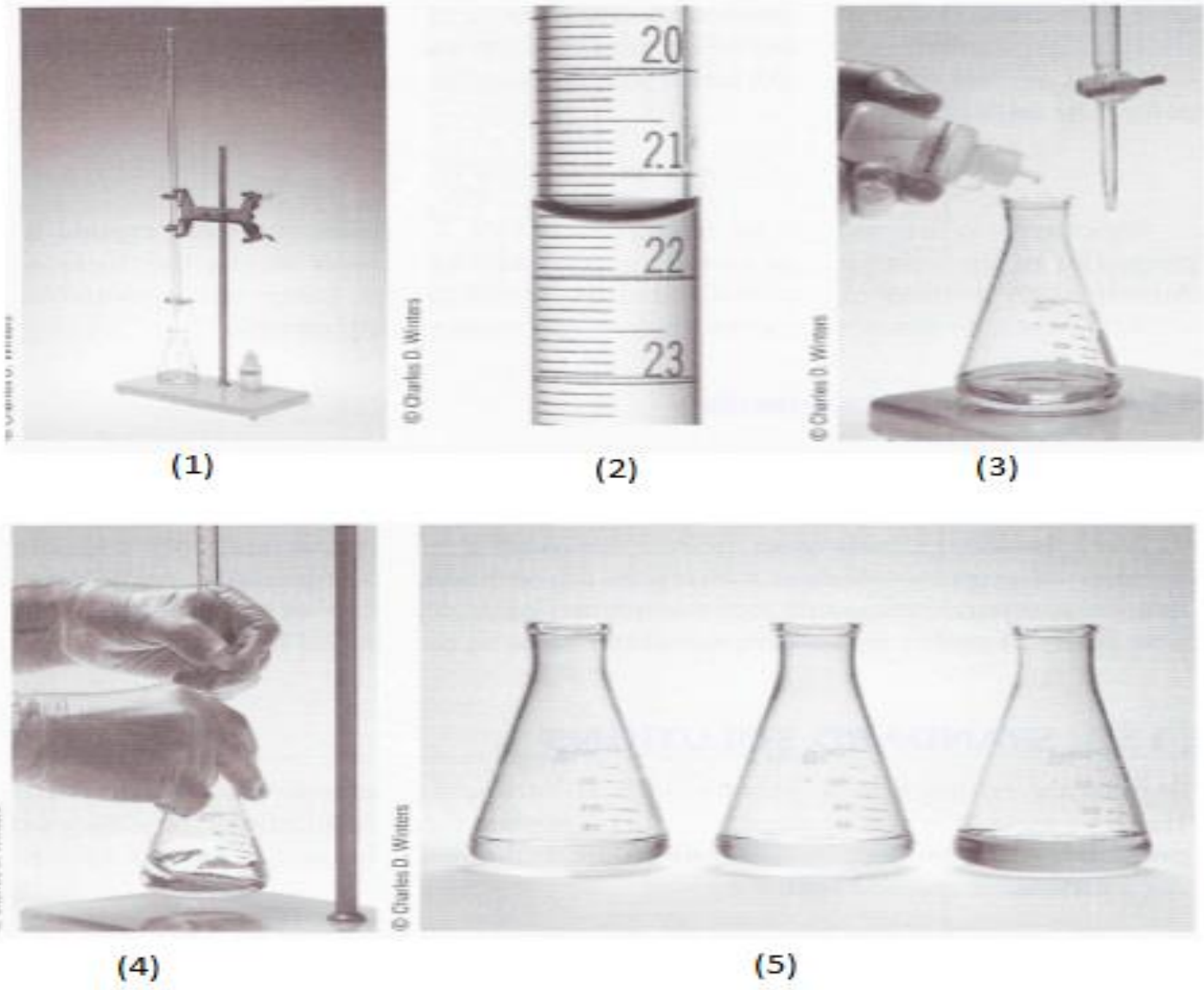
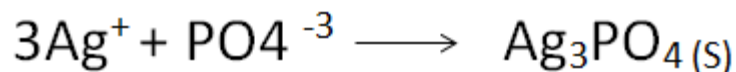


Figure 3-1: The titration process

It is sometimes necessary to add an excess of the standard titrant and then determine the excess amount by **back-titration** with a second standard titrant. For example, the amount of phosphate in a sample can be determined by adding a measured excess of standard silver nitrate to a solution of the sample, which leads to the formation of insoluble silver phosphate:



The excess silver nitrate is then back-titrated with a standard solution of potassium thiocyanate:



Here, the amount of silver nitrate is chemically equivalent to the amount of phosphate ion plus the amount of thiocyanate used for the back-titration.

Equivalence and end Points

- **Equivalence point**

The equivalence point is the point in a titration when the amount of added standard reagent is exactly equivalent to the amount of analyte.

- **End point**

The end point is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence

Standard?

- Standard Solution
 - A primary standard
 - A secondary standard
- Standardization
 - A process in which concentration of a volumetric solution is determined by using it to titrate a known mass of a primary standard.

PRIMARY STANDARD

- HIGH PURITY
- ATMOSPHERIC STABILITY
- INDEPENDENT OF HUMIDITY
- MODEST COST
- LARGE MOLAR MASS

Table 9.7**Selected Primary Standards for the Standardization of Strong Acid and Strong Base Titrants****Standardization of Acidic Titrants**

Primary Standard	Titration Reaction	Comment
Na_2CO_3	$\text{Na}_2\text{CO}_3 + 2\text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{CO}_3 + 2\text{Na}^+ + 2\text{H}_2\text{O}$	a
TRIS	$(\text{HOCH}_2)_3\text{CNH}_2 + \text{H}_3\text{O}^+ \rightarrow (\text{HOCH}_2)_3\text{CNH}_3^+ + \text{H}_2\text{O}$	b
$\text{Na}_2\text{B}_4\text{O}_7$	$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{H}_3\text{O}^+ + 3\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 4\text{H}_3\text{BO}_3$	

Standardization of Basic Titrants

Primary Standard	Titration Reaction	Comment
$\text{KHC}_8\text{H}_4\text{O}_4$	$\text{KHC}_8\text{H}_4\text{O}_4 + \text{OH}^- \rightarrow \text{K}^+ + \text{C}_8\text{H}_4\text{O}_4^{2-} + \text{H}_2\text{O}$	c
$\text{C}_6\text{H}_5\text{COOH}$	$\text{C}_6\text{H}_5\text{COOH} + \text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{O}$	d
$\text{KH}(\text{IO}_3)_2$	$\text{KH}(\text{IO}_3)_2 + \text{OH}^- \rightarrow \text{K}^+ + 2\text{IO}_3^- + \text{H}_2\text{O}$	

^aThe end point for this titration is improved by titrating to the second equivalence point, boiling the solution to expel CO_2 , and retitrating to the second equivalence point. In this case the reaction is



^bTRIS stands for *tris*-(hydroxymethyl)aminomethane.

^c $\text{KHC}_8\text{H}_4\text{O}_4$ is also known as potassium hydrogen phthalate, or KHP.

^dDue to its poor solubility in water, benzoic acid is dissolved in a small amount of ethanol before being diluted with water.

Indicators

Indicators are often added to the analyte solution to produce an observable physical change (the end point) at or near the equivalence point. Large changes in the relative concentration of analyte or titrant occur in the equivalence-point region. These concentration changes cause the indicator to change in appearance.

Typical indicator changes include the appearance or disappearance of a colour, a change in color, or the appearance or disappearance of turbidity. As an example, the indicator used in the precipitation titration of silver ion with potassium thiocyanate is a small amount of ferric chloride, which reacts with thiocyanate ions to give a red color.

The indicator reaction : $\text{Fe}^{+3} + \text{SCN}^- \longrightarrow \text{FeSCN}_2$ (Red)

We often use instruments to detect end points. These instruments respond to properties of the solution that change in a characteristic way during the titration. Among such instruments are colorimeters, turbidimeters, temperature monitors, refractometers, voltmeters, current meters, and conductivity meters.

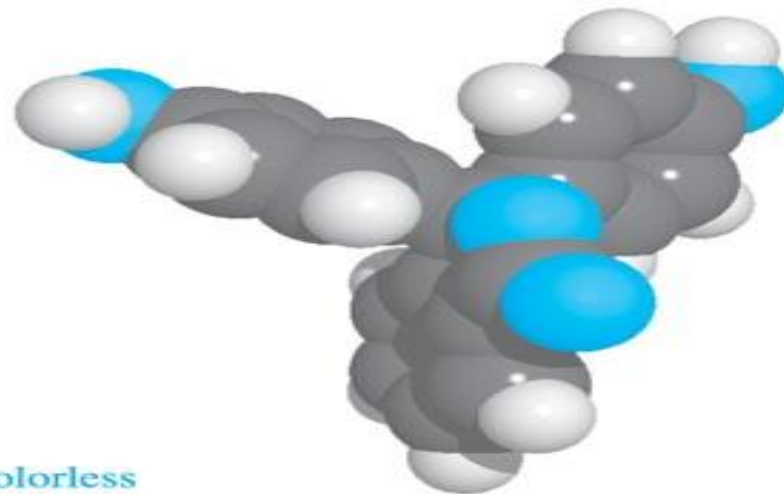
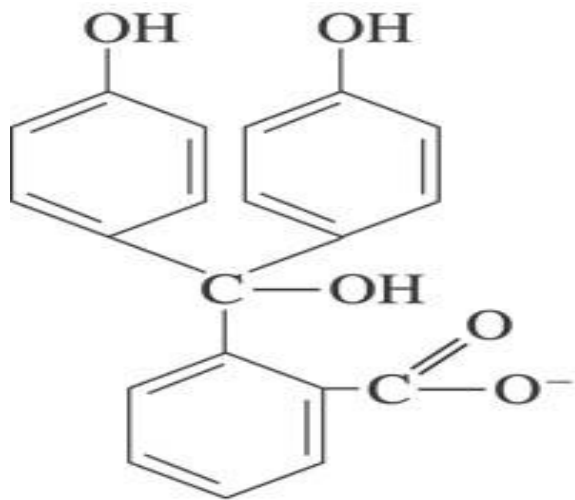
Principles of Neutralization Titrations

Like any titration, neutralization titrations depend on a chemical reaction between the analyte and a standard reagent. The point of chemical equivalence is indicated by a chemical indicator or an instrumental measurement. The discussion here focuses on the types of standard solutions and the chemical indicators that are used for neutralization titrations.

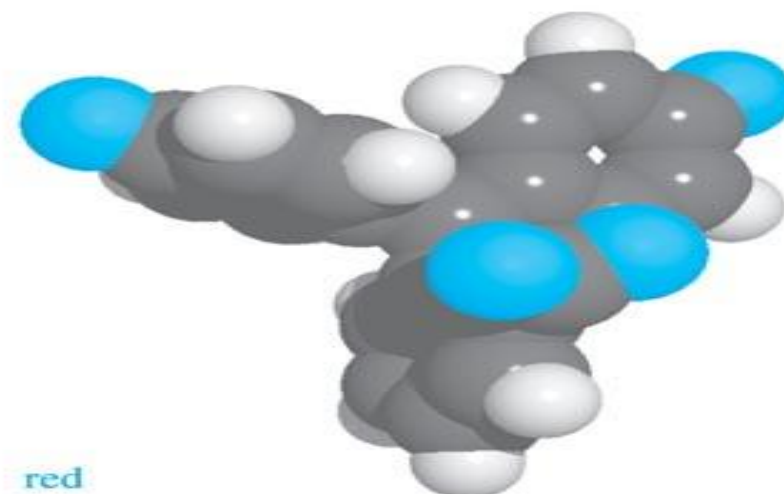
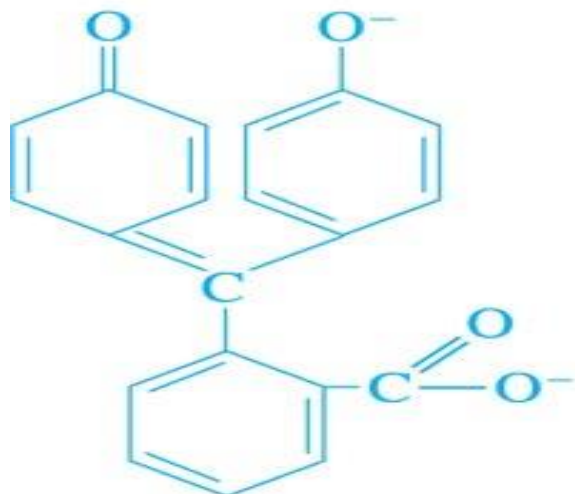
Standard Solutions

The standard solutions employed in neutralization titrations are strong acids or strong bases because these substances react more completely with an analyte than their weaker counterparts do and thus yield sharper end points. Standard solutions of acids are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid.

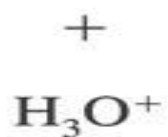
Standard solutions of bases are ordinarily prepared from solid sodium or potassium and occasionally barium hydroxides. The concentrations of these bases must be established by standardization.



colorless



red



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

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearranging leads to

$$[H_3O^+] = K_a \frac{[HIn]}{[In^-]}$$

The hydronium ion concentration determines the ratio of the acid to the conjugate base form of the indicator and thus determines the color developed by the solution.

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The color imparted to a solution by a typical indicator appears to the average observer to change rapidly only within the limited concentration ratio of approximately 10 to 0.1

$$\frac{[HIn]}{[In]} \geq \frac{10}{1}$$

and its base color when

$$\frac{[HIn]}{[In]} \leq \frac{1}{10}$$

The color appears to be intermediate for ratios between these two values. These ratios vary considerably from indicator to indicator.

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For the full acid color,

$$[\text{H}_3\text{O}^+] = 10K_a$$

and similarly 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:

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

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

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

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 $\text{InH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}$.

CALCULATING pH IN TITRATIONS OF STRONG ACIDS AND STRONG 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. Thus, for a solution of HCl with a concentration greater than about 10^{-6} M, we can write

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

where $[\text{OH}^-]$ represents the contribution of hydronium ions from the dissociation of water. An analogous relationship applies for a solution of a strong base, such as sodium hydroxide. That is,

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

Titrating a Strong Acid with a Strong Base

We will be interested here, in calculating hypothetical titration curves of pH versus volume of titrant. Three types of calculation must be done to construct the hypothetical titration curve for titrating a solution of a strong acid with a strong base. Each calculation corresponds to a distinct stage in the titration:

1. Preequivalence
2. Equivalence
3. Postequivalence

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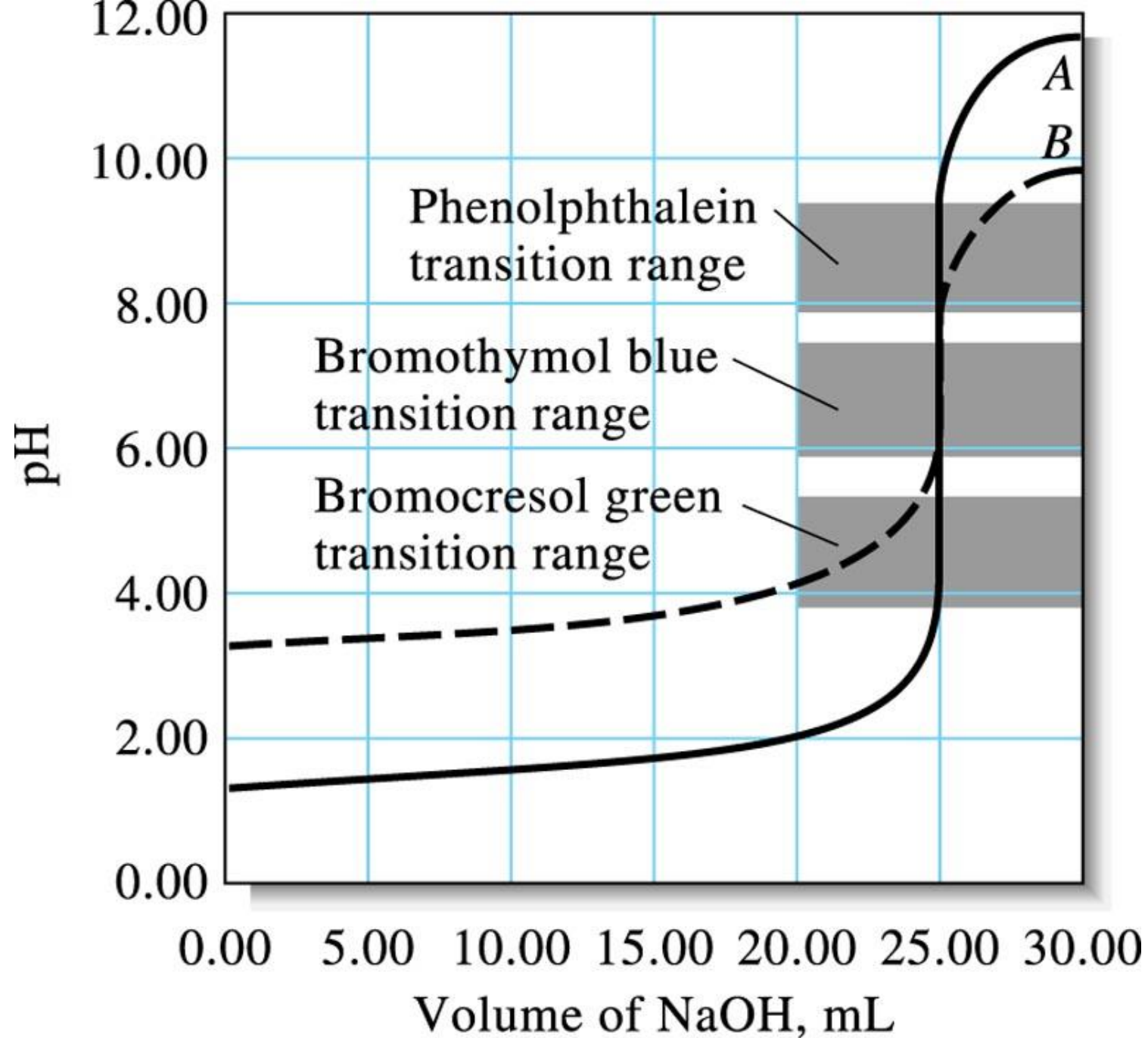
In the **preequivalence** stage, we compute the concentration of the acid from its starting concentration and the amount of base that has been added.

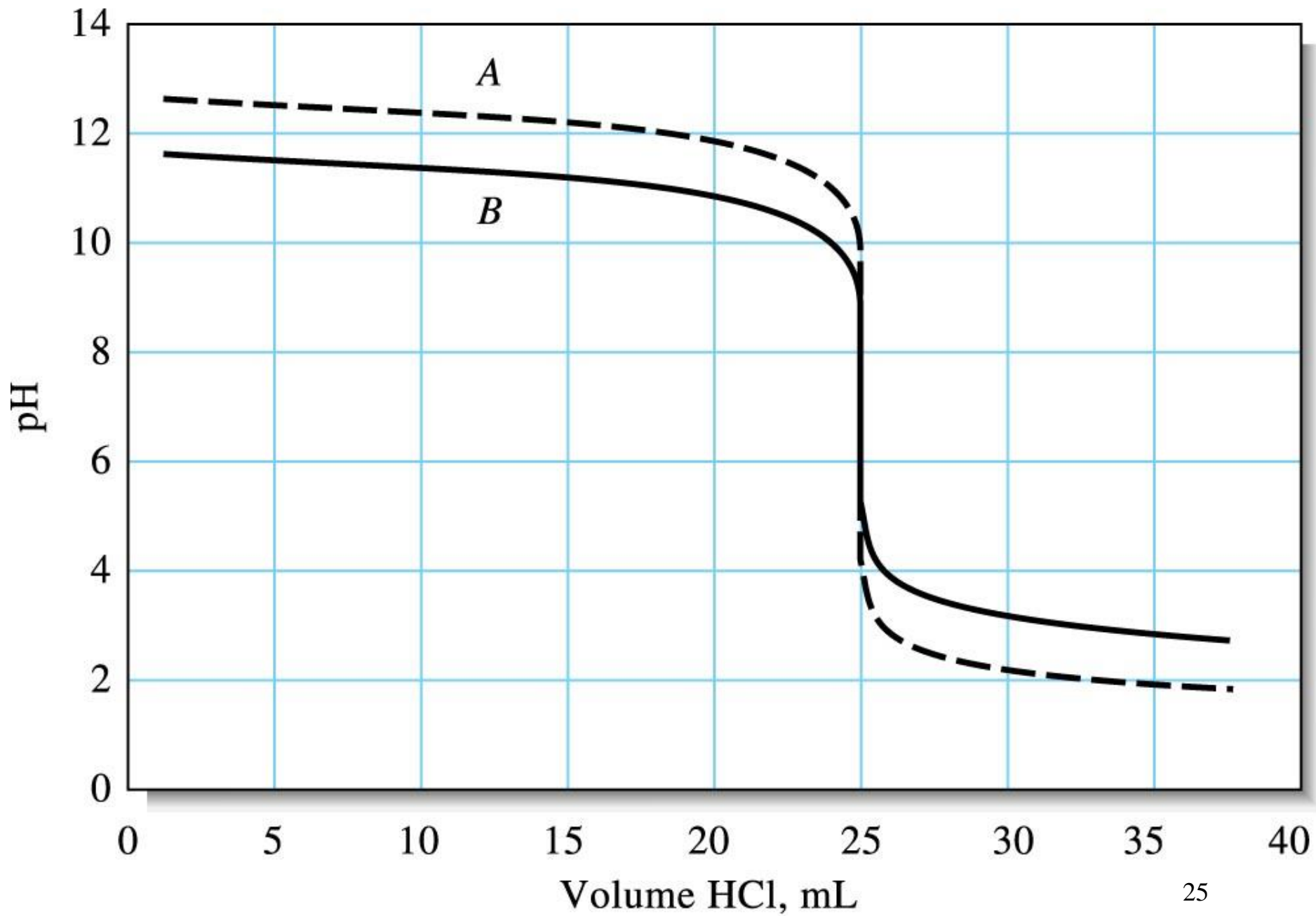
At the **equivalence** point, the hydronium and hydroxide ions are present in equal concentrations, and the hydronium ion concentration is derived directly from the ion-product constant for water.

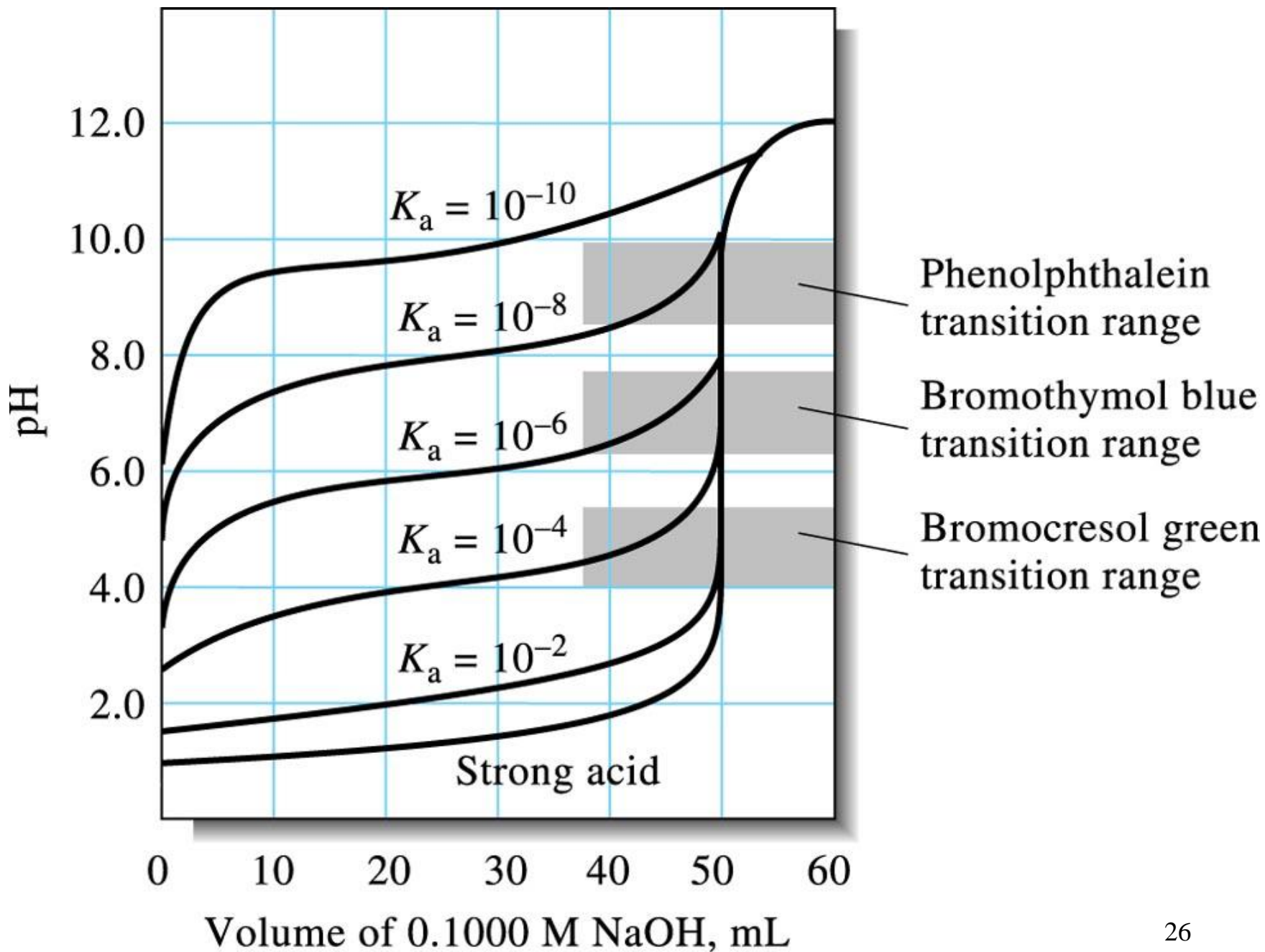
In the **postequivalence** stage, the analytical concentration of the excess base is computed, and the hydroxide ion concentration is assumed to be equal to or a multiple of the analytical concentration.

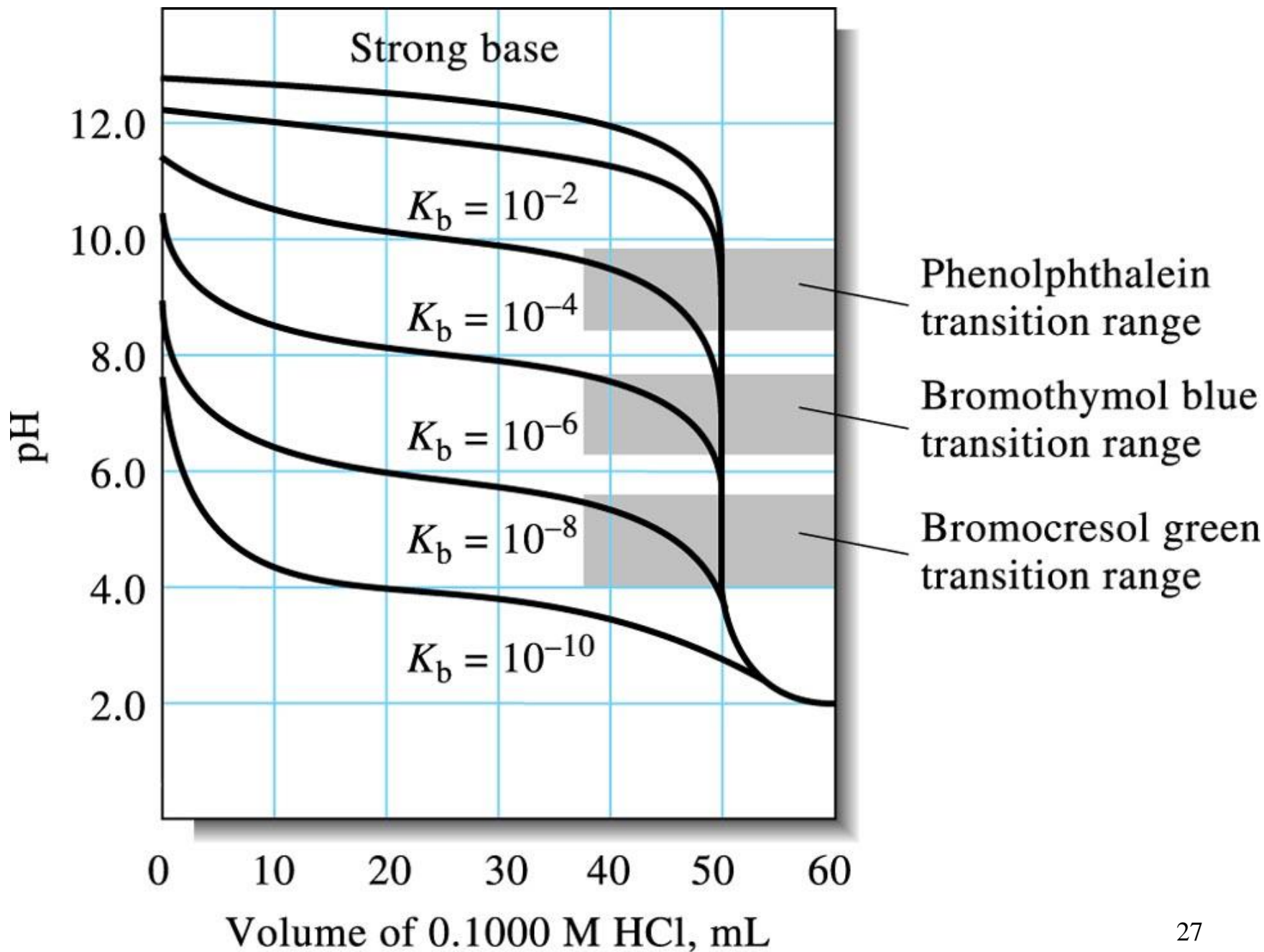
TABLE 14-2**Changes in pH during the Titration of a Strong Acid with a Strong Base**

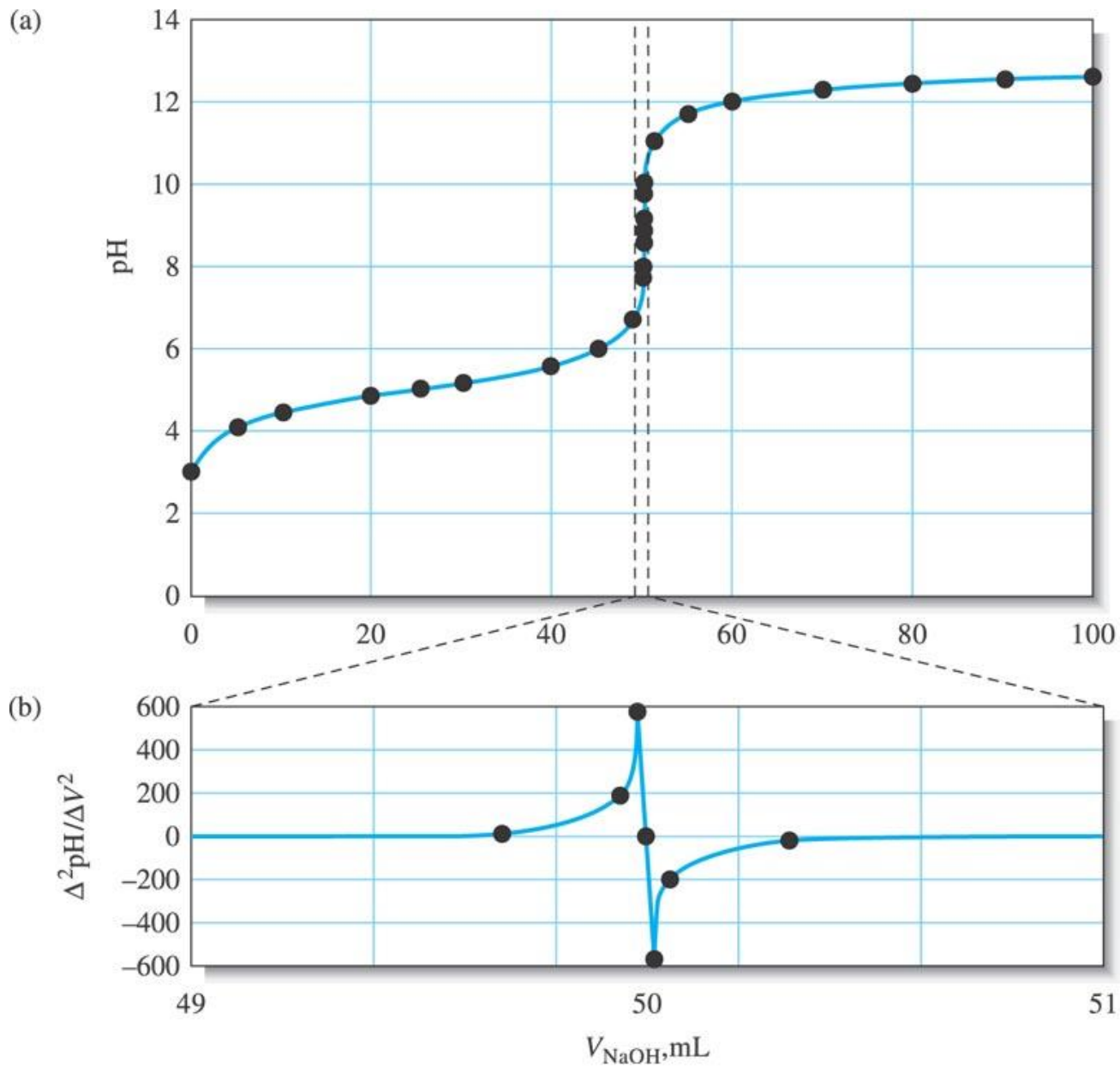
Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80











...continued...

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

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

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

$$\begin{aligned} -\log 10^{-14} &= 14.00 \\ &= \text{pH} + \text{pOH} \end{aligned}$$