

Titrations

- Titration is an analytical method in which the concentration of an analyte is determined by adding a precisely measured volume of titrant of known concentration and observing through some means when an equivalence point is reached

At equivalence point:

$$C_{\text{unk}} V_{\text{unk}} = C_{\text{titrant}} V_{\text{titrant}}$$



Titrations

- Titrations are usually used for one of four types of reactions:

- Acid-base
- Oxidation-reduction
- Complex formation
- Precipitation



Titrations

- Equivalence point vs End point
- The equivalence point is that point in the titration when stoichiometric amounts of titrant and analyte have been added
- The end point is reached when we can observe a change in the solution
- The end point will be reached beyond the equivalence point



Titrations

Blank titration

- In a blank titration, analyte is not used
- The amount of titrant needed to reach the end point is measured
- This amount indicates the volume of titrant necessary to observe the physical change at the end point
- This volume is subtracted from the volume of titrant used in determination of the unknown



Titrations

- You are probably most familiar with titrations performed using a colored indicator to identify the end point
 - An indicator is a compound, HIn, whose color depends on the pH of its environment

$$\text{HIn} \leftrightarrow \text{H}^+ + \text{In}^-$$

color1 color2
 - Under acid conditions, the form is HIn; under basic conditions it is In⁻



Titrations

- The pH at which the indicator changes color depends on its pK_a



Titration

- There are other methods to determine the end point of a titration:
 - Spectrophotometric detection
 - Precipitation reactions
 - Potentiometric detection



Titration

Spectrophotometric detection

- Beer's Law:

$$A = \epsilon b[X]$$

A = absorbance (signal)

ϵ = molar absorptivity

b = absorption path length

$[X]$ = molar concentration



Titration

Spectrophotometric detection

- If the analyte absorbs in the UV/vis spectral region, a spectrometer can be used to observe the progress of the titration
 - Measure absorbance vs titrant added
 - Correct absorbance measurements for change in volume
 - Plot corrected absorbance vs titrant added

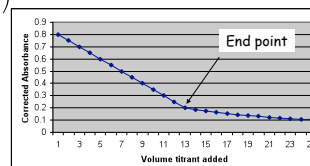


Titration

Spectrophotometric detection

Corrected absorbance—adjusts for dilution of solution

$$A_{\text{corr}} = \left(\frac{V_{\text{tot}}}{V_{\text{init}}} \right) A_{\text{obs}}$$

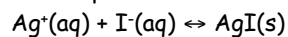


Titration

Precipitation titration

- If the K_{sp} of a compound is small, we can use precipitation as a means to determine the analyte concentration

For example:



$$K_{\text{sp}} = 8.3 \times 10^{-17}$$

Add Ag^+ to determine $[\text{I}^-]$



Titration

Precipitation titration

We can add Ag^+ to determine $[\text{I}^-]$ —because the K_{sp} is small, as long as I^- is present in solution, any added Ag^+ will precipitate as AgI

When $[\text{Ag}^+]$ increases, we have reached the end point of the titration

Monitor Ag^+ using potentiometric method



Titrations

Precipitation Titrations

Before equivalence point:

$$pAg = -\log_{10}[Ag^+]$$

$$[Ag^+] = \frac{K_{sp}}{[I^-]}$$

$$[I^-] = \frac{\text{moles } I^-(\text{init}) - \text{moles } Ag^+(\text{added})}{V_{\text{tot}}}$$



Titrations

Precipitation Titrations

At equivalence point:

$$[Ag^+][I^-] = K_{sp} = 8.3 \times 10^{-17}$$

$$[I^-] = [Ag^+] = (8.3 \times 10^{-17})^{1/2} \\ = 9.1 \times 10^{-9} \text{ M}$$

$$pAg = 8.04$$



Titrations

Precipitation Titrations

After equivalence point:

$$[Ag^+] = \frac{\text{moles } Ag^+ \text{ added} - \text{moles } I^-}{V_{\text{tot}}}$$



Titration Curve

Titration of I^- with Ag^+ to form AgI precipitate

