16 Application of Neutralization Titration

16A Reagents for Neutralization Titration

16A-1 Preparation of Standard Acid Solutions

Solution oh HCl, $HClO_4$ and H_2SO_4 are stable indefinitely.
Restandardization is not required unless evaporation occurs.

16A-2 The Standardization of Acids

Sodium carbonate: $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$

heating purified $NaHCO_3$ between 270℃ and 300℃ for one hour

two end points: The first: ≈ pH **8.3**; the second: ≈ pH **3.8**

Boiling effectively destroys this buffer by eliminating the carbonic acid:

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

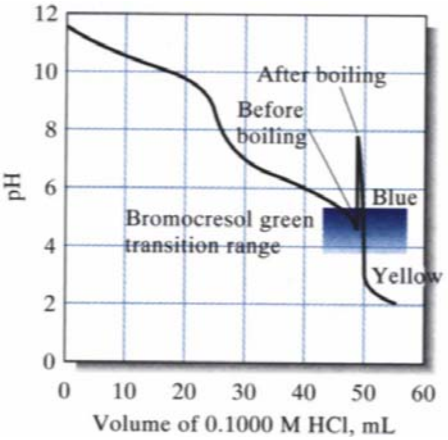


Fig. 16-1 Titration of 25.00 mL of 0.1000 M Na_2CO_3 with 0.1000 M HCl. After about 49 mL of HCl have been added, the solution is boiled, causing the increase in pH shown. The change in pH when more HCl is added is much larger.

Other Primary Standards for Acids

Tris-(hydroxymethyl)aminomethane, TRIS or THAM, $(HOCH_2)_3CNH_2$,

TRIS reacts in a 1:1 molar ratio with hydronium ions.

$$\mathbf{(HOCH_2)_3CNH_2 + H_3O^+ \rightarrow (HOCH_2)_3CNH_3^+ + H_2O}$$

Sodium tetraborate decahydrate and mercury(II) oxide

$$\mathbf{B_4O_7^{2-} + 2H_3O^+ + 3H_2O \rightarrow 4H_3BO_3}$$

Ex. 16-1 Compare the masses of (a) TRIS (121 g/mol); (b) Na_2CO_3 (106 g/mol); and (c) $Na_2B_4O_7 \cdot 10H_2O$(borax) (381 g/mol) that should be taken to standardize an approximately 0.020 molar solution of HCl for the following volumes of HCl: 20.00, 30.00, 40.00 and 50.00mL.

$$\text{mmol HCl} = \text{mL HCl} \times 0.020\ \text{mmol/mL}$$

(a) For TRIS

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

(b) For Na_2CO_3

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

(c) For $Na_2B_4O_7 \cdot 10H_2O$

$$\text{g borax} = \text{mmol HCl} \times \frac{1\ \text{mmol borax}}{2\ \text{mmolHCl}} \times \frac{381\ \text{g borax/mol}}{1000\ \text{mmol borax/mol}}$$

mL HCl	**g TRIS**	**g Na_2CO_3**	**g $Na_2B_4O_7 \cdot 10H_2O$**
20.00	0.048	0.021	0.08
30.00	0.073	0.032	0.11
40.00	0.097	0.042	0.15
50.00	0.121	0.053	0.19

16A-3 Preparation of Standard Solutions of Base

Sodium hydroxide

Potassium hydroxide and barium hydroxide

***The Effect of Carbon Dioxide upon Standard base solutions**

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

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

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

Absorption of carbon dioxide by a standardized solution of sodium or potassium hydroxide leads to a negative systematic error in analyses in which an indicator with a basic range is used. No systematic error is incurred when an indicator with an acidic range is used.

Ex. 16-2 A CO_3^{2-}-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.

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

$C_{Na_2CO_3} = 0.1962\ \text{g}/44.01\ (\text{g/mol}) \times 1/1.000\ \text{L solution}$

$= 4.458 \times 10^{-3}\ \text{M}$

Effective conc. C_{NaOH} of NaOH for acetic acid is

$C_{NaOH} = 0.05118\ \text{M NaOH} - 4.458 \times 10^{-3}\ \text{M} = 0.04672\ \text{M}$

rel error = (0.04672 - 0.05118)/0.05118 × 100 % = - 8.7 %

16A-4 The Standardization of Bases

Potassium Hydrogen Phthalate, $KHC_8H_4O_4$

a nonhygroscopic crystalline solid with a high mass (204.2 g/mol)

Other Primary Standards for Bases

Benzoic acid

Potassium hydrogen iodate, $KH(IO_3)_2$,

Advantage: a strong acid, choice of indicator less critical.

16B Typical Applications of Neutralization Titrations

16B-1 Elemental Analysis

Nitrogen

Kjeldahl method: measure of the protein content of meats, grains and animal feeds

(most proteins contain approximately the same % of N)

	meats	Dairy products	cereals
Factor	**6.25**	**6.38**	**5.70**

for -NO (nitro group), -N=N- (azo group), O^{-}-N^{+}=N- (azoxy group)

Three essential steps

(1). **Digestion**

$$\text{-CH-NH}_2 + 3H_2SO_4 \rightarrow CO_2(g) + NH_4HSO_4 + 2H_2SO_4\ [\rightarrow SO_2(g)\uparrow]$$

(2). **Distillation**

$$NH_4HSO_4 + 2NaOH \rightarrow NH_3 + 2Na^+ + SO_4^{2-} + 2H_2O$$

$$NH_3 + HCl\ (\text{excess}) \rightarrow NH_4^+ + Cl^-$$

(3) **Neutralization titration**

$$NaOH + HCl\ (\text{unreacted}) \rightarrow H_2O + Na^+ + Cl^-$$

Calculation:

mmole NH_3 = (mL)(M HCl) - (mL)(M NaOH)

***Modification method**

(a). $\text{-CH-NH}_2 + 3H_2SO_4 \rightarrow CO_2(g) + NH_4HSO_4 + 2H_2SO_4$

(b). $NH_4HSO_4 + 2NaOH \rightarrow NH_3 + 2Na^+ + SO_4^{2-} + 2H_2O$

$NH_3(g) + H_3BO_3 \rightarrow NH_4^+ + H_2BO_3^-$

(c). $HCl + H_2BO_3^- \rightarrow H_3BO_3 + Cl^-$

Ex. 16-3 A 0.7121 g sample of a wheat flour was analyzed by the Kjeldahl method. The ammonia formed by addition of conc. 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.

no. mmol HCl = 25.00 mL × 0.04977 mmol/mL = 1.2443

no. mmol NaOH = 3.97 mL × 0.04012 mmol/mL = 0.1593

no. mmol N = 1.2443 - 0.1593 = 1.0850

$$\%\,N = \frac{1.0850\ \text{mmol} \times 0.014007\ \text{gN/mmol}}{0.7121\ \text{g}} \times 100\% = 2.1341\%$$

$$\%\ \text{protein} = 2.1341\%\ N \times \frac{5.7\%\ \text{protein}}{\%\,N} = 12.16\%$$

Sulfur

$$\text{S in organic \& biological materials} \xrightarrow{O_2 \text{ buring}} SO_2 \text{ into d - } H_2O_2 \text{ soln}$$

$SO_2(g) + H_2O_2 \rightarrow H_2SO_4 \rightarrow$ titrated with standard base.

Other Elements

Table 16-1 Elemental analyses based on neutralization titrations

Element	Converted to	Absorption 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	$SiF_4(g) + H_2O \rightarrow H_2SiF_6$	NaOH
P	H_3PO_4	$12H_2MO_4 + 3NH_4^+ + H_3PO_4 \rightarrow$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 12H_2O + 3H^+$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 26OH^- \rightarrow$ $HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$	Excess NaOH with HCl

16B-2 The Determination of Inorganic Substances

Ammonium Salts

$$\text{Ammonium salts} \xrightarrow{\text{strong base}} \text{ammonia} \rightarrow \text{Kjeldahl method}$$

Nitrates and Nitrites

$$\text{nitrate or nitrite} \xrightarrow{\text{reducing agent}} \text{ammonium ion}$$

Devarda’s alloy (50% Cu, 45% Al, 5% Zn)

Arnd’s alloy (60% Cu, 40% Mg)

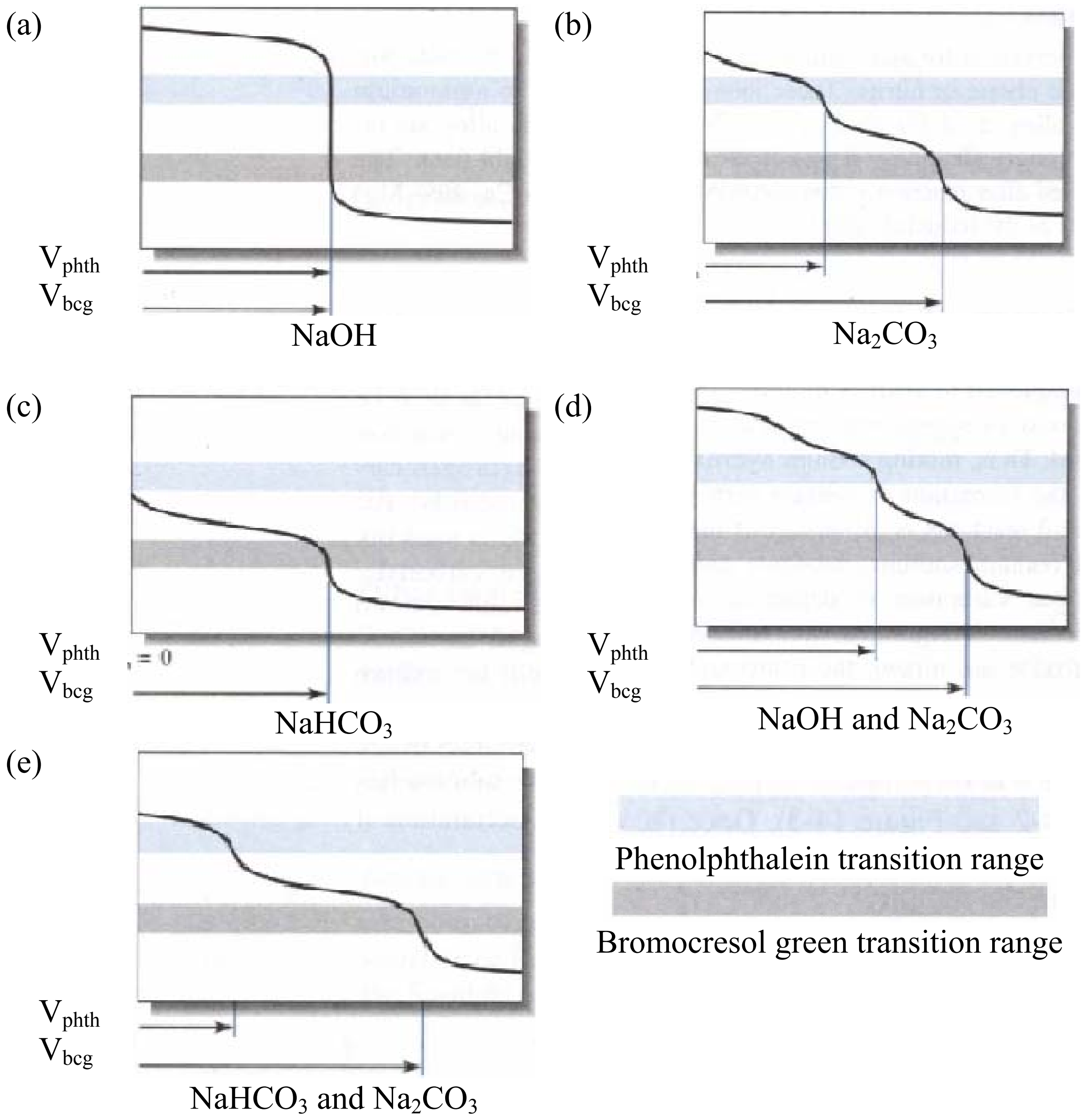
Carbonate and Carbonate Mixtures

Containing $NaHCO_3$, Na_2CO_3 and NaOH either alone or admixed.

Table 16-2 Volume relationships in the analysis of mixtures containing hydroxide, carbonate and hydrogen carbonate ions.

Constituent(s) in sample	Relationship Between V_{phth} and V_{bcg} in the Titration of an Equal Volume of Sample*
	$V_{phth} = V_{bcg}$
Na_2CO_3	$V_{phth} = \frac{1}{2}V_{bcg}$
$NaHCO_3$	$V_{phth} = 0; \quad V_{bcg} > 0$
NaOH, Na_2CO_3	$V_{phth} > \frac{1}{2}V_{bcg}$
$NaHCO_3$, Na_2CO_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 a bromocresol green end point.



(a) NaOH (b) Na_2CO_3 (c) $NaHCO_3$ (d) NaOH and Na_2CO_3 (e) $NaHCO_3$ and Na_2CO_3

Fig. 16-3 Titration curves and indicator transition ranges for the analysis of mixtures containing hydroxide, carbonate and hydrogen carbonate ions.

<u>Ex. 16-4</u>. A soln contains $NaHCO_3$, Na_2CO_3, and NaOH, either alone or in 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. Deduce the composition and calculate the molar solute conc. of the original solution.

CO_3^{2-} amount Na_2CO_3 = 22.1 mL × 0.100 mmol/mL = 2.21 mmol
↓ → <u>*22.1*</u> mL 0.100 M HCl
HCO_3^- ph.ph. end point
↓ → <u>*22.1*</u> + <u>*4.2*</u> = <u>*26.3*</u> mL
H_2CO_3 bcg. end point

amount $NaHCO_3$ + no. mmol Na_2CO_3 = 26.3 × 0.100 = 2.63 mmol

amount $NaHCO_3$= 2.63 - 2.21 = 0.42 mmol

$C_{Na_2CO_3}$ = 2.21 mmol/50.0 mL = 0.0442 M

C_{NaHCO_2} = 0.42 mmol/50.0 mL = 0.0084 M

16B-3 The Determination of Organic Functional Groups

Carboxylic and Sulfonic Acid groups

K_a: $10^{-4} \sim 10^{-6}$, indicator: phenolphthalein

Not soluble in water → dissolved in ethanol or using back-titration

Amine Groups

Aliphatic amines: $K_b \approx 10^{-5}$ can be titrated directly with a strong acid

Aromatic amines: aniline and its derivatives ($K_b \approx 10^{-10}$) too weak for titration in aqueous medium.

Cyclic aromatic amines: pyridine and its derivatives, can be titrated in nonaqueous solvent, such as anhydrous acetic acid.

Ester Groups: saponification

$R_1COOR_2 + \text{excess } OH^- \rightarrow R_1COO^- + HOR_2$

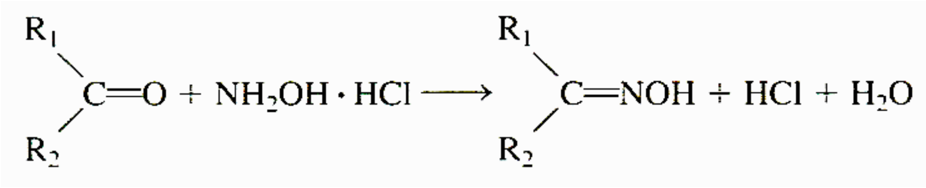
Back-titrate the excess base with standard acid

Hydroxyl Groups: esterification with carboxylic acid anhydrides or chlorides, ex: acetic anhydride and phthalic anhydride

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

$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$

Carbonyl Groups



The librated HCl is titrated with base.

16B-4 The Determination of Salts

Salt → acid or base

C. Application of Neutralization Titrations in Nonaqueous Media

1. The reactants or products might be insoluble in water.
   → high-molecular-weight organic acids and bases
2. The reactante or products might react with water.
3. The analyte is too weak an acid or base to be titrated in water.
   → Ka or Kb < 10^{-8} , ex: aromatic amines, phenols and the salte of a variety of inorganic and carboxylic acids

Disadvantages:

1. solvents are expensive and often volatile and toxic
2. require a much closer control of reagent temperature

C-1 Solvents for Nonaqueous Titrations

amphiprotic solvents

*anhydrous acetic acid
*ethanol
*ethylenediamine

$$2CH_3COOH \Leftrightarrow CH_3COOH_2^+ + CH_3COO^-$$

$$2C_2H_5OH \Leftrightarrow C_2H_5OH_2^+ + C_2H_5O^-$$

$$2NH_2CH_2CH_2NH_2 \Leftrightarrow NH_2CH_2CH_2NH_3^+ + NH_2CH_2CH_2NH^-$$

C-2 The Completeness of Acid/Base Reactions in Amphiprotic Solvents

1. the strength of the analyte as an acid or base
2. the autoprotolysis constant of the solvent
3. the inherent acidity or basicity of the solvent
4. the dielectric constant of the solvent

The Effect of Solvent Autoprotolysis Constant

in water: titration of a weak base B with a strong acid

$$B + H_3O^+ \Leftrightarrow BH^+ + H_2O$$

Kequil = Kb/Kw = $[BH^+][OH^-]/[B][H_3O^+][OH^-] = [BH^+]/[B][H_3O^+]$

Kw, the autoprotolysis constant for the solvent

a wek acid HA with a strong base in water : Kequil = Ka/Kw

In nonaqueous solvents:

the weak base B reacts with perchloric acid in anhydrous acetic acid

$B + CH_3COOH_2^+ \Leftrightarrow BH^+ + CH_3COOH$

$HClO_4 + CH_3COOH \Leftrightarrow CH_3COOH_2^+ + ClO_4^-$

$$\boxed{K_{equil} = [BH^+]/[B][CH_3COOH_2^+] = Kb'/Ks}$$

$B + CH_3COOH \Leftrightarrow BH^+ + CH_3COO^-$

The dissociation constant for the base in acetic acid : Kb'

$Kb' = [BH^+][CH_3COO^-]/[B]$

Ks: autoprotolysis constant; $Ks = [CH_3COOH_2^+][CH_3COO^-]$

Effect of Acid or base Characteristics of the Solvent

Acidic solvent : formic acid, acetic acid and sulfuric acid

→ better proton donors than proton acceptors

aniline $C_6H_5NH_2$, $K_b = 10^{-10}$

$C_6H_5NH_2 + H_2O \Leftrightarrow C_6H_5NH_3^+ + OH^-$

$C_6H_5NH_2 + CH_3COOH \Leftrightarrow C_6H_5NH_3^+ + CH_3COO^-$

Basic solvents : ethylenediamine and liquid ammonia

phenol C_6H_5OH, $Ka = 10^{-10}$

Effect of Solvent Dielectric Constant

C-3 Choice of Amphiprotic Solvents for Neutralization Titrations

C-4 End-Point Detection in Nonaqueous Titrations

C-5 Applications of Nonaqueous Acid/Base Titrations

Titration of Bases in Glacial Acetic Acid

Some Typical Application

C-6 Titration of Acids

*The Levelling Effect

*Titrating a weak Acid with a Strong Base