# Experiment 4: Analysis of an Acid-Base Titration Curve-The Gran Plot
(Adapted from Daniel C. Harris' *Quantitative Chemical Analysis*.)

Two Hours Experimental Work on Your Own (between March 30 and April 12)
Notebook Due on April 17 by 5 p.m.

Introduction

In this experiment, you will titrate a sample of pure potassium hydrogen phthalate (KHP, Harris Table 12-5) with NaOH. The net ionic equation for the titration is shown below:
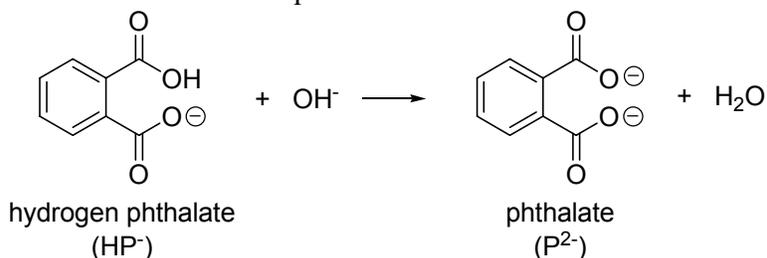
The first goal of the experiment is to standardize the NaOH solution. In General Chemistry, you relied solely on the titration endpoint to determine the NaOH concentration. However, in this course, we will make use of an entire section of the titration curve to determine the endpoint with (potentially) greater accuracy. This analysis involves the construction of a Gran plot (discussed in Harris Section 12-5). The Gran plot is arguably the most accurate way to determine K_a for hydrogen phthalate. Activity coefficients (which we covered in Chapter 8) are used in the calculations for this experiment, and significantly increase the accuracy of the results.
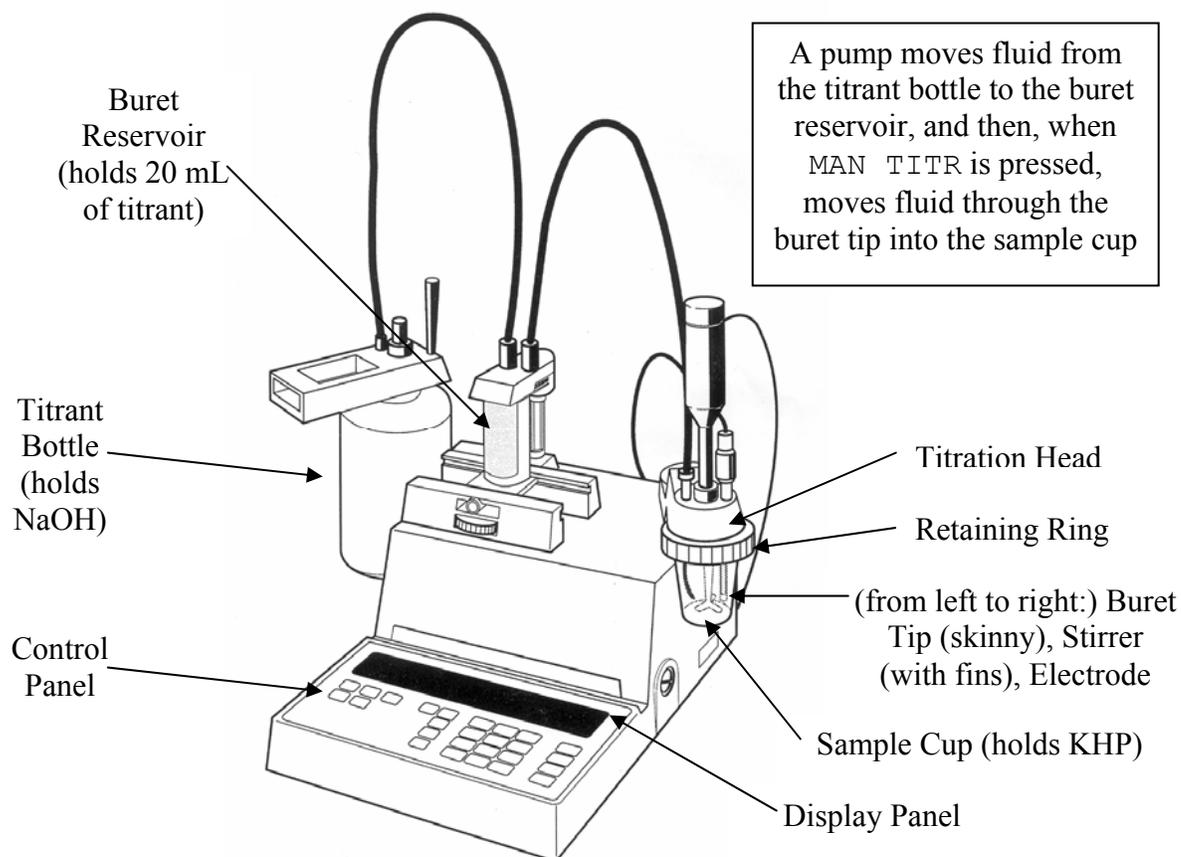
Experimental Procedure

Before you come to lab, the teaching assistant will have dried vials of potassium hydrogen phthalate at 105°C, and prepared an aqueous sodium hydroxide solution, which, when prepared, was very close to 0.1000 M. (The actual amount will be written on the board in Olin-Rice 380.) You will perform the titration using the Chemistry Department's Mettler DL12 Titrator.

In your notebook, you do **not** need to write down in detail all the instructions for the titrator. Do, however, write down brief descriptions of what you did, specific observations, and follow good, standard notebook mechanics (table of contents, date, page numbers, objective, etc.).

1. Take a vial of potassium hydrogen phthalate from the oven and cool the uncapped vial in a desiccator for at least 10 min.

Note the various components of the titrator as shown on the next page:

A pump moves fluid from the titrant bottle to the buret reservoir, and then, when MAN TITR is pressed, moves fluid through the buret tip into the sample cup

Buret Reservoir (holds 20 mL of titrant)

Titrant Bottle (holds NaOH)

Control Panel

Titration Head

Retaining Ring

(from left to right:) Buret Tip (skinny), Stirrer (with fins), Electrode

Sample Cup (holds KHP)

Display Panel

2. Meanwhile, remove the titrator pH electrode from its storage sleeve, rinse the electrode with distilled water, and carefully insert the electrode through the open hole in the titration head.

3. Calibrate the electrode as follows:

   (a) Press 3 (on the numeric keypad) and ELEC CALIB (this button is in the second column from the left) on the control panel. A light bar should start blinking to the left of BUFFER A on the display panel.

   (b) Attach the plastic sample cup containing red pH 4 buffer by loosening the grey retaining ring on the titration head (by turning the ring clockwise), raising the cup until it catches, and gently tightening the ring (by turning it counterclockwise) while holding the cup in place. Don't raise the cup so much that the stirrer doesn't have the clearance to stir!

   (c) Press the green START button at the lower right of the control panel. If everything goes well, after a few seconds, a light bar should start blinking to the left of BUFFER B on the display panel.

   (d) Holding the plastic sample cup in place, loosen the grey retaining ring and remove the sample cup. Rinse the electrode, buret tip, and stirrer thoroughly with distilled water (holding a waste beaker under the titration head), then mount the sample cup containing purple pH 10 buffer.

   (e) Again, press the green START button at the lower right of the control panel. If everything goes well, after a few seconds, you should hear three beeps, confirming that the calibration was a success!

   (f) Remove the sample cup containing the pH 10 buffer, and rinse the electrode, buret tip, and

stirrer as before.

4. Using an analytical balance, weigh out close to 0.3000 g of the potassium hydrogen phthalate (KHP), and transfer into a 50-mL volumetric flask. The mass need not be exactly 0.3000 g, but whatever the mass is should be recorded to 4 significant figures. Add some distilled water to the flask and completely dissolve the solute. Then dilute to the mark with more distilled water.

5. Pour the 50 mL of KHP solution into a clean, dry sample cup. <u>Be sure to add two drops of phenolphthalein indicator to this solution!</u>

6. Mount the sample cup onto the titration head, then press the STIR button (in the second column from the left on the control panel).

7. Now take a few moments to calculate a theoretical equivalence point based on the reported [OH⁻] and the mass of KHP (FW 204.22). (Obviously, you should do this in your notebook and not on some random scrap of paper!)

8. Press the MAIN TITR button on the rightmost column of the control panel. The display panel will show the pH of the solution to three decimal places. Record the pH after ~15 seconds. (This is the pH value with 0 mL of titrant added.)

9. Press the mL pH button (in the third column from the left on the control panel) to toggle the display readout to mL. Press and hold down the MAIN TITR button until the display reads 1.50 mL. The electronic buret will add precisely that amount of NaOH to the sample cup. Write down that volume. Press the mL pH button, wait 15 seconds, and write down the pH.

10. Press the mL pH button. Then press and hold down the MAIN TITR button until the display reads 3.00 mL. Write down that volume. Press the mL pH button, wait 15 seconds, and write down the pH.

11. Until you are within ~3 mL of the equivalence point, continue adding base in 1.50-mL aliquots, recording the volume (to the nearest 0.01 mL) and the pH (to three decimal places) 15 s after each addition.

12. Thereafter, use 0.40-mL increments until you are within 1 mL of the equivalence point. After each delivery of titrant, record the titrant volume and the pH (waiting 15 s each time).

13. At 1 mL before the equivalence point, you should start adding base only <u>0.01 mL</u> at a time. However, you only need to record the pH every <u>0.10 mL</u>. The reason you are adding base so slowly is that you want to determine (and write down) the volume at which the <u>very first faint</u> pink color is observed. Once the phenolphthalein end point is reached, add three more 0.10-mL aliquots, recording the pH each time (after waiting 15 s). <u>In your notebook, record how stable the pH readings are at this point, and briefly explain your observation.</u>

14. Finally, add three more 1.00-mL aliquots. After each delivery of titrant, record the titrant volume and the pH (yes, you should still wait 15 s before recording each pH reading).

15. When you have collected all your data, press RESET. Remove the sample cup, rinse it several times with distilled water, and dry. (Do not use any soap!) Leave the cup next to the titrator.

16. Rinse the buret tip, stirrer, and electrode thoroughly. Carefully remove the electrode from the titration head and return the electrode to its storage sleeve.

17. Clean up the rest of your glassware (leftover KHP can go down the sink). Leave the titrator turned on.

Data Analysis

(1) Plot all of the data from your titration, and tape a copy of your plot (like the one shown below) into your notebook.

Titration of Potassium Hydrogen Phthalate by ~0.1 M NaOH
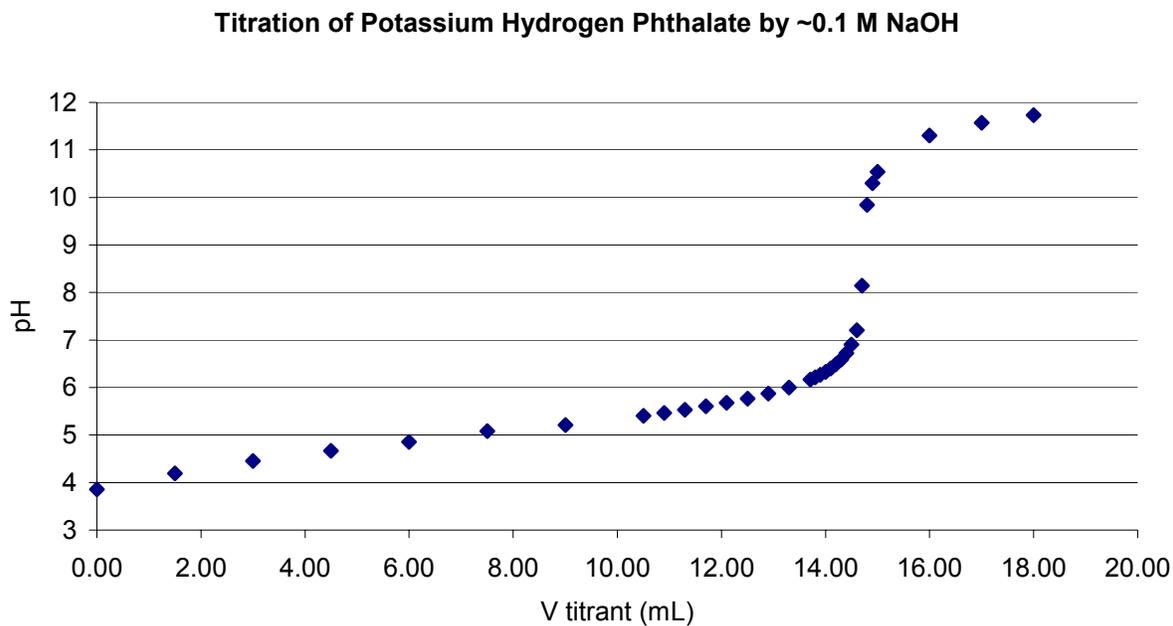
(2) Report your titration endpoints as determined by (a) the indicator and (b) a first derivative plot (see pp. 237-238 of your text). Your notebook should include a plot like this:

First Derivative of Titration Curve
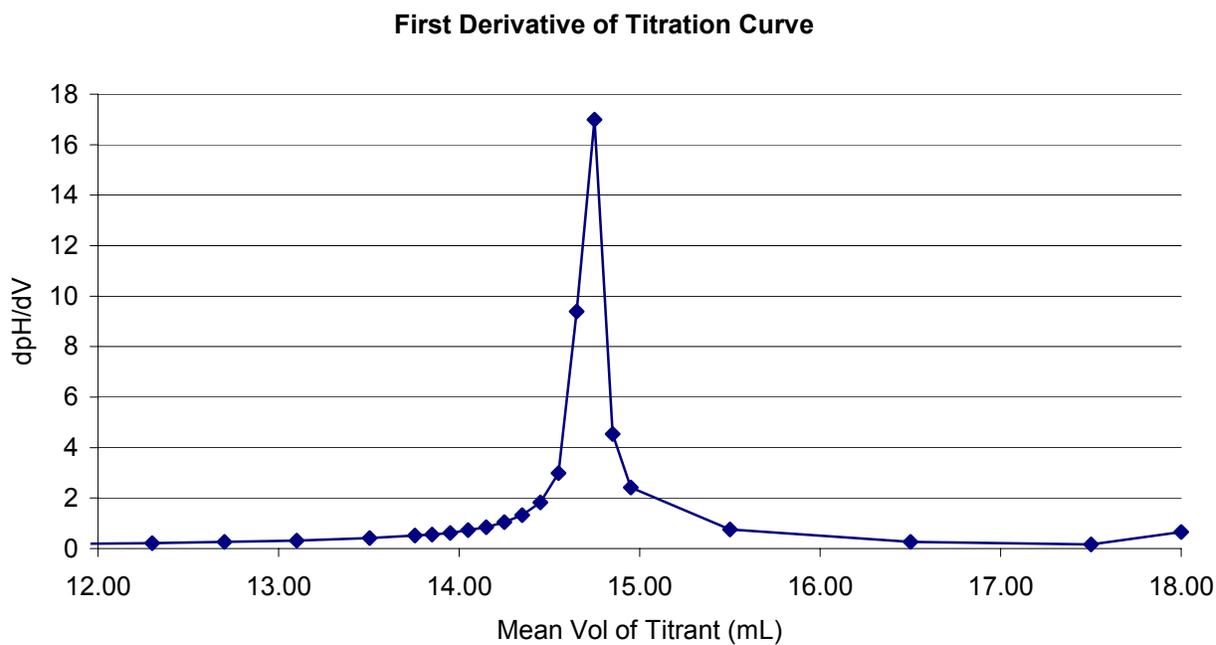
(3) Although the KHP was the "analyte" in your titration, it is actually used to standardize (that is, determine the concentration of) the OH^- solution. Use your phenolphthalein and first derivative endpoints to calculate two estimates of the concentration of $[OH^-]$ in the titrant.

(4) Construct a Gran plot ($V_{titrant}10^{-pH}$ *vs.* $V_{titrant}$). Plot for $V_{titrant}$ ranging from ~$0.8V_e$ to past V_e. Use your first derivative endpoint as your V_e value. Include a copy of the following plot in your notebook:

Preliminary Gran Plot for Titration--0.8 Ve to past Ve
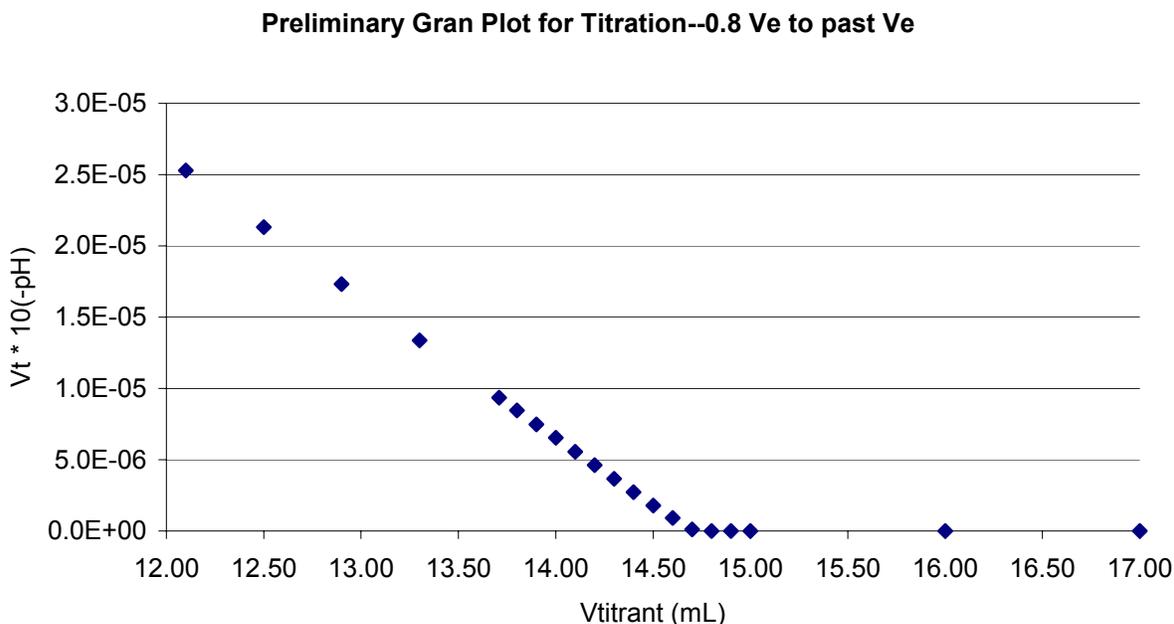
(The plot becomes non-linear when $V_{titrant}$ is very close to V_e. This is largely due to the breakdown of our assumption that mol P^{2-} = mol OH^- added. This assumption starts to fail because $[HP^-]$ is quite low close to the endpoint. Hence, the reverse of the titration reaction, $P^{2-} + H_2O \rightarrow HP^- + OH^-$, becomes non-negligible, as predicted by Le Chatelier's Principle.)

(5) Next, we want to fit a line to only the linear part of the Gran plot. First, choose and plot a subset of the data <u>before</u> V_e. Then add a trendline to these data. Do this (using Excel on the PC; Mac Excel may be slightly different) by…
- Selecting "Add Trendline" under the Chart pull-down menu.
  - Under the "Type" tab, choose a linear Trend/Regression Type.
  - Under the "Options" tab, choose to display both the equation and R-squared value on the chart. Also choose to forecast forward by 1 unit. (The idea here is, you want your plot to display the x-intercept.)
  - Click on your trendline box and go to Format Selected Data Labels. Under the Number tab, choose scientific notation and to display 3 decimal places.

The statistical parameter R^2 is the (often misused) correlation coefficient. A perfectly straight line will give a R^2 of exactly 1. Play around with the range of data you plot until your R^2 is very close to 1. When you are satisfied, print out and include this plot in your notebook (I chose to include my data from 13.70 to 14.50 mL):

Final Gran Plot
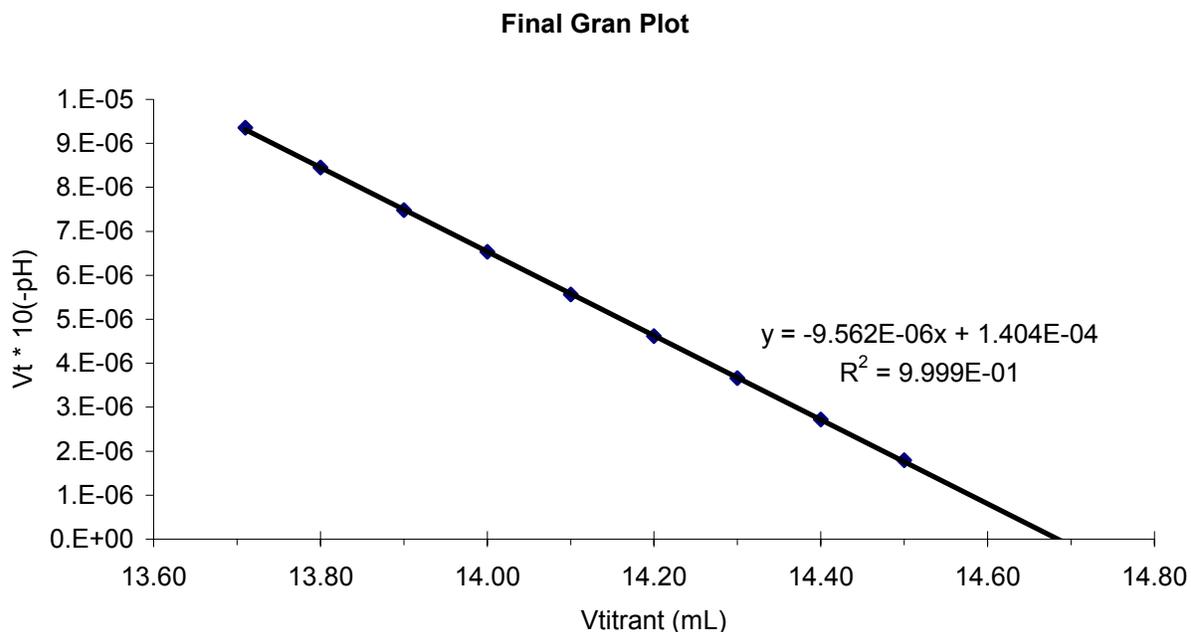
Use this plot to determine (yet another) value for V_e, solving for V_e algebraically. Then determine the OH⁻ concentration based on the Gran plot value for V_e.

(6) Find the average and standard deviation of your three measured values for [OH⁻] (that is, from the phenolphthalein data, first derivative plot, and Gran plot). By performing a Case 1 t-test, determine if there is a statistically significant difference between the average of your three measurements and the formal OH⁻ concentration prepared by your TA. If there is, explain the reason for the discrepancy.

(7) Finally, we will use the slope of your final Gran plot (which is equal to $-\dfrac{\gamma_{HP^-}}{\gamma_{P^{2-}}}K_a$) to determine a value for K_a.

    (a) Use the LINEST function to fit the same points plotted in your final Gran plot. (The slope, y-intercept, and correlation coefficient computed by LINEST should be identical to what Add Trendline reports.)

    (b) Next, compute the total ionic strength of the solution close to the endpoint. Clearly, μ is increasing throughout the titration. We will choose arbitrarily to compute μ at around the midway point of our final Gran plot: $0.95V_e$, <u>where we use the V_e determined from the Gran plot</u>. Consider the contributions of K^+, Na^+, HP^- and P^{2-}. Use the $[Na^+]$ of your TA's stock solution (Think about why this is valid, in spite of your calculation in (6)!)

    (c) Next, determine activity coefficients (at the ionic strength determined in (b)) for HP^- and P^{2-}, assuming that both ions have a hydrated radius α = 600 pm. Note that you will have to interpolate the values in Harris Table 8-1 or use the extended Debye-Huckel equation.

    (d) Compute K_a. Using the standard error in the slope computed by LINEST, also determine the standard error and the 95% confidence interval for K_a.

No concluding discussion is required. Be sure to tape in a copy of your spreadsheet in your notebook, and e-mail me a copy as well.