Analytical Chemistry I

Lecture Notes

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Dong-Sun Lee, Prof., Ph.D. *Chemistry, Seoul Women's University*

Chapter 14

Applications of Neutralization Titration

Typical Applications of Neutralization Titrations

Elemental Analysis

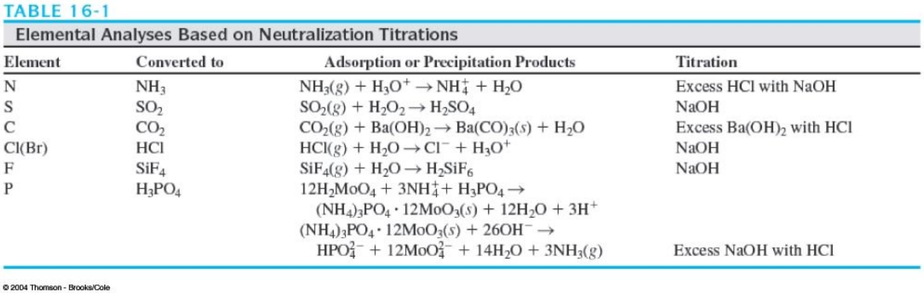
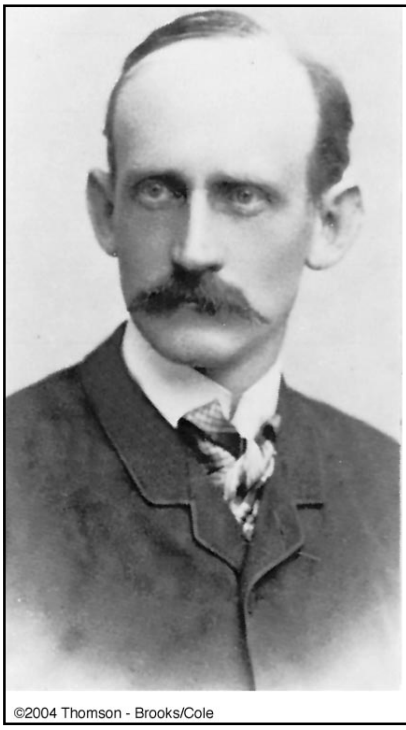


TABLE 16-1

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	$CO_2(g) + Ba(OH)_2 \rightarrow Ba(CO)_3(s) + H_2O$	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	$12H_2MoO_4 + 3NH_4^+ + H_3PO_4 \rightarrow$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 12H_2O + 3H^+$ $(NH_4)_3PO_4 \cdot 12MoO_3(s) + 26OH^- \rightarrow$ $HPO_4^{2-} + 12MoO_4^{2-} + 14H_2O + 3NH_3(g)$	Excess NaOH with HCl



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The Kjeldahl method was developed by a Danish chemist who first described it in 1883.

Digestion :

N(in protein) → NH^{4+}

Distillation of NH_3 :

$NH^{4+} + OH^{-} \rightarrow NH_3(g) + H_2O$

Collection of NH_3 *in* excess HCl :

$NH_3 + H^{+} \rightarrow NH^{4+}$

Titration of unreacted HCl :
$H^{+} + OH^{-} \rightarrow H_2O$

The Determination of Inorganic Substances

Ammonium Salts are conveniently determined by conversion to ammonia with strong base followed by distillation. Ammonia is collected and titrated as in the Kjedahl method.

Nitrates and Nitrites ions are first reduced to ammonium ion by Devarda's alloy (50% Cu, 45% Al, 5% Zn) or Arnd's alloy (60% Cu, 40% Mg). Granules of the alloy are introduced into strongly alkaline solution of the sample in Kjedahl flask. The ammonia is distilled after reaction is complete.

Carbonate and Carbonate Mixtures

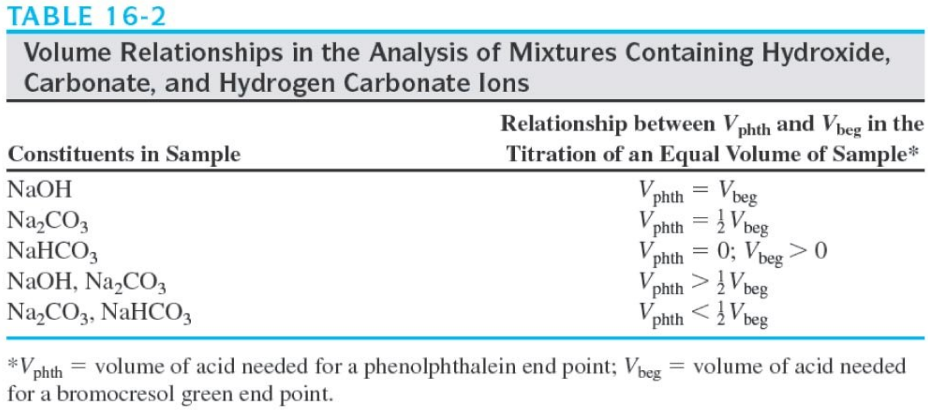
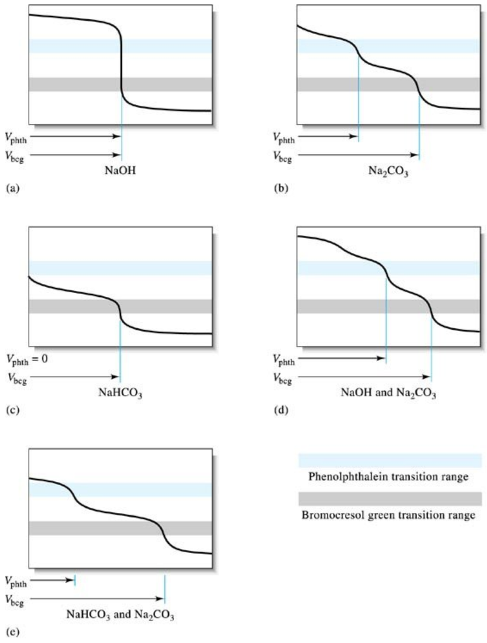


TABLE 16-2

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

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

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



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

Applications (Weak acid titrated with strong base)

1. Acidity for the examination of water and wastewater :

   Acidity as mg $CaCO_3$/L $= \{ N_{NaOH} \times Vml_{NaOH} - N_{H2SO4} \times Vml_{H2SO4} \} / Vml_{sample}$

2. Titratable acidity in food sample :

   % acidity = $\{N_{NaOH} \times Vml_{NaOH} \times \text{Eq.wt.(mg/Eq.)}_{Acid}\} / \text{Wt(mg)}_{sample}$

3. Salicylic acid, Benzoic acid, Organic acids

4. Sorenson formol titration : ex. protein hydrolysate ;

the free amino acid is treated with formaldehyde to form the methylimino or methylol derivative, reducing the basicity of the amino group so that the free carboxyl group may be titrated.

$$R—CH(NH_2)COOH + HCHO = R—CH(NHCH_2OH)COOH$$

$$\text{or } R—CH(N{=}CH_2)COOH$$

5. Kjeldahl nitrogen analysis

Applications (Strong acid titrated with strong base)

Ex : Titration of liberated acid by base

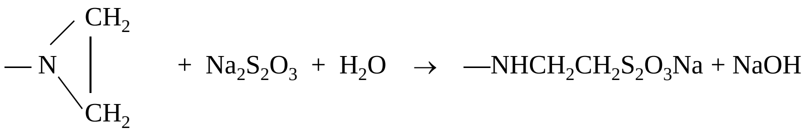
1) *Lemon oil* :

the aldehyde of the oil react with hydroxylammonium chloride to form the oxime, liberating free hydrochloric acid, which is titrated and the aldehyde content calculated as citral ;

$$RCH{=}O + HONH_3Cl \rightarrow RCH{=}NOH + HCl + H_2O$$

2) *Thiotepa* :

sodium thiosulfate reacts with each ethyleneimine group to liberate one equivalent of alkali, which is titrated with standard acid ;

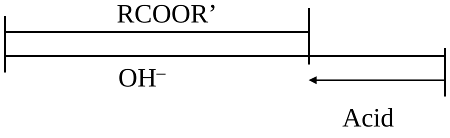


$$—N(CH_2CH_2) + Na_2S_2O_3 + H_2O \rightarrow —NHCH_2CH_2S_2O_3Na + NaOH$$

Applications (**Weak base titrated with strong acid**)

1) Alkaloid : morphine, codeine, cocaine, atropine, ephedrine
2) Calamine
3) Basicity
4) Esters ; acid-base back titration

saponification : $RCOOR' + OH^- \rightarrow RCOO^- + R'OH$



Opium Poppy (*Papaver somniferum*) , Wuhan Botanical Garden 052607 Rhowon

Kingdom: Plantae
Division: Magnoliophyta
Class: Magnoliopsida
Order: Ranunculales
Family: Papaveraceae
Genus: *Papaver*
Species: ***Papaver somniferum***

The first to process heroin was C.R. Wright, an English researcher who unwittingly synthesized heroin (diacetylmorphine) in 1874 when he boiled morphine and a common chemical, acetic anhydride, over a stove for several hours. The modern technique entails a complicated series of steps in a good laboratory.

"flower of joy"

The sap is extracted by slitting the pod vertically in parallel strokes with a special curved knife.

http://en.wikipedia.org/wiki/Opium_poppy

http://www.pbs.org/wgbh/pages/frontline/shows/heroin/transform/

The Sumerians called it Hul Gil, the 'flower of joy.'

양귀비 / 아편

Titration of Weak Base with Strong Acid

Comparison of Weak Acid/ Base with Strong Base/Acid

	Weak Acid with Strong Base	Weak Base with Strong Base
Titration reaction	$HA + OH^- \rightarrow H_2O + A^-$	$B + H_2O \rightarrow BH^+ + OH^-$
Initial	$[H^+] = \sqrt{K_a F}$	$[OH\text{-}] = \sqrt{K_b F} = 1.4 \times 10^{-3}$
Before the equivalence point $(0<V_a<V_e)$	$pH = pK_a + \log [A^-]/[HA]$	$pH = pK_b + \log[NH_4^+]/[NH_3]$
Equivalence point	$[OH^-] = \sqrt{K_b F'} = \sqrt{K_w F'/K_a}$ $F' = (F \times V_i)/(V_i + V_a)$	$[H^+] = \sqrt{K_a F'}$ $F' = (F \times V_i)/(V_i + V_a)$
After equivalence point $(V_a>V_e)$	$[OH^-] = F_{NaOH} \left\{ \frac{(V_a - V_e)}{(V_i + V_a)} \right\}$	$[H^+] = F_{HCl} \left\{ \frac{(V_a - V_e)}{(V_i + V_a)} \right\}$

The Determination of Organic functional Groups

Carboxylic acid group

Most carboxylic acids have dissociation constants that range between 10^{-4} and 10^{-6}. Carboxylic acids are not sufficiently soluble in water to permit direct titration in this medium. Where this problem exists, 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.

Sulfonic acid group

Sulfonic acids are generally strong acids and readily dissolve in water. Their titration with a base is therefore straightforward.

Amine group

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

In contrast, *aromatic amines* such as aniline and its derivatives are usually too weak for titration in aqueous medium ($K_b \approx 10^{-10}$). The same is true for cyclic amines, such as pyridine and its derivatives. Many saturated cyclic amines, such as piperidine, tend to resemble aliphatic amines in their acid-base behavior and thus can be titrated in aqueous media.

Many amines that are too weak to be titrated as bases in water are readily titrated in *non-aqueous solvents*, such as anhydrous acetic acid, which enhance their basicity.

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.

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.

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

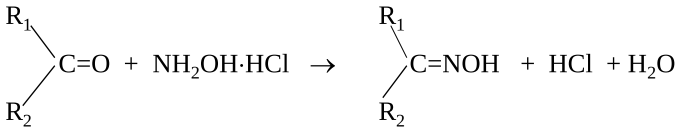
The *acetylation* is ordinarily carried out by mixing the sample with a carefully measured volume of acetic anhydride in pyridine. After heating, water is added to hydrolyze the unreacted anhydride :

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

The acetic acid is then titrated with a standard solution of alcoholic sodium or potassium hydroxide. A blank is carried through the analysis to establish the original amount of anhydride.

Carbonyl groups

Many *aldehydes* and *ketones* can be determined with a solution of *hydroxylamine hydrochloride*. The reaction, which produces an *oxime*, is



$$\overset{R_1}{\underset{R_2}{>}}C{=}O \ + \ NH_2OH\cdot HCl \ \rightarrow \ \overset{R_1}{\underset{R_2}{>}}C{=}NOH \ + \ HCl \ + H_2O$$

where may be an atom of hydrogen. The liberated HCl is titrated with base.

Here, the conditions necessary for quantitative reaction vary. Typically, 30 min suffices for aldhydes. Many ketones require refluxing with the reagents for 1 hr or more.