Chapter 13
Titrimetric Methods; Precipitation Titrimetry

Titration

- Titration
  - A procedure in which one substance (titrant) is carefully added to another (analyte) until complete reaction has occurred.
  - The quantity of titrant required for complete reaction tells how much analyte is present.

- Volumetric Analysis
  - A technique in which the volume of material needed to react with the analyte is measured

Titration Vocabulary

- Titrant
  - The substance added to the analyte in a titration (reagent solution)
- Analyte
  - The substance being analyzed
- Equivalence point
  - The point in a titration at which the quantity of titrant is exactly sufficient for stoichiometric reaction with the analyte.
Features of Titrations

- Simple, inexpensive, very accurate and precise if done correctly.
- An analytical tool involving fundamental chemistry.
- Complete reaction between the analyte and a known concentration of titrant.
- Calculation of the amount of the analyte is straightforward using consumed standard titrant solution.

Volumetric Procedures and Calculations

relate the moles of titrant to the moles of analyte

For 1:1 ratio reaction: \( \text{H}^+ + \text{OH}^- = \text{H}_2\text{O} \)

\[
\text{# moles titrant} = \text{# moles analyte} = (C \times V)_{\text{analyte}}
\]

For non 1:1 ratio reaction:

\[
\begin{align*}
5 \text{HOC}_2\text{O}_2\text{OH} + 2\text{MnO}_4^- + 6\text{H}^+ & \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \\
5 \text{moles} & \rightarrow 2 \text{moles} \\
5\text{Fe}^{3+} + \text{MnO}_4^- + \text{H}^+ & \rightarrow 5\text{Fe}^{2+} + 2\text{Mn}^{2+} + \text{H}_2\text{O} \\
5 \text{moles} & : 1 \text{mole}
\end{align*}
\]
Example - Unknown concentration of a strong acid titrated by a strong base.

- The reaction:
  \[ \text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaCl(aq)} \]
- Let's say that [HCl] is the unknown and the sample volume is 50.00 mL.
- Titrant: [NaOH] = 0.5000 M

We find that it takes 25.00 mL of NaOH to completely react with all of the HCl (i.e. neutralize), what is the concentration of [HCl] in the sample?

\[
\left[ \text{HCl} \right] \times 50.00 = \left[ 0.5000 \times 25.00 \right] \\
\left[ \text{HCl} \right] = \frac{25.00 \text{ mL} \times (0.5000 \text{ mol/L})_{\text{NaOH}}}{50.00 \text{ mL}_{\text{HCl}}} = 0.2500 \text{ M}
\]

The Equivalence Point

- Finding the equivalence point is the goal of the titration.
- If our unknown contains 0.250 moles of \( \text{CO}_3^{2-} \), and we are titrating with \( \text{H}^+ \), then the equivalence point is reached when 0.500 moles of \( \text{H}^+ \) is added.

\[
\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

1 mole : 2 mole
0.250 mole : \( x \)

\[
x = 0.500 \text{ mole}
\]

- End point
  - The point in a titration at which there is a sudden change in a physical property (e.g., indicator color, pH, conductivity, or absorbance).
  - Used as a measure of the equivalence point.
  - Usually occurs after a small excess of titrant had been added.
  - In most cases, the difference in the End Point and the Equivalence Point is insignificant and can be ignored.
- Indicator
  - A compound having a physical property (usually color) that changes abruptly near the equivalence point of a chemical reaction.
Indicators

- Colored titrant:
  - solution becomes colored at the endpoint

\[
5\text{HOC}_2\text{O}_5\text{OH} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\]

- Colored analyte:
  - solution becomes clear at the endpoint

- Indicator compound:
  - A compound that is sensitive (changes color) to the disappearance of the analyte, or appearance of excess titrant.

• Titration error
  - The difference between the observed end point and the true equivalence point in a titration.

• Blank titration
  - One in which a solution containing all reagents except analyte is titrated. The volume of titrant needed in the blank titration should be subtracted from the volume needed to titrate unknown.

Primary Standard

- A reagent that is pure and stable enough to be used directly after weighing, i.e., entire mass is considered to be pure reagent.

  1. High purity
  2. Stability toward air (O\textsubscript{2}, CO\textsubscript{2}, moisture…)
  3. Absence of hydrate water
  4. Available at moderate cost
  5. Soluble
  6. Large F.W. (why?)

Question: Can NaOH be used as a primary standard? Why?
Primary standards for bases.

• Potassium Hydrogen Phthalate (KHP)
  - Nonhygroscopic
  - High MW
  - Stable to drying
  - Inexpensive
  - $\text{HP} + \text{OH}^- \rightarrow \text{P}^2^- + \text{H}_2\text{O}$

• Other possibilities:
  - Benzoic Acid
  - Potassium Hydrogen Iodate $\text{KH(IO}_3\text{)}_2$

Primary Standards for acids

• $\text{NaHCO}_3$ – major disadvantage low MW 84.00 g/mol

• Others available such as $\text{Na}_2\text{CO}_3$.

• $\text{KHP} \rightarrow \text{NaOH} \rightarrow \text{HCl}$

• Standardization
  - The process whereby the concentration of a reagent is determined by reaction with a known quantity of a second reagent.

• Standard Solution
  - A solution whose composition is known by virtue of the way it was made from a reagent of known purity or by virtue of its reaction with a known quantity of a standard reagent.

• Direct Titration
  - One in which the analyte is treated with titrant, and the volume of titrant required for complete reaction is measured.
Back Titrations

- Back titrations are used when the reaction between an analyte and titrant are slow, or if a suitable indicator is not available.
  - Add excess titrant so that all analyte is reacted and a small amount of excess titrant is present.
  - Titrate the excess titrant with a second titrant back to the equivalence point.

Back Titration: Example

- Determine the carbonate content of limestone:
  \[ \text{CaCO}_3(s) + 2\text{H}^+ \xrightarrow{\text{heat}} \text{Ca}^{2+} + \text{CO}_2 \uparrow + \text{H}_2\text{O} \]
  - Add excess H\(^+\) and heat to drive off the CO\(_2\) from solution.
    - We end up with a solution containing H\(^+\) and Ca\(^{2+}\).
  - Titrate the excess H\(^+\) with NaOH back to the equivalence point.
    - fast reaction, available indicator.

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Back Titration: Example

Amount of H\(^+\) needed to reach the equivalence point = moles of H\(^+\) added – moles of OH\(^-\) added
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Titration Requirements

• Equilibrium constant must be large
  – reaction goes to completion.

• Must be a way to determine when the reaction has reached completion
  – through the use of an indicator.
  – by monitoring the concentration of one component.

Types of Titrations

• Acid-base
  – most common (Soda ash lab)
• Complex formation
  – (Water hardness lab)
• Precipitation
• Oxidation/reduction

Precipitation Titration
Precipitation Titration

- Titrate 50.00 mL of 0.0750 M Cl\(^-\) with 0.0500 M Ag\(^+\).
  \[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \]
  \[ K = \frac{1}{K_{sp}} = 5.6 \times 10^9 \]
- How many mL of Ag\(^+\) solution must be added to reach the equivalence point?

| Initial | 50.00 mL Cl\(_{\text{soln}}\) | 0.0750 mmol Cl\(_{\text{soln}}\) | mL Ag\(_{\text{soln}}\) | 0.0500 mmol Ag\(_{\text{soln}}\) | = 75.00 mL titrant |

- What are the concentrations of Ag\(^+\) and Cl\(^-\) in solution before reaching the equivalence point?
- Suppose 40.00 mL of titrant have been added.
  - Moles of Ag\(^+\) added:
    \[ \frac{40.00 \text{ mL titrant}}{1 \text{ mL titrant}} \times \frac{0.0500 \text{ mmol Ag}}{1 \text{ mL titrant}} = 2.000 \text{ mmol Ag}^+ \]
  - Moles Cl\(^-\) originally:
    \[ \frac{50.00 \text{ mL Cl}_{\text{soln}}}{1 \text{ mL Cl}_{\text{soln}}} \times \frac{0.0750 \text{ mmol Cl}}{1 \text{ mL Cl}_{\text{soln}}} = 3.750 \text{ mmol Cl}^- \]
  - Moles of Cl\(^-\) remaining in solution:
    \[ 3.750 - 2.000 = 1.750 \text{ mmol Cl}^- \]
    \[ \frac{1.750 \text{ mmol Cl}^-}{90.00 \text{ mL}} = 0.01944 \text{ M Cl}^- \]

- Moles of Ag\(^+\) in solution:
  - Use the equilibrium expression
    \[ [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \]

<table>
<thead>
<tr>
<th>[x]</th>
<th>Ag(^+)</th>
<th>Cl(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0</td>
<td>0.01944</td>
</tr>
<tr>
<td>Change</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>At Equilibrium</td>
<td>x</td>
<td>0.01944 +x</td>
</tr>
</tbody>
</table>

\[ [x](0.01944 + x) = 1.8 \times 10^{-10} \]

ignore \(+x\)

\[ [x] = \frac{1.8 \times 10^{-10}}{0.01944} = 9.3 \times 10^{-9} \text{ M Ag}^+ \]
• What are the concentrations of Ag⁺ and Cl⁻ at the equivalence point?
  - At the equivalence point there is no excess Cl⁻ or excess Ag⁺.
  - The concentrations of Cl⁻ and Ag⁺ are determined by the equilibrium.

\[
\text{[Ag⁺]}[\text{Cl⁻}] = 1.8 \times 10^{-10}
\]
\[
x^2 = 1.8 \times 10^{-10}
\]
\[
x = 1.3 \times 10^{-5} \text{ M Cl⁻ and Ag⁺}
\]

• What are the concentrations of Ag⁺ and Cl⁻ in solution after reaching the equivalence point?
• Suppose 85.00 mL of titrant have been added.
  - Excess moles of Ag⁺ added:
    \[
    \frac{10.00 \text{ mL titrant}}{1 \text{ mL titrant}} = 0.0500 \text{ mmol Ag⁺}
    \]
    \[
    \frac{0.5000 \text{ mmol Ag⁺}}{135.00 \text{ mL}} = 3.70 \times 10^{-3} \text{ M Ag⁺}
    \]
  - Cl⁻ in solution:
    \[
    [3.70 \times 10^{-3} + x] [x] = 1.8 \times 10^{-10}
    \]
    \[
    [x] = 1.8 \times 10^{-10} \text{ M Cl⁻}
    \]
The Titration Curve

As $p[x]$ goes down, $[x]$ goes up.

The equivalence point is where the slope of the curve is steepest (for a 1:1 rxn).

Effect of Dilution

As dilution increases, it becomes more difficult to identify the equivalence point.

Effect of $K$

The smaller the $K_{sp}$ for the dissociation reaction, the easier it will be to identify the equivalence point (larger $K$ of formation).
Indicators for Argentometric Titrations (Involving Ag⁺ ions)  
(Ag⁺ used as titrant or analyte)

- **Chemical**
  - Chromate Ion as indicating species → Mohr’s method
  - Adsorption Indicators (fluorescein) → Fajan’s (“Fay’yahns”) method
  - Fe(III) Ion → Volhard method

- **Sensors** – Potentiometric or amperometric
  - We will look at potentiometric sensors later.

Chromate Ion: The Mohr Method  
(Ag⁺ used as titrant for Cl⁻ analysis)

**Precipitation Type**
Ag₂CrO₄ precipitation in neutral pH solution (why?) is formed at the end point
Product is coloured

**Titration reaction:**
Ag⁺ + Cl⁻ ⇌ AgCl(s) [white]

**Indication reaction:**
2Ag⁺ + CrO₄²⁻ ⇌ Ag₂CrO₄(s) [red]
Adsorption indicators: Fajans Method
(Ag⁺ used as titrant for Cl⁻ analysis)
A red dye attaches to the silver salt on the surface of the analyte precipitate particle.
This happens only when the silver ion Ag⁺ is in excess, i.e., just after the equivalence point.

Fluorescein (yellow-green in soln)
↓ AgCl(s)/Ag⁺ (white)
AgCl(s)/(Ag⁺-Fluorescein)adsorption (red)

Eye Examination by an eye doctor (optometrist)

Fluorescent images obtained after the modification of (a) Au(111)/3- MPA/avidin and (b) Au(111)/mixed thiol SAM/avidin with fluorescein biotin species. The exposure times used were 3 and 30 s, respectively. The specimens were excited at 490 nm and monitored at 520 nm.

Fe(III) Ion: Volhard Method
(Ag⁺ as analyte and SCN⁻ as titrant)

- Chemical method for silver analyses with standard thiocyanate, CNS⁻, as titrant, and Fe (III) is the indicator as it forms a red complex ion with CNS⁻, FeCNS²⁺ (red) [in acidic condition, why?]

Titration reaction:

Ag⁺ + SCN⁻ ⇄ AgSCN(s) [white]

Indication reaction:

SCN⁻ + Fe³⁺ ⇄ FeSCN²⁺ (red)

The method can be adapted to chloride analyses—back titrations.

Ag⁺ (St'd, Excess) + Cl⁻ (Analyte) → AgCl(s) [white]

SCN⁻ (titrant) + Ag⁺ (left) ⇄ AgSCN(s) [white]

Fe³⁺ + SCN⁻ ⇄ FeSCN²⁺ (red)

Applications of Standard AgNO₃ Solutions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Precipitate Formed</th>
<th>Method</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>AgCl(s)</td>
<td>Volhard</td>
<td>Removal of silver salt not required</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Ag₂SO₄(s)</td>
<td>Volhard</td>
<td>Titration of excess Ag⁺ following reaction</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>Ag₂CO₃(s)</td>
<td>Volhard</td>
<td>Precipitation of K⁺ with excess amount of AgNO₃, addition of excess Ag⁺, making Ag₂CO₃(s) red in litmus solution</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>AgNO₃(s)</td>
<td>Standard</td>
<td>Direct titration with Ag⁺</td>
</tr>
<tr>
<td>SO₄²⁻, H₂SO₄</td>
<td>Ag₂SO₄(s)</td>
<td>electrometric</td>
<td>Precipitation in H₂SO₄, titration of excess Ag⁺</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>Ag₃PO₄(s)</td>
<td>Volhard</td>
<td>Precipitation in PO₄₃⁻ solution, addition of excess Ag⁺, back titration of excess Ag⁺</td>
</tr>
</tbody>
</table>