

3/8/13 MAC Notes Titration Cont'd

Acid/Base titrations : Determination of the equivalence point is characterized by a pH level that is a function of the acid/base strengths and concentrations of the analyte & titrants.

Strong Acid + Strong Base = neutral (7)

Strong Acid + weak base = still slightly Acidic

weak Acid + Strong base = still slightly Basic

$$M_A V_A = M_B V_B$$

if acid is in excess

$$[H^+] = \frac{\text{moles } H^+}{\text{total volume}} = \frac{M_A V_A - M_B V_B}{V_A + V_B}$$

if base is in excess

$$[OH^-] = \frac{\text{moles } OH^-}{\text{total volume}} = \frac{M_B V_B - M_A V_A}{V_A + V_B}$$

The end Point can be found by:

1. Indicator
2. pH probe
3. $\Delta \text{temp.}$ (thermometric)

Standardizing Titrant: Standardization is accomplished by titrating a known amount of acid or base standard.

Common Acid Standards: HCl, HClO₄ and H₂SO₄

Common Base Standard: NaOH

Metal-Ligand Complexation Reaction: (aka: Complexation Titration)

A titration in which the reaction between the analyte & the titrant form a metal-ligand complex.

A ligand - a molecule with an unshared pair of electrons that attract a metal ion.

$$\text{Formation Constant} = K_f = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\text{Dissociation Constant} = K_d = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

Common titrant (ligand) = EDTA (ethylene diamine tetraacetic acid)
 an amino carboxylic acid
 a zwitter ion

Forms strong 1:1 complexes with many metal ions.

It has 6 (six) bonding sites: 2 amino bond sites and
 4 acid bonding sites.

The equivalence point happens when the concentration of the metal ion and the ligand are stoichiometrically equal.^① This may be found by locating the inflection point on a titration curve.

- ② Visual indicator of the endpoint is a metallocromatic (organic dye) solution that yields a color change when it goes from complexed to uncomplexed. The ligand used must have a higher activity so that it can release the metal from the dye and bind with it. Many of the metallocromatic indicators are pH sensitive and reaction conditions must be adjusted.
- ③ The equivalence point may also be determined by a change in absorbance.

Redox Reaction Titrations:

a titration in which the reaction between the analyte + titrant is a redox reaction.

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Common oxidizing titrants: $\text{MnO}_4^- + \text{Cr}_2\text{O}_7^{2-}$

Common reducing titrants: $\text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-}$

For a redox titration it is common to monitor the electrochemical potential (Nernst Equation). The Nernst equation relates the voltage of a

cell (E) to the activities of the reactants + products.

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

where:
 F = faraday constant
 E° = cell voltage when activities are in unity
 Q = reaction quotient
 R = gas laws constant
 T = temp

A matrix dependent formal potential is used - that is the potential of a redox reaction for a specific set of solution conditions - such as pH and ionic composition.

Precipitation Titration: a titration reaction between the analyte + titrant that forms a precipitant.

The titration curve can be developed as a change in either the analyte or titrants concentration as a function of the titrant.

- End point can be determined using visual indicators or potentiometers.
- Visual indicators work to indicate an excess of either analyte or titrant.
- potentiometers are ion-selective electrodes that measure change in concentration