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: $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$

$$\text{# moles titrant} = \text{# moles analyte}$$

$$\text{# moles}_{\text{titrant}} = (C \cdot V)_{\text{titrant}}$$

$$\text{# moles}_{\text{analyte}} = (C \cdot V)_{\text{analyte}}$$

For non 1:1 ratio reaction:

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

5 moles : 2 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 moles : 1 mole
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?

\[
\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl}
\]

\[
[C_{\text{HCl}}] \times 50.00 = [0.5000 \times 25.00]
\]

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

The Equivalence Point vs End 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 H\(^+\), then the equivalence point is reached when 0.500 moles of H\(^+\) is added.

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

\[
1 \text{ mole} : 2 \text{ mole}
\]

\[
0.250 \text{ mole} : x
\]

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

- 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
  
- 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.

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

• 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.
  
- High purity
  - Stability toward air (O₂, CO₂, moisture...)
  - Absence of hydrate water (in most cases)
  - Available at moderate cost
  - Soluble
  - Large F.W. (why?)

Question: Can NaOH be used as a primary standard? Why?
(Hint: hygroscopic substance/reaction with components in air?)
Primary standards for bases.

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

- Other possibilities:
  - Benzoic Acid
  - Potassium Hydrogen Iodate KH(IO$_3$)$_2$

Primary Standards for acids

- NaHCO$_3$ – major disadvantage low MW 84.00 g/mol
- Others available such as Na$_2$CO$_3$.
- KHP $\rightarrow$ NaOH $\rightarrow$ 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.

Back Titration: Example

Amount of H\(^+\) needed to reach the equivalence point = moles of H\(^+\) added – moles of OH\(^-\) added
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 50.00mL of 0.0750M Cl\(^-\) with 0.0500M 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?

<table>
<thead>
<tr>
<th>Initial</th>
<th>mL soln</th>
<th>mmol Cl</th>
<th>mmol Ag</th>
<th>mL Ag(^+) soln</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.00</td>
<td>0.0750</td>
<td>0.0750</td>
<td>0.0000</td>
<td>75.00</td>
</tr>
</tbody>
</table>

- 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}} = 2.00 \text{ mmol Ag}^+ 
    
  - Moles Cl\(^-\) originally:
    \[
    \frac{50.00 \text{ mL soln}}{1 \text{ mL soln}} \times \frac{0.0750 \text{ mmol CI}}{1 \text{ mL soln}} = 3.75 \text{ mmol CI} 
    
  - Moles of Cl\(^-\) remaining in solution:
    \[
    3.75 - 2.00 = 1.75 \text{ mmol CI} 
    
  - Moles of Ag\(^+\) in solution:
    \[
    \frac{1.75 \text{ mmol CI}}{90.00 \text{ mL}} = 0.01944 \text{ M CI} 
    
- Use the equilibrium expression

\[ [\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10} \]

<table>
<thead>
<tr>
<th></th>
<th>[\text{Ag}^+]</th>
<th>[\text{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>

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

\[ [x] = \frac{1.8 \times 10^{-10}}{0.01944} = 9.3 \times 10^{-9} \text{ M Ag}^+ \]
10/12/2021

• 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.

<table>
<thead>
<tr>
<th></th>
<th>Ag⁺</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

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

• 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:
      \[
      \frac{10.00 \text{ mL titrant}}{1 \text{ mL titrant}} \times 0.0500 \text{ mmol Ag⁺} = 0.5000 \text{ mmol Ag⁺}
      \]
    – Cl⁻ in solution:
      \[
      \frac{3.704 \times 10^{-3}}{135.00 \text{ mL}} = 2.74 \times 10^{-5} \text{ M Cl⁻}
      \]
      \[
      [3.704 \times 10^{-3} + x][x] = 1.8 \times 10^{-10}
      \]
      ignore +x
      \[
      x = 1.8 \times 10^{-5}
      \]
    – Ag⁺:
      \[
      \frac{3.704 \times 10^{-5} \times 1.8 \times 10^{-5}}{2.74 \times 10^{-5}} = 4.9 \times 10^{-4} \text{ M Ag⁺}
      \]
The Titration Curve

Before the equivalence point

After the equivalence point

At the equivalence point

As \( p[x] \) goes down, \([x]\) goes up.

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

Effect of Dilution

50mL of 0.075M Cl⁻

500mL of 0.0075M Cl⁻

5000mL of 0.00075M Cl⁻

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

Titrant is 0.05M Ag⁺ for all cases

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).

\( K_{sp} = 8.3 \times 10^{-17}; \) I⁻

\( K_{sp} = 5.0 \times 10^{-13}; \) Br⁻

\( K_{sp} = 1.8 \times 10^{-10}; \) Cl⁻
Titrating Mixtures

If the difference between K_{sp} for the 2 components are different enough, then titrating a mixture is no problem.

Indicators for Argentometric Titrations (Involving Ag^{+} ions)  
(Ag^{+} used as titrant or analyte)

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

Ag_{2}CrO_{4} precipitation in neutral pH solution (why?) is formed at the end point

Product is coloured

Titration reaction:
Ag^{+} + Cl^{-} \rightleftharpoons AgCl(s) [white]

Indication reaction:
2Ag^{+} + CrO_{4}^{2-} \rightleftharpoons Ag_{2}CrO_{4}(s) [red]
**Why neutral pH is required?**

\[
\text{K}_2\text{Cr}_2\text{O}_7 \Rightarrow \text{Potassium Dichromate} \\
\text{K}_2\text{CrO}_4 \Rightarrow \text{Potassium Chromate}
\]

**Partial predominance diagram**

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**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)

\[\downarrow \text{AgCl(s)/Ag⁺ (white)}\]

\[\text{AgCl(s)/(Ag⁺-Fluorescein)}_{\text{adsorption (red)}}\]

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Eye Examination by an eye doctor (optometrist)

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)

Youtube: Chemical Cut
Chapter 13 Summary

- Determine analyte by volumetric titrations
- Advantages and disadvantages of volumetric titrations
- Primary and secondary standards, standard solution and standardization
- Back-titrations
- Titration errors
- Endpoint vs equivalence point
- Calculations of titrations
- Precipitation titrations (Argentometry with various indicators)