

# Neutralization Titration

## Introduction and Theory

Historically, analytical chemists used colored indicators in acid/base titrations. While colored indicators are still widely used, the modern glass pH electrode makes possible the direct measurement of pH during the titration. Typically, the equivalence point is determined by plotting the pH as a function of titrant volume. In this experiment, you will use both a colored indicator and a pH meter to monitor the titration of a weak acid with a strong base.

There are several ways to determine the equivalence point by graphing the pH data. The simplest graph is a plot of pH vs. the titrant volume. (Figure 1) The equivalence point is estimated from the inflection point of the titration curve. A second technique is to plot the first derivative (slope) of the pH data ( $\Delta\text{pH}/\Delta V$ ) vs. the titrant volume. (Figure 2) In this case, the equivalence point corresponds to the point where the slope is greatest (i.e., the highest point on the plot.) A third technique is to plot the second derivative [ $\Delta(\Delta\text{pH}/\Delta V)/V$ ] vs. the titrant volume. (Figure 3) In Figure 3, the equivalence point corresponds to the volume at which the second derivative is zero. (Note that the x axis in Figure 3 has been expanded.)

One problem with all three of the preceding graphical techniques is that the equivalence point is *estimated* from the graph. In addition, the most important data points are the ones surrounding the equivalence point, but they are also the most difficult to obtain. A **Gran** plot is a graphical technique that allows one to use data *before* the equivalence point (typically from  $0.8 V_e$  up to  $V_e$ .) The Gran plot also uses linear regression analysis for determining the equivalence point. The equation for the titration of an acid with a base is:

$$V_{\text{base}} \cdot 10^{-\text{pH}} = K_a (V_e - V_{\text{base}})$$

or,

$$V_{\text{base}} \cdot 10^{-\text{pH}} = K_a V_e - K_a V_{\text{base}}$$

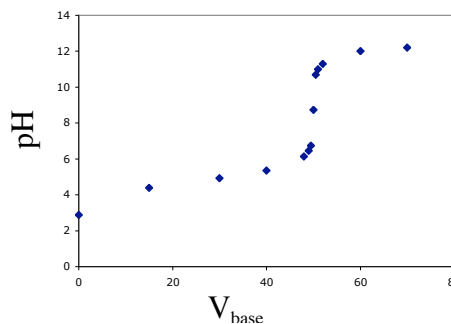


Figure 1.

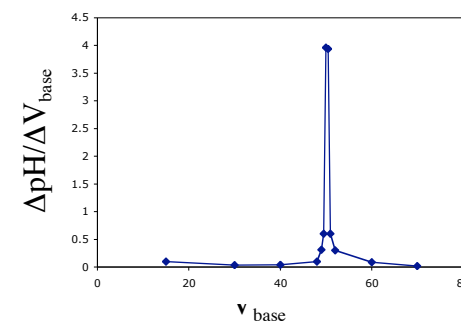


Figure 2.

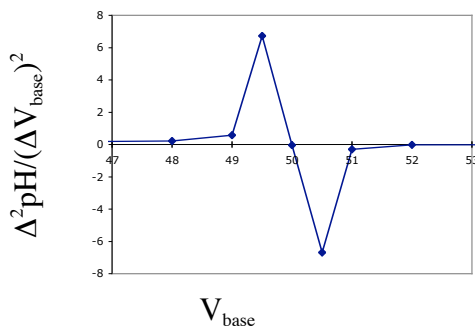


Figure 3.

where  $V_{\text{base}}$  is the volume of titrant added,  $V_e$  is the volume of base required to reach the equivalence point, and  $K_a$  is the acid dissociation constant for the acid analyte. A plot of  $V_{\text{base}} \cdot 10^{-\text{pH}}$  vs.  $V_{\text{base}}$  is a straight line with slope  $K_a$  and x-intercept of  $V_e$ . (Figure 4)

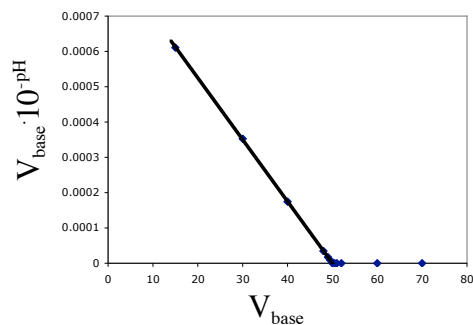


Figure 4.

**Important Point:** It is clear from Figure 4 that one should only plot for linear regression analysis those data points just before the equivalence point. Using linear regression analysis for all of your data will give you an erroneous fit. You may need to use data plots of Figures 1–3 to determine which points will be included in the Gran plot.

In this lab, you are going to titrate a weak acid (potassium acid phthalate, KHP) with a strong base (NaOH). You are going to use a colored indicator (phenolphthalein) to estimate the equivalence point of the reaction. You will use a Gran plot to determine the equivalence point of the titration and eventually the %KHP of your impure sample.

### **Procedure**

Refer to Skoog, West, Holler, Crouch Chap. 37C

1. Prepare standard NaOH solution as described in SWHC 37C-4
2. Calibrate pH meter using the manufacture's instructions. Use buffers with pH values near 7 and  
4. Rinse the electrodes well with distilled water and blot dry before immersing in a solution.
3. Standardize NaOH with potassium hydrogen phthalate (SWHC 37C-7). In addition to the phenolphthalein indicator, monitor the titration with the pH meter. Wait 30 seconds after each addition before recording the pH. Use small amounts of titrant as you approach the equivalence point. Record the volume at which the pink color is observed. Add at least five more 1 mL aliquots past the colored equivalence point. Determine the equivalence point with a Gran plot. You may need to prepare simple, first, or second derivative plots to assist in the identification of appropriate data points for the Gran plot. Use the linear regression feature of Excel to draw a line through the data. You will need to extrapolate the line to obtain the  $V_e$ .
4. Determine the %KHP in an unknown sample (SWHC 37C-8). Follow the procedure used in standardizing the NaOH solution.

5. Your lab report should contain:

- A table of information about the NaOH standardization with standard deviations and confidence intervals.
- A Gran plot from the NaOH standardization.
- A table of information about the unknown KHP titrations with standard deviations and confidence intervals.
- A copy of the following graphs for one of the trials:
  - A simple titration curve
  - A plot of the first derivative of the pH data
  - A plot of the second derivative of the pH data
  - A Gran plot

***Calculating first and second derivatives using Microsoft Excel***

To compute the first derivative, each pair of volumes (Table I) is averaged and the quantity  $\Delta\text{pH}/\Delta V_{\text{base}}$  is calculated. For a first derivative plot,  $\Delta\text{pH}/\Delta V_{\text{base}}$  is plotted against the average value of  $V_{\text{base}}$ . The second derivative and accompanying volumes are calculated in an analogous manner.

Table I. Using Microsoft Excel for computing first and second derivatives of titration data

<u>Raw data</u>		<u>First derivative</u>		<u>Second derivative</u>	
$V_{\text{base}}$	pH	Avg. $V_{\text{base}}$	$\frac{\Delta\text{pH}}{\Delta V_{\text{base}}}$	Avg. $V_{\text{base}}$	$\frac{\Delta(\Delta\text{pH}/\Delta V_{\text{base}})}{\Delta V_{\text{base}}}$
85.0	4.245				
		85.5	0.155		
86.0	4.400			86.0	0.0710
		86.5	0.226		
87.0	4.626			87.0	0.0810
		87.5	0.307		
88.0	4.933			88.0	0.0330
		88.5	0.340		
89.0	5.273			89.0	-0.0830
		89.5	0.257		
90.0	5.530			90.0	-0.0680
		90.5	0.189		
91.0	5.719			91.25	-0.0390
		92.0	0.130		
93.0	5.980				

### ***Questions***

1. Using your data, calculate the  $K_a$  of KHP.
2. Why must some of the data (points after the equivalence point) be excluded from a Gran plot? Why does the graph curve near the equivalence point and not go through zero?
3. Compare the  $V_e$  obtained with the colored indicator with the equivalence value determined from the Gran plot.
  - a) Assuming that the value obtained from the Gran plot is the “true” value, what is the relative error between the two  $V_e$  values?
  - b) Use statistical analysis to compare the two  $V_e$  values at the 95% confidence limit. Are they the same?