Titrations

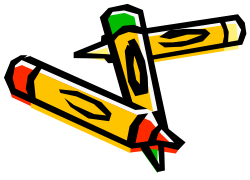
- Titration is an analytical method in which the concentration of an analyte is determined by adding a precisely measured volume of titrant of known concentration and observing through some means when an equivalence point is reached

At equivalence point:

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

Titrations

- Titrations are usually used for one of four types of reactions:
  - Acid-base
  - Oxidation-reduction
  - Complex formation
  - Precipitation



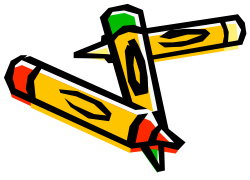
Titrations

- 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

<u>Blank titration</u>

- 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

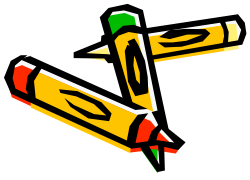
- You are probably most familiar with titrations performed using a colored indicator to identify the end point
  - An indicator is a compound, HIn, whose color depends on the pH of its environment

    $HIn \leftrightarrow H^+ + In^-$

    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



Titrations

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

Titrations

<u>Spectrophotometric detection</u>

- Beer's Law:

  $A = \varepsilon b[X]$

  - A = absorbance (signal)
  - ε = molar absorptivity
  - b = absorption path length
  - [X] = molar concentration

Titrations

Spectrophotometric detection

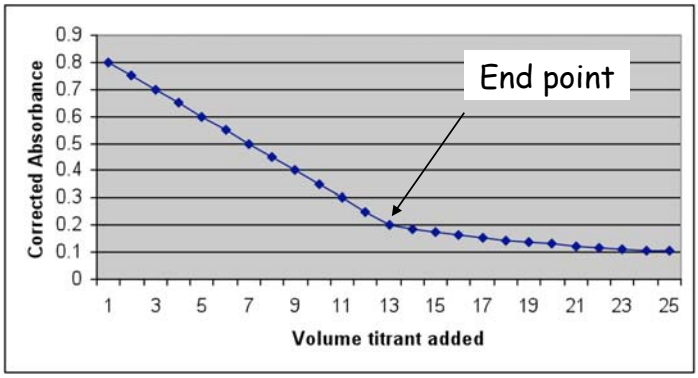
- If the analyte absorbs in the UV/vis spectral region, a spectrometer can be used to observe the progress of the titration
  - Measure absorbance *vs* titrant added
  - Correct absorbance measurements for change in volume
  - Plot corrected absorbance *vs* titrant added

Titrations

Spectrophotometric detection

Corrected absorbance—adjusts for dilution of solution

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



Titrations

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:

$Ag^+(aq) + I^-(aq) \leftrightarrow AgI(s)$

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

Add Ag^+ to determine $[I^-]$

Titrations

Precipitation titration

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

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

Monitor Ag^+ using potentiometric method

Titrations

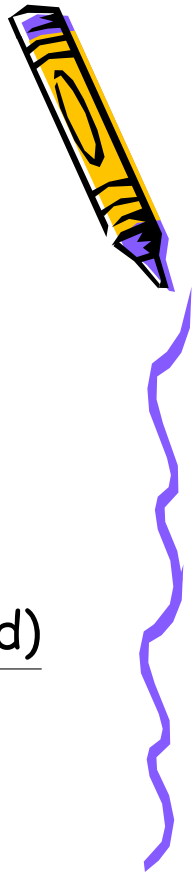
Precipitation Titrations

Before equivalence point:

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

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

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



Titrations

Precipitation Titrations

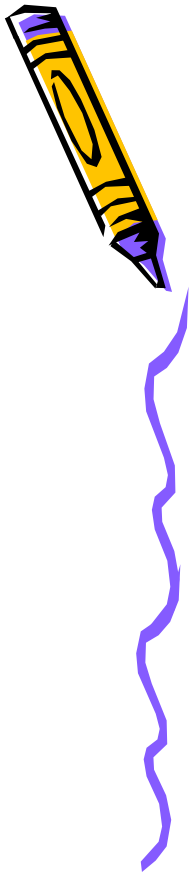
At equivalence point:

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

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

$= 9.1 \times 10^{-9}$ M

$pAg = 8.04$



Titrations

Precipitation Titrations

After equivalence point:

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

Titration Curve