Gravimetric Determination of Calcium

Definition of Gravimetric Analysis (GA)

Three important features of GA

Experimental considerations

Homogeneous Precipitation
Gravimetric Analysis

• Definition of Gravimetric Analysis:
  
a method of quantitative chemical analysis in which the species of interests is converted into a substance (of known composition) that can be separated from the sample and weighed.
  
e.g., \[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow \]

• Application of the method:
  
  • Theodore W. Richard group (Harvard University) determined atomic weights of 55 known elements using gravimetric analysis
  
  • In 1914 Theodore W. Richard won the Nobel Prize in Chemistry for determination of the atomic weights of Ag, Cl, and N.

(1868 - 1928)
Three important features of Gravimetric Analysis

For gravimetric analysis method to work:

- There must be a **quantitative** conversion of the original species to an **isolatable** compound;
- The precipitate must be **pure** or of **known purity**;
- The precipitate must be easily **handled** and **weighed**.
Gravimetric Determination of Calcium

\[ \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \downarrow \]

Is the reaction quantitative?

Is \(\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}\) isolatable?

Is \(\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}\) pure or of known purity?

Is \(\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}\) easily handled and weighed?
Is the reaction quantitative?

\[ \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \downarrow \]

- Yes.
- All \( \text{Ca}^{2+} \) ions will be converted to \( \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \).
- The molar ratio of \( \text{Ca}^{2+} \) to product is 1:1.
Is CaC$_2$O$_4$ • H$_2$O isolatable?

Ca$^{2+}$ + C$_2$O$_4^{2-}$ + H$_2$O → CaC$_2$O$_4$ • H$_2$O ↓

- Yes.
- K$_{sp}$ = 2.3 x 10$^{-9}$ (very, very small!)*
- Crystals are white, powdery, and can be filtered into a crucible.

K$_{sp}$: Solubility product, is a measure of how soluble a solid is in water at a given temperature. The smaller the K$_{sp}$ is, the less soluble it is.
(see S. S. Zumdahl, Chemical Principles, pp328-334)
Is CaC$_2$O$_4$ • H$_2$O pure or of known purity?

$\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4$ • H$_2$O ↓

If the CaC$_2$O$_4$ • H$_2$O crystals form quickly,

- the crystals will be small. $\Rightarrow$ CaC$_2$O$_4$ • H$_2$O will be unstable
- giving CaC$_2$O$_4$ and H$_2$O $\Rightarrow$ mixture of CaC$_2$O$_4$ • H$_2$O and CaC$_2$O$_4$
- co-precipitation will occur (e.g., (NH$_4$)$_2$C$_2$O$_4$ (s)) $\Rightarrow$ reduced purity.

Therefore, the key to the success of the experiment is to form the crystals \textit{slowly}!

But how to form the crystals slowly???
Homogeneous Precipitation

To generate one of the reactants (e.g., C$_2$O$_4^{2-}$) homogeneously at a rate comparable to the rate of crystal growth.

\[
\begin{align*}
\text{pH}>1 & \\
\text{H}_2\text{C}_2\text{O}_4 & \to \text{HC}_2\text{O}_4^- \\
\downarrow \text{pH} & \sim 6
\end{align*}
\]

\[
\begin{align*}
\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} & \to \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \\
\downarrow
\end{align*}
\]

• Control the pH of the starting solution to be \( \leq 1 \)
• The pH of the solution is then raised slowly by heating the solution containing urea to produce ammonia.

\[
\begin{align*}
(\text{NH}_2\text{H}_2\text{CO}) + \text{H}_2\text{O} & \to \text{CO}_2 + 2\text{NH}_3 \\
\text{NH}_3 + \text{H}^+ & \to \text{NH}_4^+
\end{align*}
\]

• The pH change will be monitored by adding the methyl red indicator:

| Red (pH<6) | pH ~ 6 | Yellow (pH>6) |
Is CaC$_2$O$_4$ • H$_2$O easily handled and weighed?

\[ \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \downarrow \]

Yes, but only when CaC$_2$O$_4$ • H$_2$O is

- dried at an appropriate temperature (100-105 °C) because

  \[ \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 \rightarrow \text{CaO} \]

- handled with appropriate use of desiccators because CaC$_2$O$_4$ • H$_2$O is moderately hygroscopic (it will take on water from air over time).
Review and Preview

• Review today’s lecture:
  • Read Lab 3 (pages 23-35 of Lab Manual)

• Preview next lecture (Data Analysis)
  • Read 169-178