## Chapter 16

## Applications of Neutralization Titrations

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## Introduction

A. Neutralizations are widely used to determine the concentrations of analytes.

B. Commonly analyzed species include acids, bases and any species that can be converted into an acid or base.

e.g., Protein in food (bread, meat)→protein →amino acids→N→$NH_3$ (+HCl)←NaOH

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**Determination of Protein in Bread**

(The Kjeldahl method)

(a) Bread sample ($m_1$) + Conc. $H_2SO_4 \xrightarrow{\Delta}$

$(protein \rightarrow)NH_4^+ \xrightarrow[NaOH]{\Delta} NH_3(\uparrow, g)$

(b) $NH_3(\uparrow, g) \xrightarrow[\text{Known, in Excess}]{\text{HCl (std)}} NH_4Cl + HCl\ (\delta)$

(c) $HCl\ (\delta) \xrightarrow[\text{Back Titration}]{\text{+ NaOH (std)}} NaCl$

(d) $n_N = n_{NH_3} = n_{\Delta HCl}$; $m_N = n_N \bullet 14$ (gram)

(e) $N\%w/w = (m_N / m_1) \bullet 100\%$

(f) $Protein\%w/w = N\%w/w \bullet 5.7$

On average there are 5.7 g protein for every gram of N.

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**The Kjeldahl Method**
(Reference method for nitrogen/protein analysis)


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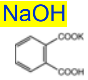
## Selected Primary Standards

- Primary standards for standardization of HCl
  (1) Sodium carbonate, $Na_2CO_3$
  (2) Borax (sodium tetraborate decahydrate), $Na_2B_4O_7 \cdot 10H_2O$
  (3) TRIS [*tris*(hydroxymethyl)aminomethane THAM)], $(HOCH_2)_3CNH_2$
- Primary standards for standardization of NaOH
  (1) Potassium hydrogen phthalate, KHP
  (2) Potassium hydrogen iodate, $KH(IO_3)_2$
  (3) Benzoic acid (limited solubility in water)

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## Standardization of Acids

1. $Na_2CO_3$

Titration of an acid using $Na_2CO_3$ involves two endpoint/equivalence point - one for each hydrogen ion accepted.

$$CO_3^{2-} \underset{K_{a2}}{\overset{+H^+}{\rightleftarrows}} HCO_3^- \qquad K_{a2} = 4.7\times10^{-11},\ pK_{a2} = 10.33$$

$pH_{eq1} = 8.3$, Ind 1: phenolphthalein (pH 10-8, R $\rightarrow$ colorless)

$$HCO_3^- \underset{K_{a1}}{\overset{+H^+}{\rightleftarrows}} H_2CO_3 \qquad K_{a1} = 4.5\times10^{-7},\ pK_{a1} = 6.36$$

$pH_{eq2} = 3.8$, Ind 2: Bromocresol green (pH 5.4-3.8, B $\rightarrow$ Y)

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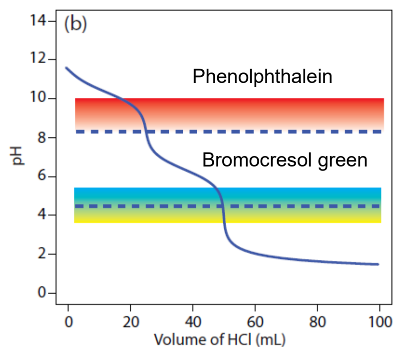


$Na_2CO_3$ is titrated with HCl

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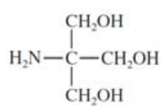
2. Tris (THAM)-tris(hydroxymethyl)aminomethane

(a) Formula is $(HOCH_2)_3CNH_2$




(b) p$K_a$ = 8.3

(c) Accepts one hydrogen ion, to form an alkylammonium ion.

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

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3. Sodium tetraborate decahydrate

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

$$H_3BO_3 \ [\text{or } B(OH)_3] + H_2O \rightarrow B(OH)_4^- + H^+$$

$$(K_a = 5.8\times10^{-10}; pK_a = 9.23)$$

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## Standardization of Bases

Commonly used standards

- potassium hydrogen phthalate ($KHC_8H_4O_4$),
- benzoic acid ($C_6H_5COOH$), an
- potassium hydrogen iodate ($KH(IO_3)_2$)]

are all one-step titrations.

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## Typical Applications of Neutralization Titrations--Kjeldahl Method

➢ Elemental Analysis

- Nonmetallic elements: N, C, Cl, S, P
- Amino acids, proteins (grains, meats, biological materials), drugs, fertilizers,

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 |

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Example16-3 A 0.7121-g sample of a 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.**

$$N \rightarrow NH_3$$

$$NH_3 + HCl \Leftrightarrow NH_4Cl$$

Amount of $NH_3$ in mmol $= 25.00\ \text{mL} \times 0.04977 - 3.97 \times 0.04012 = 1.0850$ mm

$$N\% = \frac{\text{Weight of N}}{\text{Sample Weight}} = \frac{1.0850\ \text{mmol} \times 10^{-3} \times 14.007}{0.7121} x100\% = 2.1341\%$$

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

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- The Determination of Inorganic Substances
- Ammonium salts
- Nitrates and nitrites
- Carbonate and carbonate mixtures
  - (a) NaOH
  - (b) $NaHCO_3$
  - (c) $Na_2CO_3$
  - (d) NaOH + $Na_2CO_3$
  - (e) $NaHCO_3$ + $Na_2CO_3$

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**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 phenophthalein end point requires 22.1 mL of 0.100 M HCl.

A second 50.0 mL aliquot requires 48.4 mL of 0.100 M HCl when titrated to a bromocresol green end point.

**Deduce the composition, and calculate the molar solute concentrations of the original solution.**

♣ Using two samples containing exactly the same amount of mixture solution and applying two indicators separately.

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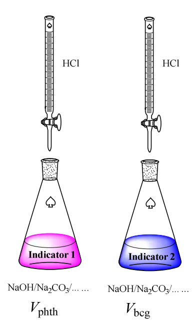
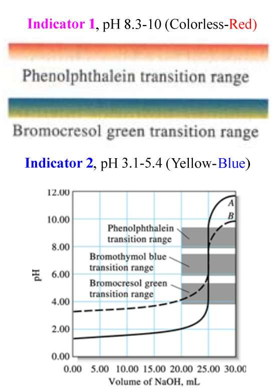
## Double Indicators Titration




Two Identical Analyte Solutions

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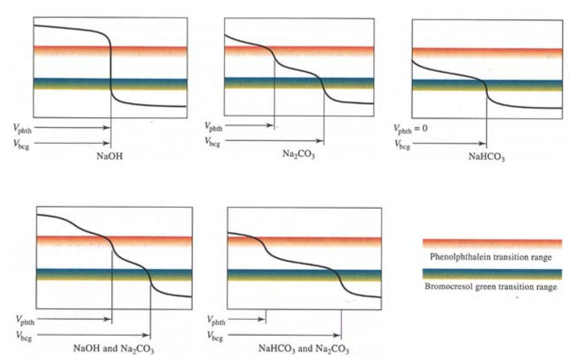


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**TABLE 14-2**

**Volume Relationships in the Analysis of Mixtures 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 | $V_{phth} = V_{bcg}$ |
| $Na_2CO_3$ | $V_{phth} = ½\ V_{bcg}$ |
| $NaHCO_3$ | $V_{phth} = 0;\ V_{bcg} > 0$ |
| NaOH, $Na_2CO_3$ | $V_{phth} > ½\ V_{bcg}$ |
| $Na_2CO_3$, $NaHCO_3$ | $V_{phth} < ½\ V_{bcg}$ |

*$V_{phth}$ = volume of acid needed for a phenolphthalein end point; $V_{bcg}$ = volume of acid needed for a bromocresol green end point

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**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 phenophthalein end point requires 22.1 mL of 0.100 M HCl. A second 50.0 mL aliquot requires 48.4 mL of 0.100 M HCl when titrated to a bromocresol green end point.

**Deduce the composition, and calculate the molar solute concentrations of the original solution.**

$V_{phth} = 22.1$ mL  $V_{beg} = 48.4$ mL

$½\ V_{beg} = 24.2$ mL  $V_{phth} < ½\ V_{beg}$

Composition: $NaHCO_3$, $Na_2CO_3$

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

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

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

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,

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

$HCO_3^- + H^+ \rightarrow H_2CO_3$

Hence,

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

The molar concentrations can then be calculated from these results as follows:

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

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

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## Chapter 16 Summary

- Commonly used standard acids and bases
- Applications of neutralization titrations
- Elemental and organic functional group analysis (Kjeldahl Method)
- Double indicators titration.

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