Titrations in General

I. Titrations: what's the point?

II. Important terms and concepts:

Titrant:

How do you choose a titrant?

Equivalence Point:

End Point:

Indicator:

- Why don't (or can't) we typically stop a titration at the equivalence point?
- How can we correct for errors introduced by not catching the equivalence point?
- Why is standardization important?

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Example Titration Scenarios

1. Acid/Base: (Colored indicator, pH meter)

Kjeldahl Nitrogen Analysis

Digestion: $\text{organic C, H, N} \xrightarrow[H_2SO_4]{\text{boiling}} NH_4^+ + CO_2 + H_2O$

Neutralization: $NH_4^+ + OH^- \rightarrow NH_3(g) + H_2O$

Distillation into standardized HCl: $NH_3 + H^+ \rightarrow NH_4^+$

Titration of excess HCl: $H^+ + OH^- \rightarrow H_2O$

2. Precipitation: (Potentiometric, indicator, Volhard, Fajans, turbidity)

3. Spectrophotometric: (Use Beer's Law: Conc. $\propto$ Absorbance.)

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What happens to the system during the course of the titration?

OR: How do we determine concentrations of species in the system as the titration progresses?

- Three scenarios to think about. Ask yourself: What is going to be the driving force in determining concentrations in each scenario?

Generic system :

$A + B \rightarrow C + D$ (KHP + NaOH $\rightarrow$ NaKP + H_2O or $Ag^+ + I^- \rightarrow AgI$)

$A = C$ (KHP = $H^+ + KP^-$ or AgI = $Ag^+ + I^-$)

1. Prior to the equivalence point:
2. At the equivalence point:
3. After the equivalence point:

Titration Curves: Visualizing changes in the system.

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Acid-Base Titrations

What determines pH in the following titration situations?

	Titration Type		
	Strong Acid w/ Strong Base	**Weak Acid w/ Strong Base**	**Weak Base w/ Strong Acid**
Initial			
Before Equivalence Point			
At Equivalence Point			
After Equivalence Point			

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Diprotic Acid (Base) Titrations

We'll use a diprotic acid as an example (H_2A)

Generalizations work as long as K_a's are *different enough*

Six regions to consider:

1. Initially, pH is determined by:
2. Before the first equivalence point, pH is determined by:
3. At the first equivalence point, pH is determined by:
4. Before the second equivalence point, pH is determined by:
5. At the second equivalence point, pH is determined by:
6. After the second equivalence point, pH is determined by:

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Equivalence Point Determination

Three Common Approaches

1. Derivatives of titration curve
2. Gran Plot
3. Indicators

Derivatives of titration curve:

A. First derivative: $\frac{dpH}{dV}$ examines the slope of the titration curve

Endpoint is where the slope is:

B. Second Derivative: $\frac{d^2pH}{dV^2} = \frac{d(dpH)}{d(dV)}$ looks at the rate of change of the slope.

Endpoint is where the 2nd derivative is:

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Equivalence Point Determination

Gran Plot:

It is difficult to get good data near the endpoint in a titration, why?

Gran plot uses data obtained prior to the endpoint to determine V_e.

- Treatment assumes that one mol of strong base will consume 1 mole of analyte acid.
- When is this assumption good?

Gran plot equation: $V_b 10^{-pH} = \frac{\gamma_{HA}}{\gamma_{A-}} K_a (V_e - V_b)$

Plot $V_b 10^{-pH}$ vs V_b, where V_b is the volume of base added

Slope is $-\frac{\gamma_{HA}}{\gamma_{A-}} K_a$, intercept is V_e

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Equivalence Point Determination

Indicators:

- Indicators for acid/base titrations are weak acids/bases themselves
- Protonated and deprotonated forms have different properties (colors)
- Choose an indicator on the basis of the pH of the transition range of your titration, why?
  1. You want the indicator to be titrated at a pH that corresponds to the equivalence point
  2. If there is too large a difference, larger titration errors result.
  3. Rule of thumb: Choose an indicator whose transition range overlaps the steepest portion of your titration curve.

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