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?

- Four 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 addition of titrant,
2. Prior to the equivalence point,
3. At the equivalence point,
4. 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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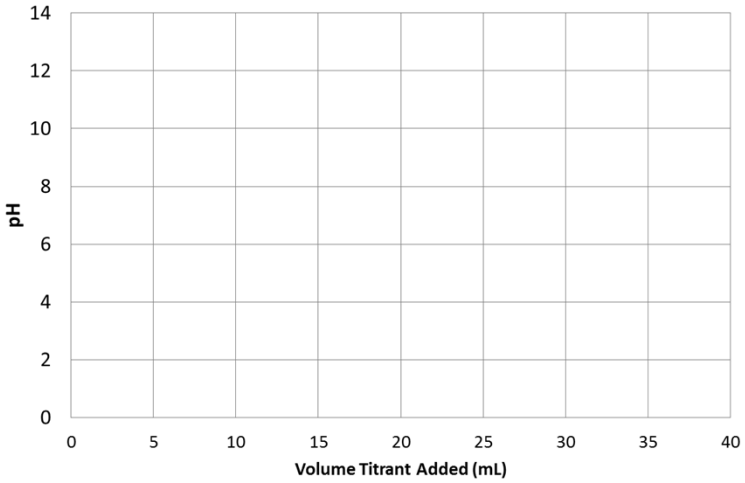
Modeling Titration Curves



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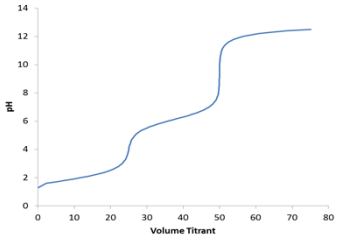
Diprotic Acid (Base) Titrations

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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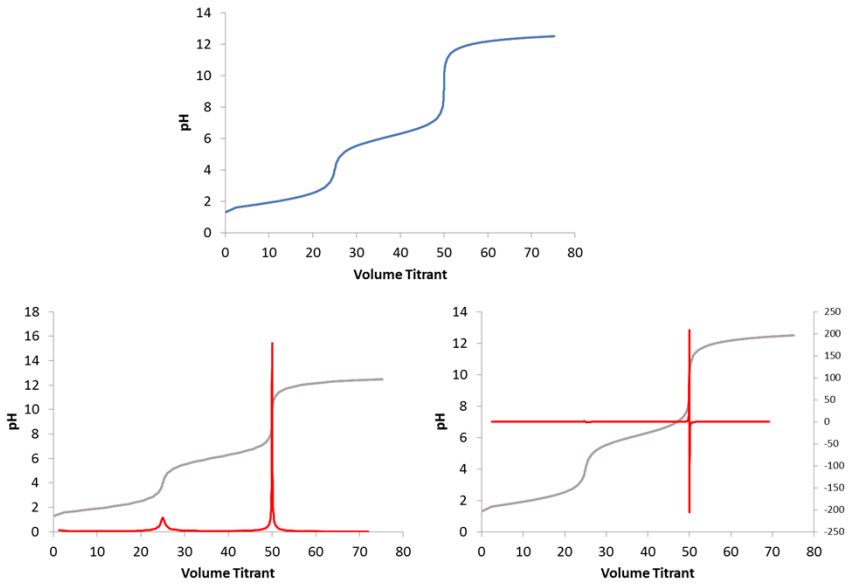
Equivalence Point Determination



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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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TABLE 10-3 Common indicators

Indicator	Transition range (pH)	Acid color	Base color	Preparation
Methyl violet	0.0–1.6	Yellow	Violet	0.05 wt% in H_2O
Cresol red	0.2–1.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Thymol blue	1.2–2.8	Red	Yellow	0.1 g in 21.5 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Cresol purple	1.2–2.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Erythrosine, disodium	2.2–3.6	Orange	Red	0.1 wt% in H_2O
Methyl orange	3.1–4.4	Red	Yellow	0.01 wt% in H_2O
Congo red	3.0–5.0	Violet	Red	0.1 wt% in H_2O
Ethyl orange	3.4–4.8	Red	Yellow	0.1 wt% in H_2O
Bromocresol green	3.8–5.4	Yellow	Blue	0.1 g in 14.3 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Methyl red	4.8–6.0	Red	Yellow	0.02 g in 60 mL ethanol. Then add 40 mL H_2O.
Chlorophenol red	4.8–6.4	Yellow	Red	0.1 g in 23.6 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Bromocresol purple	5.2–6.8	Yellow	Purple	0.1 g in 18.5 mL 0.01 M NaOH. Then add ~225 mL H_2O.
p-Nitrophenol	5.6–7.6	Colorless	Yellow	0.1 wt% in H_2O
Litmus	5.0–8.0	Red	Blue	0.1 wt% in H_2O
Bromothymol blue	6.0–7.6	Yellow	Blue	0.1 g in 16.0 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Phenol red	6.4–8.0	Yellow	Red	0.1 g in 28.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Neutral red	6.8–8.0	Red	Yellow	0.01 g in 50 mL ethanol. Then add 50 mL H_2O.
Cresol red	7.2–8.8	Yellow	Red	See above.
α-Naphtholphthalein	7.3–8.7	Pink	Green	0.1 g in 50 mL ethanol. Then add 50 mL H_2O.
Cresol purple	7.6–9.2	Yellow	Purple	See above.
Thymol blue	8.0–9.6	Yellow	Blue	See above.
Phenolphthalein	8.0–9.6	Colorless	Pink	0.05 g in 50 mL ethanol. Then add 50 mL H_2O.
Thymolphthalein	8.3–10.5	Colorless	Blue	0.04 g in 50 mL ethanol. Then add 50 mL H_2O.
Alizarin yellow	10.1–12.0	Yellow	Orange-red	0.01 wt% in H_2O
Nitramine	10.8–13.0	Colorless	Orange-brown	0.1 g in 70 mL ethanol. Then add 30 mL H_2O.
Tropaeolin O	11.1–12.7	Yellow	Orange	0.1 wt% in H_2O

Harris, *Quantitative Chemical Analysis*, 8e

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