Chapter 16

Applications of Neutralization Titrations

Applications of Neutralization Titrations

➢ Neutralization titrations are used to determine the concentration of acidic or basic analytes or analytes that can be converted to acids or bases by suitable treatment.

➢ Water is the usual solvent for neutralization titrations, because it is readily available, inexpensive, and nontoxic.

➢ Some analytes cannot be titrated in aqueous media because of low solubilities or because their strengths as acids or bases are not large enough to give satisfactory end points.

➢ Such substances can often be titrated by nonaqueous solvents, such as methyl and ethyl alcohol, glacial acetic acid, and methyl isobutyl ketone often make it possible to titrate such analytes in a solvent other than water.

➢ We shall restrict our discussions to aqueous systems.

16A Reagents for neutralization titrations

➢ Strong acids and strong bases produce the largest change in pH at the equivalence point. Hence, standard solutions for neutr. titrations are always prepared from these reagents

16A-1 Preparation of Standard Acid Solutions

➢ HCl solutions, Perchloric acid, and sulfuric acid are stable standard solutions. Restandardization is not required unless evaporation occurs.

➢Standard solutions of nitric acid are seldom encountered because of their oxidizing properties

➢ To obtain most standard acid solutions, a solution of an approximate concentration is first prepared by diluting the concentrated reagent. The diluted acid solution is then standardized against a primary-standard base.

➢ A stock solution with a known HCl concentration can also be prepared by diluting a quantity of the concentrated reagent with an equal volume of water followed by distillation.

16A-2 The Standardization of Acids

➤ Acids are frequently standardized against weighed quantities of **sodium carbonate**.

➤ Other primary standards for acids;

> ➤ Tris-(hydroxymethyl)aminomethane, $(HOCH_2)_3CNH_2$, known also as **TRIS** or THAM, is available in primary-standard purity from commercial sources. It possesses the advantage of a substantially greater mass per mole of protons consumed (121.1 g/mole) than sodium carbonate (53.0 g/mole).

$$(HOCH_2)_3CNH_2 + H_3O^+ \longrightarrow (HOCH_2)_3CNH_3^+ + H_2O$$

> ➤ **Sodium tetraborate decahydrate** $(Na_2B_4O_7.10H_2O)$ Borax, and mercury (II) oxide have also been recommended as primary standards. The reaction of an acid with the tetraborate is

$$B_4O_7^{2-} + 2H_3O^+ + 3H_2O \longrightarrow 4H_3BO_3$$
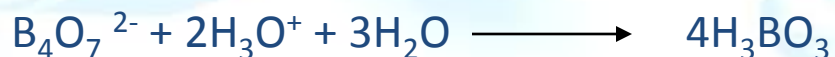
Preparing Standard Base Solutions

Sodium Carbonate

➤ Primary-standard-grade sodium carbonate is available commercially or can be prepared by heating purified sodium hydrogen carbonate between 270 to 300°C for 1 hr.

$$2HCO_3(s) \rightarrow Na_2CO_3 + H_2O + CO_2 \text{ (g)}$$

➤There are two end points in the titration of sodium carbonate.

➤ The second end point is always used for standardization because the change in pH is greater than that at the first.

➤ Alternatively, an amount of acid slightly in excess of that needed to convert the Na_2CO_3 to H_2CO_3 can be introduced.

➤The solution is boiled as before to remove carbon dioxide and cooled. The excess acid is then *back-titrated* with a dilute solution of standard base.

➤ Any indicator suitable for a strong acid/strong base titration is satisfactory.

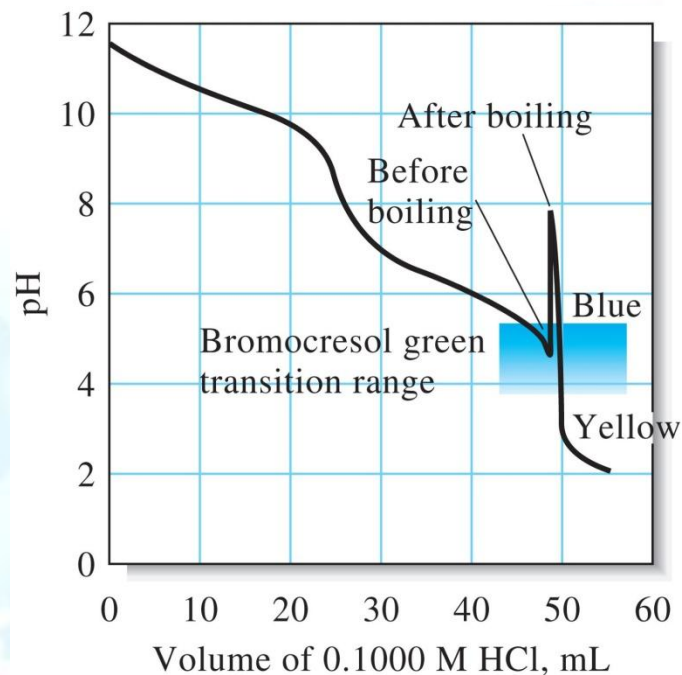➤An independent titration is used to establish the volume ratio of acid to base.

Figure 16-1   Titration of 25.00 mL of 0.1000 M Na_2CO_3 with 0.1000 M HCl. After about 49 mL of HCl have been added, the solution is boiled, causing the increase in pH shown. The change in pH when more HCl is added is much larger after boiling.

EXAMPLE 16-1

Use a spreadsheet to compare the masses of (a) TRIS (121 g/mol), (b) Na_2CO_3 (106 g/mol), and (c) $Na_2B_4O_7 \cdot 10H_2O$ (381 g/mol) required to standardize an approximately 0.020 M solution of HCl for the following volumes of HCl: 20.00, 30.00, 40.00, and 50.00 mL. Assume that the standard deviation of the mass of each of the primary standard bases is 0.1 mg and use the spreadsheet to calculate the percent relative standard deviation that this uncertainty would introduce into each of the calculated concentrations.

Solution

The spreadsheet is shown in **Figure 16-2**. The molar concentration of HCl is entered in cell B2 and the molar masses of the three primary standards in cells B3, B4, and B5. The volumes of HCl for which the calculations are desired are entered in cells A8 through A11. We will do a sample calculation for 20.00 mL of HCl and show the spreadsheet entry. In each case, the number of mmoles of HCl is calculated from

$$\text{mmol HCl} = \text{mL HCl} \times 0.020 \, \frac{\text{mmol HCl}}{\text{mL HCl}}$$

(a) TRIS

$$\text{mass TRIS} = \text{mmol HCl} \times \frac{1 \, \text{mmol TRIS}}{\text{mmol HCl}} \times \frac{121 \, \text{g TRIS/mol}}{1000 \, \text{mmol TRIS/mol}}$$

The appropriate formula for this equation is entered into cell B8 and then copied into cells B9 through B11. The relative uncertainty in the molar concentration due to the mass measurement is equal to the relative uncertainty in the mass measurement process. For the first TRIS amount (0.048 g in cell B8), the percent relative standard deviation (%RSD) is (0.0001/B8) × 100% as shown in the documentation in Figure 16-2. This formula is then copied into cells C9:C11.

(b) Na_2CO_3

$$\text{mass } Na_2CO_3 = \text{mmol HCl} \times \frac{1 \text{ mmol } Na_2CO_3}{2 \text{ mmol HCl}} \times \frac{106 \text{ g } Na_2CO_3/\text{mol}}{1000 \text{ mmol } Na_2CO_3/\text{mol}}$$

This formula is entered into cell D8 and copied into D9:D11. The relative standard deviation in cell E8 is calculated as $(0.0001/D8) \times 100\%$.

(c) $Na_2B_4O_7 \cdot 10H_2O$

The same formula as that for Na_2CO_3 is used except that the molecular mass of borax (381 g/mol) is substituted for that of Na_2CO_3. The other formulas are shown in the documentation in Figure 16-2.

Note in Figure 16-2 that the relative standard deviation in concentration using TRIS is 0.10% or less if the volume of HCl taken is more than 40.00 mL. For Na_2CO_3, more than 50.00 mL of HCl would be required for this level of uncertainty. For borax, any volume above about 26.00 mL would suffice.

	A	B	C	D	E	F	G
1	Spreadsheet to compare masses required for various bases in the standardization of 0.020 M HCl						
2	M HCl	0.020					
3	Molar mass TRIS	121 g/mol		Note:All mass measurements have standard deviations of 0.1 mg			
4	Molar mass Na_2CO_3	106 g/mol					
5	Molar mass $Na_2B_4O_7.H_2O$	381 g/mol					
6							
7	mL HCl	g TRIS	%RSD TRIS	g Na_2CO_3	%RSD Na_2CO_3	g $Na_2B_4O_7.H_2O$	%RSD $Na_2B_4O_7.H_2O$
8	20.00	0.048	0.21	0.021	0.47	0.08	0.13
9	30.00	0.073	0.14	0.032	0.31	0.11	0.09
10	40.00	0.097	0.10	0.042	0.24	0.15	0.07
11	50.00	0.121	0.08	0.053	0.19	0.19	0.05
12							
13	Documentation						
14	Cell B8=$B$2*A8*1*$B$3/1000						
15	Cell C8=(0.0001/B8)*100						
16	Cell D8=$B$2*A8*1/2*$B$4/1000						
17	Cell E8=(0.0001/D8)*100						
18	Cell F8=$B$2*A8*1/2*$B$5/1000						
19	Cell G8=(0.0001/F8)*100						

16A-3 Preparation of Standard Solutions of Base

➤ Sodium hydroxide, potassium hydroxide, and barium hydroxide are the most common bases for preparing standard solutions.

➤ Once prepared the base solution must be standardized against a primary standard acid like potassium hydrogen phthalate (KHP), benzoic acid, potassium hydrogen iodate.

The Effect of Carbon Dioxide on Standard Base Solutions

➤ The hydroxides of sodium, potassium, and barium react rapidly with atmospheric carbon dioxide to produce the corresponding carbonate:

$$CO_2(g) + 2OH^- \rightarrow CO_3^{-2} + H_2O$$

➤ If the end point of a titration occurs in acidic solution and thus requires an acid-range indicator, each carbonate ion produced from sodium or potassium hydroxide will have reacted with two hydronium ions of the acid.

➤ Because the amount of hydronium ion consumed by this reaction is identical to the amount of hydroxide lost during formation of the carbonate ion,

$$CO_3^{2-} + 2H_3O^+ \rightarrow H_2CO_3 + 2H_2O$$

no error is incurred, when an indicator with an acidic range is used.

➤ In basic solution, each carbonate ion has reacted with only one hydronium ion when the color change of the indicator is observed:

$$CO_3^{2-} + H_3O^+ \rightarrow HCO_3^- + H_2O$$

The effective concentration of the base is thus diminished by absorption of carbon dioxide and a systematic error (called a carbonate error) results.

EXAMPLE 16-2

The hydroxide concentration in a carbonate-free NaOH solution was found to be 0.05118 M immediately after preparation. If exactly 1.000 L of this solution was exposed to air for some time and absorbed 0.1962 g CO_2, calculate the relative carbonate error that would arise in the determination of acetic acid with the contaminated solution if phenolphthalein were used as an indicator.

Solution

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$c_{Na_2CO_3} = \frac{0.1962 \text{ g } CO_2}{1.000 \text{ L}} \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol } Na_2CO_3}{\text{mol } CO_2} = 4.458 \times 10^{-3} \text{ M}$$

The effective concentration c_{NaOH} of NaOH for acetic acid is then

$$c_{NaOH} = \frac{0.05118 \text{ mol NaOH}}{L} - \left(\frac{4.456 \times 10^{-3} \text{ mol } Na_2CO_3}{L} \right.$$

$$\left. \times \frac{1 \text{ mol HOAc}}{\text{mol } Na_2CO_3} \times \frac{1 \text{ mol NaOH}}{\text{mol HOAc}} \right)$$

$$= 0.04672 \text{ M}$$

$$\text{rel error} = \frac{0.04672 - 0.05118}{0.05118} \times 100\% = -8.7\%$$

➤ Carbonate ion in standard base solutions decreases the sharpness of end points and is usually removed before standardization.

➤ The best method for preparing carbonate-free sodium hydroxide solutions takes advantage of the very low solubility of sodium carbonate in concentrated solutions of the base.

➤ Water that is in equilibrium with atmospheric constituents contains only about 1.5×10^{-5} mol CO_2 /L, an amount that has a negligible effect on the strength of most standard bases.

➤ As an alternative to boiling to remove CO_2 from supersaturated solutions of CO_2, the excess gas can be removed by bubbling air through the water for several hours.

➤ This process is called **sparging** and produces a solution that contains the equilibrium concentration of CO_2.

# 16A-4 The Standardization of Bases

➤ Several primary standards are available for standardizing bases. Most are weak organic acids that require the use of an indicator with a basic transition range.

➤ *Potassium Hydrogen Phthalate,* $KHC_8H_4O_4$, KHP, is a nearly ideal primary standard.

It is a nonhygroscopic crystalline solid with a relatively large molar mass (204.2 g/mol).

➤ *Other Primary Standards for Bases,* Benzoic acid has limited solubility in water, so it is usually dissolved in ethanol prior to dilution with water and titration.

 Potassium hydrogen iodate, $KH(IO_3)_2$, is an excellent primary standard with a high molecular mass per mole of protons. In contrast to all other primary standards for bases, KH(IO3)2 has the advantage of being a strong acid, which makes it easy to choose an indicator.
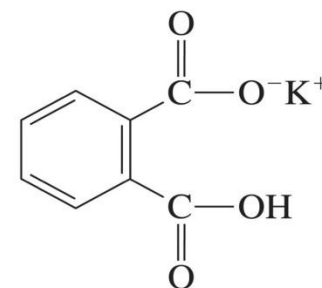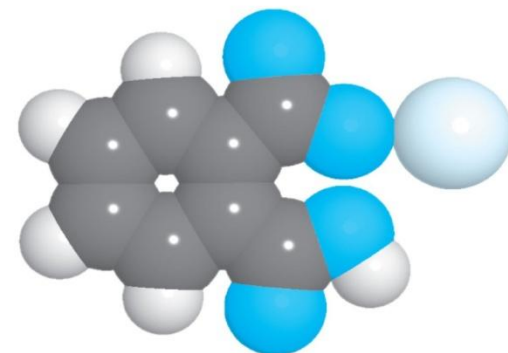
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NOTE: Solutions of bases should be stored in polyethylene bottles rather than glass because of the reaction between bases and glass. Such solutions should never be stored in glassstoppered bottles; after standing for a period, a stopper is often impossible to remove.

16B Typical applications of neutralization titrations

Neutralization titrations are used to determine the many inorganic, organic, and biological species that possess acidic or basic properties.

There are two major types of end points that are widely used in neutralization titrations

       1. a visual end point based on indicators.

       2. a potentiometric end point in which the potential of a glass/calomel electrode system is determined with a pH meter or another voltage-measuring device. The measured voltage is directly proportional to pH.

16B-1 Elemental Analysis

➢ Several important elements such as carbon, nitrogen, chlorine, bromine, fluorine, that occur in organic and biological systems are conveniently determined by methods that have an acid/base titration as the final step.

➢ Generally, the elements susceptible to this type of analysis are nonmetallic and include carbon, nitrogen, chlorine, bromine, and fluorine. Pretreatment converts the element to an inorganic acid or base that is then titrated.

Nitrogen

➤ The most common method for determining organic nitrogen is the Kjeldahl method, which is based on a neutralization titration.

➤ It is the standard process for determining the protein content of grains, meats, and biological materials.

➤ The sample is decomposed in hot, concentrated sulfuric acid to convert the bound nitrogen to ammonium ion.

➤ It is then cooled, diluted, and made basic, a process that converts the ammonium ions to ammonia.

➤ The ammonia is distilled from the basic solution, collected in an acidic solution, and determined by a neutralization titration.
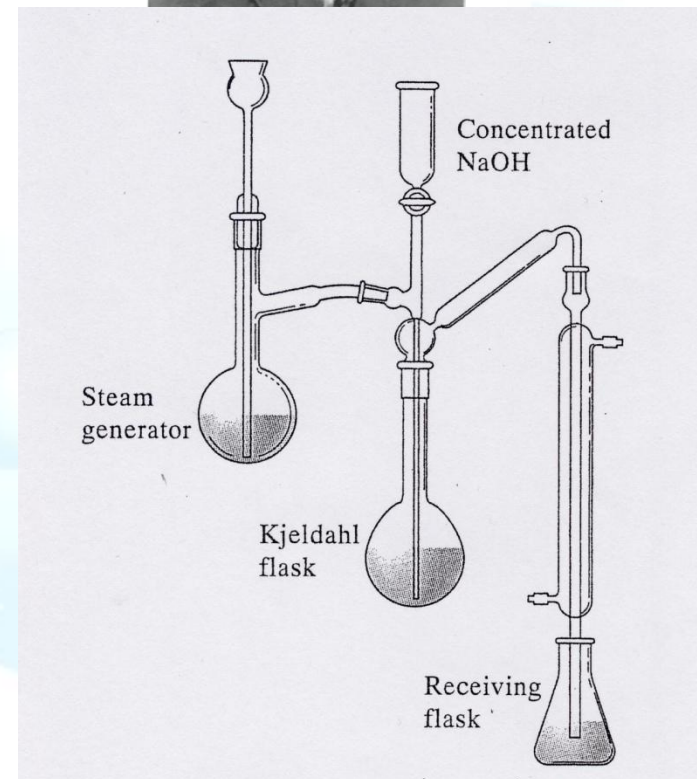
EXAMPLE 16-3

A 0.7121 g sample of wheat flour was analyzed by the Kjeldahl method. The ammonia formed by addition of concentrated base after digestion with H_2SO_4 was distilled into 25.00 mL of 0.04977 M HCl. The excess HCl was then back-titrated with 3.97 mL of 0.04012 M NaOH. Calculate the percent protein in the flour, using the 5.70 factor for cereal.

Solution

$$\text{amount HCl} = 25.00 \text{ mL HCl} \times 0.04977 \frac{\text{mmol}}{\text{mL HCl}} = 1.2443 \text{ mmol}$$

$$\text{amount NaOH} = 3.97 \text{ mL NaOH} \times 0.04012 \frac{\text{mmol}}{\text{mL NaOH}} = 0.1593 \text{ mmol}$$

$$\text{amount N} = \text{amount HCl} - \text{amount NaOH} = 1.2443 \text{ mmol}$$

$$- 0.1593 \text{ mmol} = 1.0850 \text{ mmol}$$

$$\%N = \frac{1.0850 \text{ mmol N} \times \dfrac{0.014007 \text{ g N}}{\text{mmol N}}}{0.7121 \text{ g sample}} \times 100\% = 2.1342$$

$$\% \text{ protein} = 2.1342 \ \%N \times \frac{5.70\% \text{ protein}}{\%N} = 12.16$$

* Determining Total Serum Protein

– an important clinical measurement and used in diagnosing liver malfunctions

– Although the Kjeldahl method is capable of high precision and accuracy, it is too slow and cumbersome to be routinely used in determining total serum protein.

– Methods that are commonly used include the **biuret method and the Lowry method.**

– **In the biuret method,** a reagent containing copper(II) ions is used, and a violet colored complex is formed between the Cu^{+2} ions and peptide bonds. The increase in the absorption of visible radiation is used to measure serum protein.

– In the Lowry procedure, the serum sample is pretreated with an alkaline copper solution followed by a phenolic reagent. A color develops because of reduction of phosphotungstic acid and phosphomolybdic acid to molybdenum blue.

– Both the biuret and Lowry methods use spectrophotometry for quantitative measurements.

* Other Methods for Determining Organic Nitrogen

➢ Dumas method, the sample is mixed with powdered copper(II) oxide and ignited in a combustion tube to give carbon dioxide, water, nitrogen, and small amounts of nitrogen oxides. A stream of carbon dioxide carries these products through a packing of hot copper, which reduces any oxides of nitrogen to elemental nitrogen. The mixture then is passed into a gas buret filled with concentrated potassium hydroxide. The only component not absorbed by the base is nitrogen, and its volume is measured directly.

Sulfur

➤Sulfur in organic and biological materials is determined by burning the sample in a stream of oxygen.

➤ The sulfur dioxide (as well as the sulfur trioxide) formed is collected by distillation into a dilute solution of hydrogen peroxide:

$$SO_2(g) + H_2O_2 \rightarrow H_2SO_4$$

Table 16-1 lists other elements that can be determined by neutralization methods.

TABLE 16-1

Elemental Analyses Based on Neutralization Titrations

Element	Converted to	Adsorption or Precipitation Products	Titration
N	NH_3	$NH_3(g) + H_3O^+ \rightarrow NH_4^+ + H_2O$	Excess HCl with NaOH
S	SO_2	$SO_2(g) + H_2O_2 \rightarrow H_2SO_4$	NaOH
C	CO_2	$CO_2(g) + Ba(OH)_2 \rightarrow BaCO_3(s) + H_2O$	Excess $Ba(OH)_2$ with HCl
Cl(Br)	HCl	$HCl(g) + H_2O \rightarrow Cl^- + H_3O^+$	NaOH
F	SiF_4	$3SiF_4(g) + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$	NaOH
P	H_3PO_4	$12H_2MoO_4 + 3NH_4^+ + H_3PO_4 \rightarrow$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 12H_2O + 3H^+$	
		$(NH_4)_3PO_4 \cdot 12MoO_3(s) + 26OH^- \rightarrow$ $HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$	Excess NaOH with HCl

16B-2 The Determination of Inorganic Substances

Various inorganic species can be determined by titration

1.   *Ammonium salts* are determined by conversion to ammonia with a strong base followed by distillation.

2.   *Nitrates and nitrites* are first reduced to ammonium ion by reaction with an alloy of 50% Cu, 45% Al, and 5% Zn (Devarda's alloy).

Granules of the alloy are introduced into a strongly alkaline solution of the sample in a Kjeldahl flask.

3.   *Carbonate and carbonate mixtures* require two titrations with a strong acid:

   * one using an alkaline-range indicator, such as *phenolphthalein*,

   * and the other with an acid-range indicator, such as *bromocresol green*.

The composition of the solution can then be deduced from the relative volumes of acid needed to titrate equal volumes of the sample

TABLE 16-2

Volume Relationships in the Analysis of Mixures Containing Hydroxide, Carbonate, and Hydrogen Carbonate Ions

Constituents in Sample	Relationship between V_{phth} and V_{bcg} in the Titration of an Equal Volume of Sample*
NaOH	$V_{phth} = V_{bcg}$
Na_2CO_3	$V_{phth} = \frac{1}{2} V_{bcg}$
$NaHCO_3$	$V_{phth} = 0;\ V_{bcg} > 0$
NaOH, Na_2CO_3	$V_{phth} > \frac{1}{2} V_{bcg}$
Na_2CO_3, $NaHCO_3$	$V_{phth} < \frac{1}{2} V_{bcg}$

*V_{phth} = volume of acid needed for a phenolphthalein end point; V_{bcg} = volume of acid needed for
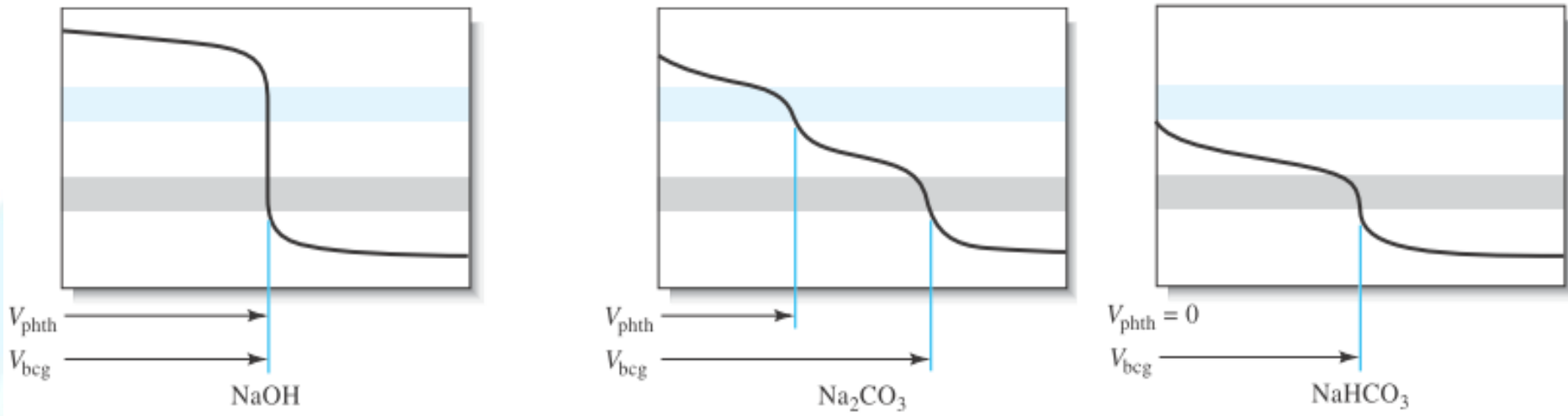
Constituents in Sample	Titration of an Equal Volume of Sample
NaOH	$V_{phth} = V_{bcg}$
Na_2CO_3	$V_{phth} = \frac{1}{2}V_{bcg}$
$NaHCO_3$	$V_{phth} = 0;\ V_{bcg} > 0$
NaOH, Na_2CO_3	$V_{phth} > \frac{1}{2}V_{bcg}$
Na_2CO_3, $NaHCO_3$	$V_{phth} < \frac{1}{2}V_{bcg}$
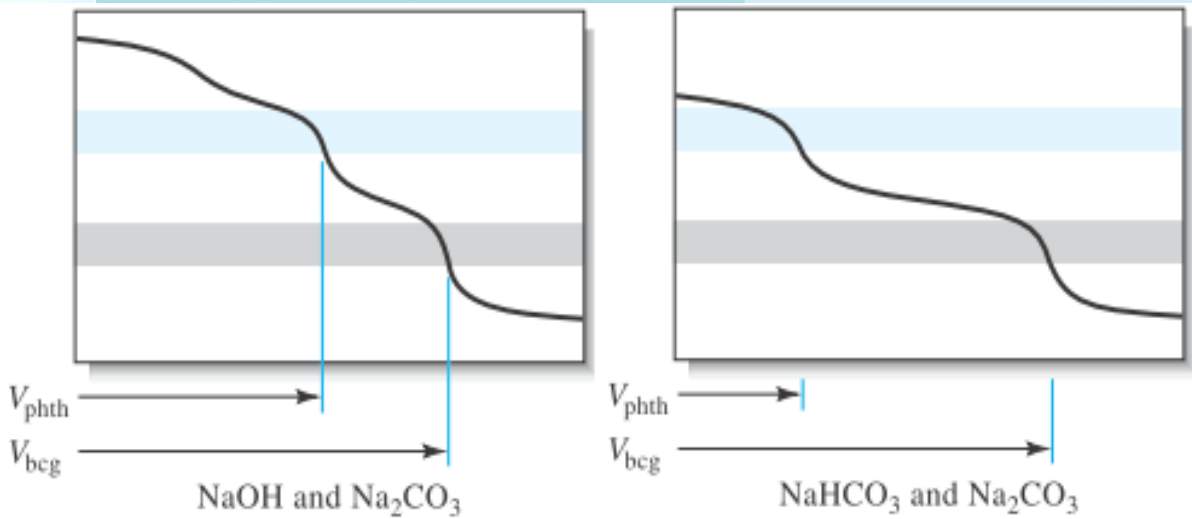
lume of acid needed for

Phenolphthalein transition range

Bromocresol green transition range

Figure 16-3 Titration curves and indicator transition ranges for the analysis of mixtures containing hydroxide, carbonate, and hydrogen carbonate ions using a strong-acid
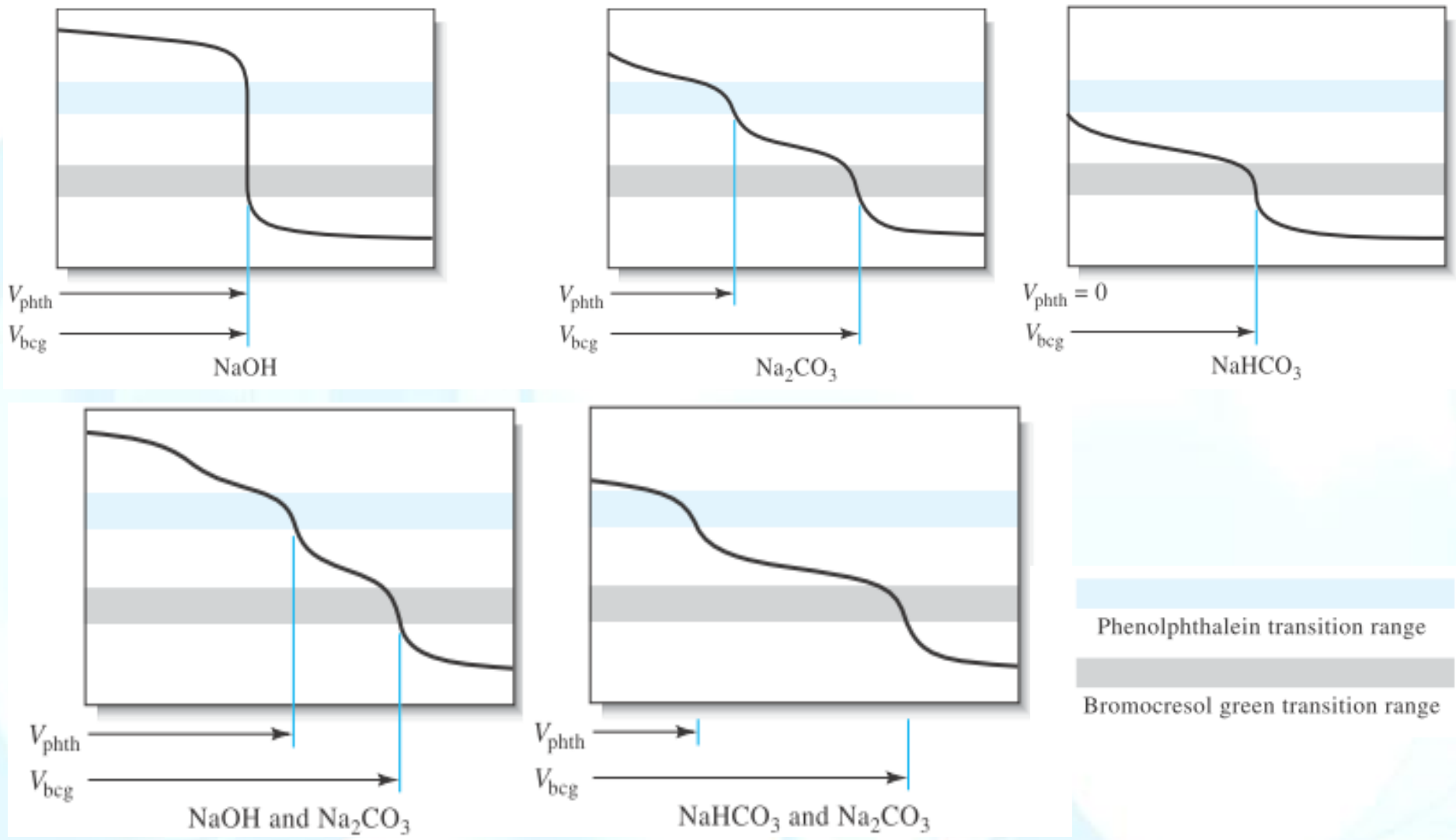
Figure 16-3 Titration curves and indicator transition ranges for the analysis of mixtures containing hydroxide, carbonate, and hydrogen carbonate ions using a strong-acid titrant.

EXAMPLE 16-4

A solution contains $NaHCO_3$, Na_2CO_3, and $NaOH$, either alone or in a permissible combination. Titration of a 50.0-mL portion to a phenolphthalein end point requires 22.1 mL of 0.100 M HCl. A second 50.0-mL aliquot requires 48.4 mL of the HCl when titrated to a bromocresol green end point. Determine the composition and the molar solute concentrations of the original solution.

Solution

If the solution contained only $NaOH$, the volume of acid required would be the same regardless of indicator (see Figure 16-3a). Similarly, we can rule out the presence of Na_2CO_3 alone because titration of this compound to a bromocresol green end point would consume just twice the volume of acid required to reach the phenolphthalein end point (see Figure 16-3b). Actually, the second titration requires 48.4 mL. Because less than half of this amount is used in the first titration, the solution must contain some $NaHCO_3$ in addition to Na_2CO_3 (see Figure 16-3e). We can then calculate the concentration of the two constituents.

When the phenolphthalein end point is reached, the CO_3^{2-} originally present is converted to HCO_3^-. Thus,

$$\text{amount } Na_2CO_3 = 22.1 \text{ mL} \times 0.100 \frac{\text{mmol}}{\text{mL}} = 2.21 \text{ mmol}$$

The titration from the phenolphthalein to the bromocresol green end point (48.4 mL − 22.1 mL = 26.3 mL) includes both the hydrogen carbonate originally present and that formed by titration of the carbonate. Therefore,

$$\text{amount } NaHCO_3 + \text{amount } Na_2CO_3 = 26.3 \text{ mL} \times 0.100 \frac{\text{mmol}}{\text{mL}} = 2.63 \text{ mmol}$$

Hence,

$$\text{amount } NaHCO_3 = 2.63 \text{ mmol} - 2.21 \text{ mmol} = 0.42 \text{ mmol}$$

$$c_{Na_2CO_3} = \frac{2.21 \text{ mmol}}{50.0 \text{ mL}} = 0.0442 \text{ M}$$

$$c_{NaHCO_3} = \frac{0.42 \text{ mmol}}{50.0 \text{ mL}} = 0.084 \text{ M}$$

16B-3 The Determination of Organic Functional Groups

Carboxylic and Sulfonic Acid Groups

➢ Most carboxylic acids have dissociation constants that range between 10^{-4} and 10^{-6}, and thus, these compounds are readily titrated.

➢ Many carboxylic acids are not soluble in water; the acid can be dissolved in ethanol and titrated with aqueous base.

➢ Alternatively, the acid can be dissolved in an excess of standard base followed by back-titration with standard acid.

➢ Neutralization titrations are often used to determine the equivalent masses of purified organic acids (see Feature 16-3). Equivalent masses serve as an aid in the qualitative identification of organic acids.

The **equivalent mass of an** acid or base is the mass of the compound that reacts with or contains one mole of protons. Thus,

the equivalent mass of KOH) is equal to its molar mass. = 56.11g/mol protons reacted

For $Ba(OH)_2$, it is the molar mass divided by 2
= 171.3 g/mol $Ba(OH)_2$ x 1 mol $Ba(OH)_2$ / 2 mol protons reacted

Amine groups

➢ Aliphatic amines generally have base dissociation constants on the order of 10-5 and can be titrated directly with a solution of strong acid.

➢ Cyclic amines with aromatic character, such as pyridine and its derivatives, are usually too weak for titration in aqueous solutions.

➢ Many saturated cyclic amines tend to resemble aliphatic amines in their acid/base behavior and can thus be titrated in aqueous media.

➢ Many amines that are too weak to be titrated as bases in water are easily titrated in nonaqueous solvents.

Ester groups

➢ Esters are commonly determined by saponification with a measured quantity of standard base:

$R_1COOR_2 + OH- \rightarrow R_1COO^- + HOR_2$ The excess base is then titrated with standard acid.

➢ Esters vary widely in their rates of saponification.

➢ Saponification is the process by which an ester is hydrolyzed in alkaline solution to give an alcohol and a conjugate base.

Hydroxyl groups

➤ Hydroxyl groups in organic compounds can be determined by esterification with various carboxylic acid anhydrides or chlorides.

➤ The two most common reagents are acetic anhydride and phthalic anhydride.

$$(CH_3CO)_2O + ROH \rightarrow CH_3COOR + CH_3COOH$$

The acetic acid is then titrated with a standard solution of alcoholic sodium or potassium hydroxide.

Carbonyl groups

➤ Many aldehydes and ketones can be determined with a solution of hydroxylamine hydrochloride. The reaction produces an oxime and the liberated HCl is titrated with a base.
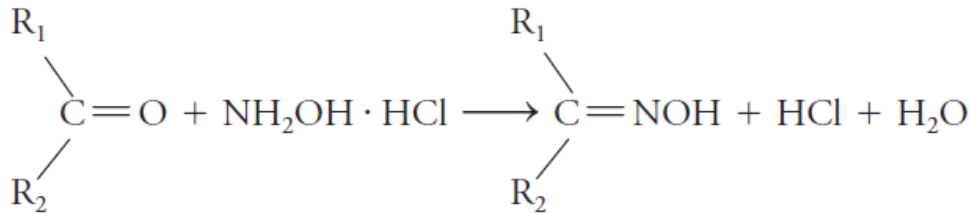
➤The liberated HCl is titrated with a base.

The Determination of Salts

➤ The total salt content of a solution can be determined accurately by acid/base titration.

➤ The salt is converted to an equivalent amount of an acid or base by passing a solution containing the salt through a column packed with an ion-exchange resin.