COMPLEXATION AND PRECIPITATION TITRATIONS

I. Complex Formation Titrations

A. The most commonly used chelon (or titrant) used in metal ion titrations is EDTA (ethylenediaminetetracetic acid).

B. EDTA is hexadentate, donating one electron pair from each of the two amine group and one electron pair from each of the four carboxylates to the bound metal ion.

C. EDTA forms a "cage" around metal ions, like a spider grasping a fly.

D. Note that ***only the fully ionized, -4-charged anion binds to metal ions***:

E. EDTA is a tetraprotic acid. If H_4Y = EDTA, then the four ionization are:

$H_4Y + H_2O \Leftrightarrow H_3Y^- + H_3O^+$	$K_1 = 1.02 \times 10^{-2}$
$H_3Y^- + H_2O \Leftrightarrow H_2Y^{2-} + H_3O^+$	$K_2 = 2.14 \times 10^{-3}$
$H_2Y^{2-} + H_2O \Leftrightarrow HY^{3-} + H_3O^+$	$K_3 = 6.92 \times 10^{-7}$
$HY^{3-} + H_2O \Leftrightarrow Y^{4-} + H_3O^+$	$K_4 = 5.50 \times 10^{-11}$

1. Between pH 3-6, H_2Y^{2-} predominates.

2. Between pH 7-9, HY^{3-} predominates.

3. At pH greater than 10, Y^{4-} predominates; thus titrations are routinely done in buffered solutions near or above pH 10.

F. The Y^{4-}- metal ion equilibrium is given by:

$$M^{n+} + Y^{4-} \Leftrightarrow MY^{(n-4)} \qquad K_{MY} = \frac{[MY^{(n-4)}]}{[M^{n+}][Y^{4-}]}$$

G. Standard solutions of EDTA are usually prepared by dissolving the $Na_2H_2Y \cdot 2H_2O$ in a volumetric flask. (Note: Most $Na_2H_2Y \cdot 2H_2O$ at normal, atmospheric conditions comes with 0.3% excess water in the crystal. The excess water must be taken into account when preparing standard solutions.)

H. Titrations curves with EDTA consist of a plot of pM versus volume of EDTA added.

1. The shapes are similar to the sigmoidal titrations of acids and bases discussed previously.
2. The curves are "easily" calculated by dividing the curve up into domains:

a. The pM before equivalence.
b. The pM at equivalence.
c. The pM after equivalence.

3. The calculations are only complicated by the need to consider ionization state of H_4Y.

II. Model Titration System: 50.00 mL 0.00500 M Ca^{2+} titrated with 0.0100 M EDTA, buffered at pH 10.0.

A. The pM before equivalence:

1. No EDTA added: pM = -log([Ca^{2+}]) = -log(0.00500) = 2.3

2. EDTA added, but before equivalence: (Assume 10.00 mL EDTA solution has been added; all other volumes in the domain would be calculated the same way).

$$Ca^{2+} + Y^{4-} \Leftrightarrow CaY^{2-}$$

a. The [Ca^{2+}] in solution comes from the untitrated Ca^{2+} and the Ca^{2+} from the back dissociation of the CaY^{2-} complexes.

b. Since the formation constant for the CaY^{2-} complex is so large, the Ca^{2+} from back dissociation is assumed to be negligible.

$$[Ca^{2+}] = \frac{\#\ moles\ Ca\ originally - \#\ moles\ EDTA\ added}{total\ volume} =$$

$$= \frac{(50mL)(0.005M) - (10mL)(0.01M)}{50 + 10} = 2.5 \cdot 10^{-3} M$$

B. At equivalence: All the Ca^{2+} is titrated to CaY^{2-}

1. The #moles Ca^{2+} initially = # moles Y^{4-} added.

2. All the free Ca^{2+} in solution comes from back dissociation of CaY^{2-} and must be calculated from the amount of CaY^{2-} in solution:

$$[CaY^{2-}] = \frac{\#\ moles\ Ca^{2+}\ initially}{total\ volume} = \frac{(50mL)(0.005M)}{50mL + 25mL} = 3.33 \cdot 10^{-3} M$$

Substituting into the formation constant expression:

$$K_{CaY^{2-}} = \frac{[CaY^{2-}]}{[Ca^{2+}][Y^{4-}]} = \frac{[CaY^{2-}]}{[Ca^{2+}][\alpha_4 C_{EDTA}]}$$

where C_{EDTA} is the total concentration of ***all*** EDTA species.

Rearranging,

$$\alpha_4 K_{CaY^{2-}} = \frac{[CaY^{2-}]}{[Ca^{2+}][C_{EDTA}]}$$

3. $\alpha_4 K_{CaY2-}$ is called a conditional formation constant, since it is pH-dependent.

3. Values for α_4 can be looked up in tables for the various pH's. (At pH 10, α_4 = 0.35; K_{CaY2-} = 5.0 x 10^{+10}). Substituting into the expressions above:

$$(0.35) \cdot (5.0 \cdot 10^{+10}) = \frac{[3.33 \cdot 10^{-3} - x]}{[x][x]} \quad \Rightarrow \quad x = [Ca^{2+}] = 4.36 \cdot 10^{-7}$$

C. Post equivalence: (Assume 35.00 mL of EDTA solution added)

1. All the calcium ion is complexed with EDTA.

2. The concentration of CaY^{2-} and the excess, free EDTA is calculated and substituted into the conditional formation constant expression to solve for the $[Ca^{2+}]$ which can only come from back dissociation.

$$[CaY^{2-}] = \frac{\#\, moles\ Ca^{2+}\ initially}{total\ volume} = \frac{(50mL)(0.005M)}{50mL + 35mL} = 2.94 \cdot 10^{-3} M$$

$$C_{EDTA} = \frac{(35mL)(0.01M) - (50mL)(0.005M)}{50mL + 35mL} = 1.18 \cdot 10^{-3} M$$

Substituting into the conditional formation constant expression:

$$5 \cdot 10^{+10} = \frac{[2.94 \cdot 10^{-3}]}{[Ca^{2+}][(0.35)(1.18 \cdot 10^{-3})]} \quad \Rightarrow \quad 1.42 \cdot 10^{-10}$$

3. Other post-equivalence points are calculated in the same fashion.

III. Properties of EDTA Titrations

A. Larger formation constants lead to larger transitions in pM at equivalence.

B. Alkaline pH leads to a larger transition in pM at equivalence.

C. Sometimes other complexing agents must be added to the titration to prevent the precipitation of metal hydroxides at the alkaline pH.

IV. Indicators for EDTA Titrations

A. Over 200 organic compounds form colored chelates with ions in a pM range that is unique to the cation and the dye selected.

B. To be useful, the dye-metal chelates usually will be visible at 10^{-6}-10^{-7} M concentration.

C. The dye is selected such that the color change corresponds to the pM at equivalence.

D. Examples of commonly used indicator dyes include...

1. Eriochrome Black T

a. Eriochrome Black T is an azo dye, best used with Mg^{2+} and Zn^{2+} titrations.
b. Excess EDTA causes a red to blue color change at near neutral pH.
c. Eriochrome Black solutions decompose easily.

2. Calmagite.

a. Similar in structure to Eriochrome Black in structure, but does not decompose as easily.
b. Similar color behavior to Eriochrome Black.
c. The is probably the most commonly used indicator.