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

Titrations

Consider the titration reaction:

$\alpha\ A + \beta\ T \rightarrow$ products

where A is the analyte and T is the titrant. At equivalence point:

$$\frac{1}{\alpha} C_A V_A = \frac{1}{\beta} C_T V_T$$

Rearranging gives

$$C_A = \frac{\alpha}{\beta} \frac{C_T V_T}{V_A}$$

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
- If properly designed, 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

Indicator	color 1	pH range	color 2
Thymol blue (1st trans)	red	1.2–2.8	yellow
Thymol blue (2nd trans)	yellow	8.0–9.6	blue
Bromophenol blue	yellow	3.0–4.6	purple
Methyl orange	red	3.1–4.4	orange
Bromocresol green	yellow	3.8–5.4	blue
Methyl red	red	4.4–6.2	yellow
Bromothymol blue	yellow	6.0–7.6	blue
Phenol red	yellow	6.4–8.0	red
Cresol red	yellow	7.2–8.8	red-purple
Phenolphthalein	colorless	8.3–10.0	fuchsia
Thymolphthalein	colorless	9.3–10.5	blue

Titrations

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

Titrations

Spectrophotometric detection

- Beer's Law:

$A = \varepsilon b[X]$

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

Titrations

Spectrophotometric detection

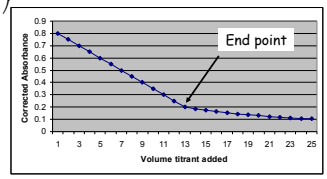
- If the analyte absorbs in the UV/vis spectral region, a spectrometer can be used to observe the progress of the titration
  - Measure absorbance *vs* titrant added
  - Correct absorbance measurements for change in volume
  - Plot corrected absorbance *vs* titrant added

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